Ioffe Institute

ABSTRACT BOOK

14th Russia/CIS/Baltic/Japan Symposium on Ferroelectricity

Young scientists school on the spectroscopic studies of critical dynamics at structural phase transitions

May 14–18, 2018

St. Petersburg, Russia

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About RCBJSF-2018

Present Symposium is a continuation of a series of meeting started in 1976 as the First Soviet-Japanese Symposium on ferroelectricity. The first meeting was jointly organized by the Nobel Prize winner professor Alexander Prokhorov and professor Jinzo Kobayashi and was held in Novosibirsk. These bilateral bi-annual symposia were continually held till 1988 (Tsukuba) and afterwards were transformed into the Russia/CIS/Baltic/Japan Symposia on Ferroelectricity (RCBJSF). In 2016 13-th RCBJSF was held in Matsue (Japan)

In 2018 the Symposium returned to Russia and it will be jointly organized by the Ioffe Institute and Peter the Great St. Petersburg Polytechnic University. We will bring together international experts on synthesis, properties, modeling and new applications of relaxor materials. The focus of the Symposium is on the fundamental understanding of structure-property relationships and on new materials.

The Symposium will present invited and contributed talks and original poster reports and will provide ample time for scientific discussions.

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Invited presentations

Pulse EPR and ENDOR study of manganese doped [(CH3)$_2$NH$_2$] [Zn(HCOO)$_3$] hybrid perovskite

M. Šimėnas,[1] L. Macalik,[2] K. Aidas,[1] V. Kalendra,[1] D. Klose,[3] M. Maczka,[2] G. Völkel,[4] A. Pöppl,[4] and J. Banys[1],*

[1]Faculty of Physics, Vilnius University, Sauletekio av. 9, LT-10222 Vilnius, Lithuania
[2]Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
P. O. Box-1410, PL-50–950 Wroclaw 2, Poland
[3]ETH Zürich, Department of Physical Chemistry,
Vladimir-Prelog-Weg 2, 8093 Zürich,
Switzerland
[4]Faculty of Physics and Earth Sciences, Universität Leipzig,
Linnestrasse 5, D-04103 Leipzig, Germany
[*]Corresponding Author: juras.banys@ff.vu.lt

We use pulse EPR and ENDOR spectroscopy to investigate the manganese doped [(CH$_3$)$_2$NH$_2$] [Zn(HCOO)$_3$] hybrid framework based on the perovskite architecture (see Figure 1) [1]. This compound exhibits a structural phase transition at 163 K to a ferroelectric ordered phase. The echo-detected field sweep Mn^{2+} spectrum of the disordered phase reveals a significant EPR transition-dependent relaxation. The ^{1}H ENDOR pattern indicates several protons in the vicinity of the Mn^{2+} center in agreement with the density functional theory calculations. A multifrequency (X, Q and W-band) electron spin echo envelope modulation (ESEEM) technique reveals a peculiar signal which is unaffected by the external magnetic field. The temperature dependence of the longitudinal relaxation time indicates a coupling between the Mn^{2+} electron spins and a hard optical phonon mode, which undergoes a damping at the phase transition point. The temperature dependent measurements of the phase memory time reveal methyl group motion in the ordered phase.

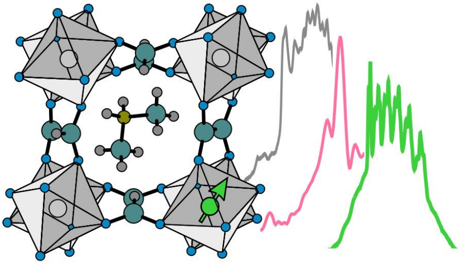

Figure 1. Structure of [(CH$_3$)$_2$NH$_2$][Zn(HCOO)$_3$] hybrid perovskite in the ordered phase (left). ^{1}H ENDOR, ESEEM and EDFS spectra of the Mn^{2+} centers in this compound (right).

References

[1] M. Šimėnas et. al., *J. Phys. Chem. C.*, 121, 27225–27232 (2017)

Local dynamics in relaxor ferroelectrics and its relation to supercooled liquid

T. Egami[1,2]

[1]Shull Wollan Center — Joint Institute for Neutron Sciences, University of Tennessee, Knoxville, TN37996 USA
[2]Oak Ridge National Laboratory, Oak Ridge, TN37831, USA
*Corresponding Author: egami@utk.edu

In relaxor ferroelectrics some phonons are localized because of strong chemical and lattice disorder, and dynamic ferroelectric fluctuations are active up to the Burns temperature. Usually the atomic dynamics is studied by inelastic neutron or x-ray scattering to measure the dynamic structure factor, S(Q, E), where Q and E are the momentum and energy exchange in scattering. However, in relaxor the dynamic fluctuations are local and strongly damped, so that it is difficult to observe it in S(Q, E). To capture such fluctuations we Fourier-transform S(Q, E) to the dynamic pair-density-function (DyPDF), g(r, E), a frequency-resolved PDF. We show in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Ba(Zr, Ti)O_3$ (BZT) DyPDF can describe the local dynamics and elucidate their behavior. For PMN local ferroelectric fluctuations explain the origin of fluctuations up to Burns temperature. In BZT local ferroelectric instability related to the formation of nano-polar regions explains the high permittivity of this lead-free ferroelectrics. Such local dynamics is seen in all strongly disordered systems such as liquids and glasses. Relaxor ferroelectric phenomena are just the ferroelectric version of a glassy behavior. We show that glassy behaviors in various properties are all similar and form a class of ill-condensed matter with frustrated order.

Caloric Effects in Multiferroic Composites (x)$La_{0.7}Pb_{0.3}MnO_3$ — (1-x) $PbTiO_3$

I. N. Flerov,[1,2,*] E. A. Mikhaleva,[1] A. V. Kartashev,[1,3] and M. V. Gorev[1,2]

[1]Kirensky Institute of Physics, Federal Research Center KSC SB RAS,
660036, Krasnoyarsk, Russia
[2]Siberian Federal University, 660074, Krasnoyarsk, Russia
[3]Astafiev Krasnoyarks State Pedagogical University, 660049, Krasnoyarsk, Russia
[*]Corresponding Author: flerov@iph.krasn.ru

Electro(ECE)-, magneto(MCE)- and baro(BCE)-caloric effects in ferroics associated with a change of the entropy and/or temperature under variation of the external field are the most pronounced in the region of the phase transitions and considered as an important tool in the field of studies of the origin and fundamental properties of materials. On the other hand, ferroics demonstrating a large caloric response are promising as a solid-state alternative to gas compression cooling technologies [1].

The study of the paired caloric effects in $La_{0.7}Pb_{0.3}MnO_3$ (MCE and BCE) [2] and $PbTiO_3$ (ECE and BCE) [3] have shown that caloric efficiency of monoferroics can be elevated using two from three distinct external fields (electric, magnetic, mechanical stress). Such a way is also promising for single-phase and composite multiferroics which accommodate multiple ferroic order parameter states and display direct or indirect cross coupling properties between the different ferroic order states.

In the present paper, ceramic ferromagnet- ferroelectric composites (x)$La_{0.7}Pb_{0.3}MnO_3$ — (1–x)$PbTiO_3$ ($x = 0.18; 0.32; 0.69; 0.81; 0.85$) were studied. The detailed experimental information on MCE, ECE and BCE, magnetization, heat capacity, entropy, thermal dilatation, susceptibility to hydrostatic pressure and magnetic and electric fields was obtained. A good agreement was found between caloric parameters determined by the direct and indirect methods. Caloric and multicaloric efficiency as well as relative cooling power of composites were discussed and compared with those of the initial compounds $La_{0.7}Pb_{0.3}MnO_3$ and $PbTiO_3$. It was shown that variation of a relationship between ferromagnetic and ferroelectric components can significantly increase: first, barocaloric and magnetocaloric efficiency of compositional material due to the mechanical stress appearing between grains of different ferroic phases under magnetic field and, second, intensive ECE due to the displacement of the ferroelectric phase transition towards the tricritical point.

The obtained experimental and calculated data make it possible to consider that ferromagnetic–ferroelectric composites are really promising materials for use as effective solid-state refrigerants in mono- and multicaloric cooling cycles built on MCE, ECE and BCE.

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References

[1] N. A. Zarkevich, D. D. Johnson, V K Pecharsky, *J. Phys. D: Appl. Phys.*, 51, 024002 (2018).
[2] A. V. Kartashev, E. A. Mikhaleva et al., *J. Appl. Phys.*, 113, 073901 (2013).
[3] E. A. Mikhaleva, I. N. Flerov et al., *Phys. Solid State*, 54 1832–1840 (2012).

The First Observation of New Quantum Phenomena in Ferro-and Piezoelectrics: Shift Photovoltaic Current

J. Spanier[1], and V. M. Fridkin [2,*]

[1]Drexel University, Dept. of Physics, 3141 Chestnut Str. Philadelphia PA, USA
[2]Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics " RAS,
Leninski Ave, Moscow, Russia
[*]Corresponding Author: fridkinv@gmail.com

As well known, the bulk photovoltaic current in the crystals without center of symmetry consists of two parts: ballistic and shift currents. The first prediction of the shift photovoltaic current as a new quantum phenomenon was done more than 30 years ago [1]. Recently the "ab initio " theory of the shift current has been developed [2, 3]. Very short relaxation times of the shift current (of atomic values) and the absence of corresponding Hall effect did not permit its experimental observations. Therefore, this quantum phenomenon has never been observed. In the present paper the first experimental observation of the shift photovoltaic current and its comparison with theoretical predictions was performed [4] for piezoelectric crystals bismuth germanate and bismuth silicate by means of simultaneous measurements of the linear and circular bulk photovoltaic effect in magnetic field.

References

[1] V. Belinicher and B. Sturman, Sov. Phys. Uspekhi, **23**, 199 (1980)
[2] S. Young and A. Rappe, Phys. Rev. Lett., **109**, 116601 (2012)
[3] B. Sturman and V. Fridkin, The Photovoltaic and Photorefractive Effects in Noncentrosymmetric Materials (Gordon and Breach, Philadelphia, 1992)
[4] Z. Gu, D. Imbrenda, A. Bennett-Jackson, M. Falmbigl, A. Podpirka, T. Parker, D. Shreiber, M. Ivill, V. Fridkin, and J. Spanier, Phys.Rev.Lett., **118,** 096601 (2017)

Dielectric and magnetodielectric properties in solid oxygen as a correlated molecular solid

Sumio Ishihara,[1,*] Naomichi Sato,[1] and Makoto Naka[2]

[1]Department of Physics, Tohoku University, Sendai 980-8578 Japan
[2]Waseda Institute for Advanced Study, Waseda University, Tokyo 169-8050, Japan, University
[*]Corresponding Author: ishihara@cmpt.phys.tohoku.ac.jp

There is a long history of the researches on solid oxygen. A minimal unit of the solid oxygen is an O_2 molecule in which the highest orbitals of the doubly degenerate Π_g molecular orbitals are occupied by two electrons. Because of the strong intra-molecule Hund coupling, the O_2 molecule is a magnetic molecule with the spin amplitude of $S=1$. The long-range antiferromagnetic order realized below 23.9K at ambient pressure is termed the α phase. A number of electronic-structural phases under high pressure have been confirmed so far. This is owing to the electron correlation, the magnetism in O_2 molecules and the flexible structure framework. Recently, a new phase is suggested by the optical absorption measurements under high magnetic field of the order of 100T [1]. In addition, the second-harmonic generation (SHG) is observed under the high pressure [2], suggesting a possibility of a new electronic and structure phase without a space inversion symmetry. It is highly required that the electronic structure as well as the dielectric properties are reinvestigated from the viewpoint of the modern condensed-matter physics researches.

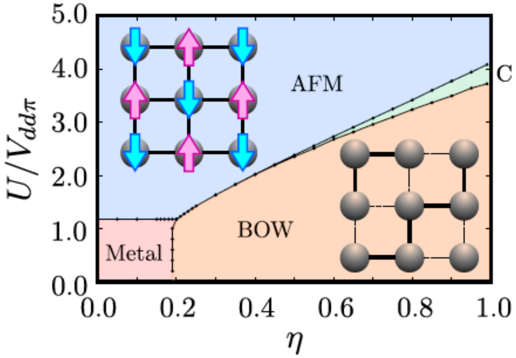

Figure 1. Electronic phase diagram in a plane of the electron-electron interaction (U) and the electron-lattice interaction (η).

In this talk, we introduce recent our theoretical researches of the electronic structure as well as the dielectric/magneto-dielectric properties of solid oxygen as a correlated electron system with flexible crystal structure. We introduce 1) the magnetic and molecular structures under high magnetic field, 2) a correlation between the optical spectra and magnetism, and 3) the dielectric properties under high pressure. A calculated phase diagram is shown in Fig. 1.

The authors appreciate fruitful discussion with T. Kimura (University of Tokyo), Y. H. Matsuda (University of Tokyo), and T. Aoyama (Tohoku University).

References

[1] T. Nomura et al. Phys. Rev. Lett. 112, 247201 (2014)
[2] T. Aoyama et al. JPS meeting, 27aAM-4 (2014).

Pd nanoparticles supported on ferroelectric $BaTiO_3$

Jun Kano

Grad. Sch. of Sci. Tech., Okayama Univ.
jun@psun.phys.okayama-u.ac.jp

Composite compounds such as precious metal nanoparticles loaded on oxide support are widely used as a catalyst. Since precious metal has metallic surface, high catalytic activity can be expected due to reactive surface. So immobilization of nano-sized precious metal on the oxide support is essential role for high catalytic activation. It is known that catalytic activity is also affected by chemical and physical properties of support [1,2]. Any interaction between metal and support will have some influence on catalytic activity.

We expect that ferroelectric support can change the electronic state of metal nanoparticle owing to the effect of a spontaneous polarization, realizing a new type of catalyst assisted by the ferroelectricity. In order to investigate the electronic state of metal affected by the electric polarization, X-ray absorption near edge structure (XANES) has been carried out for Pd loaded on ferroelectric $BaTiO_3$ surface.

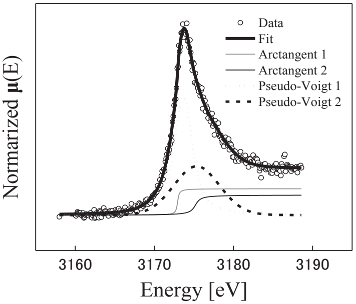

Fig. 1. Pd-L3 edge XANES spectrum of $PdO_x/BaTiO_3$ and its fit result. Two type of function are used. Pseudo-Voight is used for peak function. Arctangent is used for background function.

Figure 1(a) shows a Pd-L3 edge XANES spectrum of $PdO_x/BaTiO_3$ and its fit result. Pd nanoparticles shows unusual valence state, Pd^{4+}. We confirmed that $PdO_x/\gamma\text{-}Al_2O_3$ shows only Pd^{2+} absorption. This result indicates that Pd nanoparticles on $BaTiO_3$ has surface structure including Pd^{4+} because of that Pd-L3 edge XANES measurement is surface sensitive. Bulk sensitive measurement (Pd-K edge XANES) confirms that core structure of Pd nanoparticles is formed by only Pd^{2+}. To understand these results, we suppose a core-shell structure. PdO_x particles on $BaTiO_3$ are basically PdO. Since Pd^{4+} is realized at a surface, PdO may be stabilized with oxygen terminated. For easy understanding, we suppose electric polarization aligns toward to the PdO_x particles as in Fig. 2 (this direction represents P^+). By the effect of P^+, Pd cations and O anions are relatively displaced to upper and down side, respectively, forming *zig-zag* atomic arrangement. Such atomic configuration can break Pd-O planar coordination, resulting that foreground Pd atoms are floated at the surface of PdO (see Fig. 2(b)). These Pd atoms can bind outer O_2, realizing six coordinated Pd. In case of P^- (alignment of P^- is opposite direction of P^+), oxygen cannot adsorb with surface Pd atom because Pd atoms are displaced into core side, indicating no realization of Pd^{4+} state.

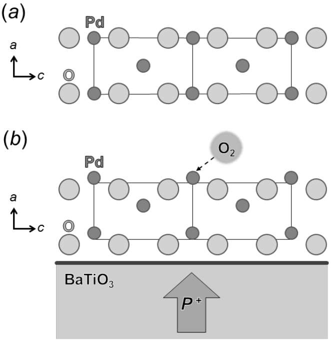

Fig. 1. Cross section view of crystal structure. (a) is PdO. (b) is interface of PdO-$BaTiO_3$. Polarization direction is along to PdO side

References

[1] S. J. Tauster, *Acc. Chem. Res.* **20,** 389-394 (1987).
[2] H. Tanaka *et al.*, *J. Alloys Compd.* **408-412,** 1071-1077 (2006).

Emergent Piezoelectric Materials: structure, properties, applications

A. L. Kholkin[1,2*]

[1]Physics Department and CICECO – Aveiro Institute of Materials, University of Aveiro,
Campus de Santiago, 3810-193 Aveiro, Portugal
[2]School of Natural Sciences and Mathematics, Ural Federal University, 19 Mira street,
Ekaterinburg, Russia
[*]Corresponding Author: kholkin@ua.pt; kholkin@urfu.ru

Recent studies revealed several new classes of piezoelectrics including 2D materials (graphene) [1] and biomolecular crystals (self-assembled peptides, amino acids, nucleotides) [2,3,4] Piezoelectricity in these occurs because of symmetry breaking on the surface in the first case and presence of highly anisotropic hydrogen bonds in the second. Graphene in contact with oxides offers extremely high piezoelectric activity due to polarity of C-O bonds, while peptide nanotubes (PNTs) demonstrate remarkable electromechanica; properties (similar to $LiNbO_3$) due to self-assembly and intrinsic softness of directed hydrogen bonds. Remarkably stable structure, possibility of functionalization together with biocompatibility and easy synthesis and nanofabrication, make graphene, PNTs and other biomolecular crystals (e.g. amino acid glycine [4]) attractive alternatives to traditional lead-based piezoelectrics.

In this presentation, the mechanisms of piezoelectric effect in these structures will be discussed and methods for their studies will be introduced. Hybrid Piezoresponse Force Microscopy (Hybrid-PFM) will be presented allowing measuring piezoresponse during acquisition of force-distance curves [5]. Several types of demonstrators including piezoelectric membranes based on 2D materials (graphene), cantilevers based on PNTs, and piezoelectric scaffolds for cardiomyocite cells [6] will be presented. Recent results on piezoelectricity and pyroelectricity in PNTs show that they are very attractive for various piezoelectric applications in biomedicine, because of their intrinsic biocompatibility combined with mesoporous structure and ability to work in contact with living cells and biological liquids. Scaling of piezomaterials down to nanosize is expected to dramatically improve their performance, thus making piezoelectric nanodevices much more sensitive than the traditional ones.

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References

[1] G. da Cunha et al. Nat. Commun. 6, 7572, 2015.
[2] A. L. Kholkin et al. ACS Nano 4, 610 (2010).
[3] S. Guerin et al. Nature Mater. 17, 180 (2018).
[4] I. Bdikin et al. J. Appl. Phys. 118, 072007 (2015).
[4] E. Seyedhosseini et al. ACS Appl. Mat. Interfaces 9, 20029 (1917).
[5] A. Kalinin et al. Ultramicroscopy 185, 249 (2018).
[6] P. J. Gouveia et al. Biomaterials 139, 213 (2017).

Brillouin light scattering study of acoustic response of PMN crystal under dc electric field

S. G. Lushnikov,[1,*] A. I. Fedoseev,[1] and S. Kojima[2]

[1]Ioffe Institute, Politekhnicheskaya 26, St.-Petersburg, Russia
[2]Institute of Materials Science, Tsukuba University, Ibaraki 305–8573, Tsukuba, Japan
[*]Corresponding Author: sergey.lushnikov@mail.ioffe.ru

It is well known that PMN single crystals that preserve a cubic symmetry up to helium temperatures under normal conditions experience a phase transition to a ferroelectric phase at Tc ~ 210 K if an external dc electric field exceeding a certain threshold is applied (E_{th}). The resulting phase diagram depends on the direction and regime of application of the field and also on the temperature regime (cooling or heating at E = 0 — ZFC, ZFH, or cooling or heating at E ≠ 0 — FC, FH) [1–4].

In this report we present the results of Brillouin investigations of the effect of electric field in all possible regimes of its application on the behavior of a quasi-longitudinal acoustic phonon (QLA) with $\mathbf{q}_{\mathbf{ph}} \| [110]$ in a 180-degree light scattering geometry. The electric field was applied in the [111], [$\bar{1}$10], and [100] directions in the temperature interval 85–295 K. The light was excited by an ion Ar+ laser with wavelength $\lambda = 514.5$ nm. The light scattered from the sample was analyzed by a high-contrast Sandercock 3+3 tandem Fabry–Perot interferometer. The free spectral range of the interferometer was 75 GHz. A high-voltage power supply (HJPM-P, Matsusada Precision Inc.) was used to apply a dc electric field of 5.3 kV/cm. In the temperature measurements, the sample was placed in a heat/cooling stage (THMS600), the temperature of which was varied with a stabilization of +/– 0.1 K.

Three measurement regimes were used: (a) ZFC-FH, (b) FC-ZFH and (c) FC-FH, in which the sample was first cooled with steps of 10 K to the liquid nitrogen temperature. At this temperature an electric field switching corresponding to the regime was performed, and the measurements were carried out with the same steps to room temperature. The temperature dependences of the shift, intensity, and half-width of the QLA phonon obtained after processing the spectra were analyzed within the framework of existing E–T phase diagrams and modern concepts of the physics of relaxor ferroelectrics.

References

[1] R. Sommer, N.K. Yushin, and J.J. van der Klink, *Phys. Rev.*, vol B48, 13230 (1993)
[2] E.V. Colla, E.Y. Koroleva, N.M. Okuneva, and S.B. Vakhrushev, *Phys. Rev. Lett.*, vol 74, 1681 (1995)
[3] Z.-G. Ye, *Key Engineering Materials*, vol 155&156, 81 (1998)
[4] S.G. Lushnikov, J.-H. Ko, and Seiji Kojima, *JETP Lett.*, vol 79, 555 (2004)

Delay Time of Phase Transition in Polar Phase in Relaxors

R. F. Mamin*

Zavoisky Physical-Technical Institute of FIC KazanSC RAS,
Sibirskii tract 10/7, Kazan, Russia
*Corresponding Author: mamin@kfti.knc.ru

Relaxor ferroelectrics with diffuse phase transitions, commonly called relaxors, have been subject to intensive research. Interest in these compounds is determined by a combination of ferroelectric, piezoelectric and optical properties and the ability to use these materials in optoelectronics and data storage systems. The distinguishing features of relaxors are a strongly diffuse maximum in the temperature behavior of permittivity, the shift of this maximum toward higher temperatures with rising measuring field frequency, and a strong frequency dependence of permittivity at very low frequencies.

Numerous experimental data show that the properties of the low-temperature phase depend on the history of samples, so nonergodic behavior is observed in the low-temperature phase [1]. In an applied electric field, the transition to a uniform state of polarization is observed in the low-temperature phase after zero-field cooling. Such a phase transition was observed in [1] after a sufficiently long delay time had passed from the beginning of field application. The dependences of delay time t_0 of the phase transition on temperature T and external electric field E were established. The observed regularities have been discussed using an approach which had be developed earlier [2] on the basis of the model of diffuse phase transition in the system with defects [3]. It is shown that in the frame of that approach the delay phase transition in polar phase in relaxor could be explain if the dynamic of electron system would be take in consideration [2]. For examine that model we investigate the effect of illumination on the delay time t_0 of the phase transition in $PbMg_{1/3}Nb_{2/3}O_3$ in [110] orientation. It is show that delay time t_0 of the phase transition becomes shorter when the sample is illuminated.

The reported study was partially supported by RFBR, research project No. 18-02-00675a.

References

[1] E. V. Colla, E. Yu. Koroleva, N. M. Okuneva, S. B. Vakhrushev, *PRL* **74**, 1681–1684 (1995).
[2] R. F. Mamin, R. Blinc, *Physics of the Solid State* 45, 942–945 (2003).
[3] R.F. Mamin, *Physics of the Solid State* 43, 13141319 (2001).

Dynamics of boson peak and fracton in glass and single crystal

T. Mori,[1,*] Y. Fujii,[2] A. Koreeda,[2] S. Kojima[1]

[1]Division of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki, Japan
[2]Department of Physical Sciences, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga, Japan
[*]Corresponding Author: mori@ims.tsukuba.ac.jp

In disordered materials, the boson peak (BP) is a universal feature of atomic vibration observed in the terahertz region and it is one of the unresolved issue in glass physics [1]. The BP closely relates to the low temperature universal thermal properties of glassy system which is also unsolved problem. Meanwhile, for polymer glass, it is recognized that the so-called fracton [2] excitation universally appear in the frequency range above the BP frequency, whose ascription is attributed to self-similar connectivity of structural units.

Interestingly, such universal dynamics of disordered materials also appears even in some particular single crystals [3,4]. As revealed by recent studies, the BP behavior appears in single crystals, such as some thermoelectric materials [3,5] and pure relaxor materials [6], where the off centering rattling phonon modes may play the crucial role in the contribution of the universal glass-like thermal properties in the single crystals [5]. In addition, the fracton in single crystal appears in the pure relaxor substances [4,7], by the connection of the dipole-dipole moments having a fractal structure, which will be a key to explain the huge dielectric response.

In this paper, we show how to detect these universal excitations by terahertz spectroscopy and inelastic light scattering [8], and discuss the difference of behaviors of BP and fracton between actual glass materials and single crystals.

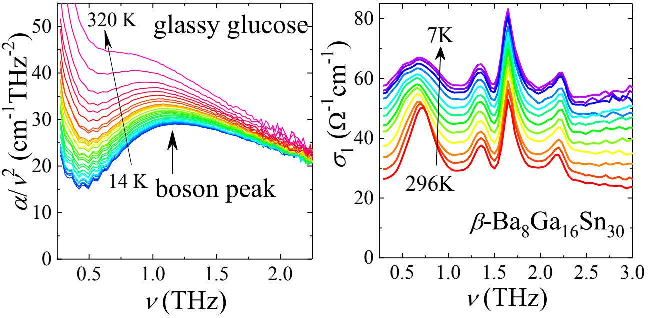

Figure 1. Boson peak in glassy material (left: glassy glucose) [8] and off-center rattling phonon in single crystal (right: thermoelectric material β-Ba$_8$Ga$_{16}$Sn$_{30}$) [3] detected by THz spectroscopy. The lowest optical phonon of β-Ba$_8$Ga$_{16}$Sn$_{30}$ corresponds to the boson peak in glassy material.

References

[1] T. Nakayama, *Rep. Prog. Phys.* **65**, 1195 (2002)
[2] S. Alexander and R. Orach, *J. Phys. (Paris), Lett.* **43**, 625 (1982)
[3] T. Mori et al., *Phys. Rev. Lett.* **106**, 015501 (2011)
[4] A. Koreeda et al., *Phys. Rev. Lett.* **109**, 197601 (2012)
[5] T. Takabatake et al., *Rev. Mod. Phys.* **86**, 669 (2014)
[6] M. Tachibana and E. Takayama-Muromachi, *Phys. Rev. B* **79**, 100104(R) (2009)
[7] S. Tsukada et al., *Sci. Rep.* **7**, 17508 (2017)
[8] M. Kabeya, *Phys. Rev. B* **94**, 224204 (2016)

Quenching behavior of electrical and piezoelectric properties on Bi-based Perovskite Ceramics

H. Nagata, T. Miura and T. Takenaka

[1]Department of Electrical Engineering, Faculty of Science and Technology,
Tokyo University of Science, Yamazaki 2641 Noda, Chiba, Japan
*Corresponding Author: h-nagata@rs.noda.tus.ac.jp

Bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT), is a perovskite-structure ferroelectric ceramic with a rhombohedral symmetry (*R3c*) at room temperature (RT). BNT-based solid solutions have relatively high piezoelectric properties in lead-free piezoelectric materials and enable the easy preparation of dense ceramics, which is an advantage for manufacture; therefore, BNT-based solid solutions have attracted attention as lead-free piezoelectric ceramics. However, BNT has the problem of having a low depolarization temperature T_d of approximately 180 ºC, resulting in a working temperature below T_d. In particular, the morphotropic phase boundaries (MPBs) of BNT-based solid solutions have a low T_d of approximately 100 ºC, even though an MPB has excellent piezoelectric properties. That is, the piezoelectric constant and T_d show a trade-off relationship, so that the elevation of T_d without the deterioration of piezoelectric activities is strongly demanded for practical piezoelectric applications using BNT-based ceramics.

Recently, quenching treatment helped to enlarge, rhombohedral lattice strain, $|90^\circ\text{-}\alpha|$ and gave us BNT ceramics with higher T_d[1]. As for BNT, it has been reported that T_d of Li-substituted BNT-based solid solution, $(Bi_{0.5}Na_{0.5(1\text{-}x)}Li_{0.5x})TiO_3$ (abbreviated as BNLT100*x*, respectively), increased at the rhombohedral composition[2]. In this study, therefore, quenching effects for electrical properties of BNLT100*x* ceramics were investigated to obtain higher T_d.

BNLT100*x* (x = 0.02, 0.04, 0.08) ceramics were prepared by a conventional ceramic fabrication process. Quenching procedure during a sintering process was done at 1100˚C for each composition. Piezoelectric properties were calculated using a resonance and antiresonance method. The T_d were determined by the temperature dependence of dielectric and piezoelectric properties.

Figure 1 shows depolarization temperatures T_d of OF- and q-BNLT100*x* as a function of Li-substituted amount *x*. The T_d of BNLT8 quenched at 1100˚C reached 237˚C, and it was almost 70˚C higher than that prepared by the ordinary cooling process. We also found that, from the measurement of resonance and antiresonance method, an electromechanical coupling factor k_{33} of both ordinary fired BNLT100*x* and quenched one were almost the same value. So there is no degradation of piezoelectric properties in quenching procedure compared to ordinary cooling process. In addition, from the XRD patterns, $|90^\circ\text{-}\alpha|$ of the quenching samples were larger than that of ordinary firing. From this result, we found that Td is related to the magnitude of the $|90^\circ\text{-}\alpha|$ for BNLT100*x*, a trend which is similar in pure BNT[1].

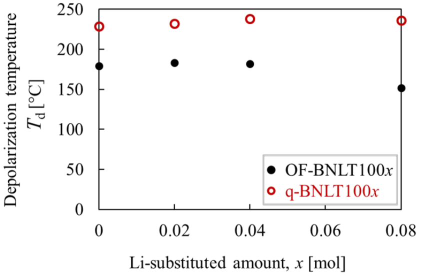

Figure 1 Depolarization temperature T_d of OF- and q-BNLT100*x* as a function of Li-substituted amount *x*.

[1] H.Muramatsu, H.Nagata, and T.Takenaka, *Jpn. J. Appl. Phys.*, **55** (2016) 10TB07.

[2] Y.Hiruma, K.Yoshii, H.Nagata, and T.Takenaka, *Jpn. J. Appl. Phys.*, **103** (2008) 084121.

Ultrafast Control of Polar Materials Studied by Time-resolved Linear and Nonlinear Spectroscopy

Yoichi Okimoto[1,*]

[1]Department of Chemistry, Tokyo Institute of Technology

[*]Corresponding Author: okimoto.y.aa@m.titech.ac.jp

Solid materials with a polar structure have widely been studied so far, because the polar materials, including ferroelectrics, show various interesting mechanical, electrical, and optical phenomena originated from the lack of the inversion symmetry. Very recently, some studies to optically control the polar natures have been reported in some polar materials[1,2] especially using femtosecond laser pulses. In this presentation, we demonstrate our recent trials of ultrafast control of the polarity in an organic ferroelectrics in terms of femtosecond time-resolved spectroscopy.

The target material is a proton-mediated organic co-crystal, [H-dppz][Hca] (dppz = 2,3-di(2-pyridinyl)pyrazine, Hca = chloranilate). This material is an organic ferroelectrics at room temperature (T_c=402 K) developed by Horiuchi *et al.* [3] We irradiated the co-crystal with a femtosecond pulse whose photon energy is around 1 THz (about 30 cm^{-1}) and investigated variation of the intensity of the second harmonic (SH) light generated from the polar co-crystal. The time profile of observed change of SH intensity exactly follows that of the applied THz pulse and the magnitude of the relative SH change reached up to 15 %, indicating ultrafast change of the ferroelectricity.

By contrast, with irradiating the co-crystal using a pulse covered mid-infrared (around 40 THz) photon energy region, a component proportional to square of the applied field was observed in the time profile of the SH change, in addition to a linear component proportional to the field as observed in the 1THz excitation. The result suggests that the change of the polarity of the co-crystal cannot follow the optical electric field of 40 THz. In this presentation, I'd like to talk about the microscopic origin of the SH change by light as well as the ultrafast dynamics of the ferroelectric nature of the co-crystal on the time scale of 10-1000 fs.

This work was done in collaboration with T. Umanodan, K. Yokoyama, T. Ishikawa, S. Koshihara, K. Oka, M. Azuma (Tokyo Tech), H. Hirori, K. Tanaka (Kyoto univ.) and J. Itatani (Univ. of Tokyo).

References

[1] T. Umanodan, Y. Okimoto *et al.*, J. Phys. Soc. Jpn. **84**, 073707 (2015).
[2] Y. Okimoto *et al.*, Phys. Rev. Applied **7**, 064016 (2017).
[3] S. Horiuchi *et al.*, J. Am. Chem. Soc. **135**, 4492 (2013).

Revealing hidden structural instabilities in fluoroperovskites ABF_3

R.V. Pisarev[1*], R.M. Dubrovin,[1] S.A. Kizhaev,[1] P.P. Syrnikov,[1] and J.-Y. Gesland[2]

[1]Ioffe Institute, RAS, 194021, St. Petersburg, Russia
[2]Faculté des Sciences et Techniques, Le Mans Université, 72085 Le Mans Cedex 9, France
[*]Corresponding Author: pisarev@mail.ioffe.ru

The search for new multiferroics with efficient coupling between lattice, orbital and magnetic degrees of freedom is a vital topic in the present day condensed matter physics promising large potential for various device applications. There is skepticism that fluoroperovskites ABF_3 are of any interest with regard to the multiferroicity, but recent theoretical papers predict the existence of ferroelectric instability in cubic fluoroperovskites [1,2]. In order to test these predictions, we performed the studies of temperature (5÷400 K) and frequency (10÷1000 kHz) dependences of the complex dielectric permittivity $\varepsilon(T)$ in a large group of fluoroperovskites with different structures, tolerance factors *t,* and phase transitions.

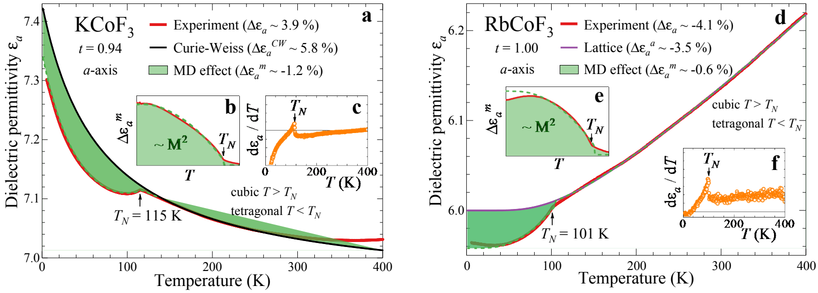

Figure 1. Dielectric permittivity $\varepsilon(T)$ in cubic fluoroperovskites $KCoF_3$ and $RbCoF_3$.

All studied fluoroperovskites revealed different temperature behavior of $\varepsilon(T)$. For example, $KCoF_3$ and $RbCoF_3$ demonstrated drastically different behavior of $\varepsilon_a(T)$ (see Fig. 1) though they both possess similar structural, magnetic and other properties. In $RbCoF_3$, $\varepsilon_a(T)$ shows a conventional behavior for ionic crystals and can be well fitted by the Einstein-type function above T_N (see Fig. 1d). In marked contrast, in $KCoF_3$ the main trend is the increase of $\varepsilon(T)$ with decreasing temperature which is well described by the Curie-Weiss function up to T_N. Though the value t=0.94 for $KCoF_3$ is exactly in the middle of the cubic structure stability range (0.88<t<1.00) the growth of $\varepsilon(T)$ clearly evidences a "hidden" structural instability. In contrast, $RbCoF_3$ (t=1.00) falls exactly at the boundary between the cubic and hexagonal structures.

These observations allowed us to suppose decisive importance of the tolerance factor t in controlling structural stability or instability of fluoroperovskites. This statement was remarkably supported by the study of other fluoroperovskites. Thus, the hexagonal $CsMnF_3$ with the largest value of t=1.03 shows temperature behavior of $\varepsilon(T)$ similar to that in $RbCoF_3$. Spectacular results were obtained in the orthorhombic $NaMnF_3$ with the lowest tolerance factor t=0.78. A dramatic growth of $\varepsilon(T)$ by 170 % takes place in this material at low temperatures which is accompanied by the largest ever observed magnetodielectric effect of 26 %. These findings allow us to name $NaMnF_3$ a novel *magnetic incipient ferroelectric* which can potentially be transformed into a multiferroic state using chemical and strain engineering [2].

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References

[1] A.C. Garcia-Castro et al., Phys. Rev. B89, 104107 (2014).
[2] A.C. Garcia-Castro et al., Phys. Rev. Lett. 116, 117202 (2016).

Epitaxial growth of ferroelectric HfO_2 thin films

T. Shimizu,[1,*] T. Mimura,[1] and H. Funakubo[1, 2]

[1]School of Materials and Chemical Technology, Tokyo Institute of Technology,
4259 Nagatsuta, Midori, Yokohama, 226-8502, Japan
[2]Materials Research Center for Element Strategy, Tokyo Institute of Technology,
4259 Nagatsuta, Midori, Yokohama, 226-8502, Japan
[*]Corresponding Author: shimizu.t.aa@m.titech.ac.jp

HfO_2 ferroelectric materials, which was recently discovered, gives great opportunities to develop novel functional device with ferroelectricity because of excellent compatibilities with current semiconductor technologies. This new type materials exhibits ferroelectricity even in a quite thin film below 15 nm, in which the ferroelectricity is hardly expected with conventional perovskite and its related materials. The ferroelectricity of HfO_2-based materials originates from metastable and polar orthorhombic phase shown in Fig. 1. It is essential to investigate crystal structure of HfO_2 orthorhombic phase because the ferroelectricity closely relates to crystal structures. The epitaxial thin film is suitable for investigation of nature of ferroelectricity as well as crystal structure for the materials of which single crystals is not readily obtained. Conversely, almost previous study on HfO_2-based ferroelectric films were performed using polycrystalline films. Furthermore these films often includes parasitic monoclinic or tetragonal phases. Hence the discussion on crystal and domain structure is quite limited except for studies with high resolution transmission microscopes (TEMs). We had succeeded in growth of epitaxial and uniaxial film of HfO_2 films by pulsed laser deposition techniques and these results can be found in several literatures.

The epitaxial HfO_2 films were grown on Yttria-stabilized Zirconia (YSZ) single crystalline substrates or Sn-doped In_2O_3 (ITO) buffered YSZ substrates. Our study on epitaxial growth of the films by ceramics targets with various Y concentrations, orthorhombic films are reproducibly grown in case with a 7%$YO_{1.5}$-substituted HfO_2 target. Figure 2 (a) shows scanning TEM images of 7%$YO_{1.5}$-substituted HfO_2 films on ITO buffered YSZ substrates. This images shows that 7%$YO_{1.5}$-substituted HfO_2 films were epitaxially grown on underlying ITO layer and also the films have orthorhombic structure because inset magnified image agree with simulated one for orthorhombic phase. Figure 2(b) shows ferroelectric hysteresis loops measured for 7%$YO_{1.5}$-substituted HfO_2 films on ITO/(110)YSZ substrate. By taking account of domain configuration, we can estimate spontaneous polarization of around 45 μC/cm² agreeing with the first principle calculations. Other our recent results for structural investigations and ferroelectric properties will be discussed in the presentation.

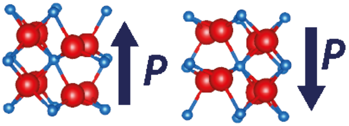

Fig. 1 Crystal structure of ferroelectric orthorhombic HfO_2.

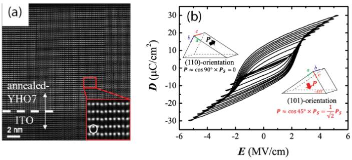

Fig. 2 (a) Scanning TEM image of 7%$YO_{1.5}$ substituted HfO_2 epitaxial film on ITO//YSZ substrate. (b) D-E hysteresis curve measured on 7%$YO_{1.5}$ substituted HfO_2/ ITO//YSZ stacks with Pt top electrode.

References

[1] T. S. Böscke, et al., APL, 99, 102903–1–4 (2011).
[2] M. H. Park, et al., Adv. Mater., **27,** 1811–1831 (2015).
[3] T. Shimizu, et al., *APL*, **107**, 032910–1–5 (2015).
[4] K. Katayama, et al., *JAP*, **119**, 134101–1–7 (2016).
[5] M. Mimura, et al., *APL*, **109**, 052903 (2016).K. Katayama et al., *APL*, **109**, 112901 (2016).
[6] T. Shimizu et al., Sci. Rep. **6,** 32931 (2016).
[7] S. Clima et al., *APL*, **104**, 092906 (2014).

Domain Shape in Uniaxial Ferroelectrics

V. Ya. Shur

School of Natural Sciences and Mathematics, Ural Federal University, 51 Lenin Ave,
620000 Ekaterinburg, Russia
Corresponding Author: vladimir.shur@urfu.ru

The variety of domains shapes appeared in uniaxial ferroelectrics will be presented, classified and described systematically. The obtained experimental results will be discussed using unified kinetic approach based on the analogy between domain structure evolution and phase growth during first-order phase transformation.

The classical theoretical approach predicted only the regular polygonal shape of isolated domains defined by crystal symmetry [1,2]. Recent systematic investigations of domain shapes allowed revealing wide shape variety which can be divided into several groups: (i) circular shapes, (ii) regular polygons, (iii) irregular polygons, (iv) irregular shapes. The kinetic approach to domain growth based on step (pair of kinks) generation and kink motion has been used for explanation of all obtained shapes [3]. The nucleation probabilities are determined by the local value of the sum of the external field and partially screened (residual) depolarization field. The bulk screening allows stabilizing any metastable domain shape even with charged domain walls.

The key role of the bulk screening retardation in formation of self-assembled nanodomain structures is demonstrated. The domain shape complication due to screening ineffectiveness was demonstrated experimentally and by computer simulation [3]. Two limiting variants of the step nucleation have been considered: (a) stochastic with equiprobable position of nucleation sites, (b) determined with step generation at fixed points and anisotropic kink motion.

Stochastic nucleation leads to formation of the circular domains. Determined nucleation stimulated formation of the regular polygonal domains. The convex polygons with walls parallel to the main crystallographic axis appeared for effective screening: (a) hexagons for C_{3v} symmetry (lithium niobate, lithium tantalate and lead germanate), (b) squares for C_4 symmetry, (strontium-barium niobate), (c) rectangles for C_2 symmetry (potassium titanyl phosphate [4]). Screening retardation leads to formation of the irregular polygons and stars [5]. The artificial nucleation sites allowed to decrease the number of polygon vertexes. The fast restoration of the initial hexagon and rhombus shapes after domain merging was attributed to formation of the short-lived super-mobile walls with high kink concentration [6].

The stochastic nucleation obtained at the elevated temperatures leads to lack of the domain shape stability effect and open the way to formation of the complicated fractal and dendrite domain shapes [7,8]. The dendrite (snowflakes) domain structures can be created by several mechanisms: (i) appearance of the isolated domains (discrete switching) with subsequent merging, (ii) lack of the domain shape stability, (iii) domain shrinkage under the action of the pyroelectric field or spontaneous backswitching, (iv) domain growth at the elevated temperature in the crystals covered by artificial dielectric layer [9].

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References

[1] V. Gopalan, V. Dierolf, D.A. Scrymgeour, *Annu. Rev. Mater. Res.,* 37, 449–489 (2007)
[2] L. Tian, D.A. Scrymgeour, V. Gopalan, *J. Appl. Phys.,* 97, 114111 (2005)
[3] V.Ya. Shur. *J. Mater. Sci*., 41, 199–210 (2006)
[4] V.Ya. Shur et. al., *Appl. Phys. Lett*., 109, 132901 (2016)
[5] A.I. Lobov et. al., *Ferroelectrics*, 341, 109–116 (2006)
[6] V.Ya. Shur et. al., *Ferroelectrics*, 360, 111–119 (2007)
[7] V.Ya. Shur et. al., *J. Appl. Phys*., 112, 104113 (2012)
[8] V.Ya. Shur et. al., *J. Appl. Phys*., 119, 144101 (2016)
[9] V.Ya. Shur, A.R. Akhmatkhanov, *Phil. Trans. R. Soc.* A, 376, 20170204 (2018)

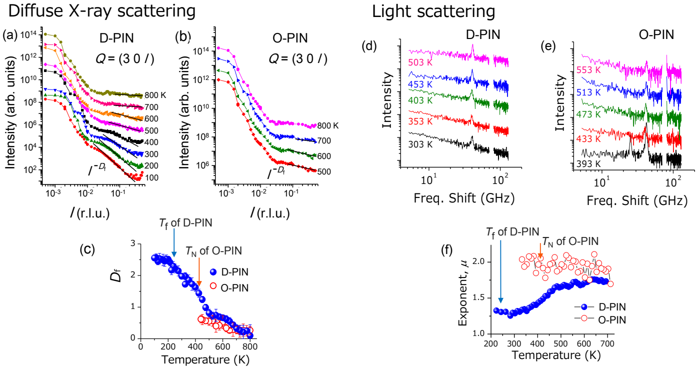
Inhomogeneity and ferroelectric instability in $Pb(In_{1/2}Nb_{1/2})O_3$ by changing In/Nb-arrangement

S. Tsukada,[1*] K. Ohwada,[2] H. Ohwa,[3] S. Mori,[4] S. Kojima,[5] N. Yasuda,[3]
H. Terauchi,[6] and Y. Akishige[7]

[1] Faculty of Education, Shimane University, Matsue, Shimane, Japan
[2] Synchrotron Radiation Research Center, KPSI, QST, Sayo, Hyogo, Japan
[3] School of Engineering, Gifu University, Gifu, Japan
[4] Department of Materials Science, Osaka Prefecture University, Sakai, Osaka, Japan
[5] Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan
[6] School of Science, Kwansei Gakuin University, Sanda, Hyogo, Japan
[7] Office of the Vice President for Research, Shimane University, Matsue, Shimane, Japan

*Corresponding Author: tsukada@edu.shimane-u.ac.jp

Role of inhomogeneity in phase transitions is important issue to be solved. We have approached this issue in relaxors and ferroelectrics by light spectroscopy and X-ray diffraction techniques.[1] In the present talk, we review our previous works and we report investigations of the phase transitions in single crystals of $Pb(In_{1/2}Nb_{1/2})O_3$ via changing the In/Nb-arrangement in the B site of the ABO_3 perovskite structure. $Pb(In_{1/2}Nb_{1/2})O_3$ is an intriguing system in which the inhomogeneous structure and dielectric properties can be controlled by thermal treatment. We studied the static properties using synchrotron diffuse X-ray scattering (Figs. a-c) and the dynamic properties of the structure using inelastic light scattering (Figs. d-f). These properties depend on the degree of randomness with which the B site is occupied. When the distribution of occupied In/Nb sites is regular (ordered), the antiferroelectric phase is stabilized by a change in the collective transverse-acoustic wave, which suppresses long-range ferroelectric order and the growth of the inhomogeneous structure. However, when the B site is occupied randomly (disordered), a fractal structure grows as the temperature decreases below $T^* \sim 475$ K, and nanosized ferroelectric domains are produced by the percolation of self-similar and static polar nanoregions.[2]



Figs. a-c: Diffuse scattering intensities along the transverse [001] direction near the 300 Bragg peak for Disordered $Pb(In_{1/2}Nb_{1/2})O_3$ (D-PIN) and Ordered PIN (O-PIN). The fractal dimensions determined by fitting clearly show different temperature dependence between D-PIN and O-PIN. Figs. d-f: Light-scattering spectra from D-PIN and O-PIN observed in the backscattering geometry under cross-nicol configuration. The spectra were converted to reduced intensity and the determined exponent μ also shows different temperature dependence between D-PIN and O-PIN.

References

[1] For example, S. Tsukada, *et al.* Phys. Rev. **87**, 014101 (2013)./ Phys. Rev. **97**, 024116 (2018).
[2] S. Tsukada, *et al.* Sci. Rep. **7**, 17508 (2017). / K. Ohwada, *et al.* Phys. Rev. B **77**, 94136 (2008).

Nano- and Microdomain Engineering in $LiNbO_3$ Thin Films and Optical Waveguides

T. R. Volk and R. V. Gainutdinov

Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics" of RAS,
Moscow, Russia
*Corresponding Author: volk-1234@yandex.ru

Nano- and microdomain patterns have attracted increased attention in view of their applicability, in particular for the nonlinear-optical frequency conversion and ferroelectric high-density nonvolatile memory. We present our results on investigations of specified nano- and microdomain patterns written in thin (300–500 nm thick) ion-sliced $LiNbO_3$ single-crystal films composing LNOI ($LiNbO_3$-on-insulator) sandwiches and in Ti-indiffused $LiNbO_3$ optical waveguides. The patterns were fabricated by dc-voltages of an AFM tip and electron-beam irradiation. All written patterns are completely stable in real time.

In LNOI sandwiches 1D and 2D domain patterns of specified design were written by AFM method [1–3]. In the written patterns a static conduction on the domain walls (DWC) was found, which exceeds the conductance of surrounding domains not less than by five orders of magnitude. DWC shows no decay in real time; its stability is owing to the stability of written domains. The effects of DWC on the domain formation, in particular on the kinetics of domain motion, domain equilibrium shape and limiting discreteness of nanosized domain patterns were found. Writing by AFM-tip voltages in ion-sliced $LiNbO_3$ films permits the manipulation of the sizes and shapes of written stable patterns in wide limits from nanosized domain dots to large (of tens of microns) arbitrarily-shaped patterns by means of varying the exposure conditions and inter-domain spacing.

Based on the approach developed for electron-beam domain writing in $LiNbO_3$ crystals ([4, 5] and references therein), domain gratings were fabricated in Ti-indiffused planar and ridge optical waveguides on $LiNbO_3$.

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References

[1] R. V. Gainutdinov, T. R. Volk and *H. H. Zhang, Appl. Phys. Lett.,* 107, 162903 (2015)
[2] T. R. Volk, R. V. Gainutdinov, and H. H. Zhang, *Appl. Phys. Lett.,* 110, 132905 (2017)
[3] T. R. Volk, R. V. Gainutdinov, and H. H. Zhang, *CRYSTALS*, 7, 137 (2017)
[4] T. R. Volk, L. S. Kokhanchik, R. V. Gainutdinov, Ya. V. Bodnarchuk, and Feng Chen, *Ferroelectrics*, 500, 129–140 (2016)
[5] L. S. Kokhanchik, Ya. V. Bodnarchuk, and T. R. Volk, *J. Appl. Phys.*,122, 104105 (2017)

Restoration of Soft Modes in Raman Spectra of Antiferroeelectric (Pb-La)(Zr-Sn-Ti)O_3 Ceramics

A. N. Vtyurin[1,2],* A. S. Krylov[1], S. N. Krylova[1], A. S. Oreshonkov[1,2],
Xiaoyong Wei[3], Yujun Feng[3], Ran Xu[3] and Tian Zhao[3]

[1]Kirensky Institute of Physics, Krasnoyarsk, 660036, Russia
[2]Siberian Federal University, Krasnoyarsk, 660041, Russia
[3]Electronic Materials Research Laboratory & Intl. Center for Dielectric Research,
Xi'an Jiaotong University, Xi'an, 710049, China
*Corresponding Author: vtyurin@iph.krasn.ru

Since their discovery in 1950s, PZT-type materials have been the most widely used piezoelectric ceramics[1]. With increasing Ti content above $x = 0.06$, the solid solution changes from antiferroelectric to ferroelectric. The six structural phases in the solid solution $Pb(Zr_xTi_{1-x})O_3$ have been observed at ambient pressure are an antiferroelectric phase for compositions near $PbZrO_3$ ($x < 0.06$), ferroelectric low-temperature and high-temperature rhombohedral phases for most Zr-rich alloys, a monoclinic ferroelectric phase near (50 % Zr)/(50 % Ti) composition, a tetragonal ferroelectric phase for Ti-rich alloys, and a cubic paraelectric phase for all compositions at sufficiently high temperature. Recently it was found by inelastic and diffuse X-ray scattering techniques[2] that in pure lead zirconate phase transition from cubic into antiferroelectric phase is driven by phonon soft mode condensation. Here we report low frequency Raman scattering study of phase transition from cubic into antiferroelectric phase in $(Pb_{0.97}La_{0.02})(Zr_{0.864}Sn_{0.04}Ti_{0.096})\ O_3$ composition.

Raman spectra have been obtained with Jobin Yvon — Horiba T-64000 triple spectrometer with N2 cooled CCD matrix. Spectra were excited by Ar+ laser (514.5 nm, 500 mW). Data collection time was 600 s for one spectrum, temperature stabilization better than 0.1 K. To interpret results program package VASP was used for first principle simulations and LADY — for empirical simulations of lattice disorder effects.

The spectrum of higher temperature cubic phase consists of weak and extremely wide bands, as assumed to be in a highly disordered lattice and agrees with previous data[3]. Under cooling a set a new lines appears; their frequencies show only slight anomalies aside from normal temperature drift, while their widths increase very quickly coming to the transitions point from below. In particular low frequency mode at about 50 cm^{-1} exhibits strong maximum of its damping above 400 K (see Fig. 1).

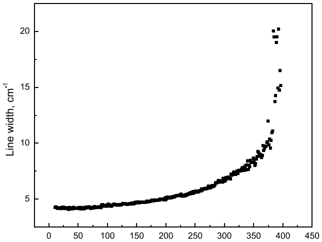

Figure 1. Line width vs. temperature for 50 cm^{-1} Raman line.

Results are discussed in terms of overdumped soft modes interacting via their dumpings at the phase transition.

References

[1] M. E. Lines, A. M. Glass. Principles and Application of Ferroelectrics and Related Materials. Clarendon Press, Oxford, 1977.
[2] A. K. Tagantsev, K. Vaideeswaran, S. B. Vakhrushev et al., *Nat. Communs*. 4, 2229, (2013).
[3] I. Jankowska-Sumara. *Phase Transit.* 87, 685 (2014).

Charge Screening Strategy for Controlling Domain Structure in Nano-scale Ferroelectric Systems

T. Yamada,[1,2*] D. Ito,[1] T. Sluka,[3] O. Sakata,[4,5] H. Funakubo,[5] T. Namazu,[6]
M. Yoshino,[1] N. Setter[3,7], and T. Nagasaki[1]

[1]Department of Energy Engineering, Nagoya University, Nagoya 464-8603, Japan
[2]PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan
[3]Ceramics Laboratory, Swiss Federal Institute of Technology-EPFL, Lausanne CH-1015 Switzerland
[4]Synchrotron X-ray Station at SPring-8 and Synchrotron X-ray Group, National Institute for Materials Science, Sayo 679-5148, Japan
[5]School of Materials and Chemical Technology, Tokyo Institute of Technology, Yokohama 226-8503, Japan
[6]Department of Mechanical Engineering, Aichi Institute of Technology, Toyota 470-0392, Japan
[7]Department of Materials Science and Engineering, Tel-Aviv University, Ramat Aviv, 69978, Israel

*Corresponding Author: t-yamada@energy.nagoya-u.ac.jp

Domain structure control in nano-scale ferroelectric systems has been considered invaluable for improving dielectric and piezoelectric responses. Despite the significant need to control the domain structure, approaches for this are limited. For thin films, the most common approaches are to vary the orientation and strain of the films by selecting an appropriate substrate. However, the imperfect charge screening at the interface and/or surface, which generates a depolarizing field, can also affect the domain structure. This influence is larger for smaller structures.

In this presentation, we focus on such an influence in ferroelectric nanorods, the dimensionality of which is different from that of thin films. We fabricated epitaxial tetragonal $Pb(Zr_{0.35}Ti_{0.65})O_3$ (PZT) nanorods by two different methods: 1) partial etching of an epitaxial film on $SrTiO_3$ and Si substrates using a focused ion beam (hereafter, FIB-rods), and 2) self-assembled growth on $SrTiO_3$ substrates by pulsed laser deposition (PLD) at an elevated oxygen pressure (hereafter, PLD-rods).

Using the FIB-rods with different widths, the influence of imperfect charge screening on the domain structure was investigated by synchrotron X-ray diffraction (XRD) (Fig.1(a)). We found that the *c*-domain fraction in the PZT nanorods drastically increased with decreasing rod width (Fig.1(b)). The preferred formation of the *c*-domain in narrow rods can be rationalized in terms of the large depolarizing field in the *a*-domain. Indeed, the *a*-domain formation prevailed by depositing Pt on the sidewall of rods. Phase field simulations also supported the experimental observations (Fig.1(c)).

The self-assembled PLD-rods exhibited remarkably large piezoelectric response. The field induced lattice strain measured by synchrotron XRD showed that d_{33}^* of (001) rods was the same as that of single crystal and d_{33}^* of (111) rods was even larger than that of crystal. The former can be explained by the reduced substrate clamping in the nanorods. The latter implies that the imperfect charge screening facilitated the field-induced phase transition in the nanorods.

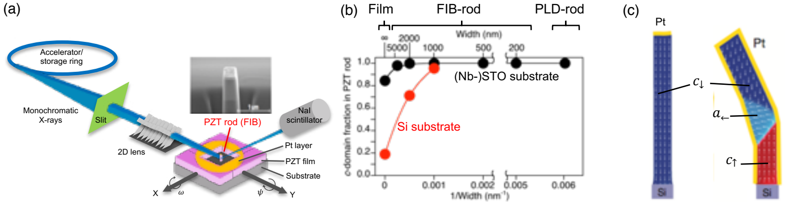

Figure 1. (a) schematic illustration of synchrotron XRD for measuring a FIB-rod, (b) *c*-domain fraction as a function of the inverse PZT rod width, and (c) phase field simulations for PZT rods with/without sidewall metallization.

References

T. Yamada et al., *Jpn. J. Appl. Phys.*, **54**, 10NA07 (2015), *IEEE Trans. Ultrason., Ferroelect., Freq. Control*, **63**, 1642 (2016), and *Sci. Rep.*, **7**, 5236 (2017).

Oral presentations

The Influence of Screening Efficiency on Domain Kinetics in KTP Single Crystals

A. R. Akhmatkhanov*, **E. M. Vaskina, M. A. Chuvakova, E. V. Pelegova, A. A. Esin, E. A. Gachegova, and V. Ya. Shur**

[1]School of Natural Sciences and Mathematics, Ural Federal University, 51 Lenin Ave.,
620000 Ekaterinburg, Russia
*Corresponding Author: Andrey.Akhmatkhanov@urfu.ru

The influence of screening efficiency on domain kinetics has been studied experimentally in potassium titanyl phosphate ($KTiOPO_4$, KTP) single crystals using complementary experimental methods.

KTP crystals with periodical ferroelectric domain structures are one of the most promising materials for nonlinear optics, in which the main types of nonlinear optical interactions have been demonstrated. It was shown previously in lithium niobate and lithium tantalate single crystals that the domain structure kinetics including the formation of tailored domain structures is tightly related to inefficiency of the bulk screening of residual depolarization field [1]. Despite the growing interest to formation of tailored regular domain structures in KTP the systematical study of influence of bulk screening efficiency on domain kinetics in these crystals is absent. In this work we present the study of influence of artificial dielectric layer and polarization reversal at elevated temperatures on domain structure evolution and kinetics of the domain walls in KTP crystals.

The studied KTP samples representing 1-mm-thick plates cut perpendicular to polar axis were grown by top-seeded solution method ("Crystals of Siberia", Novosibirsk). The bulk conductivity of the samples was $2 \cdot 10^{-7}$ $Ohm^{-1}cm^{-1}$ at room temperature. The artificial dielectric layer representing the photoresist layer AZ nlof2020 (AZ Microchemicals, Germany) was deposited on Z+ polar surface by spin coating. The polarization reversal with artificial dielectric layer was carried out using the liquid electrodes (saturated aqueous solution of LiCl). The polarization reversal at elevated temperatures was realized in the temperature controlled microscope stage THS600 (Linkam, UK). The circular ITO electrodes deposited by magnetron sputtering were used for external field application.

In situ visualization of domain kinetics during polarization reversal with artificial dielectric layer allowed revealing the formation and growth of large number of narrow domain streamers oriented along [010] direction. It was shown that the streamer velocity (6–60 mm/s) is about ten times higher than the velocity of macroscopic domain walls (2–5.5 mm/s). The visualization of static domain structure after partial polarization reversal by piezoresponse force microscopy has shown that the domain streamer is formed by [100] and [010]-oriented domain walls. The streamers are initially formed at Z- polar surface and then reached the Z+ polar surface. The minimal measured streamer width was about 500 nm and minimal distance between the neighboring streamers — about 100 nm. The measured switching currents were approximated using the modified Kolmogorov-Avrami approach taking into account the decrease on the growth dimensionality when the domain streamers reach the opposite electrode edge.

The polarization reversal in the temperature range from −70 °C up to 300 °C has shown that temperature increase leads to increase of the input of fast and superfast domain walls [2, 3] to the switching process leading to strong elongation of growing domains. The domain wall velocities were measured and corresponding activation energies were extracted from the experimental data.

The research was made possible in part by Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006) by RFBR (grant 16–02–00724), and by President of Russian Federation grant for young scientists (Contract 14.Y30.17.2837-MK). The equipment of the Ural Center for Shared Use "Modern nanotechnology" Ural Federal University was used.

References

[1] V. Ya. Shur, A. R. Akhmatkhanov, *Philos. Trans. R. Soc. A*, 376, 20170204 (2018)
[2] V.Ya. Shur, et al., *Appl. Phys. Lett.*, 109, 132901 (2016)
[3] V.Ya. Shur, et al., *Appl. Phys. Lett.*, 111, 152907 (2017)

Pre-transitional processes in antiferroelectric lead zirconate doped by Ti studied by diffuse and inelastic X-ray scattering

D. A. Andronikova[1,2], Yu. A· Bronwald[1,2], R. G· Burkovsky[2], I. N· Leontiev[3], N. G. Leontiev[4], A. Bosak[5], D. Chernyshov[6], A. Q. R. Baron[7], A. V. Filimonov[2] and S. B.· Vakhrushev [1,2]

[1]Ioffe Institute, 26 Polytechnicheskaya, St Petersburg, Russia
[2]Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya, SPb, Russia
[3]Southern Federal University, ul. Bolshaya Sadovaya 105/42, Rostov-on-Don, Russia
[4]Don State Agrarian University, ul. Lenina 21, Zernograd, Rostov oblast, Russia
[5]European Synchrotron Radiation Facility, BP 220, Grenoble Cedex, France
[6]Swiss-Norwegian Beamlines, ESRF, BP 220, Grenoble Cedex, France
[7]SPring-8, RIKEN and JASRI, 1–1–1 Kouto, Sayo, Hyogo 679, Japan
*Corresponding Author: andronikova.daria@gmail.com

Lead-zirconate titanate ($PbZr_{1-x}Ti_xO_3$, PZT) is one of the most actively studied and widely used ferroelectric materials. One of the reasons of the interest is a complex phase diagram of lead zirconate and lead titanate solid solution, which defines variety of physical properties and crystal structures depending on titanium concentration. Other reasons of popularity are high piezolelectric properties, demonstrated by PZT around morthotropic phase boundary [1], and prospects of application of antiferrolectric properties [2], demonstrated by PZT with low Ti concentration.

Pure lead zirconate (x=0) is the prototypical antiferroelectric material. Between the cubic perovskite paraelectric phase and the antiferroelectric phase, in the narrow temperature range, intermediate ferroelectric phase exists [3]. Addition of titanium increases the temperature range of stability of this phase. Cubic-to-intermediate phase transition is accompanied by doubling of the cell parameters of the paraelectric cubic lattice along two directions [4] and results in the appearance of M-superstructure with coordinate (H±1/2 K±1/2 0) in the diffraction pattern. Observation of additional satellites around M-point by electron diffraction [4] results in conclusion about complex domain pattern, characterized by antiphase domain boundary in lead displacement.

Recent studies [5, 6] of pure lead zirconate reveals complex pattern of dynamical correlations in paraelectric phase. Diffuse scattering distribution indicates disordering of oxygen octahedral tilts and Pb displacements is shown in the high-temperature cubic phase. To study temperature behavior of these correlations X-ray diffuse scattering measurements have been done in wide temperature range in PZT with small titanium concentration ($x < 0.04$). To characterize dynamical origin of DS lattice dynamics have been studied using inelastic X-ray scattering. Obtained temperature evolution of DS and pre-transitional dynamical peculiarities will be shown in presentation and discussed in the context of mode coupling.

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References

[1]. G. H. Haertling, Journal of the American Ceramic Society 82(4), 797 (1999).
[2] K. M. Rabe, Functional metal oxides: New science and novel applications, (Wiley-VCH Verlag GmbH & Co.)
[3] Michiyoshi Tanaka, et.al.Japanese Journal of Applied Physics, 21(2R):291, 1982.
[4] J Ricote, et.al. Journal of Physics: Condensed Matter, 10(8):1767, 1998.
[5] M. Pasciak et.al. Phase Transitions, 2014
[6] Zhang N., et.al. J. Appl. Cryst. (2015). 48, 1637–1644 1.

Polarization Switching in Crystals and Films of 2-methylbenzimidazole

E. V. Balashova[1,*], **B. B. Krichevtsov**[1], **F. B. Svinarev**[1], **G. A. Pankova**[2],
N. V. Zaitseva[1], **A. V. Ankudinov**[1,3], **G. A. Lityagin**[4]

[1]Ioffe Institute, Politechnicheskaya 26, Saint Petersburg, Russia
[2]Institute of macromolecular compounds, Saint Petersburg, Russia
[3]ITMO University, Saint Petersburg, Russia
[4]Peter the Great St. Petersburg polytechnic University, Saint Petersburg, Russia
[*]Corresponding Author: balashova@mail.ioffe.ru

Recently, a number of new organic and semi-organic ferroelectrics with high spontaneous polarization values have been discovered [1, 2]. Crystals of a chemically inert single-component organic ferroelectric of 2-methylbenzimidazole $C_8N_2H_8$ (MBI) [1] having a pseudotetragonal symmetry of the $P4_2/n$ (Pn) group looks promising because the spontaneous polarization is Ps $\cong 5$ µC/cm^2 [1], polarization switching takes place for different orientations of electric field, and the coercive field is much smaller than in polymers. The purpose of the work was to grow MBI crystals and films, to study their block and crystal structure, and the switching of polarization at different temperatures as a function of the frequency and amplitude of the electric field.

Crystals of 2-methylbenzimidazole were obtained by evaporation and by slow cooling method from a saturated solution of MBI powder in ethanol. The results of 3D-XRD analysis of crystal structure, study of mechanical properties by means of atomic force microscopy, as well as weak- and strong-signal dielectric response are presented. Simulations of the hysteresis loops are carried out within the framework of the special case of the Kolmogorov-Avrami-Ishibashi model. The temperature dependence the activation field E_a of domain wall motion, values of domain wall energy and energy barrier are presented.

MBI films were grown on the substrates of sapphire Al_2O_3, quartz SiO_2, bismuth germanate, glass by evaporation. As shown by optical and X-ray studies, the films have a texture consisting of blocks, which are split crystals of the spherulite type. Study of ferroelectric domains was performed by means of PiezoAFM in Kelvin mode. Dielectric hysteresis loops in MBI films are observed both for in-plane and out-of-plane orientation of the electric field. The value of switchable polarization increases with heating and decreases with increasing frequency. The maximum remnant polarization Pr ~ 4.5 µC/cm^2 (at T = 373 K) is close to that in a single crystals. The difference in the behavior of the hysteresis loops in MBI single crystals and films is associated with the specific structure of the blocks.

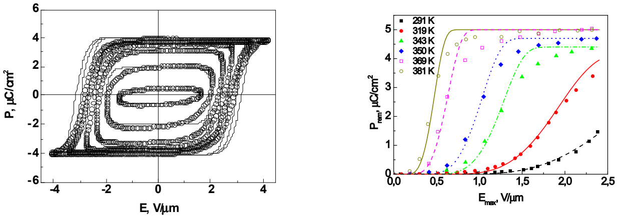
(a) (b)

Figure 1. (a) Dielectric hysteresis loops for different values of the amplitude of the applied field. (b) Dependence of remnant polarization P_{rem} on E_{max}. Lines — calculations, points — experiment.

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References

[1] Horiuchi S. et al. Nature Communications, **Vol.** 3, Art.2322 (2012).
[2] R. K. Saripalli, D. Swain, S. Prasad, et al. J. Appl. Phys., Vol. 121, p.114101 (2017).

Some aspects of electrocaloric effect in ferroelectrics

E. Birks*, A. Sternberg

Institute of Solid State Physics, University of Latvia, 8 Kengaraga str., Riga, Latvia
*Corresponding Author: birks@lanet.lv

In spite of exploding number of studies of electrocaloric effect (ECE) in ferroelectrics, published in the last decade, the clear answer about potential of the effect in applications, first of all cooling devices, in not clear. Such situation to big extend is related with weak common picture about mechanisms, contributing in electrocaloric effect in ferroelectric materials. In this presentation some common issues regarding evaluation and interpretation of electrocaloric effect are discussed.

The indirect method of evaluation, based on using of Maxwell relations, dominates in published studies of ECE. The method is apparently convenient, but requests clear understanding about nature of measured polarisation (P) since Maxwell relations are applicable only to temperature dependence of homogeneous intrinsic polarisation. This requirement is usually being left without attention, creating unconvincing results, where not only level but even sign of the calculated ECE are disputable [1].

The dependence of specific heat on applied electric field (E) is requested for indirect evaluation of temperature change (DT), created by ECE. However, the specific heat is determined as a change of temperature in result of supplied heat and is being measured in dependence on temperature at fixed electric field (usually E=0). The applicability of specific heat values, obtained in such a way, for adiabatic process, used in the case of ECE, is considered.

Since P and E are vectors, the role of mutual orientation between them on behaviour of ECE is considered. In simplest, one dimensional case it allows to describe DT(E) loop at bipolar pulses. In 3-dimensional case direction of E parallel and perpendicular to electric field in ferroelectric phase is distinguished. Absence of spontaneous polarisation can lead to negative ECE in perpendicular direction of E, even considering intrinsic polarisation.

Influence of electric field on disorder is frequently used in interpretation of electrocaloric effect [2]. This simple comprehension is inappropriate not only because order-disorder phenomena are not quite common to ferroelectrics of perovskite structure, but even in interpretation of entropy in general [3].

References

[1] E. Birks, M. Dunce, J. Peräntie, J. Hagberg, A. Sternberg, J. Appl.Phys., vol.121, 224102 (2017)
[2] Y.-B. Ma, N. Novak, J. Koruza, T. Yang, K. Albe, B.-X. Xu, Phys.Rev.B, 94, 100104(R) (2016)
[3] F. L. Lambert, J. Chem. Educ., vol.79, 187–192 (2002)

Percolation Behaviour in Lead-free Relaxor Ferroelectric Solid Solutions

A. A. Bokov[1,*] J. Zhuang,[2,1] W. Ren[2] and Z.-G. Ye,[1,2]

[1]Department of Chemistry & 4D LABS Simon Fraser University,
Burnaby, BC, V5A 1S6, Canada
[2]Electronic Materials Research Laboratory & International Center for Dielectric
Research, Xi'an Jiaotong University, Xi'an, 710049, China
[*]Corresponding Author: abokov@sfu.ca

The percolation theory is often used to interpret the sequence of phases which is observed in relaxors with the change of temperature. In relaxors the polar nanoregions growing upon cooling from paraelectric to relaxor phases are considered as finite percolation clusters which transform to infinite cluster at the percolation threshold temperature associated with the glassy freezing temperature, T_f, or the ferroelectric Curie temperature, T_C. In the present work we show that in relaxor ferroelectric solid solutions the percolation behavior can be observed not only for the size of polar clusters as a function of temperature, but also for the size of compositional clusters as a function of concentration of ferroactive ions. Using the experimental techniques of x-ray diffraction, dielectric spectroscopy, piezoresponse force microscopy (PFM) and the measurements of polarization-field hysteresis loops, we studied the solid solutions of classical perovskite ferroelectric (1-x)$BaTiO_3$ – x$ABO_3$where ABO_3 =$BaZrO_3$, $BaSnO_3$, $BaHfO_3$, and $DyFeO_3$. The analysis of experimental data based on the percolation theory revealed the existence of a critical concentration, x_c, which is larger than the relaxor-to-normal ferroelectric crossover concentration and above which the infinite percolation cluster and the related relaxor phase cannot be developed. The temperature of the transition into the relaxor ferroelectric cluster state was found to follow the critical behavior $T^*\propto(x_c - x)^{\xi}$ with the critical exponent $\xi \approx 0.5$. The characteristics of polar clusters are estimated from the PFM data and the electric field and frequency dependences of polarization.

Chemical and hydrostatic pressure effects on phase transitions in $PbHfO_3$

R. G. Burkovsky,[1,*] D. A. Andronikova,[2] I. A. Bronwald[1], G. A. Lityagin[1], M. A. Knjazeva[1], A. Bosak[3], K. Roleder[4] and A. V. Filimonov[1]

[1]Peter the Great Saint-Petersburg Polytechnic University, Politekhnicheskaya 29, St.-Petersburg, Russia
[2]Ioffe Institute, Politekhnicheskaya 26, St.-Petersburg, Russia
[3]European Synchrotron Radiation Facility
[4]Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland
[*]Corresponding Author: roman.burkovsky@gmail.com

Antiferroelectric perovskite crystals $PbZrO_3$ and $PbHfO_3$ are technologically important materials with complex picture of phase transitions [1,2]. Among the parameters that affect strongly the stability of particular phases are temperature, pressure and chemical doping. We report on our recent X-ray scattering experiments, aiming at pinpointing the similarities and differences between the effects of hydrostatic pressure and doping by Sn^{4+} ions of $PbHfO_3$. The latter can be understood as chemical pressure, since Sn^{4+} ions have slightly smaller ionic radii [3]. Specifically we have studied pure $PbHfO_3$ and $0.7PbHfO_3$-$0.3PbSnO_3$. It is shown that both hydrostatic and chemical pressure trigger the appearance of the intermediate high-temperature phase that is free from modulations in lead sublattice, but with distortions in oxygen sublattice. This high-temperature phase is characterized by the increase of generalized susceptibility at incommensurate wavevectors on cooling, as evidenced by diffuse scattering measurements. This increase in susceptibility is a precursor for the incommensurate phase formation. Along these similarities, there are substantial differences between the effects of hydrostatic and chemical pressures. In particular, hydrostatic pressure leads to the strong increase of temperature, above which the cubic phase becomes stable. Sn^{4+} doping, on the other hand, keeps the cubic transition temperature largely intact, but leads to the decrease of IC and AFE phase transition temperatures. IC phase transition sequence is more complex in the case of hydrostatic pressure, where modulations with two different wavevectors take place consequently on cooling. Both hydrostatic pressure and Sn^{4+}-doping appear to enhance oxygen sublattice instability with respect to octahedral tilts.

References

[1] R. B. Burkovsky et al., Scientific Reports 7, 41512 (2017).
[2] G. A. Samara, Physical Review B 1, 3777 (1970).
[3] I. Jankowska-Sumara et al, Journal of Applied Physics 122, 104104 (2017).

NMR studies of confined and bulk KDP and DKDP.

N.I. Uskova[1], E.V. Charnaya[1,*], D. Yu. Podorozhkin[1],
S.V. Baryshnikov[2], A. Yu. Milinskiy[2]

[1]Physics Department, St. Petersburg State University, St. Petersburg, 198504 Russia
[2]Blagoveschensk State Pedagogical University, Blagoveschensk, 675002 Russia
[*]Corresponding author: charnaya@mail.ru

The potassium dihydrogen phosphate (KDP) and its deuterated analogue (DKDP) are among the most known ferroelectric crystals. Due to their importance in fundamental and applied physics, great efforts were focused on studies of size effects on ferroelectric properties of KDP and DKDP, in particular, on the structural phase transition in the KDP and DKDP confined nanoparticles (see, for instance, [1,2] and references therein). Results of such studies, which were carried out by calorimetric and dielectric methods, are rather controversial. Since NMR is very sensitive to local structural transformations and is not affected by water freezing or melting in porous matrices we used NMR to investigate the impact of nanoconfinement on the ferroelectric phase transition in deuterated KDP embedded into opals. The results obtained were compared with those of NMR studies for relevant bulk samples.

Opals (photonic crystals) consist of close packed amorphous silica spheres with a 270 nm mean diameter. Between spheres there is an interconnected network of octahedral and tetrahedral nanopores. The ferroelectric nanoparticles formed in pores from saturated solution upon drying at 450 K. We studied variously deuterated samples from KDP to DKDP with more than 95 % level of deuteration. The static and magic angle spinning (MAS) NMR measurements were performed using an Avance400 Bruker spectrometer. The ^{31}P free induction decay was recorded after a 90-degree pulse and was Fourier transformed to get the static or MAS NMR spectrum. The ^{31}P nuclei have spin ½. Then the ^{31}P NMR lineshape for powder or nanocomposite samples is mainly determined by the chemical shift anisotropy. The most sensitive to the phase transition is the anisotropy of the chemical shift tensor which is related to the principle components of the tensor as $\delta = \delta_{zz} - \delta_{iso}$, $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$. The ferroelectric phase transition for the static NMR is seen from the changes in the lineshape, while the intensity of the sedebands changes through the phase transition in MAS NMR. Fig. 1 shows an example of the MAS NMR spectra for the opal sample with nanoparticles deuterated up to 95 %. For all opal nanocomposites under study we observed a noticeable decrease and diffusion of the ferroelectric phase transition despite a quite large size of pores in the opals.

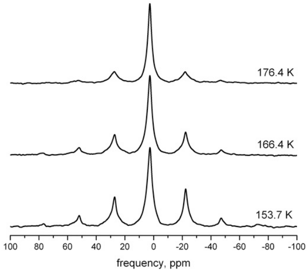

Fig. 1. Three ^{31}P MAS NMR spectra for the opal with nanoparticles deuterated up to 95 %. The structural changes occur between 176.4 and 166.4 K. Note that the ferroelectric phase transition in the relevant bulk sample is seen near 230 K.

References

[1] A. Ciżman, T. Marciniszyn, E. Rysiakiewicz-Pasek, et al, Phase Transit. 86, 910, 2013. 2.

[2] N.I. Uskova, D. Yu. Podorozhkin, E.V. Charnaya, et al, S.V. Baryshnikov, Ferroelectrics 514, 50, 2017.

Synchrotron In-situ diffraction experiments with ferroelectric crystals and thin films

Dmitry Chernsyhov

Swiss-Norwegian Beam Lines at the European Synchrotron Radiation Facility, Grenoble, France
dmitry.chernyshov@esrf.eu

A deliberate manipulation with ferroelectric properties requires a detailed mapping of crystal and domain structures as a function of external stimuli. The report aims to show how in-situ diffraction experiments with synchrotron light contribute in the coherent picture of structural evolution at different length and time scales. The main focus is on perovskite-like materials and discussion of the characteristic diffraction signatures of ferroelectric behavior as a function of electric field and temperature. A twinning of PMN-PT and PIN-PMN-PT crystals with composition close to the morphotropic border was followed as function of temperature and electric field, the results are rationalized in terms of change of symmetry and associated polarization. 3D mapping of reciprocal space was used to untangle structural deformations and domain re-distributions and estimate their contributions to electromechanical properties. The role of structural disorder is illustrated with diffuse scattering as a function of temperature and electric field. In-situ diffraction experiments of epitaxial films of KxNa1-xNbO3(100)||Pt(111)@Si(100) are used to exemplify the power of this technique for ferroelectric films.

Domain Formation Induced in Congruent Lithium Niobate by Electron Beam Irradiation

D. S. Chezganov,[*] E. O. Vlasov, L. V. Gimadeeva, M. A. Chuvakova, and V. Ya. Shur

School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., Ekaterinburg, Russia
[*]Corresponding Author: chezganov.dmitry@urfu.ru

We have studied the features of domain structure formation induced by an electron beam irradiation at the room and elevated temperatures in congruent lithium niobate (CLN) crystals covered by artificial dielectric layer. The results were explained in terms of kinetic approach [1].

The samples represented the 0.5-mm-thick Z-cut CLN plates. The formation of domain structures has been made by irradiation of the Z- polar surface covered by dielectric layer using scanning electron microscopes Auriga Crossbeam and Merlin (Carl Zeiss). The irradiation parameters and beam positioning were controlled by electron beam lithography system Elphy Multibeam (Raith). The irradiation at the temperature up to 250°C was performed using thermal stage C1003 (Gatan Inc.). The dot and stripe irradiation were used. The static domain structures were visualized by scanning electron microscopy (SEM) after selective chemical etching in pure HF during 90 s at the room temperature.

The dose dependence of shape and size of isolated domains was measured after dot irradiation. The hexagonal shape of domains appeared at room temperature. The lack of domain shape stability leading to formation of the self-assembled domains was obtained at elevated temperatures (Fig. 1(a) — 1(d)). The temperature dependence of the threshold charge dose value was established.

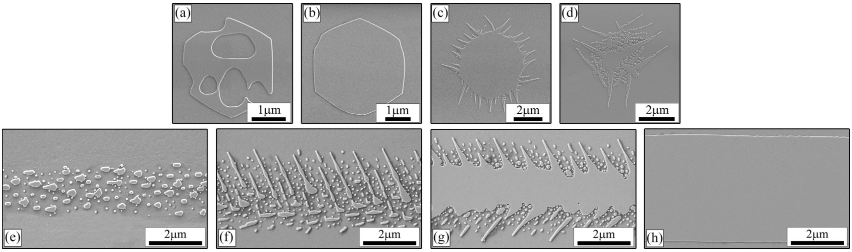

Figure 1. SEM images of the domains at Z– polar surface obtained by: (a) — (d) dot irradiation, (e) –(h) stripe irradiation. (a), (e) –(h) Room temperature, (b) 75°C, (c) 200°C, (d) 225°C. Charge dose: (a) — (d) 120 pC, (e) 1 mC/cm^2, (f) 2 mC/cm^2, (g) 26 mC/cm^2, (h) 56 mC/cm^2.

Four types of domain structures have been revealed after stripe irradiation at room temperature (Fig. 1(e) — 1(h)): (1) isolated nanodomains; (2) isolated domain rays oriented along Y+ directions; (3) solid domains with jagged walls (“fish-bone” structure); (4) continuous solid stripe domains. The obtained domain patterns have been considered as subsequent stages of domain structure evolution [2]. The domain structure evolution was characterized by dose dependences of domain density, length, and period of domain rays and stripe domain width. The threshold irradiated charge dose necessary for formation of solid stripe domain has been revealed. The revealed temperature dependence of the stripe domain shapes was discussed.

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References

[1] V. Ya. Shur, *J. Mater. Sci.*, 41, 199–210 (2006)
[2] E. O. Vlasov, et al., *Scanning*, 2018, Article ID7809826 (2018)

Optical Transitions in $TlGaSe_2$ Ferroelectric — Semiconductor in the Visible Range

Asuman Çengiz[1,2], Yurii M. Chumakov[1,4,*], and MirHasan Yu. Seyidov[1,3]

[1]Department of Physics, Gebze Technical University, 41400 Gebze, Kocaeli, Turkey
[2]Department of Physics, Kocaeli University, 41380 Kocaeli, Turkey
[3]Institute of Physics Azerbaijan National Academy of Sciences,
AZ - 1143 Baku, Azerbaijan
[4]Institute of Applied Physics of Academy of Sciences of Moldova,
MD-2028 Chisinau, Moldova
[*]Corresponding Author: yurii.chumakov@gtu.edu.tr

In this work the optical absorption characteristics of $TlGaSe_2$ ferroelectric — semiconductor in the visible part of the spectrum are presented and discussed. $TlGaSe_2$ is well — known semiconductor — ferroelectrics which undergoes two successive phase transitions during cooling. An incommensurate (ICN) transition at temperature T_i~ 120 K with a modulation vector near the $\boldsymbol{k} = (\delta; \delta; 0.25)$ point in the Brillouin zone, and upon further cooling at temperature T_c ~ 110 K, a commensurate (C) phase transition to the quadruple period ferroelectric phase with the modulation vector $\boldsymbol{k} = (0; 0; 0.25)$. The INC — phase is modulated along the **c** — direction perpendicular to the plane of layers. Above T_i $TlGaSe_2$ belongs to the C_{2h}^6 space group, while below T_c the space group symmetry of crystal is not known yet. The transmission spectra of $TlGaSe_2$ were recorded at normal light incidence on mirror surface of samples in the wavelength range of 400–900 nm in the temperature range of 19 to ~ 300 K. The optical band gaps at different temperatures were determined from the extrapolation of the linear region of the square or square root of the absorption curve. As a result, layered semiconductor $TlGaSe_2$ is interpreted as a direct band gap semiconductor with a band — gap ~ 2.04–2.14 eV at 300 K. Nevertheless, other electronic inter — band transitions can occur on the optical transmission spectrum of $TlGaSe_2$. We find that optical absorption edge of $TlGaSe_2$ is characterized by the presence of an Urbach — like tail and a high — energy Tauc absorption region. Findings reveals that "amorphized" structure of $TlGaSe_2$ which is prominent in near conduction/valance band energy states, cannot be ignored for the understanding of the optical transition mechanisms in of this semiconductor. Our main funding shows that the electronic band structure and optical properties of $TlGaSe_2$ are very sensitive to disorder. The crystallographic analysis of the thermal motion of atoms in $TlGaSe_2$ has reveal that defects in this compound are related with existence of vacancies caused by absence of Se atoms in some unit cells. The theoretical band structure calculations found that the presence of vacancies in $TlGaSe_2$ has led to increasing of localized states near the top of valence and on bottom of conduction bands. We first illustrate that Se — vacancies in the crystal structure of studied compound can dramatically modify optical absorption characteristics of $TlGaSe_2$ in the region of just above an Urbach edge as well as strongly affect a structural phase transitions in this crystal.

Microstructure and Electrical Properties of Porous PZT Films Prepared by PVP Assisted Process

Liubov Delimova[1], **Nina Zaitseva**[1], **Ekaterina Gushchina**[1], **Dmitry Seregin**[2],
Konstantin Vorotilov[2], **Alexander Sigov**[2]

[1] Ioffe Institute RAS, Saint-Petersburg, Russian Federation
[2] Moscow Technological University (MIREA), Moscow, Russian Federation
e-mail: ladel@mail.ioffe.ru

Porous ferroelectric films are a new physical object whose properties significantly differ from the properties of dense films. We report structural and electrical properties of porous lead zirconate titanate (PZT) films prepared by sol-gel technique with the use of polyvinylpyrrolidone (PVP) with different molecular weights and concentration as a porogen. PVP molecules incorporate into the film structure and undergo thermal destruction after a heat treatment leaving empty porous. X-ray diffraction, scanning electron microscopy, piezoelectric force microscopy, ellipsometry, dielectric hysteresis, capacitance-voltage curves, leakage currents, and polarization dependences of transient current and photovoltaic current are used for characterization of the films structure and properties. The XRD study of dense PZT films shows the predominant (111) perovskite texture and the weaker (100) one, that is typical for columnar grain films deposited on Pt with (111) orientation. Porous PZT films demonstrate also only perovskite phase, however it is hard to make conclusion concerning their texture due to increasing the reflexes intensity caused by the substrate. The films demonstrate (110), (100), (211), (210) peaks, whereas (111) reflex is hard to detect due to strong Pt (111) peak. The lattice parameters calculated from the measured interplane distances under the assumption of a pseudocubic lattice are increased with the PVP content. Possible reason may be reducing internal mechanical stresses in porous films. The remanent polarization magnitude decreases with the porosity increase, especially pronounced when PVP content exceeds 6 wt.%.

Earlier, we have found the correlation between the grain-boundary conduction and transient current behavior [1]. The transient current, measured in the dense PZT films at varied preliminary polarization, shows the current peaks in case the applied bias is directed along the polarization, which corresponds to the nonconductive grain boundaries [1]. The porous PZT films with low porosity (PVP content up to 6 wt.%) demonstrate the same behavior of transient current, indicating that the current flows inside the grains. The films with PVP content above 6 wt.% reveals intermediate behavior, where the current peaks either do not appear at all or the peaks arise both in case the bias is directed along the polarization and against it. These results indicate significantly change of perovskite grain structure with the increase in porosity. The similar results are found under the photocurrent measurement in polarized short-circuited PZT films. In depolarized state of the dense or porous PZT films with PVP content below 6 wt.%, the downward short-circuited photocurrent is measured, which is evidence for the presence of the downward internal electric field in the film. The photocurrent measured in the polarized films can be explained by the bulk photovoltaic effect when the photocurrent inside the grain is induced in the polarization direction. The photocurrent measured in PZT films with PVP content above 6 wt.% does not depend on preliminary polarization. The possible mechanisms responsible for the photocurrent behavior are discussed.

References

[1] L. Delimova, E. Guschina, D. Seregin, K. Vorotilov, A. Sigov. JAP 121, 224104 (2017).

Magnetic properties of h-$YMnO_3$ and h-$HoMnO_3$

I. V. Yatsyk[a, b], **T. P. Gavrilova**[a, b], **R. M. Eremina**[a, b,*]

[a]Kazan E. K. Zavoisky Physical-Technical Institute (KPhTI) of the Kazan Scientific Center of the
Russian Academy of Sciences, Sibirsky tract, 10/7, Kazan, 420029, Russia
[b]Kazan (Volga Region) Federal University, Kremlevskaya st., 18, Kazan, 420008, Russia
*REremina@yandex.ru

Multiferroic rare earth manganites $RMnO_3$ have attracted a great attention due to their manifestations of significant couplings between the magnetic and electric order parameters. Generally, $RMnO_3$ has two kinds of multiferroic structures: hexagonal and orthorhombic depending on the rare earth R^{3+} ionic size from 1.11 Å to 0.94 Å. The orthorhombic structure with a Pnma space group forms the stable crystal structure of $RMnO_3$ perovskite oxides with R = La to Dy, which belongs to the magnetic ferroelectrics induced by magnetic ordering. Furthermore, another family of compounds with smaller ionic size (for R = Y, Ho, Er, Yb, Lu, etc.) forms the stable hexagonal structure with $P6_3cm$ space group. The critical point of the structure transition is located near $YMnO_3$ (Y^{3+} = 1.06 Å) and $HoMnO_3$ (Ho^{3+} = 1.05 Å) [1]. The coexistence of ferroic orders in $RMnO_3$ with hexagonal or orthorhombic structure yields complex physics in the intimate interactions among charge, orbital, lattice, and spin degrees of freedom. It also has fascinating physical properties which might lead to promising applications.

$HoMnO_3$ is a high-T_C ferroelectric T_C=875 K material with the very large value of polarization P~56 mC/m^2 directed along the *c* axis caused by vertical Ho–O displacements. $YMnO_3$ is also a high-T_C ferroelectric T_C=933 K material with P~14.6 mC/m^2. Here we present the investigation of magnetic properties of h-$YMnO_3$ and h-$HoMnO_3$ by the electron spin resonance method. Electron spin resonance (ESR) measurements were carried out on a Bruker EMX/plus and Bruker ELEXSYS E680 spectrometers in the temperature range of 5 - 320K at the frequencies 9.4GHz and 34.2GHz. In all temperature range the ESR spectrum of h-$YMnO_3$ and h-$HoMnO_3$ consists of one exchange-narrowed resonance line. As shown in [1], the Dzyaloshinskii - Moriya antisymmetric anisotropic exchange interaction is allowed in the structure of $HoMnO_3$. Consequently, this interaction should make a significant contribution to the ESR linewidth. To derive the contribution of the uniform Dzyaloshinskii-Moriya (DM) interaction to the linewidth in hexagonal manganites, we consider the following Heisenberg Hamiltonian:

$$\acute{I} = J\cdot\left(\bar{S}_i\cdot\bar{S}_j\right)+\sum_{i,i+1}D_{ij}{}'\left[S_i\times S_j\right]+g\mu_B HS_Z,$$

where J is the isotropic superexchange coupling parameter between spins of Mn^{3+} ions and **D** denotes the DM vector. The isotropic exchange interaction between Mn^{3+} spins is J($HoMnO_3$)=2.44 meV, J($YMnO_3$) = 2.45 meV, DM antisymmetric anisotropic interaction is D=0.38 meV in $HoMnO_3$ [1] and D=0.48 meV in$YMnO_3$ [2], respectively. The anisotropic parameters D can be used for estimation of the angular dependence of the linewidth in the high temperature limit k_BT>>J. The DM vector is directed along the *c* axis and leads to the strong anisotropic broadening of the ESR linewidth: ~ 8000-16000 Oe in $HoMnO_3$ and 3000-6000 Oe in YMnO, respectively.

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References

[1] N. J. Laurita, Yi Luo, Rongwei Hu, Meixia Wu, S. W. Cheong, O. Tchernyshyov, N. P. Armitage, Phys.Rev.Lett. **119**, 227601 (2017)

[2] C. Toulouse, J. Liu, Y. Gallais, M.-A. Measson, A. Sacuto, and M. Cazayous, L. Chaix, V. Simonet and S. de Brion, L. Pinsard-Godart, F. Willaert, J. B. Brubach, and P. Roy, S. Petit, Phys.Rev.B **89**, 094415 (2014)

New Phase Transition of $YbFe_2O_4$ due to Short Range Magnetic Order

K. Fujiwara[1,*], T. Karasudani[1], K. Kakurai[2], W. T. Lee[3], T. Fujii[1], K. Todori[1],
M. Takesada[4] and N. Ikeda[1]
[1]Grad. Sch. of Nat. Sci. and Tech., Okayama Univ, 3-1-1 Tsushimanaka, Kita-ku, Okayama, Japan
[2]CROSS Tokai, IQBRC Bldg, 162-1 Shirakata, Tokai, Naka, Ibaraki, Japan
[3]ANSTO, New Illawarra Rd, Lucas Heights NSW, Australia
[4]Dept. of Phys., Hokkaido Univ., Kita 8, Nishi 5, Kita-ku, Sapporo, Hokkaido, Japan
[*]Corresponding Author: sc422225@s.okayama-u.ac.jp

Multiferroic materials have attracted much researchers' attention because they have strong interaction between magnetic and dielectric ordering, that do not be described in the Maxwell's equation.

The mixed valence iron material *R*Fe_2O_4 (R = Lu, Yb, Y etc.) is expected new ferroelectric material which may have an electric polarization by polar charge ordering in the doubly stacked triangular layer (W-layer) of mixed valenced iron ions. [1]

We had found in $YbFe_2O_4$ that the crystal produced by conventional synthesis method contains about 10% of iron deficiency. We had succeeded in making stoichiometric samples with suppressed iron deficiency. In the crystal made with conventional method, the competition of the ordering between ferromagnetic and anti-ferroic magnetic below T_{LT} (~150K) had been reported. But our stoichiometric sample shows only ferri-magnetic order and T_{LT} was restrained [2].

In this study, we report the neutron diffraction experiment and Mössbauer spectroscopic measurement of the stoichiometric $YbFe_2O_4$. No competition between anti-ferromagnetism and ferrimagnetism near T_{LT} was observed [3]. Furthermore, broad magnetic scattering was observed around 1/3 1/3 0 just above the magnetic transition (T_N ~ 245K) and it disappears at 300 K.

Also we found an internal magnetic field above T_N for stoichiometric $YbFe_2O_4$ in Mössbauer spectroscopy. Such field had reported only below T_N in the conventional sample. The internal magnetic field of the stoichiometric $YbFe_2O_4$ disappears at 300 K (Fig.1). A peak of specific heat was found for this sample at 300K.

From these data, we suppose there possibly is new phase transition near 300 K where the development of short-range magnetic ordering plays important role.

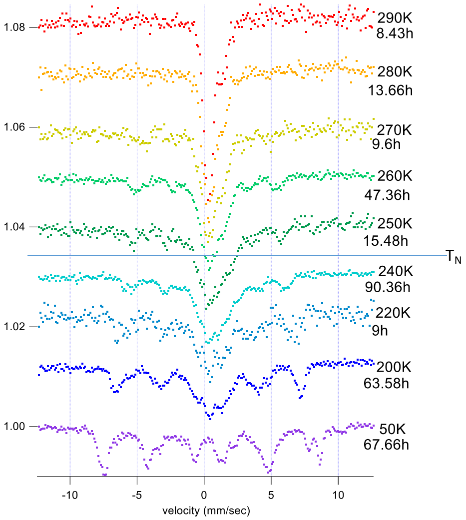


Figure 1. Mössbauer spectral of stoichiometric $YbFe_2O_4$.

References

[1] N. Ikeda et al., *Nature,* **436**, 1136 (2005)

[2] K. Fujiwara etal., *Trans. Mat. Res. Soc. Japan,* **41**, 139-142 (2016)

[3] A. D. Christianson et al., *PRL,* **100**, 107601 (2008)

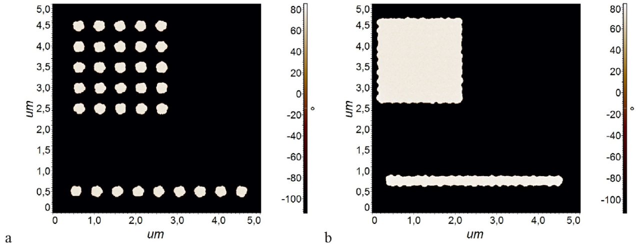
Domain formation processes in LNOI structures in AFM tip field

R. V. Gainutdinov[1], T. R. Volk[1], H. H. Zhang[2]

[1] Shubnikov Institute of Crystallography of Federal Scientific Research Centre “Crystallography and Photonics” of Russian Academy of Sciences, Leninsky pr. 59, Moscow, Russia
[2]Jinan Jingzheng Electronics Co. Ltd., Jingshidong Road, Yaogu Industrial Park B1806, Building No. 1, Jinan, People’s Republic of China

Corresponding Author: radmir@crys.ras.ru

Recently, new generation of sandwich type waveguides denoted as LNOI “$LiNbO_3$ film on an insulator” have attracted increasing interest. Interest to such structures is associated with the creation of various optical devices in the integral (waveguide) performance. In particular, it is the use of the devices based on such waveguides for conversion the frequency of laser radiation in the phase quasi-phase-matching (QPM) mode on a ferroelectric domain structure. Thus, the problem of the formation of micro- and submicrometer domain structures with specified design in LNOI devices arises. It requires studying the mechanisms of the domain formation in such structures. Here the results of studies of the domain formation in thin LNOI structures in the field of the atomic force microscope tip are presented. Images of domains were obtained with the method of piezoresponse force microscopy (PFM). For the first time, local piezoelectric hysteresis loops were obtained in LNOI structures when a train of pulses with determined off-duty ratio was applied to AFM tip. Analysis of the hysteresis loops revealed the low-frequency dispersion of the coercive field E_c and the bias field E_b, as well as the absence of backswitching up to the pulse duration of 1 ms. Observed dynamics of domains revealed the undoubted influence of domain wall pinning on the interface. Time and field kinetics of switching in AFM tip field (the dependence of the domain diameter on the magnitude of the applied voltage U and the pulse duration t_p) are studied. For the first time, one-dimensional and two-dimensional regular domain structures are recorded in the films (Fig. 1). The effect of domains coalescence as they approach each other is found to be associated, presumably, with the absence of electrostatic repulsion between domains due to the higher conductivity of the domain walls.



a b

Figure 1. 1D and 2D domain structures recorded in LNOI with AFM tip field with different distances between record points (a – 500 nm, b – 200 nm).

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References

[1] G. Poberaj, H. Hu, W. Sohler and P. Guenter, Laser& Photonics Rev., **6**, 488, (2012).

Ferroelectricity in channel-like structures loaded with water molecules

B. Gorshunov[1*], M. Belyanchikov[1], Z. Bedran[1], E. Zhukova[1], V. Torgashev[2], V. Thomas[3], M. Savinov[4], P. Bednyakov[4], A. Dudka[5], A. Zhugayevych[6], S. Tretiak[6,7], F. Uhlig[8], J. Smiatek[8], M. Fyta[8], M. Dressel[1,8]

[1]Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700 Russia
[2]Faculty of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia
[3]Institute of Geology and Mineralogy, RAS, 630090 Novosibirsk, Russia
[4]Institute of Physics AS CR, Na Slovance 2, 18221 Praha 8, Czech Republic
[5]Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, 119333 Moscow, Russia
[6]Skolkovo Institute of Science and Technology, Moscow 143026, Russia
[7]Center for Integrated Nanotechnologies (CINT), LANL, Los Alamos, NM 87545, U.S.A.
[8]1. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany
*Corresponding Author: bpgorshunov@gmail.com

Water molecules, H_2O, have a large electrical dipole moment. Thus the dipole-dipole interaction between the molecules might lead to ordering, i.e., emergence of a (anti)ferroelectric state. Such state is not observed in bulk liquid water and ice due to suppression of dipole-dipole interactions by shorter-range highly-directional hydrogen bonds (H-bonds). It is suggested, however, that the so-called water ferroelectricity can be realized if water is subject to certain special conditions when the role of H-bonds is diminished, e.g., when H_2O molecules or molecular groups are confined within micro- or nano-sized spaces, organized in one-dimensional chains or smeared over two-dimensional interface (see, e.g., [1,2]). This type of confined-water ferroelectricity is believed to play a significant role in variety of processes and areas of natural sciences (e.g., geology, mineralogy, meteorology, soil chemistry, biology, pharmaceutics, food industry and materials science), including the living organisms (water in cells and membrane channels, proteins hydration shells). Along with a large number of theoretical studies and computer simulations of the phenomenon, the respective *experimental* observations are rather poor and often controversial. We performed a series of experiments using objects that are model systems for this type of research. These are dielectrics whose crystal lattice contains channels of nanosized cages in which *distinct* H_2O molecules are placed during crystal growth. The molecules are only weakly coupled with the crystalline matrix that keeps them at a distance (5-10 Å) large enough to suppress the H-bonding, but relatively close for an effective electrical dipole-dipole interaction. Using broad-band (1 Hz up to 10^{14} Hz) spectroscopy, we have studied the temperature-dependent dynamics of water subsystems in artificial and natural crystals of beryl and cordierite. In the water molecular subsystem of beryl, we have discovered an incipient ferroelectric phase [3] and single-particle librational and translational excitations of confined H_2O molecules [4,5]. The specific potential profile experienced by the molecules localized within the cages of cordierite leads to their rich relaxor-like dynamics.

The work was supported by the Russian Ministry of Education and Science (Program '5top100'), Project N3.9896.2017/BY and MIPT grant for visiting professors.

References

[1] C. Luo et al., *Nano Lett*. 8, 2607–2612 (2008)
[2] W.-H. Zhao et al., *Chem. Sci*. 5, 1757–1764 (2014)
[3] B. Gorshunov, et al., *Nat. Comm*. 7:12842 doi: 10.1038/ncomms12842 (2016)
[4] E. Zhukova et al., *J. Chem. Physics*, 140, 224317 (2014)
[5] M. Belyanchikov et al., Physical Chemistry Chemical Physics, **19**, 30740-30748 (2017)

First-principles based investigation of the electrocaloric effect: inverse effect, defect tuning and irreversibilities

A. Grünebohm,[1,*] M. Marathe[2] and C. Ederer[3]

[1]Faculty of Physics and CENIDE, University of Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany
[2]Institut de Ciència de Materials de Barcelona, Campus de la UAB, 0819 Bellaterra, Spain

[3]Materials Theory, ETH Zürich, Wolfgang-Pauli-Str. 27, 8093 Zürich, Switzerland
[*]Corresponding Author: anna@thp.uni-due.de

The electro-caloric effect (ECE) is the isothermal entropy or adiabatic temperature change of a polar material induced by an electrical field, which is promising for novel cooling devices. Commonly, field application reduces the entropy. However, in some cases also the inverse ECE, i.e. a field-induced increase of the entropy has been observed.
It is important to fundamentally understand the factors promoting an inverse ECE in order to avoid unintended superposition of conventional and inverse ECE.
Here, we use molecular dynamics simulations based on an effective Hamiltonian derived from first principles, to study the ECE in the prototypical ferroelectric material $BaTiO_3$ [1].
We analyze the conditions giving rise to large inverse caloric responses focusing on ferroelectric transitions [2] and defect doping [3].
In both cases, we also discuss irreversibilities of the response due to thermal hysteresis [4] and ferroelectric switching.

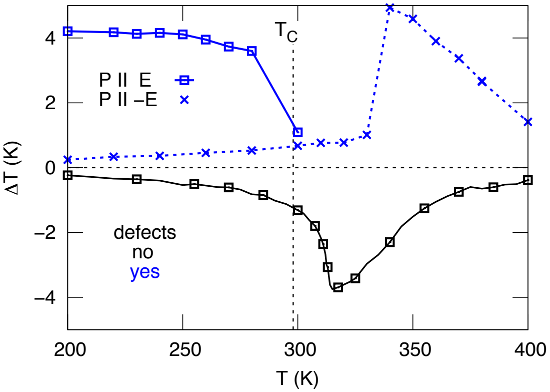


Figure 1. Adiabatic temperature change of $BaTiO_3$ found under field removal. Black: conventional ECE without defects; Blue: inverse ECE in the presence of anti-parallel defect dipoles. As illustrated by symbols, the response below T_C is not reversible and depends on the previous poling conditions.

References

[1] M. Marathe *et al.*, Phys. Rev. B **93**, 054110 (2016)
[2] M. Marathe et al, Phys. Rev. B **96**, 014102 (2017)
[3] A. Grünebohm and T. Nishimatsu, Phys. Rev. B **93**, 134101 (2016)
[4] M. Marathe, C. Ederer, A. Grünebohm, PSS B **255**, 1700308 (2017).

Ferroelectricity evolution mechanism in κ-alumina-type oxides

Tsukasa Katayama[1], Shintaro Yasui[1], Takuya Osakabe[1], Yosuke Hamasaki[1], Tomoyasu Taniyama[1], Mitsuru Itoh[1], Hiroki Moriwake[2], Ayako Konishi[2], Takanori Kikuchi[3], Takahisa Shiraishi[3], and Akiriro Akama[3]

[1]Laboratory for Materials and Structures, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[2]Nanostructures Research Laboratory, Japan Fine Ceramics Center
2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan
[3]Institute for Materials Research, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
e-mail: itoh.m.aa@m.titech.ac.jp

κ-Al_2O_3-type structure, isostructural with ε-Fe_2O_3 and $GaFeO_3$-type structures, has attracted researchers' attention due to their magnetic and ferroelectric properties. κ-Al_2O_3-type structure is composed of alternative stacking of spinel and corundum layers along c-direction. Electric polarization appears along –c direction of *Pna*2_1 space group and its switching under electric field is caused by the shifts of oxygens and cations. Previous paper has adopted *Pnna* structure as a paraelectric phase during the switching [1]. In this model, crystallographic positions of C and D change to D and C, respectively. It gives a polarization switching energy of 0.5 eV/formula, being fairly large compared to the typical perovskite type ferroelectrics. In this study, we have proposed the mechanism of the polarization switching in κ-Al_2O_3-type structure both by cation substitution experiments and calculation.

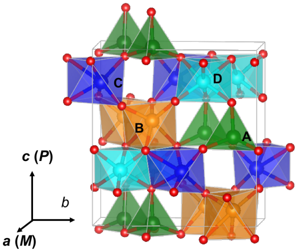


Fig.1 Crystal structure of k-Al_2O_3 structure.

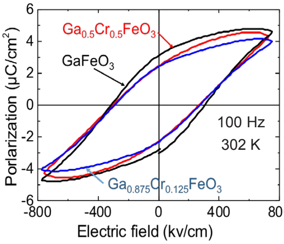


Fig.2 D-E loops for $Ga_{1-x}Cr_xFeO_3$ (x=0, 0.125, 0.5).

We have reexamined the polarization mechanism by the calculation [2]. As a result, coordination exchange between IV and VI was found to take place between A and B, which gives smaller energy for the polarization switching of 0.09 eV/formula. Selective occupation of cation in four of the cations sites, A, B, C, and D can give a good hint for the polarization mechanism. Cr^{3+} ion, for example, can occupy preferentially octahedral D-site [3] and cannot occupy tetrahedral A-site according to the ligand field theory. Therefore, Cr substitution for Ga in D site of $GaFeO_3$ would disturb the polarization switching according to the previous model [1]. However, and polarization and coercive field do not change with the increase of Cr content, as shown in Fig.2. This result validates our switching model [2], in which coordination exchange occurs between A and B sites.

References

[1] D. Stoeffler, *J. Phys.*: *Condens. Matter,* 185502(2012).
[2] A. Konishi *et al.*, unpublished.
[3] R. Saha *et al.*, *J. Solid State Chem*., 2353(2011).

Probing relaxations, non-linearities and domains of PMN-10PT ceramics via broadband dielectric spectroscopy

R. Katiliūte,[1] M. Ivanov,[1,*] M. Vrabelj,[2] L. Fulanovic,[2,3] A. Bradeško,[2,3] Z. Kutnjak,[2,3] J. Banys[1] and B. Malič[2,3]

[1]Faculty of Physics, Vilnius University, Saulėtekio al. 9, 10222 Vilnius, Lithuania
[2]Jožef Stefan Institute, Jamova c. 39, 1000 Ljubljana, Slovenia
[3]Jožef Stefan International Postgraduate School, Jamova c. 39, Ljubljana, 1000 Slovenia
[*]Corresponding Author: maksim.ivanov@ff.vu.lt

Relaxor-based solid solutions, especially the ones with lead titanate as the second member, have a lot of potential applications due to their exceptional properties: piezoelectric, high dielectric permittivity, electrocaloric effect, etc. These are due to various mechanisms, including high mobility of domain walls and presence of polar nano regions or ferroelectric nanodomains. The $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.1PbTiO_3$ (PMN-10PT) relaxor ferroelectric ceramics exhibit large dielectric permittivity anomaly and a phase transition to the ferroelectric state in the vicinity of room temperature. These properties make it a good candidate to study influence of various dopants on functionalities. Manganese is a nice candidate to study, as it can be incorporated isovalently, ant it is known to significantly reduce dielectric losses and electrical conductivity in lead-based perovskites.

We studied the influence of Mn doping on dielectric properties of high density (>95%) PMN-10PT ceramics by means of broadband dielectric spectroscopy in 20 Hz – 40 GHz range using flat capacitor (low frequencies), coaxial lines and waveguides (microwave range). The Mn-addition significantly decreases the dielectric permittivity and losses with strong indication of suppression of domain wall movement and mobility of polar nanoregions. This is further corroborated by nonlinear dielectric spectroscopy, which shows a significant decrease in non-linearities as well as suppression of dispersion of third order non-linear susceptibility. Various relaxational processes were resolved and will be discussed during the presentation.

Effect of magnetic fields on the fatigue processes in triglycine sulfate crystals

E. S. Ivanova*, R. V. Gainutdinov, E. A. Petrzhik, A. K. Lashkova, and T. R. Volk

Shubnikov Institute of Crystallography, Federal Scientific Research Center Crystallography and Photonics, Russian Academy of Sciences, Leninskii pr., Moscow, Russia
*e-mail: ivanova.el.ser@gmail.com

We report on the nanoscopic studies of the fatigue processes in triglycine sulfate (TGS) crystals and on the effects of a weak static magnetic fields on these processes.

According to the conclusions drawn in [1], the qualitative criterion of defect state of TGS is the density and distribution of a nanorelief observed on the polar (010) cleavage, which consists of rounded islands and pits of submicron lateral sizes and height/depth of 0.63 nm. This relief in TGS samples under study was investigated by atomic-force microscopy (AFM) in a tapping mode. An aged (fatigued) state of the crystal was created by a long-term (>100 h) treatment of the samples under a sinusoidal electric field $E = 1$ kV/cm > Ec with a frequency f=50 Hz and an amplitude $E = 1$ kV/cm>Ec (where Ec is the coercive field). This procedure resulted in a strong broadening and bias of the P-E hysteresis loops. Simultaneously, AFM investigations have found a significant increase in the density of nanorelief and broadening of its size distribution [2]. In line with the macroscopic data, this modification of the nanorelief evidences of a fatigued state. The application of a static magnetic field (2 T, 20 min) to a fatigued crystal resulted in post-effects which manifested as a long-term evolution of the nanorelief [3]. In the first days, the average size of nanorelief decreased and the size distribution became narrower. However, in a decade the nanorelief returned to its initial (fatigued) state.

Assuming the nanorelief on the polar surface to be a manifestation of defect clusters existing in the crystal bulk, one can interpret the observed fatigue effects as a coarsening of defect clusters, whereas their evolution after applying a weak magnetic field evidences of a short-term disintegration.

The approach to the magneto-stimulated effects in non-magnetic crystals (to which TGS belongs), in particular the origin of “magnetic memory” observed in the given work, are widely discussed in the literature (e.g. [4]).

References

[1] N. V. Belugina, R. V. Gainutdinov, A. L. Tolstikhina, V. V. Dolbinina, N. I. Sorokina, and O. A. Alekseeva, *Crystallogr. Rep*. **56**, 1070 (2011).

[2] E.S. Ivanova, E. A. Petrzhik, R. V. Gainutdinov, A. K. Lashkova, and T. R. Volk, *Phys. Solid State* **59**, 569 (2017).

[3] R.V. Gainutdinov, E. S. Ivanova, E. A. Petrzhik, A. K. Lashkova, and T. R. Volk, *JETP Lett.* **106**, 97 (2017).

[4] V.I. Alshits, E. V. Darinskaya, M. V. Koldaeva, E. A. Petrzhik. Magnetoplastic effect in nonmagnetic crystals. In: Dislocations in Solids, V. 14 / Ed. J. P. Hirth. Elsevier, Amsterdam. (2008). P. 333–437.

Complex studies of the induced phase transition kinetics in [001], [011] and [111] -oriented single-crystal relaxor solid solutions

L. S. Kamzina* and L. A. Kulakova

Ioffe Institute, Russian Academy of Sciences, Politekhnicheskaya 26,
St. Petersburg, 194021 Russia
Corresponding Author: kamzin@mail.ioffe.ru

The electric field-induced dynamics of the phase transition to a ferroelectric phase in $33PbIn_{1/2}Nb_{1/2}O_3–35PbMg_{1/3}Nb_{2/3}O_3–32PbTiO_3$ (PT32) and $PbMg_{1/3}Nb_{2/3}O_3−29\ PbTiO_3$ (PT29) crystals have been studied in different geometries of applying an external electric field E || [001], E || [011] and E || [111]. The optical transmission at two wavelengths (λ=632.8 nm, λ=1300 nm), dielectric permittivity, the sound velocity and the sound damping have been measured simultaneously at room temperature. It was found that even in small fields (E ~ 2 kV / cm) applied in the [011] and [111] directions, the maximum changes of all three characteristics, as well as the coincidence of the time dependences of the optical transmission at different wavelengths, occur in one and the same time interval. It is established that in the same interval of fields applied along [001] direction, the anomalies of the optical properties do not coincide in time with the anomalies of the acoustic and dielectric properties (Fig.1 and 2). The results are explained by the induction of single-domain and multidomain phases.

Fig.1

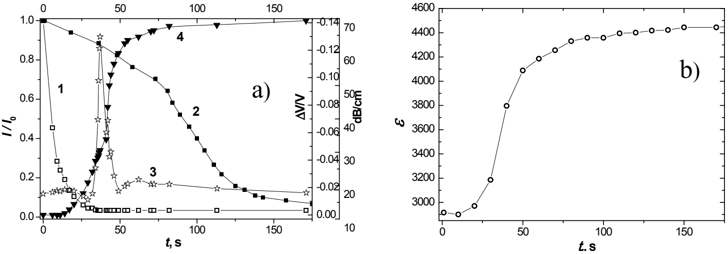
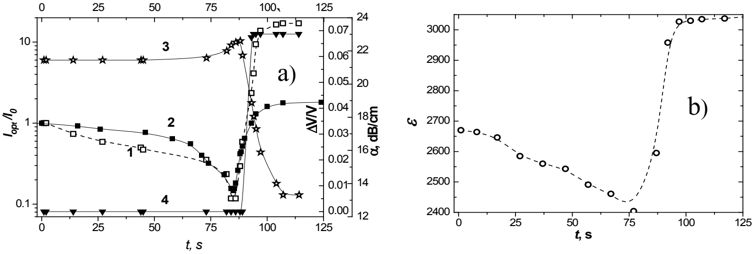


Fig.2



Time dependences of the main characteristics of the PT29 crystal in an electric field applied along [001] (Figure 1) and PT32 in an electric field applied along [011] (Figure 2), **a**: optical transmission (1, 2) at different wavelengths of light, λ, nm: 1 - 632.8, 2 - 1300 ; attenuation coefficients (3) and the sound velocity (4); **b**: the dielectric constants.

Electric polarization induced by phase separation in magnetically ordered and paramagnetic states of RMn_2O_5 (R=Gd, Bi).

B. Kh. Khannanov[1], V.A. Sanina[1], E.I. Golovenchits[1], M.P. Scheglov[1]

[1]A.F. Ioffe Physical Technical Institute RAS, 26 Politekhnicheskaya str., St. Petersburg, Russia
*Corresponding Author: khannanov@mail.ioffe.ru

The electric polarization hysteresis loops and remanent polarization were revealed in multiferroics RMn_2O_5 (R=Gd, Bi) at wide temperature interval (5K — 330K) [1]. The long-range ferroelectric order having an exchange-striction magnetic nature had been observed at low temperatures ($T \leq T_C = 30–35$ K). Along with this, an electrical polarization of a different nature had been found at temperatures $T >> T_C$. A generally accepted point of view is that RMn_2O_5 has sp.gr. *Pbam* (at room temperature). We believe that the high-temperature polarization we observed was caused by the frozen superparaelectric state, which was formed by the restricted polar domains resulting from phase separation and charge carriers self-organization. Charge ordering in RMn2O5 and the e_g electron transfer between Mn^{3+}-Mn^{4+} ion pairs are key factors responsible for polar electric states of these multiferroics at all temperatures. The double exchange between Mn^{3+}-Mn^{4+} ions induces the phase separation in RMn2O5 which is similar to phase separation in $LnAMnO_3$ (A- Sr, Ba, Ca) manganites containing Mn^{3+} and Mn^{4+} ions as well. Phase separation exists at all temperatures and makes the formation of local conductive domains containing Mn^{3+} — Mn^{4+} ion pairs with ferromagnetically oriented spins energetically favorable. The phase separation domains are located in a dielectric antiferromagnetic (paramagnetic) matrix of the original crystal. We believe that the polarization we observed was caused by the frozen superparaelectric state. Theoretically, the frozen superparaelectric state was considered in the system of isolated ferroelectric nanoscale domains in a dielectric matrix [2]. In this state, hysteresis loops and remanent polarizations are observed. The frozen superparaelectric state turns into the conventional superparaelectric one near T* (T* = 100–330 K), in which the hysteresis loops are destroyed. The T* values correspond to the temperatures at which the potential barriers of the restricted polar domain reorientations become equal to the kinetic energy of the itinerant electrons (leakage). The application of magnetic field H increases the barriers at the phase separation domain boundaries due to the double exchange growth, thus increasing the T* temperatures. The electric polarization hysteresis loops were measured using the version of the PUND method presented in [3], which was adapted to studies of the local polar domains. The emergence of the local phase separation domains was confirmed in the high-sensitivity 3-crystal X-ray diffractometer measurements and in the permittivity and conductivity investigations. We revealed correlations between properties of the local phase separation domains and hysteresis loops. It has recently been shown [4] that the RMn_2O_5 symmetry at room temperature is a noncentral symmetry, which means that the electri c polarization should be existed at room temperature. The authors did not discuss the possible nature of such a polarization. We showed that the electric polarization observed by us at T >> Tc is due to the local non-centrosymmetrical phase separation domains that form a frozen superparaelectric state.

References

[1] B. Kh. Khannanov, V.A. Sanina, E.I. Golovenchits, M.P. Scheglov Journal of Magnetim and Magnetic Materials 421 (2017) 326–335.

[2] M.D. Glinchuk, E.A. Eliseev, and A.N. Morozovska, Phys.Rev. B. 78 (2008) 134107

[3] S.M. Feng, Y.S. Chai, J.L. Zhu, N. Manivannan, Y.S. Oh, L.J. Wang, Y.S. Yang, C.Q. Jin, Kee Hoon Kim, NewJ.Phys.12(2010)073006

[4] V. Baledent, S. Chattopadhyay, P. Fertey, M.B. Lepetit, M. Greenblatt, B. Wanklyn, F.O. Saouma, J.I. Jang, and P. Foury-Leylekian, Phys. Rev. Lett. 114 (2015) 117601

Vibrational dynamics of ferroelectric K($Ta_{1-x}Nb_x$)O_3 studied by inelastic light scattering

M. M. Rahaman,[1,2] **Š. Svirskas,**[3] **J. Banys,**[3] **and S. Kojima**[1*]

[1]Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan
[2]Department of Materials Science and Engineering, University of Rajshahi, Rajshahi, 6205, Bangladesh

[3] Faculty of Physics, Vilnius University, Saulėtekio al. 9/IIIb., LT-10222 Vilnius, Lithuania

[*]Corresponding Author: kojima@bk.tsukuba.ac.jp

Lead free ferroelectric materials are important for the application to piezoelectric, pyroelectric, and electrooptic devices. $KTa_{1-x}Nb_xO_3$(KTN) with perovskite structure has attracted much attention due to its huge second order electrooptic effect just above the Curie temperature (T_C). KTN undergoes a ferroelectric phase transition, which shows relaxor features with the weak random fields caused by the B-site disorder [1-4]. We studied the vibrational properties using Raman and Brillouin scattering.

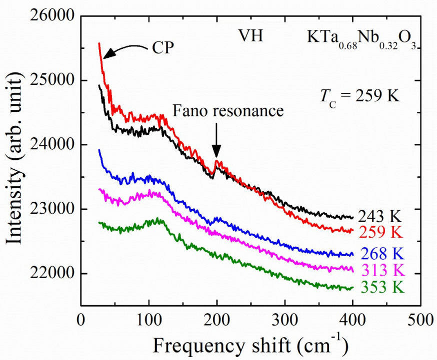


Figure 1. Temperature dependence of Raman scattering spectra of a $KTa_{0.68}Nb_{0.32}O_3$ crystal.

The temperature dependence of Raman scattering spectra of the KTN crystal is shown in Fig. 1. The Fano resonance was observed at about 194 cm^{-1}, and its origin is the coupling between polarization fluctuations of polar nanoregions (PNRs) and the Slater mode [3]. The change of the parameters of the Fano resonance was observed in the vicinity of the T_C. These vibrational dynamics is discussed in relation to a ferroelectric phase transition with the weak random fields. The breaking of symmetry in the cubic phase caused by PNRs is also discussed on the basis of the vibrational dynamics.

References

[1] R. Ohta, J. Zushi, T. Ariizumi, S. Kojima, Appl. Phys. Lett. **98**, 092909 (2015).
[2] M. M. Rahaman, T. Imai, T. Sakamoto, and S. Kojima, Appl. Phys. Lett. **111**, 032904 (2017).
[3] M. M. Rahaman, T. Imai, T. Sakamoto, S. Tsukada, and S. Kojima, Scientific Reports **6**, 23898 (2016).
[4] M. M. Rahaman, T. Imai, T. Sakamoto, M. A. Helal, S. Tsukada, S. Tsukada, and S. Kojima, J. Alloy. Comp. **735**, 1063 (2018).

Domain writing in $LiNbO_3$ ferroelectric crystals by electron beam irradiation: composition influence and conductivity

L. S. Kokhanchik,[1,*] S. M. Shandarov,[2] and T. R. Volk[3]

[1]Institute of Microelectronics Technology and High Purity Materials RAS, 6, Academician Ossipyan str, Chernogolovka, Moscow region, Russia
[2] Tomsk State University of Control Systems and Radioelectronics, 40, Pr. Lenina, Tomsk, Russia
[3] Institute of Crystallography RAS, 59, Leninskiy Prospekt, Moscow, 119333, Russia
[*]Corresponding Author: mlk@iptm.ru

Microdomain patterns of specified design have attracted increased attention in view of their applicability for the nonlinear-optical frequency conversion, in particular in integrated schemes. Domain electron-beam writing (DEBW) provides a possibility to fabricate domains on the nonpolar surfaces of ferroelectric crystals, which is of interest for some integrated schemes on $LiNbO_3$ nonpolar surfaces. In addition to some practical aspects, this DEBW geometry is accessible for 3D characterization of the written domains [1].

In this report we summarize our results on DEBW in $LiNbO_3$ crystals with different composition and conductivity. The samples under study were optically polished Y-cut $LiNbO_3$ plates. The following compositions were investigated and compared: a nominally pure congruent $LiNbO_3$ (CLN); $LiNbO_3$ doped with 4 at.% Zn (LN-4Zn); $LiNbO_3$ doped with 0,5 mol% TiO_2 (LN-Ti) and a chemically reduced $LiNbO_3$ denoted as RLN. RLN samples were obtained by annealing a CLN plate in hydrogen at 550^0 C, which enhances the conductivity up to 10^{-11} to 10^{-13} $Ohm^{-1}cm^{-1}$ as compared with $G = (10^{-16}–10^{-18})$ $Ohm^{-1}cm^{-1}$ in the CLN.

Micro-domain patterns were written on Y-cut surface in SEM using various irradiation parameters — acceleration voltage (U), current (I) and dose ($D=Q/S_{irr}$). We compared the «starting» conditions of the domain appearance (U_{st}, I_{st}, Q_{st} and D_{st}) and domain characteristics depend on the EB parameters and irradiation duration. Mechanism of ferroelectric switching under EB irradiation was discussed in the framework of EB charging of insulators. Under domain creation the charging balance in the samples with different composition was achieved. The common property of the domain length graphs $L_d(t_{irr})$ is their linearity, which was observed in the whole range of U and I applied under study (5–25 kV; 0,1–1nA). Assuming the charge equilibrium to be achieved, this linearity was interpreted [2] as the result of domain frontal growth under high external fields by the viscous friction law. The slopes of linear $L_d(t_{irr})$ as well as L_d values depended on the composition and were different for CLN, LN-4Zn and LN-Ti, but were drastically less in RLN than in other investigated crystals. On the contrary the starting values Q_{st} and D_{st} in RLN increased greatly [3]. The DEBW characteristics observed in $LiNbO_3$ crystals of different composition are discussed depend on variations of intrinsic defect structure and conductivity.

Using DEBW and accumulated experience [4], big micro-domain patterns were written in Ti: $LiNbO_3$ optical waveguide on Y-cut $LiNbO_3$. Changing of the length L_d of the domains, created in crystal layers with different Ti concentration due to the voltage U variations, was observed. The results obtained permit us to match the conditions of DEBW to the waveguide parameters in order to optimize the uniformity and continuity of written patterns.

The work was supported by RFBR (grants № 16–29–11777- ofi-m, 16–02–00439 a and 16–29–14046-ofi-m)

References

[1] L. S. Kokhanchik, R. V. Gainutdinov, S. D. Lavrov, E. D. Mishina, T. R. Volk, *Appl.Phys.Lett.,* 105,142910 (2014)
[2] L. S. Kokhanchik, T. R. Volk, *Appl.Phys.B,*110, 367 (2013)
[3] L. S. Kokhanchik, Ya. V. Bodnarchuk, T. R. Volk, *J. Appl.Phys.*122,104105 (2017)
[4] L. S. Kokhanchik, R. V. Gainutdinov, S. D. Lavrov, E. D. Mishina, T. R. Volk, *Ferroelectrics,480,* 49(2015)

Electrophysical Properties of Nanocrystalline $BaTiO_3$

Leonid N. Korotkov[1], Mikhail A. Kashirin[1], Nikita A. Emelianov[2],
Wisam M. Al Mandalawi[1], and Tatiana N. Korotkova[3]

[1] Voronezh State Technical University,
Moskovsky pr. 14, 394026, Voronezh, Russian Federation
[2] Kursk State University, Radishcheva st., 33 , 305000, Kursk, Russian Federation[3]
[3]Voronezh Institute of the RF Ministry of Internal Affairs,
pr. Patriotov 53, 394065, Voronezh, Russian Federation
e-mail: l_korotkov@mail.ru

Influence of thermal treatment on crystalline structure, FTIR spectra and dielectric properties of initially cubic perovskite $BaTiO_3$ nanoparticles with average size of 100 nm (Sigma–Aldrich, USA) was studied. It was found that annealing leads to formation of ferroelectric tetragonal phase and increasing of tetragonal distortion of crystalline cell.

For the experiments the samples in the form of disc (diameter and thickness were 10 mm and 1 mm, respectively) were used. The electrodes were made by silver paste coating. Before experiments the sample was placed in a thermostat where the temperature was varied from 20 to 300 °C and measured with an error less than ± 1 °C.

Experimental results show that an appearance of ferroelectricity in the nanostructured $BaTiO_3$ and its dielectric permittivity variation (ε) is caused by the decrease of lattice defects concentration owing to thermal annealing. Such defects lead, in particular, to the specific dependence of T_C on d.c. field.

Observed dispersion of dielectric permittivity (ε) and dielectric nonlinearity of the material under study within the ferroelectric phase are caused by the domain mechanism mainly. It was found that anomalous hysteresis of ε observed at cycle temperature variation in the vicinity of Curie temperature (T_C) is due to interaction of interphasic boundaries with lattice defects.

Studies of d.c. electrical conductivity revealed that charge transport is realized mainly through the granule volume. Considerable contribution to a.c. conductivity gives displacement currents which are caused by both the domain wall motion and the Maxwell–Wagner polarization. The last one supposedly due to a migration of charge carries in granule interfaces.

Dependences of magnetization on magnetic field strength were studied for both the nanostructured and the bulk ferroelectric $BaTiO_3$. It was found that nanostructured barium titanate demonstrates ferromagnetic and diamagnetic properties simultaneously. The annealing of nanostructured $BaTiO_3$ in H_2 atmosphere under experimental conditions leads to a significant increase of the spontaneous magnetization and decrease of the diamagnetic response. Analysis of experimental results shows that defects in grains surfaces of the the nanostructured $BaTiO_3$ (probably oxygen vacancies) are mainly responsible for electron states, which produce ferromagnetic and diamagnetic responses.

Transitions in Multiferroics $HoFe_{3-x}Ga_x(BO_3)_4$

A.S. Krylov,[*] E.M. Moshkina, I.A. Gudim, S.N. Krylova and A.N. Vtyurin

Kirensky Institute of Physics, Federal Research Center KSC SB RAS,
Academgorodok 50/38, Krasnoyarsk, Russia
[*]Corresponding Author: shusy@iph.krasn.ru

Multiferroic materials showing the coexistence of at least two ferroic orders ((anti)ferroelectric, (anti)ferromagnetic and (anti)ferroelastic) are expected to find potential applications in many devices. Amongst these properties the coexistence of ferroelectricity and ferromagnetism is highly desired. Besides their coexistence, of utmost importance is a strong coupling between the two ferroic orders. In multiferroic materials, the coupling interaction between the different order parameters can produce additional functionalities. The application of multiferroics will make possible to significantly enlarge the functional possibilities of spintronics.

Crystals of the $RFe_3(BO_3)_4$ family (R is rare earth ion) were reported to possess multiferroic features, demonstrating both structural and magnetic phase transitions [1–4], where transition points may be varied by rare earth composition. In this work we used Raman spectroscopy to study $HoFe_{3-x}Ga_x(BO_3)_4$ single crystals.

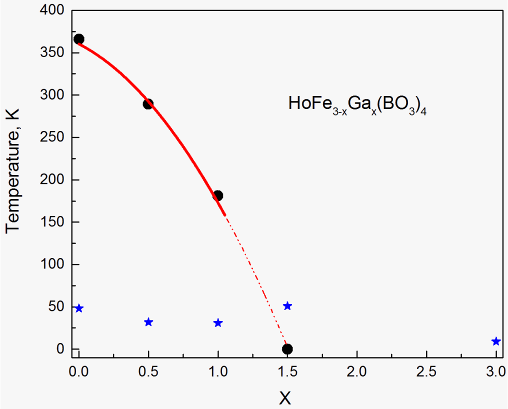


Figure 1. Phase diagram Composition–Temperature

Temperature measurements were performed in the temperature range 10–400 K. The aim of this study is to investigate possible existence of a soft mode related to structural order parameter and effects of magnetic transitions on Raman spectra. Analysis of the experimental Raman spectra, temperature dependences of the provisions of the centers of lines, their width and relative intensity was carried out, as well as theoretical temperature approximation for a number of lines. A number of anomalies in the temperature dependences of the spectral lines associated with the occurrence of magnetic order. It was found that significant changes are observed in the spectrum of low-frequency range (below 100 cm^{-1}) — there is a mode corresponding to two-magnon scattering. Phase diagram Composition–Temperature presented in Figure 1.

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References

[1] A.K. Zvezdin et al. *JETP Lett.* 81, 272 (2005)
[2] A.M. Kuzmenkoet al. *JETP Lett.* 94, 294 (2011)
[3] A.S. Krylov et al.*Solid State Commun.* 174, 26 (2013)
[4] E. Moshkina et al. *Cryst. Growth. Des.* 16, 6915 (2016)

Electrocaloric Properties of (Pb, La)(Zr, Ti)O_3 ceramics

Hiroshi Maiwa[1,*]

[1]Department of Materials and Human and Environmental Sciences, Shonan Institute of Technology,
1–1–25 Tsujido-Nishikaigan, Fujisawa, Japan
*Corresponding Author: maiwa@mate.shonan-it.ac.jp

The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field. There are some problems with conventional refrigerators. Since the conventional refrigerator operates by using a compressor, vibration is inevitable. Conventional refrigerators also use Freon as refrigerants; however, the use of Freon has been implicated in ozone depletion. Other disadvantages include the difficulty of downscaling. Thermoelectric cooling is possible using a Peltier device, considered a solid-state cooling device; however, low efficiency has been a hindrance to wider application. From the viewpoint of innovation in refrigeration, cooling based on new mechanisms are expected.

In this study, the electrocaloric temperature change, ΔT, due to applied ΔE was calculated in PZT films. The ΔT of the ferroelectric and (Pb, La)(Zr, Ti)O_3 ceramics were estimated and measured directly. The dP/dT between 30 °C and 100 °C for PLZT(9.1/65/35) were –0.098 $\mu C/cm^2K$. Estimated ΔT from Equation for PLZT(9.1/65/35) were 0.52K. Compared with 0.23K of PLZT(7/65/35), it was considered that the values of the PLZT(9.1/65/35) were enhanced with higher La substitution. Figure 1 shows the strain-electric field (s-E) loops and the temperature-electric field (T-E) loops of PLZT(9.1/65/35) ceramics. The round T-E and S-E shapes formed around polarization switches observed in the PLZT(9.1/65/35) loop is characteristic of relaxor-ferroelectric materials. The decreasing transition temperature and increasing polarization movements in relaxor ferroelectrics provide large temperature change. Preparation of anti-ferroelectric PLZT(4/90/10) are in progress. The properties will be included in the presentation.

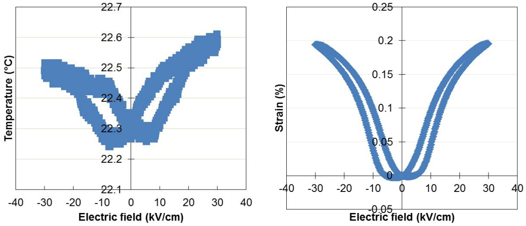

Figure 1. s-E and T-E loops of PLZT(9.1/65/35) ceramics.

Electronic Properties of Multiferroics with Spinel structure: First principles calculation

Husnu Koc[1], **Selami Palaz**[2], **Amirullah M. Mamedov** [3,4*], **and Ekmel Ozbay**[3]

[1] Siirt University, Faculty of Science and Letters, Department of Physics, Siirt, Turkey
[2] Harran University, Faculty of Science, Department of Physics, Sanliurfa, Turkey
[3] Nanotechnology Research Center, Bilkent University, Bilkent, Ankara, Turkey
[4] Baku State University, International Scientific Center, Baku, Azerbaijan
[*]Corresponding Author: mamedov46@gmail.com

In the present work, the structural, electronic and mechanical properties of isostructural $LiVCuO_4$ and $LiCu_2O_4$ have been investigated by using density functional theory. The spin polarized generalized gradiend approximation has been used for modeling exchange-cerrelation effects. The structural optimization of these multiferroics compounds have been performed by using VASP-code, and the lattice parameters and magnetic moments have been calculated. From our calculation has been determined that the $LiVCuO_4$ compound is a narrow band gap compounds, while the $LiCu_2O_4$ compound is metallic in nature. Considering spin states from electronic band structure and density of state (DOS) of $LiVCuO_4$ compound, it have been identified as E_g=0.37 eV for spin up and E_g=1.86 eV for spin down. Mechanical and magnetoelastic properties have also been computed. The second-order elastic constants have been calculated, and the other related quantities such as the Young's modulus, shear modulus, Poisson's ratio, anisotropy factor, sound velocities, Debye temperature, hardness, magnetoelastic cofficient and magnetostriction cofficient have also been estimated in the present work.

A Crystal Optical Study of Short Range Polar Order in the Ferroelectric Phase: Doped Incipient Ferroelectrics

P. A. Markovin,[1,*] V. A. Trepakov,[1] M. E. Guzhva,[1,2] O. E. Kvyatkovskii,[1]
A. G. Razdobarin[1] and M. Itoh[3]

[1]Ioffe Institute, 194021, 26 Politekhnicheskaya, Saint-Petersburg, Russia
[2]Saint-Petersburg Mining University, 199106, 21 line, Saint-Petersburg, Russia
[3]Tokyo Institute of Technology, 4259 Nagatuta, Midori, Yokohama 226-8503, Japan
[*]Corresponding Author: P.Markovin@mail.ioffe.ru

Just recently we developed a method for calculating the magnitude and temperature dependence of the root-mean-square fluctuations of the polarization (short-range, local polar order) $P_{sh} = \langle P^2{}_{fl}\rangle^{1/2}$ below the ferroelectric transition temperature T_c from temperature changes in the spontaneous polar contribution to the principal values of the refractive index $\delta n_i^S(T)$ if the average spontaneous polarization $P_s = \langle P\rangle$ characterizing the long-range order is determined from independent measurements (e. q., for example, from dielectric hysteresis loops) [1]. This method is particularly important to study systems with the coexistence of the long-range and short-range orders below T_c, where the contributions of the short range and long-range orders are comparable in magnitude. Among these objects are, in particular, incipient ferroelectrics $SrTiO_3$ and $KTaO_3$ doped with impurities ($Sr_{1-x}Ca_xTiO_3$, $SrTi(^{16}O_{1-x}{}^{18}O_x)_3$, $KTa_{1-x}Nb_xO_3$, etc.) in which impurity concentrations above a critical value x_c, induce ferroelectric ordering. The quantity $\langle P^2\rangle^{/2}$, which includes the long-range and short-range orders, is turned out to be significantly greater than $P_s = \langle P\rangle$ revealing distinctly existence of developed spatial fluctuations of the order parameter, the behavior of which qualitatively differs from the behavior of classical thermodynamic fluctuations near T_c.

In the present work we estimated quantitatively the role of the short (P_{sh})- and long (P_s) range ordering in the formation of the impurity-induced polar state in incipient ferroelectrics. The temperature dependence of the principal values of the refraction (specific optical retardation) of light in $Sr_{1-x}Ca_xTiO_3$ with x = 0.014 (SCT-1.4), $SrTi(^{16}O_{0.03}{}^{18}O_{0.97})_3$ (STO-18), $KTa_{1-x}Nb_xO_3$ with x = 0.018 (KTN) and nominally pure $SrTiO_3$ (STO) single crystals have been measured and the magnitudes and temperature variations of polar contributions to the refraction in STO-18, SCT-1.4 and KTN were derived. Additionally, the temperature dependences of the morphic birefringence for SCT-1.4 and electro-optic coefficients at room temperature were measured in SCT-1.4 and STO. Dielectric hysteresis loops were measured in SCT-1.4, $Sr_{1-x}Ca_xTiO_3$ with x=0.007 (SCT-0.7) and KTN at different temperatures to calculate P_s.

Ab initio calculations of equilibrium structures and total energies of three low-temperature phases for $SrTiO_3$ and $CaTiO_3$ are performed too. On these theoretical grounds the symmetry of the ground state of the solid solution $Sr_{1-x}Ca_xTiO_3$ is identified, which is important for correct calculations of P_{sh} and P_s in SCT from our measurements.

As a result we determined the magnitude and temperature dependence of P_{sh} polarization in SCT-1.4, which appears only because of strong spatial fluctuations (“local” or “short-range” ordering) and leads to the contribution of short-range order to the polar phase below and above T_C and the magnitude and temperature dependence of the long-range order polarization P_s. P_{sh} and P_s were also evaluated in SCT-0.7, STO-18 and KTN at low temperature below T_c.

References

[1] P.A. Markovin, V.A. Trepakov, A.K. Tagantsev, A. Deineka, and D.A. Andreev, Phys. Sol. State, 58, 134 - 139, (2016)

Mode-distribution analysis of quasielastic neutron scattering in the relaxor ferroelectrics (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$

M. Matsuura[1,*] T. Kikuchi[2] and Y. Kawakita[3]

[1]Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaraki 319-1106, Japan

[1]Material Research and Development HQ, Sumitomo Rubber Industries, Ltd., Tsutsui, Chuo, Kobe, Hyogo 651-0071, Japan

[3]Neutron Science Section, Japan Proton Accelerator Research Complex, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan
[*]Corresponding Author: m_matsuura@cross.or.jp

Relaxor ferroelectrics have gained much scientific and industrial attention due to their extremely high piezoelectric and dielectric responses in a wide temperature range [1]. Another characteristic feature of relaxor is their dielectric relaxation in a wide frequency range from 100Hz to GHz [2]. These characteristic features have been ascribed to randomly oriented polar nanoregions (PNRs), which have local ferroelectric polarizations in a nanometer-scale. Below the onset temperature of PNRs, characteristic diffuse scatterings are commonly observed in lead-based relaxors [4]. The diffuse scattering with anisotropic Q-pattern resembles a butterfly or an ellipsoidal shape. The thermal variation of the diffuse scattering roughly agrees with the dielectric susceptibility ε'(T), suggesting one-to-one correspondence between diffuse scattering and PNRs.

As PNRs grow on cooling, relaxation process of PNRs becomes slow, which leads to narrowing quasi-elastic neutron scattering (QENS) of the diffuse scattering near Bragg peaks. When size of PNRs distributes in a wide length scale, the width of QENS are expected to distribute in a wide energy range. To study the distribution in the relaxation time of PNRs, we measured QENS in the relaxor ferroelectrics (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-$x$$PbTiO_3$ (x=0.37) by using neutron backscattering spectrometer DNA installed at J-PARC MLF. However, analyses of QENS data are model dependent in many cases, which may result in wrong interpretation. In order to extract the intrinsic distribution of relaxation time, we used maximum entropy method in QENS data analysis, which were recently developed by one of the authors [3]. Figure 1 shows an example of QENS data and distribution of relaxation mode of relaxor ferroelectrics. We will discuss temperature and wave vector dependences of the distribution in relaxation.

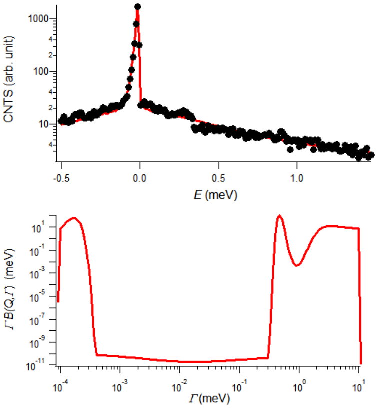

Figure 1. (a) Quasielastic neutron scattering (QENS) of PMN-37%PT measured at (100) at T=500 K. (b) Distribution of Lorentzian width Γ obtained by the mode-distribution analysis for the QENS in (a).

References
[1] S.-E. Park and T. R. Shrout, J. Appl. Phys., 82, 1804, (1997).
[2] V. Bovtun et al., Ferroelectrics, 298, 23 (2004).
[3] T. Kikuchi et al. Phys. Rev. E, 87, 062314 (2013).

Doped-HfO$_2$ Ferroelectric Film Formation using Ion Implantation

**S. Migita,[1,*] H. Ota,[1] H. Yamada,[1] K. Shibuya,[1] A. Sawa,[1] T. Matsukawa,[1]
and A. Toriumi[2]**

[1]AIST, Umezono 1-1-1, Tsukuba, Japan
[2]Material Engineering, The University of Tokyo, Hongo 7-3-1, Tokyo, Japan
[*]Corresponding Author: s-migita@aist.go.jp

Ferroelectric doped-HfO$_2$ films are unique that several kinds of metal dopants such as Si, Al, and rare earth elements are effective for the achievement of ferroelectric property in HfO$_2$ films [1, 2] and the maximum polarization is attainable in ultrathin films around 10 nm thickness [3]. Precise control of dopant concentration in such ultrathin film using conventional deposition techniques such as atomic layer deposition (ALD) and physical vapor deposition (PVD) is a severe process. At the same time, ion implantation technique, which is a well-established process for the LSI fabrication, will be applicable when the amount of dopants becomes small. For example, the number of Si atom in a 10-nm-thick HfO$_2$ film with 3-%-doping (in metal composition) corresponds to 8.5×10^{14} atoms/cm^2. This number is within the range of ion implantation technique. In this work, we applied the ion implantation technique for the formation of Si-doped HfO$_2$ films and examined the ferroelectric properties of metal-insulator-metal capacitors.

10-nm-thick HfO$_2$ films were deposited by RF sputtering technique at room temperature onto TaN electrode films prepared on Si substrates. The HfO$_2$ films are amorphous at this stage. Si ion implantation was processed at the energy of 3 keV, which was designed by simulation. The doses of Si ions were varied between 5×10^{14} and 1.5×10^{15} atoms/cm^2. Samples were then annealed for crystallization at 700 °C for 1 min in a vacuum chamber. The process was finished by deposition of top electrodes, lithography and dry etching.

Polarization characteristics of the capacitors are shown in **Fig. 1**. Ferroelectric film is successfully obtained by the ion implantation technique. It is also observable that the electrical property changes with the dose. As far as we know, formation of ferroelectric thin films using ion implantation has never been reported in traditional ferroelectric materials. HfO$_2$ films are the special case because the film thickness is thin and the necessary dopant concentration is extremely small. We believe that this technique will be powerful for the exploration of new dopant elements for ferroelectric HfO$_2$ films.

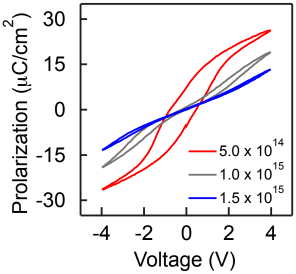

Figure 1. P-V characteristics of Si-doped HfO$_2$ films prepared by Si ion implantation into amorphous HfO$_2$ films at 3 keV with different doses, and annealed at 700 °C for 1 min.

Acknowledgement

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References

[1] U. Schroeder *et al.*, *ECS J. Solid State Sci. Technol.* **2**, N69 (2013); *Jpn. J. Appl. Phys.* **53**, 08LE02 (2014).
[2] L. Xu, A. Toriumi *et al.*, *J. Appl. Phys.* **122**, 124104 (2017).
[3] S. Migita *et al.*, *Jpn, J. Appl. Phys.* **57**, 04FB01 (2018).

Soft-mode informatics: Theoretical calculations of ferrolectricity in thin-film HfO_2 using comprehensive soft-mode analysis

Hiroki Moriwake[*1,2], **Ayako Konishi**[1,2], **Atsushi Togo**[3], **Takao Shimizu**[4], **Hiroshi Funakubo**[4]

[1] Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, Japan
[2] Department Center for Materials research by Information Integration (CMI2) National Institute for Materials Science (NIMS), Tsukuba, JAPAN
[3] Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan
[4] Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Yokohama, Japan
[*]Corresponding Author: moriwake@jfcc.or.jp

Hafnium oxide (HfO_2) has been used as high-k gate dielectric materials in Si semiconductor devices. Recently, ferroelectric behaver of thin film HfO_2 was reported. However, the origin and the mechanism of ferroelectric phase transition of thin film HfO_2 are still not well known. If the origins of this ferroelectricity can be understood, hafnia-based materials may find applications in nonvolatile memories and ferroelectric field effect transistors as well. Therefore, in this study, we tried to elucidate the mechanism of ferroelectric phase transition of thin film HfO_2 using comprehensive soft-mode analysis. Our calculation results are shown in Fig.1. Under ambient pressure, no soft-mode observed in tetragonal $P4_2/nmc$ phase. However, under slight negative (tensile) pressure (–3GPa), soft-mode path to experimentally observed ferroelectric $Pca2_1$ phase were found. This soft-mode path is quite sensitive to pressure, if we apply positive (compressive) pressure, even in zero pressure, it vanished. In thin film form, volume change by first-order phase transition tetragonal to monoclinic should be suppressed by constrain from substrate. In this situation, ferroelectric phase transition through this soft-mode path can be occurred.

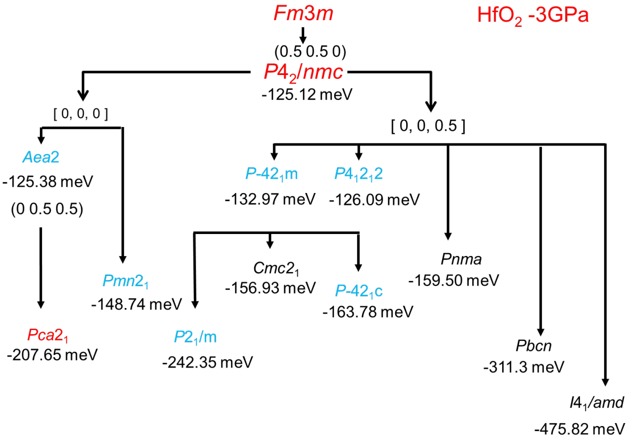

Figure 1. Calculation results of comprehensive soft-mode analysis of HfO_2 under –3GPa.

References

[1] A. Togo and I. Tanaka, *Phys. Rev.* B, 87, 184104 (2013)

Investigation of structures and dynamics of domain walls by synchrotron x-ray and neutron scattering

Kenji Ohwada,[1,4*] **Masato Matsuura,**[2] **Shinya Tsukada,**[3]
Kentaro Deno,[4] **Jun'ichiro Mizuki,**[4, 1] **and Makoto Iwata**[5]

[1]Synchrotron Radiation Research Center, KPSI, QST, 1-1-1 Kouto, Sayo, Hyogo, Japan
[2] Neutron Science and Technology Center, CROSS, Tokai, Ibaraki, Japan
[3]Faculty of Education, Shimane University, Matsue City, Shimane, Japan
[4]School of Sci. and Tech., Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo, Japan
[5]Graduate School of Engineering, Nagoya Institute of Technology, Nagoya, Aichi, Japan
*Corresponding Author: ohwada.kenji@qst.go.jp

We have investigated the origin of the large dielectric/piezoelectric susceptibility in relaxor ferroelectrics from a view point of structures and dynamics for a long time. Sub-micrometer sized domains are typical higher-order structures in the relaxor ferroelectrics and the relation between the domain size and the susceptibility have been clarified [1]. On the other hand, the normal ferroelectrics such as $BaTiO_3$ have also been reported to show large enhancement of the susceptibility by a factor of 10 by decreasing the domain size. This is so-called domain engineering and the resultant domain structures are called as engineered domains [2]. Since the mechanism of the large susceptibility originating from the domains has not been clarified, the function of the domain wall (= interface) is recently and commonly considered to be important [3, 4]. However, the domain wall thickness is at most a few nm and the volume fraction of the domain wall regions is too much small compared with the bulk volume. How the domain walls affect the bulk and contribute to the large susceptibility? For solving the problems, it is essential to access the structures and the dynamics of the domain walls, if possible, directly.

In this paper we show two challenges to investigate the structures and dynamics of domain walls directly by using synchrotron x-ray and neutron scattering techniques. One is the neutron quasielastic scattering of $BaTiO_3$ with engineered domain configuration. The other is the synchrotron x-ray scattering study of the $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ ($x = 0.3$). The former experiment will provide us information of the domain wall dynamics with the micro-eV resolution, while, the latter experiment will provide us information of the change of the structural morphology of the domain wall near critical temperature ($T_c \sim 420$ K).

References

[1] For example, K. Ohwada *et al.*, Ferroelectrics (accepted for publication), Phys. Rev. B **92**, 174121 (2015), Phys. Rev. B **90**, 104109 (2014).
[2] S. Wada *et al.*, J. Appl. Phys. 98, 014109 (2005), Ferroelectrics 355, 37 (2007), Nihon Kessho Gakkaishi, 54, 81 (2012).
[3] M. Iwata *et al.*, Jpn. J. Appl. Phys. 54, 021502(2015).
[4] J. Hlinka, J. Adv. Dielect. 02, 1241006 (2012).
[5] P. Chu *et al.*, Scientific Report 05007 (2014).

Direct observation of bent electronic band structure in $BaTiO_3$

**Norihiro Oshime[1*], Jun Kano[1,2], Eiji Ikenaga[3], Shintaro Yasui[4], Satoshi Hinokuma[5],
Naoshi Ikeda[1], Yosuke Hamasaki[6], Sou Yasuhara[4], Takayoshi Yokoya[7],
Mitsuru Itoh[4], Tatsuo Fujii[1], and Akira Yasui[8]**

[1]*Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan.*
[2]*Laboratoire SPMS, CentraleSupélec 8-10 rue Joliot-Curie 91190 Gif-Sur-Yvette, France.*
[3]*Institute of Materials and Systems for Sustainability, Nagoya University, Nagoya 464-8603, Japan.*
[4]*Laboratory for Materials and Structures, Tokyo Institute of Technology, Yokohama 226-8503, Japan.*
[5]*Department of Applied Chemistry and Biochemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan.* [6]*Department of Chemistry, Faculty of Science, Gakushuin University, Tokyo 171-8588, Japan.* [7]*Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan.* [8]*Japan Synchrotron Radiation Research Institute, JASRI, Sayo, Hyogo 679-5198, Japan.*
*Corresponding Author: sc421235@s.okayama-u.ac.jp

Electric polarization causes an electrostatic potential gradient along to the polarization in ferroelectric oxides [1], involving the bent band structure. The gradational potential drives rectified electron transfer in ferroelectric tunneling junctions [2] and photovoltaic devices [3]. The energy level of the band bending structure is described by layer-by-layer shift along the polarization orientation [4]. We consider that depth profile analysis of the energy shift is important for the understanding of electronic structure in ferroelectrics. In this study, direct observation of bent band structure in ferroelectric $BaTiO_3$ (BTO) has been performed using angular-resolved hard x-ray photoemission spectroscopy (AR-HAXPES).

Figure 1 shows the depth dependence of binding energies of the valence band (VB) in BTO thin film with 5 nm thickness. The VB consists of three electronic states one nearly pure O-2*p* orbital and two hybridization states originated from O-2*p* and Ti-3*d* orbitals, which correspond to regions A, B and C, respectively.

In the internal layer of BTO (corresponding to emission angle 15°-45°), the binding energy of regions A, B and C monotonically increases with the increase of depth. The energy shift follows with a potential slope where electric polarization is pointing into the Nb doped $SrTiO_3$ (NSTO) substrate. Thus we assigned this behavior as ferroelectric band bending (FeBB) induced by electric polarization. In the surface and BTO/NSTO interface regions, incomplete screening and Schottky barrier appeared, respectively. Note that the binding energy of region B and C in FeBB shows larger shift than region A, revealing that band bending can be affected by the hybridized states in ferroelectric oxide.

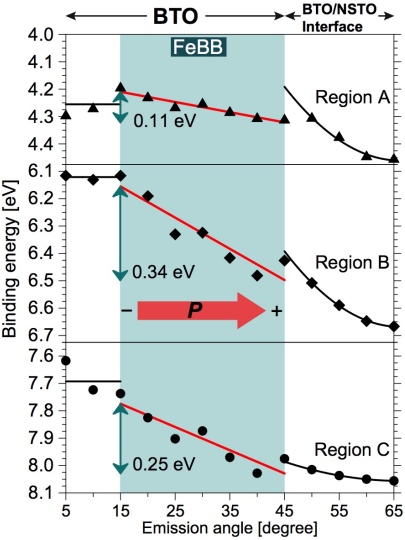

Fig. 1. The depth dependence of binding energy of VB in BTO. AR-HAXPES can observe depth profile of BTO with the emission angles 5°-45°.

References

[1] M. Y. Zhuravlev et al., *Phys. Rev. Lett.* **94**, 246802 (2005).
[2] E. Y. Tsymbal and A. Gruverman, *Nat. Mater.* **12**, 602 (2013).
[3] H. Matsuo et al., *Appl. Phys. Lett.* **108**, 032901 (2016).
[4] X. Liu et al., *Phys. Rev. Lett.* **116**, 197602 (2016).

Structure and ferroelectric properties of KNN- based perovskite ceramics

E. D. Politova[1*], N. V. Golubko[1], G. M. Kaleva[1], A. V. Mosunov[1], N. V. Sadovskaya[1], S. Yu. Stefanovich[1], D. A. Kiselev[2], A. M. Kislyuk[2], P. K. Panda[3]

[1]L.Ya.Karpov Institute of Physical Chemistry; Vorontsovo pole, 10, Moscow 105064 Russia,
[2]National University of Science and Technology "MISiS",
Leninskii pr. 4, Moscow, 119991 Russia
[3]National Aerospace Laboratories, Kodihalli, Bangalore-560017 India
*Corresponding Author: politova@nifhi.ru

Lead-free ferroelectric materials on the base of $(K_{0.5}Na_{0.5})$ NbO_3 (KNN) are being intensively studied in order to replace widely used the Pb-based ones [1–3]. In this work, effects of modification of compositions by donor and acceptor dopants in the A- and B-sites of perovskite lattice on structure, dielectric, ferroelectric and piezoelectric properties of ceramics from Morphotropic Phase Boundary in the systems $(K_{0.5}Na_{0.5})$ NbO_3 (KNN) and $(K_{0.5}Na_{0.5})$ NbO_3 — $BaTiO_3$ (KNN-BT) additionally doped by Ni^{3+} cations have been studied. Ceramic samples were prepared by the two-step solid-state reaction method at temperatures $T_1 = 1073$ K (6 h), $T_2 = 1223$ K (6 h), $T_3 = 1423$ K (2 h).

The samples were characterized using the X-ray Diffraction, Second Harmonic Generation (SHG), and Dielectric Spectroscopy methods. Microstructure of the samples was examined by the Scanning Electron Microscopy (SEM) method and the surface morphology and as-grown domain structure of the samples were characterized by the Piezoresponse Force Microscopy (PFM) method.

Depending on composition and sintering conditions changes in the unit cell volume were observed. Ferroelectric phase transitions were revealed at $T_{pt} \sim 400$ K and at $T_m \sim 600$ K in the dielectric permittivity versus temperature curves. An increase in the $BaTiO_3$ content leads to slight decrease in the T_m and T_{pt} values. Increase in the spontaneous polarization value was observed in modified ceramics using the SHG method. At the room temperature, non monotonous changes of dielectric parameters and spontaneous polarization values were observed in modified compositions studied. Using the PFM method the as-grown domain structure was observed in ceramics prepared. The hysteresis behavior of the piezoresponse of the ceramic confirmed their ferroelectric switching behavior. Finally, effective d_{33} piezoelectric coefficient values reached d_{33}=300 pm/V in the KNN-BT ceramics and d_{33}=200 pm/V in the samples additionally doped by Ni^{3+} cations. The results obtained confirmed prospects of new lead-free materials development by modification of the KNN- based compositions close to the MPB by the aliovalent cation substitutions.

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References

[1] K. Wang, F.-Z. Yao, W. Jo, D. Gobeljic, V. V. Shvartsman, D. C. Lupascu, J.-F. Li, J. Rodel, Temperature-insensitive (K, Na)NbO_3-based lead-free piezoactuator ceramics, *Adv. Funct. Mater*. 23, 4079–4086 (2013).
[2] P. K. Panda and B. Sahoo, PZT to Lead-Free Piezo Ceramics, *Ferroelectrics* **474**, 128–143 (2015).
[3] J. G. Wu, D. Q. Xiao, J. G. Zhu, Potassium-sodium niobate lead-free piezoelectric materials: Past, present, and future of phase boundaries, *Chem. Rev.* **115**, 2559–2595 (2015).

Investigations of nonlinear-optical response and inelastic light scattering on local inhomogeneities in strontium barium niobate crystals of different chemical compositions

A. M. Pugachev[1], I.V. Zaitseva[1], V.K. Malinovsky[1], N.V. Surovtsev[1], L.I. Ivleva[2], P.A. Lykov[2]

[1]Institute of Automation and Electrometry, Siberian Branch of the Russian Academy of Sciences, 630090, Novosibirsk, Russia
[2]Prokhorov General Physics Institute, RAS, 119991, Moscow, Russia
*Corresponding Author: *apg@iae.nsk.su*

The generation of the second optical harmonic (SHG) and Raman spectra (Raman spectra) on a series of strontium barium niobate $Sr_xBa_{1-x}Nb_2O_6$ (SBN x) crystals of various stoichiometric compositions (x = 0.3, 0.5, 0.6, 0.75) that exhibit the properties of both an ordinary ferroelectric (x = 0.3), and the ferroelectric with diffuse phase transition (x = 0.6, 0.75). The crystals were grown in the Prokhorov General Physics Institute. The aim of this research is investigation of local noncentrosimmetric inhomogenities in the paraelectric phase in ferroelectric crystals [1]. The temperature dependences of the signal of the second optical harmonic with a high spectral resolution (not worse than 1 cm^{-1}) were measured upon excitation by pulsed laser radiation of a wavelength of 1064 nm, as well as Raman spectra in the spectral range 8–200 cm^{-1}. It is found that in the high-temperature phase the SHG signal is reliably detected in all the investigated SBN samples, which indicates the presence and temperature evolution of local noncentrosymmetric inhomogeneities in the paraelectric phase. When comparing the obtained experimental results with measurements of the dielectric constant in SBN crystals [2], it was shown that analysis of the temperature derivative of the second harmonic signal proposed in [3] reliably describes the parameters of the phase transition from ferroelectric to paraelectric phase. It was shown experimentally that in all the investigated SBN crystals both in the ferroelectric and paraelectric phases, the spectral width of the SHG (Hyper- Rayleigh scattering) response does not exceed the spectral resolution of the spectrometer (~ 1 cm^{-1}). This indicates that the lifetimes of the polar local regions are in the range of not less than 5 ps (additional contributions comparable in integral intensity to the SHG signal are not found). The dependence of the shape of the central peak in Raman spectra on the stoichiometric composition of the SBN crystals is discussed. In particular, it is shown that, in ferroelectrics with a diffuse phase transition (x> 0.6), the central peak in the spectral density presentation is determined by a set of relaxation times. This description of the central peak is fundamentally different from the case of an ordinary ferroelectric in which the central peak is determined by a single relaxation time.

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References

[1] G. Burns, B.A. Scott. Solid State Comm. 13, 423 (1973).
[2] T. Lukasiewicz, M.A. Swirkowicz, J. Dec, W. Hofman, W. Szyrski. Journal of Crystal Growth 310, 1464 (2008).
[3] A.M. Pugachev, I.V. Zaytseva, V.I. Kovalevskii, V.K. Malinovsky, N.V. Surovtsev, Yu.M. Borzdov, I.P. Raevski, S.I. Raevskaya, M.A. Malitskaya. Ferroelectrics, 501, 9–14 (2016)

Phase State and Lattice Dynamics of Multiferroic Heterostructures Based on Bismuth Ferrite

D.S. Babarikin,[1] D.V. Stryukov,[2] A.S. Anokhin,[2] A.V. Pavlenko,[2] V.B. Shirokov,[1,2] V.M. Mukhortov,[1,2] and A.G. Razumnaya,[1,*]

[1]Faculty of Physics, Southern Federal University, Zorge str. 5, Rostov-on-Don, Russia
[2]Southern Scientific Center of RAS, Rostov-on-Don, 344006, Russia
[*]Corresponding Author: razumnaya1@gmail.com

The heterostructures with alternating layers of multiferroic and ferroelectric materials offer a promising platform for the development of fundamentally new lead-free ferroelectric random access memory elements due to the functional cross-coupling of magnetic (multiferroic) and ferroelectric properties.

In the current work the $Bi_{0.98}Nd_{0.02}FeO_3/Ba_{1-x}Sr_xTiO_3$ (BFO/BST*x*) heterostructures with different composition of the BST*x* buffer layers ($x = 0.2$; 0.6; 0.8) have been synthesized and studied using x-ray diffraction and Raman spectroscopy with the objective to determine the specific features of their structure and lattice dynamics. The BFO/BST*x* heterostructures were grown by rf-sputtering on a cubic MgO substrate. The thicknesses of the BFO and BST*x* layers were ~100 nm.

The out-of-plane and in-plane unit cell parameters of the layers, the modulation period, and the orientation relationships between the film and the substrate have been determined using X-ray diffraction. According to X-ray diffraction examination and Raman spectroscopy, the crystal structure of the BFO and BST*x* layers in BFO/BST*x*/(001) MgO heterostructures is pseudotetragonal at room temperature. It was revealed that the tetragonal distortion of the BST*x* layers increases with increasing of the Ba concentration, while in the BFO layers it remains virtually unchanged.

The surface microstructure of the heterostructures was studied using an atomic force microscope. The analysis of the surface morphology revealed that the BFO films showed a three-dimensional growth mechanism, and the islands are strictly oriented with respect to each other and the substrate and to the crystallographic axes of the MgO substrate.

The polarized Raman spectra of the heterostructures have been measured in a broad temperature range. Besides phonon modes, Raman spectra contains a band observed at 610 cm^{-1}, which corresponds to the maximum density of states of the magnon branch at the Brillouin zone boundary, and an intense band in the second-order Raman spectra with the maximum at ~1250 cm^{-1}, which corresponds to the density of states of two-magnon excitations. It has been found that the intensity of the band at ~1250 cm^{-1} decreases linearly with increasing temperature. The extrapolation of the temperature dependence of the integrated intensity of this band suggests that in these heterostructures magnetic ordering exists up to ~700 K.

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Raman Spectra and Optical Non-linear Properties of Tellurium Oxides

E. M. Roginskii*[1,3], Ph. Thomas[2] and M.B.Smirnov[3]

[1]Spectroscopy of the solid state laboratory, Ioffe Institute, Politekhnicheskaya st. 26,
Saint-Petersburg, Russia

[2]Institute of Research on Ceramics (IRCER) UMR 7315 CNRS, Centre Européen de la
Céramique, Université de Limoges, 12 rue Atlantis, 87068 Limoges Cedex, France
[3]Physical Faculty, Saint-Petersburg State University, Stary Petergof, Ulyanovskaya st.1, Russia

*Corresponding Author: e.roginskii@mail.ioffe.ru

Since the beginning of 90th the extraordinary high optic non-linearity of tellurium dioxide TeO_2 in both crystalline and glassy states attracts attention of specialists searching for advanced materials for new optoelectronic devices [1]. It was found that the non-linear refractive index of glassy α-TeO_2 is maximal among other oxide glasses and is 50 times higher than that of the silica glass [2]. Large body of studies (experimental and theoretical) was devoted to searching a chemical composition of the tellurite glasses with optimal non-linear optical (NLO) properties. The paper [3] reports on extremely high value of third order nonlinear susceptibility with of β-TeO_3 with respect to the one of α-TeO_2. However, no experimental confirmation was reported up to now because the crystalline β-TeO_3 is available only in powder form. Besides, the compound is unstable and under moderate heating decomposes into TeO_2 and O_2. These results induces alternative study to confirm or disprove extra high nonlinear optical properties of the crystal. We report here the results of comprehensive investigation within Density functional theory (DFT) of electronic structure dynamical and optical (linear and nonlinear) properties of α-TeO_2 and β-TeO_3.

One of the most important parameter of the electronic structure which influence on optical properties is the band gap (E_g). The calculated value of E_g for TeO_3 within local density approximation (LDA) is strongly underestimated with respect to experimental value E_g=3.25 (see. Fig. 1), the same result was obtained in paper [3]. This error result in strong overestimation of nonlinear properties. The bandstructure calculation of α-TeO_2 and β-TeO_3 by quasiparticle GW approximation was performed to find the E_g values in a good agreement with experimental data. Then Habbard like term corrections to the density functional was applied by using the data obtained with GW approximation. The phonon and raman spectra and the nonlinear properties was estimated for both TeO_2 and TeO_3 crystals. It is found that $\chi^{(3)}$ (β-TeO_3) is about twice as lower than $\chi^{(3)}$ (α-TeO_2) in spite of the fact that the electronic bandgap is narrower in β-TeO_3.

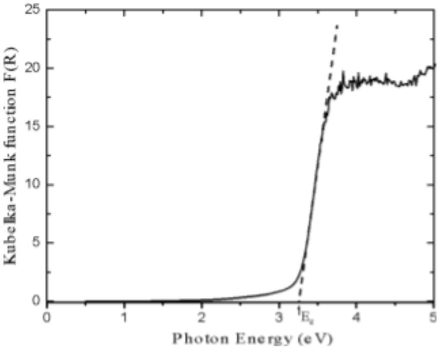


Figure 1: Diffuse reflectance data for powder β-TeO_3 sample: Kubelka-Munk function versus the photon energy.

References

1. H. Nasu, T. Uchigaki, K. Kmiya, and K. Kubodera, Jpn. J. Appl.Phys., 1992 3, 3899.
2. S.-H. Kim, T. Yoko, and S. Sakka, J. Am. Ceram. Soc. 1993, 76, 2486.
3. A. Plat, J. Cornette, M. Colas, A.P. Mirgorodsky, M.B. Smirnov, O. Noguera, O.Masson, P. Thomas, J. Alloys and Compounds 2014, 587 120.

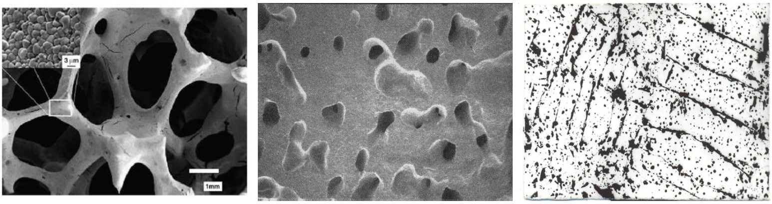
Recent Advances in Porous Piezoceramics Applications

A. N. Rybyanets [1,*]

[1]**Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia**
[*]**e-mail:** arybyanets@gmail.com

Large-scale production of composite materials and their intensive use in ultrasonic transducers has required overcoming not only technological problems but also psychological revolution in gospels views of technologists and designers of piezoceramic material. The refusal from former trends to manufacture high-density, chemically perfect and structure indefectible ceramic materials and switchover to fabrication and use of "imperfect" materials (lead-metaniobate ceramics, porous ceramics and ceramic matrix composites) has required a long time [1]. Porous piezoelectric ceramics are important for a variety of applications such as medical ultrasonic devices, nondestructive testing, underwater acoustics etc.

In this work, a brief review of fabrication methods, mathematical models and applications of porous piezoceramics are presented. The results of microstructure analysis and microstructure-properties interrelations are discussed. A recent advances in fabrication methods of nano- and microporous piezoceramics, and ceramic matrix piezocomposites, as well as new application fields (baromembrane process and HIFU devices) are discussed.



(a) (b) (c)

Figure 1. SEM micrographs of different porous ceramics structures: (a) open cell PZT ceramics, fabricated by polymer foam method; (b) closed cell (Na, Li)NbO3 ceramics, obtained by burning out of polymer granules; (c) PKN ceramics with intracrystalline porosity, obtained by the fast-sintering method.

Two recently appeared applications of porous piezoceramics are considered: piezoelectrically active membranes for reverse osmosis, ultra- and microfiltration and HIFU transdusers based on ferroelecally hard porous focusing elements. The results of experimental studies of micro- and nanoporous piezosubstrates, piezoelectrically active nanoporous selective layers, hybrid and composite piezoelectrically active and ultrasonically activated membranes are presented. Theoretical aspects of ferroelectrically hard porous ceramics application in HIFU transducers as well as systematical experimental data are presented.

Technological aspects of large-scale manufacture and application of porous piezoceramics in HIFU, NDT and medical ultrasonic transducers are considered. A novel advances in fabrication methods of nano- and microporous piezoceramics and derivative ceramic matrix piezocomposites are considered.

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References

[1] A. N. Rybyanets, *IEEE Trans. UFFC*, vol. 58, N7, P. 1492–1507 (2011).

Micro-Raman and AFM Observations of Domain in Barium Titanate

A. Sakai,* R. Kashiwagi, and Y. Yamamoto
Department of Information and Electronic Engineering, Muroran Institute of Technology,
27-1 Mizumoto-cho, Muroran 050-8585, Japan
*Corresponding Author: sakai@mmm.muroran-it.ac.jp

Mappings of 90º domains in a $BaTaO_3$ single crystal have been obtained by micro-Raman scattering and atomic force microscopy (AFM). In order to take a sensitive detection of the domain structure, we used the optical flat surfaces (100) of the single crystal with a single domain in the tetragonal phase at room temperature. After the sample was heat up to the cubic phase through the transition temperature, the domains are obtained in the tetragonal phase.

Micro-Raman scattering spectra were observed by a back scattering configuration with a spatial resolution of 2μm. The scan area is 30×30μm with 1μm step so that the Raman image consists of 30×30 pixels (900 spectra). Figure 1 shows the mapping of the peak position of the 160cm^{-1} mode. The stripe structure of domain is clear detected at the position of the domain observed by the optical microscope.

Figure 2 shows the AFM image observed by the contact mode. The value of the bending angle θ is in good agreement with the theoretical value. Temperature dependence of the AFM image and bending angle will be shown at the conference.

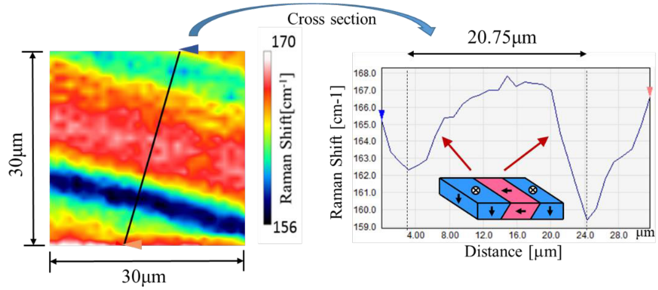

Fig.1. Mapping of the domain structure of the BTO single crystal by micro-Raman scattering.

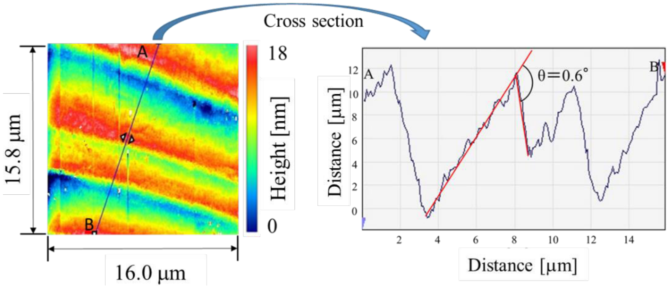

Fig.2. AFM image of the domain structure of the BTO single crystal.

The background specific heat of ferroelectrics

I. Shnaidshtein,[*] and S. Grabovsky

Faculty of Physics, Lomonosov Moscow State University, Moscow, Russia
[*]shnaidshtein@physics.msu.ru

The heat capacity of a ferroelectric crystal in a wide temperature range can be represented as the sum of the anomalous and background specific heats. Anomalous or excess is called the part of the specific heat, which depends on the phase transition parameter and its derivatives. This part of the heat capacity is not observed if measurements are taken at a fixed value of the phase transition parameter. The background heat capacity of a crystal is the sum of its lattice heat capacity and other contributions that do not depend on the derivatives of the phase transition parameter, for example, the contribution to the heat capacity of thermal expansion. Calculation of the background heat capacity is a necessary stage in the interpretation of the experimental data on the temperature dependence of the heat capacity for ferroelectric crystals.

Since the background specific heat of a crystal is substantially determined by its lattice heat capacity, the determination of the background specific heat from the experimental temperature dependence of the heat capacity of the crystal makes it possible to obtain independent information on its phonon spectrum. Conversely, the existing data on the phonon spectrum of the crystal make it easier to determination its background specific heat.

Calculation of the background specific heat is quite facilitated in the presence of a sufficiently detailed temperature dependence of the heat capacity over a wide temperature interval including the ferroelectric phase transition. Obtaining such the dependences requires special thorough when planning and making a calorimetric experiment.

We made a comparative review of various methods for determining the background specific heat of ferroelectric crystals. The experimental and computational approaches are analyzed using examples of such model ferroelectrics as triglycine sulfate, potassium dihydrophosphate, barium titanate and gadolinium molybdate. Also detailed are the results relating to prospective for applications crystals of lanthanum borogermanate and solid solutions based on lead titanate magnoniobate.

The specificity of ferroelectric crystals is that, as a rule, in their phonon spectrum the most active are one or several polar optical modes being discussed. This circumstance can be used both in constructing the lattice specific heat from data on the phonon spectrum of the ferroelectric crystal, and in constructing the interpolation schemes necessary for interpretation the temperature dependencies of the heat capacity of ferroelectrics.

Modeling of the irreversible phenomena of polarization and deformation in ceramics

A. S. Skaliukh

Southern Federal University, Rostov on Don, Russia
Corresponding Author: *a.s.skaliukh@gmail.com*

Modeling of micro- and nanocomposites with active elements requires the development of effective mathematical models of polarization and deformation of polycrystalline ferroelectric continuous medium. Of a particular interest are the problems in the three-dimensional formulation, where one has to deal with irreversible processes. Such processes are associated with phase transitions of a representative volume by the type "solid body" — "solid body", and mathematically are modeled by nonlinear relationships. Two sets of unknown functions are introduced into the model, which are reversible and irreversible parameters, and, as a consequence, formulated the constitutive relations separately for these parts. The most interesting cases arise in non-uniform fields, in cases where electric fields grow, while mechanical fields decrease, or vice versa. Least studied the case of partial polarization, when the direction of the electric field does not coincide with any of the principal axes of mechanical stresses tensor.

Within the framework of a quasi static process, we constructed a three-dimensional model of polarization and depolarization of polycrystalline ferroelectric perovskite-type materials, then investigated the anisotropy classes of a representative volume under various external electric and mechanical fields, and constructed algorithms for determining of the residual and induced vectors of polarization and the residual and reversible tensors of deformation.

Irreversible parameters of the process are found from the equations in differentials constructed using the energy criterion of domain switching, energy ratios that take into account for break down the mechanisms fixation of domain walls, and energy losses in the cyclic process of deformation and polarization. Reversible parameters are found from the general relations of thermodynamics, in the form of functional dependences for elastic, piezoelectric and dielectric characteristics in the kind of linear relationships from the residual parameters.

The case is considered when the direction of the residual polarization vector does not coincide with any of the principal directions of the residual strain tensor. A comparison is made with the results of the Jiles-Atherton model, large and small strain and dielectric loops of hysteresis are constructed, and the cases of introducing anisotropy for reversible parameters are investigated. It is shown that the constructed model successfully extends to many types of ceramics. It can be implanted into a finite element complex to calculate the physical characteristics of working elements of piezoceramic sensors.

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Electrocaloric and Accompaining Effects in $BaTiO_3$–$SrTiO_3$ Solid Solution

E. Smirnova*, G. Sotnikova, N. Zaitseva, A. Kapralov, G. Gavrilov

Ioffe Institute, 26 Politekhnicheskaya, St Petersburg 194021, Russian Federation

Corresponding Author: esmirnoffa@gmail.com

In the past decades, the electrocaloric effect (ECE) are of much interest since the solid-state cooling systems based on ECE can be developed to substitute ordinary mechanical vapor compression refrigeration systems.

The ECE is a phenomenon in which a material shows reversible temperature changes under applied electric field [1, 2]. The temperature change δT is proportional to polarization change under electric field (∂P (E) / ∂T) and the electrocaloric effect in ferroelectric (FE) transitions can reach maximum values. Therefore one of the possible directions of searching for electrocaloric materials is the study of the ECE in the temperature range of FE phase transitions [3].

The ECE is inextricably linked with the accompanying effects that determine its magnitude, such as pyro- and piezoelectric effects, thermal expansion, elastic properties and heat capacity [1]. The behavior of the listed phenomena differs in field and temperature dependences.

We present the study of ECE and related effects such as pyro- and piezoeffects, as well as temperature changes in the elastic properties of electric field in ferroelectric with the first-order phase transition, to reveal the mechanisms that determine the electrocaloric effect in such materials. A solid solution of barium-strontium titanate 0.68 BaTiO3-0.32 SrTiO3 (BST) with the first-order ferroelectric transition was selected as the object of investigation [4].

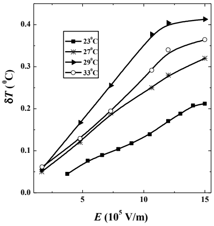

Figure 1. Plots of ECE-induced sample temperature change δT vs. applied bias field E for BST ceramics .

The results of the complex study allow us to analyze the influence of various mechanisms that contribute to both pyroelectric and electrocaloric effects in a ferroelectric with a first-order phase transition and to assess the role of the secondary pyroelectric effect in the electrocaloric effect.

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References
[1] J.F.Nye., Physical properties of crystals, .Oxford of the Claredon Press, 385 p.(1964).
[2] W.N.Lawless, Phys.Rev.B.**16**, .433 (1977).
[3] M. Valant, Progress in Materials Science, **57**, 980 (2012).
[4] V.V. Lemanov, E.P.Smirnova, P.P.Sirnikov, E.A Tarakanov, Phys. Rev. B. **52**, 3151 (1996).

Compositional Control of Divalent Cations Mobility in $Ca_3(VO_4)_2$-type Ferroelectric/Optical Nonlinear Materials

S. Yu. Stefanovich and B. I. Lazoryak

Chemistry Department, Lomonosov Moscow State University
Leninskie Gory 1, Moscow, Russia
Sergey Stefanovich: *stefan@tech.chem.msu.ru*

Oxide ferroelectrics often contain single-valent cations such as lithium, sodium, or potassium responsible for ionic-conductive or ion-exchange properties at moderate temperatures. Along with adjustable domain structure these properties open additional technical possibilities for engineering of integrated optics devices. Divalent cation conductivity is still unknown to co-exist with ferroelectricity.

Vanadates $Ca_9M(VO_4)_7$ (M = REE, Y or Bi) structurally related to high-temperature ferroelectric $Ca_3(VO_4)_2$ [1] possess ferroelectric-ionic conductor phase transitions at 1000–1200 *K* [2]. They are shown to have high optical nonlinearities [3], and are also able to generate laser radiation when M = Nd, Tm, Er, Yb [4]. Their large-size Czochralski-grown crystals [5] are now widely investigated as promising nonlinear and laser materials. At around ferroelectric phase transitions the $Ca_9M(VO_4)_7$ demonstrate Ca^{2+}-ionic conductivity usually equal 10^{-2}–10^{1} $Ohm^{-1}cm^{-1}$, which is comparable with K^+-ionic conductivity near ferroelectric phase transitions in $KTiOPO_4$.

Examined in this work structural and dielectric characteristics, differential thermal analysis, and second harmonic generation (SHG) evidence that $Ca_{10.5-x}Pb_x(VO_4)_7$ solid solution ($0 \le x \le 4.5$) belongs to whitlockite-type ferroelectrics. SHG activity strongly increases with x up to its maximum at x = *4.5, where it has a record value among* all studied before $Ca_3(XO_4)_2$related compounds (X=P, V). Ferroelectric Curie temperatures of $Ca_3(VO_4)_2$ drops from its known value $T_c = 1368$ *K* (x = 0) to 770 K (x = *4*.5). Two-order increased Ca^{2+}- ion conductivity of $Ca_{10.5-x}Pb_x(VO_4)_7$ in vicinity of 1000 K at x = 44.5 in combination with their ferroelectric and optical nonlinear properties extends applicability of high-temperature ion-exchange technologies to new promising materials.

Influence of guest atoms on ferroelectric, optical nonlinear and ion-conductive properties of $Ca_3(VO_4)_2$ — derived vanadates are studied in details for a group of compositions $Ca_{8-x-y}MePb_xBi_{2/3y}(VO_4)_7$, where Me = Mg, Zn, Cd. It is found, that lead substitution for calcium is as a major factor controlling ferroelectricity, ionic-conductivity and non-linear optical activity (NOA) in $Ca_3(VO_4)_2$-based materials. Concentration of bismuth is on the second place in augmenting of NOA in the whitlockites. Atoms of other tested elements (Me = Mg, Zn, Cd) have little influence on NOA and ferroelectric properties. However, located inside the conductivity channels in the crystals these atoms are blocking Ca^{2+} mobility. As the result, two- to three-orders ionic conductivity reduction characterizes the $Ca_{8-x-y}MePb_xBi_{2/3y}(VO_4)_7$ in comparison with ionic conductivity of pure $Ca_3(VO_4)_2$ in technically important middle-temperature range 700–1000 K.

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References

[1] Glass A. M., Abrahams S. C., Ballman A. A., Loiacono G. Ferroelectrics **17**, 579 (1977)
[2] Lazoryak B. I., Belik A. A., Stefanovich S. Yu. *et. al*. Dokl. Phys. Chem.. **384,** 144 (2002)
[3] Sleight A. W. Huang J. US Patent 5.202.891. 1993
[4] Chen X., Zhuang N. F., Hu H. L., Zhuang F. J., Chen J. Z. Appl.Phys., **B88,** 449 (2007)
[5] Dobrotvorskaya, M.V., Gorobets Y. N., Kosmyna M. B. *et. al*. Crystallogr. Rep. **57,** 959 (2012)

Depth profiling of dopant concentration and pyroelectric properties of $LiNbO_3$ single crystals high-temperature treated in the presence of metal ions

G. Suchaneck[1,*], U. V. Yakhnevych[2], A. Eydam[1], D. Yu. Sugak[2,3], I. I. Syvorotka[2,3], V.G. Haiduchok[2,3], S. B. Ubizskii[2], G. Gerlach[1]

[1]Solid State Electronics Laboratory, TU Dresden, 01062 Dresden, Germany
[2]Department of Semiconductor Electronics, Lviv Polytechnic National University, 12 Bandera street, Lviv, Ukraine
[3]Scientific Research Company "Electron-Carat", 202 Stryiska street, Lviv, Ukraine

[*]Corresponding Author: Gunnar.Suchaneck@tu-dresden.de

Lithium niobate is one of the most frequently used oxide crystals. Its versatility is based on excellent nonlinear electro-optic, as well as piezoelectric and pyroelectric properties of the intrinsic material. Due to certain $LiNbO_3$ "soft" structure characteristics, single crystals can be doped by a large number of impurities allowing the targeted modification of the crystal properties. Usually, doping is carried out during the crystal growth.

In this work, the less common after-growth diffusion method is applied incorporating dopants into the crystal during a high-temperature treatment in an appropriate environment containing metal ions. Optical spectra of $LiNbO_3$ single crystals (7×15×32 mm, X, Y, Z) doped with Cu, Fe, Co, and Cr were recorded along the main crystallographic axes perpendicular to the direction of diffusion in order to obtain the dopant depth distribution [1]. For studying of pyroelectric properties, plates with a size of 7×15×1.8 mm, (X, Y, Z) were cut out, electroded with Cu and covered by a graphite lacquer to enhance laser light absorption. Depth profiling of the pyroelectric properties was performed by (i) an approximate laser intensity modulation method (LIMM) applied to both sides of the sample which is valid near the surface up to about 25% of thickness [2], and (ii) a thermal square-wave method at constant frequency which records the time dependence of the pyroelectric response [3]. TSWM assumes a constant heating rate during pulse time and a constant propagation speed of the temperature oscillation. Since TSWM consists of constraints related to the penetration depth of the temperature oscillation, its validity is limited in our 1.8 mm thick $LiNbO_3$ samples to a region of 20 to 80% of crystal thickness.

Optical spectra revealed an incorporation of ions to depths of less than 700 μm. The dopant concentration maxima were located at a depth of 170…700 μm from the crystal edge. They depend on the type of ion and the conditions of heat treatment, i.e. the duration and the temperature of annealing. For undoped $LiNbO_3$ single crystals, a thickness-independent pyroelectric coefficient was obtained. The pyroelectric coefficient profile of doped $LiNbO_3$ crystals was attributed to peculiarities of the dopant concentration profile.

References

[1] D. Sugak, I.I. Syvorotka, U. Yakhnevych, et al., *Acta Phys. Pol. A,* 133 (2018) *in press*
[2] B. Ploss, R. Emmerich, S. Bauer, *J. Appl. Phys*. 72, 5363-5370 (1992)
[3] O.V. Malyshkina, A.A. Movchikova, G. Suchaneck, *Fiz. Tverd. Tela* 49, 2045-2048 (2007)

Ferroelectricity in PMN-17PT single crystals

Š. Svirskas,[1,*] D. Jablonskas[1], S. Kojima,[2] and J. Banys[1]

[1]Faculty of Physics, Vilnius University, Saulėtekio al. 9/IIIb., LT-10222 Vilnius, Lithuania
[2]Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
[*]Corresponding Author: sarunas.svirskas@ff.vu.lt

Relaxor ferroelectrics are materials exhibiting a broad dielectric anomaly which expands over 10 orders in magnitude of frequency. This anomaly is not related to a structural phase transition. It is thought to be caused by the random fields (RFs) [1] which arise due to the compositional heterogeneity in the perovskite lattice.

Canonical relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) has a charge disorder in the B-site of perovskite lattice. The charge disorder is the main factor which enhances random fields and thus relaxor properties in PMN. RFs can be controlled by substituting B-site with a “compatible” ion which has a valence which keeps charge neutrality in the lattice. This can be achieved by mixing PMN with lead titanate (PT). The (1-x)PMN-xPT solid solutions has one of the most exciting phase diagrams in the solid state physics. It exhibits crossover from pseudocubic-rhombohedral to tetragonal phase through the region called morphotropic phase boundary [2]. These compositions are technologically important due to their excellent electromechanical properties.

The increase of PT concentration enhances the ferroelectric properties in PMN-xPT system. Several works on structural properties of compositions below the morphotropic phase boundary revealed that rhombohedral phase occurs in a compositions with quite low concentration of PT [3,4]. Although some other works contradict these findings and claim that the rhombohedral phase appears only for concentrations above 25 % of PT [5,6].

In this contribution we will discuss the presence of a ferroelectric phase transition in PMN-17PT single crystal from the point of macroscopic responses. The dielectric spectra were investigated in 20 Hz – 50 GHz frequency range. The relaxation dynamics revealed features of an order-disorder phase transition in a PMN-17PT single crystal. The measurements of ferroelectric hysteresis loops favors the idea that ferroelectric phase appears spontaneously with the temperature. The crystal is in a ferroelectric phase at the room temperature and the electric field induced phase transition cannot be observed in a zero-field cooled sample.

References

[1] V. Westphal, W. Kleemann, and M.D. Glinchuk, Phys. Rev. Lett. **68**, 847 (1992).
[2] S.W. Choi, T.R. Shrout, S.J. Jang, and A.S. Bhalla, Mater. Lett. **8**, 253 (1989).
[3] Z.-G. Ye, Y. Bing, J. Gao, A.A. Bokov, P. Stephens, B. Noheda, and G. Shirane, Phys. Rev. B **67**, 104104 (2003).
[4] B. Dkhil, J.M. Kiat, G. Calvarin, G. Baldinozzi, S.B. Vakhrushev, and E. Suard, Phys. Rev. B **65**, 024104 (2001).
[5] G. Xu, D. Viehland, J.F. Li, P.M. Gehring, and G. Shirane, Phys. Rev. B **68**, 212410 (2003).
[6] P.M. Gehring, W. Chen, Z.-G. Ye, and G. Shirane, J. Phys. Condens. Matter **16**, 7113 (2004).

Dynamical hierarchy of ferroelectric nanocrystals of $BaTiO_3$ and $PbTiO_3$ synthesized in supercritical hydrothermal condition

Masaki Takesada[1*], Yuki Sugawara[1], Kiwamu Sue[2], Hiroshi Takashima[2], Yukiya Hakuta[3]
[1]Department of Physics, Hokkaido University, Sapporo 060-0810, JAPAN
[2]AIST, Umezono 1-1-1 Tsukuba 305-8565
[3]Advanced Operando-measurement Technology OIL, AIST, Kashiwanoha 5-1-5, Kashiwa 277-858, JAPAN
[*]E-mail: mt@phys.sci.hokudai.ac.jp

The ferroelectricity in perovskite oxides of $BaTiO_3$ and $PbTiO_3$ has been extensively studied from the view point of fundamental physics and practical applications for more than half a century. In the recent miniaturization of devices, interests of ferroelectricity shift from macroscopic to nano-sized physical properties. It has been reported that the ferroelectricity and the dielectricity indicate frail stability with decreasing the size of system as the size effect. The existence of the critical size of ferroelectricity has been discussed. The reported critical sizes for the existence of ferroelectricity in $BaTiO_3$ and $PbTiO_3$ are about 30 nm and 10 nm, respectively. [1,2] The ferroelectric phase transition disappears below the critical size. Because a long-range force of dipole-dipole interaction is modulated in nano-sized system, however, it may no longer be a phase transition phenomenon but should be called ferroelectric nano-ordering. Recently from a first principal calculation Naumov et al. predicted the geometrical toroidal ordering in nanocrystals. [3] A dynamical behavior of ferroelectric nano-ordering attracts attention in vicinity of critical size from the viewpoint of the limit of statistical physics.

In the present study the broadband light scattering has been performed in the $BaTiO_3$ and $PbTiO_3$ nanocrystals to clarify the dynamics of the ferroelectric nano-ordering near the reported critical sizes using a Sandercock-type tandem Fabry-Perot interferometer and a triple monochromator. The broadband light scattering spectra of ferroelectric nanocrystals of $BaTiO_3$ and $PbTiO_3$ compose of a characteristic central peak component. Since the central peak is not able to be reproduced by a simple Debye-type relaxation, the dynamical structure in ferroelectric nanocrystals of $BaTiO_3$ and $PbTiO_3$ could be derived from the hierarchical structure with geometrical toroidal nano-ordering and in the fractal structure. We will discuss the results of broadband light scattering spectra from the view point of fracton.

1. Z. Zhao et al., Phys. Rev. B 70 (2004) 024107.
2. K. Ishikawa et al., Phys. Rev. B 37 5852 (1988).
3. Ivan I. Naumov et al., Nature 432, (2004) 737.

Structure, Dielectric and Piezoelectric Properties of the $BiScO_3$-$PbTiO_3$-$PbMg_{1/3}Nb_{2/3}O_3$ Ceramics

M. V. Talanov,[1,*] A. A. Bush,[2] K. E. Kamentsev,[2] V. P. Sirotinkin,[2] and A. G. Segalla[3]

[1] Research Institute of Physics, Southern Federal University, Stachki av. 194, Rostov-on-Don, Russia
[2]Restarch Institute of Solid state electronics materials, Moscow Technological University (MIREA),
pr. Vtrnadskogo, 78, Moscow, Russia
[3]Research and production complex No 3, “ELPA” Research Institute,
Panfilovski pr., 10, Zelenograd, Russia
[*]Corresponding Author: tmikle-man@mail.ru

The solid solutions of relaxor ferroelectrics $Pb(Mg_{1/3}Nb_{2/3})\ O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})\ O_3$ (PZN) with the classic ferroelectric $PbTiO_3$ (PT) are greatly promising for practical applications as elements of actuators, sensors, transducers and other piezoelectric devices [1]. The single crystals of these solid solutions with the compositions near the morphotropic phase boundaries (MPB) that separate tetragonal and rhombohedral parts of the x-T phase diagrams possess the highest piezoelectric responses (d_{33}>2500 pC/N, k_{33}>0.90) [2]. However the low Curie temperature (T_c ~120–150ºC) of the relaxor-PT solid solutions seriously limits the range of their potential applications. Recently, the (1-x)$BiScO_3$(BS) xPT solid solutions have been intensively investigated. These solid solutions are characterized by high values of piezoelectric coefficients (d_{33}>450 pC/N) and Curie temperature (T_c > 450˚C) when their compositions are close to the MPB (x=0.64) [3]. The most effective way to connect the merits of various binary systems, in particular, the highest piezoelectric response of relaxor-PT systems, and high T_c of the BS-PT system, is the design of multicomponent systems. To date, there is a whole family of multicomponent solid solutions between BS, PT and various relaxor ferroelectrics: PZN [4], $Pb(Ni_{1/3}Nb_{2/3})\ O_3$ [5] and others. However, the available information about the dielectric and piezoelectric properties of the BS-PT-PMN ceramics is very limited, despite the fact that solid solutions based on PMN are key materials for various applications [6]. Thus, the aim of this work is the construction and refinement of the phase diagram for the ternary BS-PT-PMN system in a wide range of the BS content, the determination of the structure-property relationships of the solid solutions and the choice of the most promising compositions for practical applications in piezoelectric devices.

The phase structure, dielectric, ferroelectric, and piezoelectric properties of (1–2x)$BiScO_3$ — $x$$PbTiO_3$ — $x$$PbMg_{1/3}Nb_{2/3}O_3$ ceramics with x=0.30–0.46 were studied [7]. It was found that an increase of x leads to a structural phase transition between the rhombohedral and tetragonal phases through an intermediate monoclinic phase, a crossover from the nonergodic relaxor state to the ferroelectric one, as well as a change in the order of phase transition from the second-order to the first-order. The assumption have been made about the existence of a tricritical point on the phase diagram at x≈0.42 near which the dielectric response is enhanced. The observed structure-property relationships of the studied solid solutions are discussed. It is shown that the solid solutions with x=0.42 are characterized by high piezoelectric parameters (d_{33}=509 pC/N, d_{31} = –178 pC/N, d_h = 153 pC/N), which make possible their applications in sonar equipment.

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References

[1] K. Uchino, *Piezoelectric actuators and ultrasonic motors*, Boston: Kluwer (1997)
[2] S. E. Park, T. R. Shrout, *J Appl Phys.*, 82, 1804–1811 (1997)
[3] R. E. Eitel et al., *Jpn J Appl Phys.*, 40, 5999–6002 (2001)
[4] Z. Yao et al., *J Appl Phys.*, 109, 014105(1–8) (2011)
[5] D. Wang et al., *Jpn J Appl Phys.*, 52, 101101(1–5) (2013)
[6] C. J. Stringer et al., *J Amer Ceram Soc.*, 91, 1781–1787 (2008)
[7] M. V. Talanov et al., *J Amer Ceram Soc.*, 101, 683–693 (2018)

Relationship between Chirality and Ferroelectricity of Alanine doped Triglycine sulfate crystals

Yukana Terasawa,[1] Kazuhiko Ishikawa,[1] Masaaki Ichiki,[2] and Toru Asahi [1,3*]

[1] Graduate School of Advanced Science and Engineering, Waseda University, 2-2 Wakamatsu-cho
Shinjuku-ku, Tokyo, Japan, 162-8480,
[2] Research Center for Ubiquitous MEMS and Micro Engineering, National Institute of Advanced
Industrial Science and Technology (AIST), 1-2-1 namiki, tsukuba-shi, Ibaraki, Japan, 305-8564,

[3] Research Organization for Nano & Life Inovation, Waseda University, Tokyo, Japan, 513
Wasedatsurumaki-cho Shinjuku-ku, Tokyo, Japan, 162-0041
*Corresponding Author: tasahi@waseda.jp

When we grow chiral crystals composed of achiral molecules, we get the same amount of left-handed crystals and right-handed crystals (spontaneous resolution [1]). Although we can distinguish left and right of these crystals by X-ray diffraction analysis, this is very complicated method and takes long time. As far, there is no method to grow chiral crystals which have chirality that we desire.

We have studied on chirality of Triglycine sulfate (TGS) crystals, which is one of chiral crystals composed of achiral molecules. Especially, alanine doped Triglycine sulfate (ATGS) crystals have very interesting property in chirality. From our study, we found that L-alanine doped Triglycine sulfate (LATGS) crystals form left-handed crystals, on the other hand, D-alanine doped Triglycine sulfate (DATGS) crystals form right-handed crystals. That is to say alanine can control the chirality of TGS crystal. Furthermore, we can consider that the bias of chirality of TGS crystal is due to steric hindrance of alanine molecule.

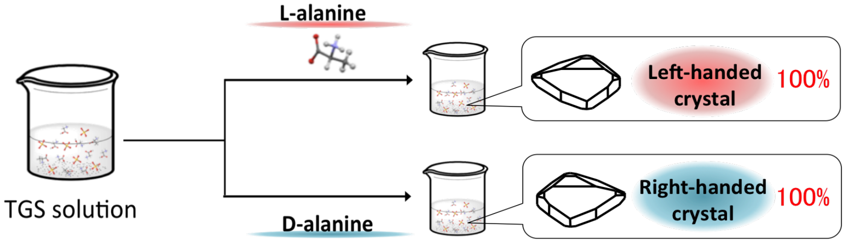

Figure 1. Chirality of LATGS crystals and DATGS crystals

TGS crystals also show ferroelectricity below $\boldsymbol{T}_{\mathrm{C}}$, so we measured *P*-*E* hysteresis curve. As the results, internal bias ($\boldsymbol{E}_{\mathrm{I.B.}}$) of LATGS crystal showed large positive values and that of DATGS crystal showed large negative values compared to that of TGS crystal. From these results, we consider that there is a relationship between chirality and $\boldsymbol{E}_{\mathrm{I.B.}}$ of ATGS crystal. So in this presentation, we will explain details on chirality and $\boldsymbol{E}_{\mathrm{I.B.}}$ of ATGS crystal.

Reference

[1] L. Pasteur, *Annales de Chemie et de Physique*, 24, 442-459 (1848).

Magnetoelectric States of Complex Oxides: Experiment, Crystallographic and Thermodynamic Description

N. V. Ter-Oganessian

Institute of Physics, Southern Federal University, 194 Stachki st., Rostov-on-Don, Russia
nikita.teroganessian@gmail.com

The quest for new multiferroic materials showing magnetoelectric properties above room temperature and with considerable coupling of electrical and magnetic subsystems continues and new compounds are constantly discovered. In this talk we would like summarize our theoretical and experimental research on several complex oxides. The first group of compounds are antiferromagnetic spinels Co_3O_4, $MnGa_2O_4$, and $MnAl_2O_4$, which are shown to display linear magnetoelectric effect below their Neel temperature. Linear magnetoelectric effect was also shown to emerge in $CoAl_2O_4$ with low inversion and significant spin frustration, which allows making important conclusions on the magnetic ground state and its dependence on cation inversion. Two other examples include goethite, α-FeOOH, which is theoretically predicted to display linear magnetoelectric effect below its Neel temperature of 400 K and $PbCu_3TeO_7$, which shows complex magnetic field induced magnetoelectric states.

The work is financially supported by the Ministry of Education and Science of the Russian Federation (state assignment Grant No. 3.5710.2017/8.9).

Crystal Structure and Lattice Dynamics of Piezoelectric Diphenylalanine Nanotubes

S. G. Vasilev,[1,*] P. S. Zelenovskiy,[1] S. G. Arkhipov[2,3], V. Svitlyk,[4]
V. Ya. Shur[1], S. Kopyl[5] and A. L. Kholkin[1,5]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave, 620000 Ekaterinburg, Russia
[2]Novosibirsk State University, 2 Pirogova str., 630090 Novosibirsk, Russia
3Institute of Solid State Chemistry and Mechanochemistry,
18 Kutateladze str., 630128 Novosibirsk, Russia
[4]European Synchrotron Radiation Facility, 71 avenue de Martyrs, Grenoble, 38000, France
[5]Physics Department & CICECO — Aveiro Institute of Materials, University of Aveiro,
3810–193, Aveiro, Portugal
[*]Corresponding Author: semen.vasilev@urfu.ru

Diphenylalanine (FF) is a model object for the investigation of bioorganic molecules self-assembly and formation of tubular structures [1]. Moreover, FF microtubes have attracted research interest in recent decade due to excellent piezoelectric and pyroelectric properties [2] and their potential for biocompatible piezoelectric and pyroelectric elements for medical devices [3].

We have studied single crystalline microtubes consist of FF nanotubes and needle-like solvate crystals of cycled FF monomers grown from the solution. Both microtubes and solvate crystals have typical length up to 5 mm and diameter 50–100 µm. Studies were performed at the European Synchrotron Radiation Facility (ESRF), ID27 High Pressure Beamline. We have performed two types of single crystal X-ray diffraction experiments for the determination of: 1) FF structure at low temperatures, and 2) the change of the crystal structure of FF and cycled FF dipeptides at ambient conditions. The structures were solved at different temperatures measurements were performed in temperature range from 290 to 95 K. The investigated temperature dependence of the cell parameters allowed to reveal an anomaly in the vicinity of 200 K.

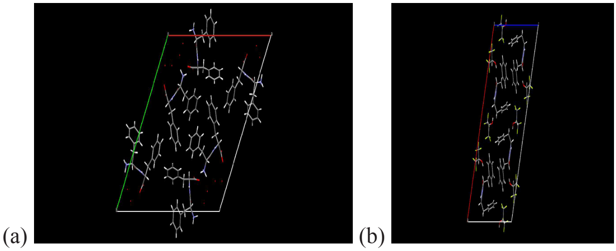

Figure 1. Solved crystal cell (a) FF microtube consisting of individual nanotubes, and (b) solvate crystal of cycled FF monomers.

The research was carried out using equipment of Ural Center for Shared Use “Modern Nanotechnologies” Ural Federal University with the financial support by the grant of the President of the Russian Federation for young scientists (Contract 14.Y30.17.2294-MK) and the Government of the Russian Federation (Resolution 211, Contract 02.A03.21.0006). S.K. and A.L.K. thank the joint project Portugal-Turkey (TUBITAK/0006/2014 and No. 115F227). We acknowledge ESRF for providing beamtime for these studies.

References

[1] E. Gazit, *The Royal Society of Chemistry*, 36, 1263–1269 (2007)
[2] A. Kholkin et al., *ACS Nano*, 4, 610–614 (2010)
[3] I. Coondoo et al., Electrically Active Materials for Medical Devices (Imperial College Press), 297–316 (2016)

Dielectric Properties of Water and Ice: a Unified Treatment

A.A. Volkov

A. M. Prokhorov General Physics Institute, Russian Academy of Sciences,
119991Vavilov st., 38, Moscow, Russia
aavol@bk.ru

Water's dielectric properties are central to understanding many vital biologic, technologic and environmental processes. Surprisingly, in spite of a giant body of scientific efforts a detailed insight into the atom-molecular mechanisms occurring in water and ice is still missing. Traditionally, water and ice are studied separately by independent scientific schools. Both substances possess a large dielectric constant of close value: ε(0)~87 and ε(0)~96 for water and ice at the freezing temperature. First value is associated with the dipole moment of an individual H_2O molecule, while in the second case «the dipole moment per 0–0 link seems to be a more pertinent take-off concept» [1]. Successful attempt was demonstrated to treat the dielectric constant of water in terms of ferroelectricity [2]. There is no idea, however, how to extend the ferroelectric model to ice. The concept of ferroelectric ice develops independently [3].

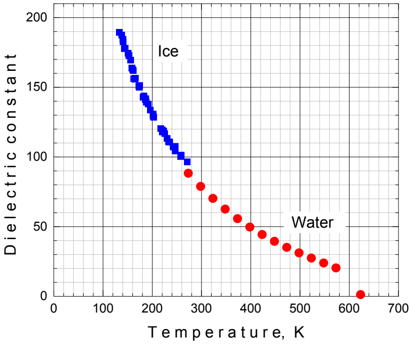

Figure 1. Static dielectric constants, ε(0), of water and ice [4, 5].

Figure 1 shows the temperature behavior of the dielectric constants of water and ice. The curve provokes to think about the uniform origin of water (red) and ice (blue) pieces. In our recent study we have developed a conceptually new model of the water structure [6]. The model implies a high concentration of the inherent H_3O^+ and OH^- ions. The dielectric response is due to bipolar diffusion of the ions and their interconversion with the neutral H_2O molecules via the proton exchange. Here we show that the model gives a unified approach to understanding of the water and ice dielectric response formation.

References

[1] A. von Hippel, *IEEE Trans. Electr. Insul*. **23**, pp. 801–840 (1988).
[2] J. C. del Valle et al., *Ferroelectrics* **466**, pp. 166–180 (2104).
[3] H. Fukaszawa et al., *The Astrophysical Journal* **652**, pp. L57 — L60 (2006).
[4] M. Uematsu and E. U. Franck, *J. Phys. Chem. Ref. Data* **9**, pp.1291–1306 (1980).
[5] G. P. Johari and E. Whalley, *J. Chem. Phys*. **75**, 1333–1340 (1981).
[6] A.A. Volkov et al., *J. Mol. Liquids* **248**, pp. 564–568 (2017).

Nonlinear dynamics of phosphorous chalcogenide ferroelectrics with many-well local potentials

I. Zamaraite,[1*] A. Dziaugys,[1] R. Yevych,[2] M. Medulych,[2] J. Banys,[1] Yu. Vysochanskii[2]

[1] Vilnius University, Vilnius, Lithuania
[2] Uzhgorod University, Uzhgorod, Ukraine
[*]Corresponding Author: ilona.zamaraite@ff.vu.lt

For $Sn_2P_2S_6$ (SPS) ferroelectrics the second order phase transition at $T_0 \sim 337$ K with mixed displacive — order/disorder character is occurred [1]. Observed evolution of the soft mode spectrum is enough complicate — several low energy optic branches linearly interact at heating and relaxational central peak growths near the phase transition temperature. By DFT methodology it was found [2] that local potential for the spontaneous polarization fluctuations in SPS ferroelectrics has three — well shape. This peculiarity is related to Sn^{2+} cations electron lone pair stereoactivity [2, 3] and to valence fluctuations $P^{4+} + P^{4+}$ — $P^{3+} + P^{5+}$ inside $(P_2S_6)^{4-}$ anions [4]. Microscopic origin of ferroelectric lattice instability in SPS can be described as second order Jahn-Teller effect and their thermodynamics is considered in the frame of Blume-Emery-Grffiths model. At accounting of electronic correlation, the presentation of Anderson's electron pairs flipping can be involved. At this the electronic recharging and lattice instability can be presented as pseudospin fluctuations in anharmonic potential with complicate shape. The anharmonic quantum oscillator (AQO) model is proposed [4] for description of temperature–pressure phase diagram of SPS. This model we generalize by taking onto of two inequal interacting systems of oscillators and applicate for analysis of ferroelectric dynamics at temperature and pressure variation.

As direct confirmation of three-well shape of the local potential in SPS, we present our observation of antiferroelectric — like double dielectric poops in this proper uniaxial ferroelectrics. Qualitively this phenomenon can be explained as repopulation of pseudospins between possible three states (–1, 0 +1) during repolarization process at external electric field influence. The calculations give us the stable and metasrable solutions which describe ferroelectric and antiferroelectric phases and corresponding types of loops depending on parameters of AQO model. The temperature — electric field diagram in the parameters of AQO model is described. Experimental condition for realization of "ferroelectric" or "antiferroelectric" loops are investigated.

References

[1] Yu. M. Vysochanskii et al. Phase transitions in ferroelectric phosphorous chalcogenide crystals. Vilnius University Publishing House, 453 (2008)
[2] K. Z. Rushchanskii, Yu. M. Vysochanskii, D. Strauch, *Physical Review Letters*, 99, 207601–1–207601–4 9 (2007)
[3] K. Glukhov et al., *International Journal of Molecular Sciences*, 13, 14356–14384 (2012).
[4] R. Yevych et al., *Low Temperature Physics*, 42, 1477–1486 (2016)

Posters

On ultrafast switching of the ferroelectric polarization by midinfrared pulses

V.A. Abalmassov

Institute of Automation and Electrometry SB RAS, Academician Koptyug ave. 1, Novosibirsk, Russia
abalmassov@iae.nsk.su

The appearance of high-power coherent sources of THz radiation recently has made possible resonant excitation of high amplitude phonon modes with the resulting change in various material properties [1]. In [2] the author has proposed a mechanism of switching of the ferroelectric polarization by the resonant excitation of the high-frequency vibrational mode nonlinearly coupled to the low-frequency ferroelectric mode through the term in the ferroelectric phase. The coupling constant was calculated in frame of the density functional theory. The follow-up experiment [3] has demonstrated the transient switching of the polarization in $LiNbO_3$. The 150 fs midinfrared pulse at 19 THz with the maximum available in the experiment fluence of 95 mJ cm^{-2} (electric field about 20 MV cm^{-1}) reversed the polarization in an irradiated part of the sample but after about 200 fs the polarization switched back to its initial direction.

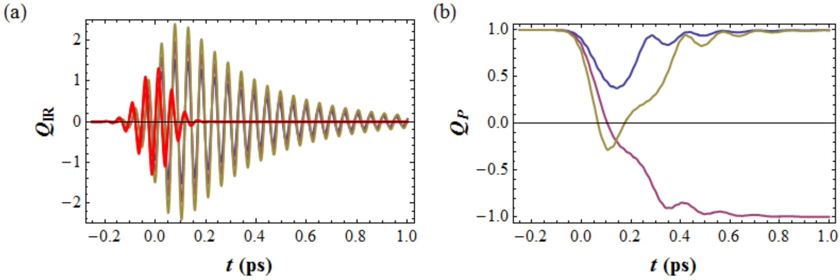

Figure 1. (a) Midinfrared excitation impulse (red) and the resulting phonon mode at three excitation fluences *J* (blue), 1.29*J* (purple) and 1.57*J* (gold). (b) The corresponding polarization mode

We analyze the theoretical approach used in [2, 3] and argue that the coupling terms obtained there are valid only in the limit of very fast dynamics because the corresponding potential was calculated with the other phonon modes frozen. At the same time the thermodynamic potential obtained for fixed generalized forces (relaxed ions positions) is used instead to describe the ferroelectric soft mode dynamics [4]. Due to the symmetry restrictions the coupling term of interest in the paraelectric phase in is. Taking this into account and solving the dynamics equations numerically as in [2, 3] we show (Figure 1) that this coupling actually can lead to the polarization reversal and can explain the observed in [3] polarization dynamics.

References

[1] T. Kampfrath, K. Tanaka and K.A. Nelson, *Nature Photonics*, 7, 680 (2013)
[2] A. Subedi, *Phys. Rev. B*, 92, 214303 (2015)
[3] R. Mankowsky et al., *Phys. Rev. Lett.*, 118, 197601 (2017)
[4] V.L. Ginzburg, A.P. Levanyuk and A.A. Sobyanin, *Phys. Rep.*, 57, 151 (1980)

Ferroelectric phase transition in KDP from Monte Carlo simulations

V.A. Abalmassov

Institute of Automation and Electrometry SB RAS,
Academician Koptyug ave. 1, Novosibirsk, Russia
abalmassov@iae.nsk.su

Ferroelectric phase transition in KDP (KH_2PO_4) is triggered by the protons ordering in double-well potentials of hydrogen bonds. The Hamiltonian of the proton subsystem can be written in a Ising-like form. Because of the frustrating interactions only a sophisticated modification of the mean field theory, four-particles cluster approximation [1], is able to adequately describe the thermodynamic properties of the phase transition.

Monte Carlo simulations have been done earlier to find the critical temperature [2]. However, the energy parameters scheme used there was slightly different from that which is traditionally used.

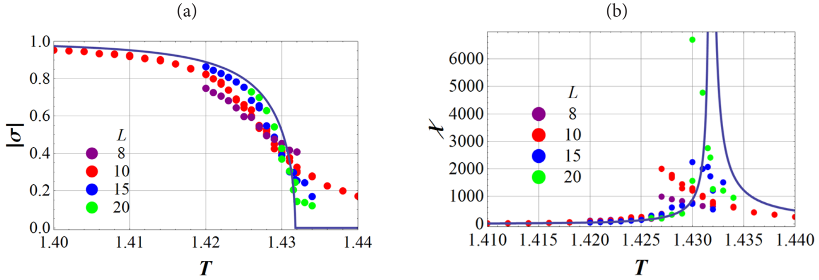

Figure 1. (a) average spin and (b) dielectric susceptibility as a function of temperature for different sample sizes L. The solid line corresponds to the cluster approximation

We used the Metropolis algorithm to calculate the thermodynamic quantities of the KDP crystal in the vicinity of the phase transition neglecting the protons tunneling in double well potentials. The sample had a cubic form with L unit cells on each side (8 pseudospins in the unit cell). Up to 10^7 Monte Carlo cycles per spin were performed. We set for the moment the long-range interaction parameter γ to zero which should give the second order phase transition. For the other energy (Slater-Takagi) parameters we take $\omega/\varepsilon = 8.5$ which corresponds well to the experimental data [3]. We note a very good agreement between Monte Carlo and four-particles cluster approximation results (Figure 1).

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project No. 18–02–00399.

References

[1] R. Blinc and S. Svetina, Phys. Rev. 147, 430 (1966)
[2] G.S. Pawley and J.E. Tibballs, Ferroelectrics Letters 44, 33 (1982)
[3] V.A. Abalmassov, A.M. Pugachev, N.V. Surovtsev, Fiz Tverd Tela 53, 1301 (2011)

Local studies of the electro-mechanical properties and domain dynamics in rare earth doped $BiFeO_3$ ceramics

**A. S. Abramov[1,*], D. O. Alikin[1,4], M. M. Neradovskiy[1,2],
A. P. Turygin[1], R. O. Rokeah[1], A. V. Nikitin[3],
D. V. Karpinsky[3], V. Ya. Shur[1], A. L. Kholkin[1,4]**

[1]School of Natural Sciences and Mathematics, Ural Federal University,
620000 Ekaterinburg, Russia
[2]Université Côte d'Azur, CNRS, InPhyNi, 06100 Nice, France
[3]Scientific-Practical Materials Research Centre of NAS of Belarus, BY-220072 Minsk, Belarus
[4]Department of Physics & CICECO — Aveiro Institute of Materials, University of Aveiro, Aveiro,
3810–193 Portugal
[*]Corresponding Author: alexander.abramov@urfu.ru

Nowadays, the researcher attention is focused on the piezoelectric and electromechanical properties of the bismuth ferrite material, where in thin film form high remnant polarization was discovered [1]. Large polarization and related piezoelectric response is highly desirable for $BiFeO_3$ (BFO) ceramics which are possible to be applied in various electromechanical devices. The main issues impeding using the BFO in devices are high electrical conductivity and low phase stability [2]. These problems partially can be solved by rare earth elements doping which reduces impurities of secondary phases, thereby stabilizing the perovskite phase and, as a consequence, reduce leakage current [3,4]. In addition, realization of morphotropic phase boundary structural state realizes the coexistence of structural phases, which tends to improve ceramic's magnetic and piezoelectric properties [5].

In this work we implemented advanced multi-frequency piezoresponse force microscopy (PFM) and spectroscopy techniques for the local study of the rare earth doped BFO ceramics (Pr, La, Sm). We developed evaluation of effective piezoelectric coefficients with additional electrostatic compensation ad showed that particularly diminished electromechanical response of BFO ceramics is not related to defect impact but is consequence of "leaky" phase boundaries impact. The method revealed negligible difference of effective d_{33} on doping at the local scale while macroscopic response was significantly reduced and differed from composition to composition.

Here we also developed PFM voltage spectroscopy and local switching for the investigation of the domain wall dynamics in ceramics materials. The mobility of domain walls in an inhomogeneous system was studied. The impact domain wall orientation into its kinetics is discussed as well as initial domain state and defect environment.

The equipment of the Ural Center for Shared Use "Modern nanotechnology" was used. The reported study was funded by RFBR (grant No. 17–52–04074) and BRFFR (grant No. F17RM-036). This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01–0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 778070.

References

[1] J. Wang, et al., *Science.*, 299, 1719–1722 (2003).
[2] T. Rojac, et al., *J Am Ceram Soc.*, 97, 1993–2011 (2014).
[3] S. Fujino, et al., *Appl Phys Lett.*, 92, 82–85 (2008).
[4] A. Ghosh, D. Damjanovic, *Appl Phys Lett*., 99, 232906 (2011).
[5] I. O. Troyanchuk, et al., *Phys. Rev*., 83, 054109 (2011).

Study of structure and dielectric response of the ferroelectric composites $(1\text{-}x)NaNO_2+(x)KNO_2$ at x=0.05, 0.1 and 0.2

O. Alekseeva[1], A. Naberezhnov[1,2], E. Stukova [3], M. Reehuis [4]

[1] Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation
[2] Ioffe Institute, 26 Polytekhnicheskaya St., St. Petersburg, 194021, Russian Federation
[3]Amur State University
21 Ignatievskoe Str, Blagoveshchensk, 675027, Russian Federation
[4]Helmholtz Zentrum Berlin
14109, Germany, Berlin, Hahn-Meitner-Platz 1
E-mail alekseevaolga0@gmail.com

The results of the neutron diffraction study of ferroelectric polycrystalline composites (1-x) $NaNO_2+(x)KNO_2$ at x=5, 10 and 20 vol. % and pure $NaNO_2$ are reported. The dielectric properties study [1] of these composites has shown the existence of an anomaly in the dielectric response: it was found two maxima on the temperature dependence of the real part of the permittivity ε '(T) on heating. One of them was observed at the temperature of 437 K (both in composites and in the pure $NaNO_2$ powder) and refered to the ferroelectric phase transition in $NaNO_2$. The second one was observed at T≈424 K in the low-frequency region $f \sim 10^{-1}–10^5$ Hz. Upon cooling only one wide maximum was observed near T≈418 K. This anomaly could be attributed, for instance, with a shift of the temperature of transition in incommensurate phase of $NaNO_2$ taking place in these composites. However, the clarification of microscopic nature of observed dielectric response anomalies requires structural studies.

The main results of the structural studies are the following:

The temperature dependencies of $NaNO_2$ order parameter η(T) in these composites were obtained (Fig. 1). They don't depend on KNO_2 concentration and coincide with η(T) for pure $NaNO_2$. Curie temperature values practically coincide on heating and cooling. Anomaly of dielectric response observed in the composites at T~420 K does not relate to any structural transition

The increase (~10-15 K) of structure phase transition temperature for KNO_2 in the composites at different KNO_2 concentrations is observed.

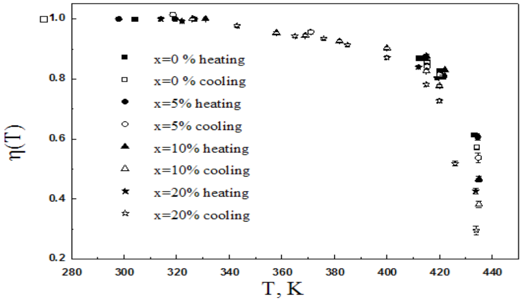

Fig. 1 Temperature dependence of the order parameter in the composites and pure $NaNO_2$.

References:

Stukova E. V., Baryshnikov S. V., Koroleva E. Yu. Shift of phase transitions in $NaNO_{2(1-x)}/KNO_{2(x)}$ ferroelectric composites. Russian physics journal, 2015, Volume 58, Issue 2, pp 221–22.

Study of kinetics of growth of $NaNbO_3$ nanocrystals formed in the glass matrix

S. B. Vakhrushev[1,2], E. Yu. Koroleva [1,2], A.A. Lipovskii [2], A.A. Naberezhnov[1,2], D.K· Tagantsev [2], O.A. Alekseeva [2], P. Yu. Vanina[2], D. Yu. Chernyshev[3]

[1] Ioffe Institute, 26 Polytekhnicheskaya St., St. Petersburg, 194021, Russia
[2] Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russia
[3]European Synchrotron radiation facility, Grenoble, France
E-mail: alekseevaolga0@gmail.com

Ferroelectric glass-ceramics containing niobate-group crystals have attracted much attention because of their promising properties for a variety of applications, such as electro-optics, high energy storage capacitors and nonlinear and photorefractive materials. Nevertheless, a set of questions opened because of nanoscale-range size of crystalline grains in these materials is still unanswered. These are initial stage of formation of the crystallites, behavior of crystalline structure and phase transition in the nanocrystals, which depend on their size and surrounding glass matrix. The kinetics of their crystalline lattice formation from initial nanoscale niobium-rich droplets in glass is also unknown.

In this contribution the results of X-ray diffraction study of growth kinetics, time evolution of structure and phase transition sequence of $NaNbO_3$ nanocrystals formed in the glass matrix are reported. We have studied the growth of $NaNbO_3$ nanocrystals in the sample containing 31% of Nb_2O_5 at three temperatures: 542, 532 and 522 ºC. Figure 1 shows changes of intensity of NaNbO3 (100) peak during the growth of $NaNbO_3$ nanocrystals. Analysis have shown that the structure corresponds to the tetragonal phase (space group ***P4/mbm***) as in bulk samples. The average size of $NaNbO_3$ nanocrystals was estimated. The nanocrystals' size evolution in the course of the growth at different temperatures is presented in Figure 2.

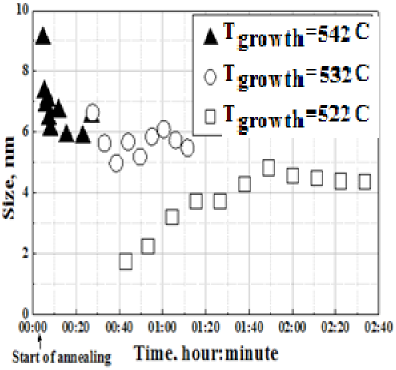

Fig. 1. Time evolution of (100) reflection intensity of $NaNbO_3$ during growth process at 3 temperatures.

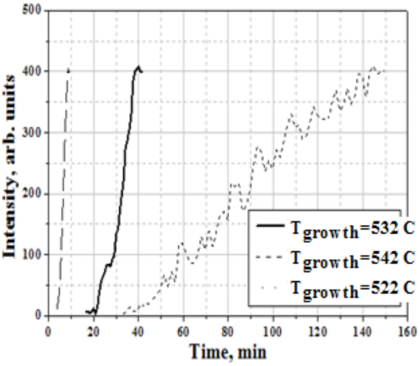

Fig. 2. Nanocrystals' size evolution in the course of growth at different temperatures

Domain structure and local polarization reversal in sol-gel $BiFeO_3$ thin films

D. O. Alikin[1,3,*], D. S. Chezganov[1], A. S. Abramov[1],
E. B. Araujo[2], V. Ya. Shur[1], A. L. Kholkin[1,3]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
Kuibysheva 48, Ekaterinburg, Russia
[2]São Paulo State University, Ilha Solteira — SP, São Paulo, Brazil
[3]Department of Physics & CICECO — Aveiro Institute of Materials, University of Aveiro,
3810–193, Aveiro, Portugal
[*]Corresponding Author: denis.alikin@urfu.ru

Bismuth ferrite (BFO) is one of the promising materials for photovoltaic applications since discovery of its abnormal photovoltaic effect and high values of photocurrent [1]. Recently, possibility to control photoconductivity by an arrangement of domain walls was demonstrated in BFO thin films [2]. Thus, microscopic insight into domain wall kinetics is motivated by the needs of domain wall engineering.

In this work we studied microstructure and domain structure relationship and its influence on the polarization dynamics. Both orientation analysis by electronic backscattered diffraction and extraction of spontaneous polarization from piezoresponse force microscopy (PFM) data demonstrated self-organized formation of 'cluster-like' domain structure with specific orientation of polarization orthogonal to the substrate (Figure 1). Despite the fact that BFO is a multiaxial material, domain structure was preliminary aligned along the one spatial axis and represented as "clusters" of grains with domain state similar to single domain state. These clusters were separated by grain boundaries possessing specific electronic transport (analogue of charged domain walls).

The unusual domain structure of the films allowed studying details of local polarization reversal in a inhomogeneous system with different interfaces: conductive and insulator grain boundaries. Two types of polarization reversal were found: nucleation of the domain under the tip and de-pinning of the existing domain walls from the insulator interface. Once created domain walls were interacting electrostatically with grain boundaries differently, depends on the interface conductivity. Finite element modelling with Landau-Ginsburg-Devonshire treatment was used to explore peculiarities of domain kinetics in an inhomogeneous electric field. Obtained results give a new understanding of the grain boundaries impact to the properties of ferroelectric thin films.

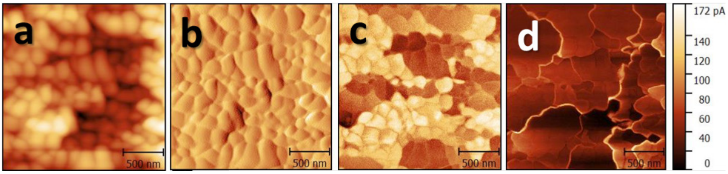

Figure 1. Domain structure in BFO thin films: a) topography, b) deflection signal (differential topography), c) vertical PFM phase, d) photocurrent.

The equipment of the Ural Center for Shared Use "Modern nanotechnology" was used. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 778070".

References

[1] S. Y. Yang, J. Seidel, S. J. Byrnes, *Nat. Nanotechnol.*, 5, 143 (2010).
[2] A. Bhatnagar, Chaudhuri R., Kim A. H., *Nat. Commun.*, 4, 2835 (2013).

Lattice dynamics in $PbZr_{0.8}Ti_{0.2}O_3$ probed by neutron and X-ray scattering techniques

D.A. Andronikova[1,2], Yu.A. Bronwald[1,2], R.G. Burkovsky[2], A. Bosak[3], D. Chernyshov[4], P.M. Gehring[5], A.V. Filimonov[2] and S.B. Vakhrushev [1,2]

[1]Ioffe Institute, 26 Polytechnicheskaya, St Petersburg, Russia
[2]Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya, SPb, Russia
[3]European Synchrotron Radiation Facility, BP 220, Grenoble Cedex, France
[4]Swiss-Norwegian Beamlines, ESRF, BP 220, Grenoble Cedex, France
[5]NIST Center for Neutron Research, National Institute of Standards and Technology,
100 Bureau Drive, MS6100, Gaithersburg, USA
*Corresponding Author: andronikova.daria@gmail.com

Lead-zirconate titanate $PbZr_{1-x}Ti_xO_3$ (PZT) is widely used and well-known piezoelectric material [1]. At Ti concentration range x=0.06–0.45 (so-called “rhombohedral” region of the phase diagram) two ferroelectric phases exist. Space group of the low-temperature rhombohedral phase (RLT) is R3c. This phase is characterized by cation displacements along [111] direction and oxygen octahedral antiphase rotation, doubled unit cell in three directions [2]. The high-temperature phase (RHT) has space group symmetry R3m [2], cations have similar displacements but oxygen octahedrals rotate along the same direction in all oxygen layers (in-phase rotations) [3]. Using transmission electron microscopy it has been obtained that RHT phase is characterized by appearance of weak M-superstructure peaks (h+½ k+½ l) in diffraction pattern, RLT phase — by appearance of R-superstructure peaks (h+½ k+½ l+½). Recently it has been obtained that RLT structure is characterized not only by ordered antiphase oxygen octahedral rotations, but also by some in-phase tilt components [4]. These in-phase oxygen rotations lead to weak DS at M-points. During transition from RLT to RHT while ordered antiphase tilts become disordered, in-phase tilts remain. Since both rhombohedral phases and the paraelectric phase [5] are characterized by disorder in oxygen octahedral rotations, neutron scattering technique is needed to study corresponding pre-transitional processes. In this presentation results of X-ray and neutron inelastic scattering will be compared and discussed in the context of understanding of phase transitions microscopic mechanisms.

References

[1] D.A. Berlincourt, C. Cmolik, and H. Jaffe, Proc. IRE48, 220 (1960).
[2] A.M. Glazer, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.28, 3384,1972.
[3] D. Viehland et.al. Ferroelectrics, Vol. 183, pp. 311–319 (1996)
[4] N. Zhang et al. J. Appl. Cryst. 48, 1637–1644 (2015).
[5] N. Zhang et al. Acta Cryst. B67, 461–466 (2011).

Pressure induced ferroelectric phase transition in $GdFe_3(BO_3)_4$ by first-principles calculations

N. D. Andryushin,[1,*] M. S. Pavlovski,[2] and V. I. Zinenko[2]

[1]Siberian Federal University, 660041, Krasnoyarsk, Russia
[2]Kirensky Institute of Physics, Federal Research Center, 660036, Krasnoyarsk, Russia
[*]Corresponding Author: and@iph.krasn.ru

A gadolinium ferroborate, $GdFe_3(BO_3)_4$, crystallizes in nonpolar trigonal space group (R32). The boron ions surrounded by three oxygen ions in form of triangle. The Gd ions surrounded by six oxygen ions in form of triangular prism. Structural phase transition in the crystal, which retains the trigonal symmetry, was observed under hydrostatic pressure of 25.6 GPa, in experimental study [1]. The transition is connected with abrupt change of the unit cell volume by 8%. The precise symmetry group of the high pressure phase $GdFe_3(BO_3)_4$ was not exactly determined.

In the present work theoretical study of gadolinium ferroborate is performed. The calculations were carried out by means of the Vienna ab initio package (VASP). The parameters of crystal lattice and coordinates of ions were optimized for $GdFe_3(BO_3)_4$ crystal in R32 phase and are in a proper agreement with experimental data. The calculation of lattice dynamics of the crystal revealed that there is no soft modes in the center of the Brillouin zone (gamma point) in $GdFe_3(BO_3)_4$ (space group R32). However, the same simulation with applied external pressure showed that one of the polar modes became instable (imaginary value of frequency) at some pressure.

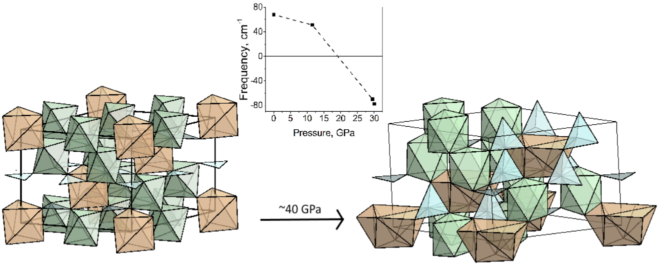

Figure 1. The calculated structures of $GdFe_3(BO_3)_4$ in the R32 phase without applied external pressure and in the R3 phase with applied external pressure ~40 GPa. The calculated pressure dependence of polar mode frequency in the R32 phase. Imaginary frequencies are shown in the real negative frequency range.

The atomic displacements connected with polar soft mode induce structural transition from space group R32 to R3. The structure of the $GdFe_3(BO_3)_4$ in high pressure phase (R3) was obtained from the relaxation calculation and external pressure simulation. The three of four BO3 triangles in the unit cell become BO_4 tetrahedrons and ions of Gd surround by nine ions of oxygen in this phase because of more dense structure. The structural transition also cause significant changes in calculated phonon spectra. We suppose that the phase transition observed in the experiment [1] was ferroelectric in accordance with our calculation.

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References

[1] A. G. Gavriliuk et al., *JETP Letters*, Vol. 80, № 6 pp. 426–432 (2004)

Lattice Dynamics of Two-layer Heterostructures Based on Barium-Strontium Titanate

Ya. Yu. Matyash,[1] N.V. Lyanguzov[2], A.S. Anokhin,[2,*] Yu I. Golovko[2], V.M. Mukhortov[2] and A.G. Razumnaya [1]

[1]Faculty of Physics, Southern Federal University, Zorge str. 5, Rostov-on-Don, Russia
[2]Southern Scientific Center of RAS, Rostov-on-Don, 344006, Russia
[*]Corresponding Author: anokhin.andrey@gmail.com

Currently, ferroelectric heterostructures consisting of layers of various compositions are the subject of intensive investigations because their properties can be improved due to the effect of deformation of a unit cell in thin layers. The deformation of a unit cell in heterostructures is controlled by the varying of the layer composition, selecting a substrate material or a buffer layer.

The effect of the sequence of the $Ba_{0.8}Sr_{0.2}TiO_3$ (BST08) and $Ba_{0.4}Sr_{0.6}TiO_3$ (BST04) layers deposition on the lattice distortions and dielectric properties in the two-layer BST08/BST04 and BST04/BST08 heterostructures was studied by means of X-ray diffraction and Raman spectroscopy. The symmetrical two-layer BST08/BST04 and BST04/BST08 heterostructures were deposited on cubic (001) MgO substrates by rf sputtering. The thicknesses of layers BST08 and BST04 were 45, 75 and 300 nm.

The investigations of the Polarized Raman spectra of the heterostructures show that the features of the behavior of the low-frequency transverse "soft" mode associated with the value of the static dielectric permittivity depend on the BST08 and BST04 layers deposition sequence. Note that in the Raman spectra of the BST08/BST04/MgO and the BST04/BST08/MgO heterostructures with 45 nm layer thicknesses, the frequencies of the soft E modes (104 and 89 cm^{-1}, respectively) are significantly different. With an increase of the BST08 and BST04 layers thickness up to 75 nm, the soft mode shift is ~ 10 cm^{-1} in the spectra of the BST08/BST04/MgO (100 cm^{-1}) and BST04/BST08/MgO (90 cm^{-1}) heterostructures. In the spectra of the BST08/BST04/MgO and BST04/BST08/MgO heterostructures with a layer thickness of 300 nm, the soft mode frequency is 102 and 97 cm^{-1}, respectively. Thus, the effect of the sequence of the layers deposition on the lattice distortions decreases with increasing of the layer thickness.

An increase in the frequency E(TO) of the soft mode in the BST08/BST04/MgO heterostructures indicates the presence of compressive stresses in the BST04 and BST08 layers. This result is in good agreement with the results of x-ray diffraction studies, which have shown the increasing of a value of tetragonal distortion in heterostructures, where the BST04 layer is the bottom layer. Thus, the values of internal mechanical stresses and the values of misfit strain depend on the sequence of layers deposition. The values of the dielectric constant, spontaneous polarization and the Curie temperature can be controlled by the changing of the order of the layers in two-layers the heterostructures.

This work was performed in the framework of the State task of the SSC RAS (Project No. State. Reg.: 01201354247).

Piezoelectric and Elastic parameters of L-Hist.H_3PO_3 Crystals Measured by Method of Electro-Mechanic Resonance

E. V. Balashova,[1,*] B. B. Krichevtsov,[1] S. N. Popov,[1] P. N. Brunkov,[1] G. A. Pankova,[2] A. A. Zolotarev[3]

[1]Ioffe Institute, Politechnicheskaya 26, Saint Petersburg, Russia
[2]Institute of macromolecular compounds, Bolshoy pr. 31, Saint Petersburg, Russia
[3]Saint Petersburg state university, 11 Lieutenant Shmid Emb., Saint Petersburg, Russia
*Corresponding Author: balashova@mail.ioffe.ru

At present new materials with high values of nonlinear optical-, pyro-, and piezoelectric coefficients, obtained on basis on protein amino acid compounds with various inorganic and organic acids and salts, are actively searched for and studied. Interest in them is associated with the need to obtain ecological, cheap and light functional materials for nonlinear optics, the development of magnetoelectric devices based on ferrite-piezoelectric structures, pressure sensors and actuators, radiation sensors, including the terahertz range.

In the present work we report on the synthesis of single crystals of the L-histidine compound with phosphorous acid (L-Hist • H_3PO_3), the results of elemental analysis, X-ray diffraction studies of the crystal structure, and the values of elastic and piezoelectric coefficients obtained by electromechanical resonance.

The crystals were synthesized by slow cooling method from an aqueous solution at a molar ratio of 1:2 components of histidine and phosphorous acid. Elemental analysis of the crystals obtained showed a stoichiometric ratio of organic and inorganic components of 1:1. The grown crystals reached sizes of ~ 3 * 3 * 6 mm. X-ray diffraction studies by Oxford Diffraction Rigaku Xcalibur diffractometer confirmed the previously described crystal structure with monoclinic $P2_1$ symmetry [1]. For measurements on the elastic, piezoelectric and dielectric properties of histidine phosphite crystals, the electromechanical resonance technique of the plates was used. Compression-expansion oscillations along the length and thickness of the plates were studied. The dielectric spectra of capacitance C and tgδ in the frequency range 100 kHz — 1 MHz and in the temperature range T = (295–340) K were investigated with the E7–20 LCR meter, and in the frequency range 100 kHz — 2 MHz with the LCR model E4980A, Agilent Technologies (Fig.1).

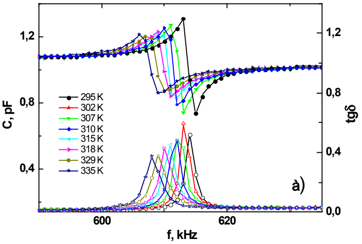

Figure 1. Frequency dependences of capacitance C and tgδ at different temperatures.

Based on the experimental data, the elastic compliance values s_{33} and s_{22}, the Young's modulus Y_{ii}^E, the piezoelectric coefficients d_{23} and d_{22}, the electromechanical coupling coefficients k_{2i} were calculated.

The work was supported by RFBR grant N16–02–00399

References

[1] Averbuch-Pouchot M.T.// Zeitschrift für Kristallographie, Vol. 207, p.111 (1993).

Size effects in ferroelectric diisopropylammonium bromide

S.V. Baryshnikov[1*], A. Yu. Milinskiy[1], E.V. Charnaya[2], I.V. Egorova[1]

[1]Blagoveschensk State Pedagogical University, Blagoveschensk, Russia
[2]Physics Department, St. Petersburg State University, St. Petersburg, Russia
[*]Corresponding author: svbar2003@list.ru

Molecular ferroelectrics are an interesting object to study [1–3]. They exhibit all the basic physical properties observed in inorganic ferroelectrics of the $BaTiO_3$ type, however, additional effects arise in organic ferroelectrics due to Van der Waals forces. The diisopropylammonium bromide $C_6H_{16}BrN$ (DIPAB) [4] is a new organic ferroelectric which has a high Curie temperature of 426 K and spontaneous polarization of ~ 23 μK/cm^2, which is comparable with that in $BaTiO_3$. Unlike inorganic ferroelectrics, DIPAB is more lightweight and mechanically flexible, which makes it to be promising for practical applications. Here we report results of dielectric studies of a nanocomposite based on DIPAB embedded into a porous alumina film with 60 nm pores.

The embedding of DIPAB into the pores was carried out from a saturated solution in methyl alcohol followed by slow cooling during several hours. The excess DIPAB layer on the sample surface was removed with a damp tissue. Dielectric measurements were carried out in the temperature range from 300 to 450 K at frequencies of 10^3–10^6 Hz. The results of dielectric measurements for a crystalline powder sample (bulk) and porous Al_2O_3 film filled with DIPAB at a frequency of 10^4 Hz are shown in Fig. 1.

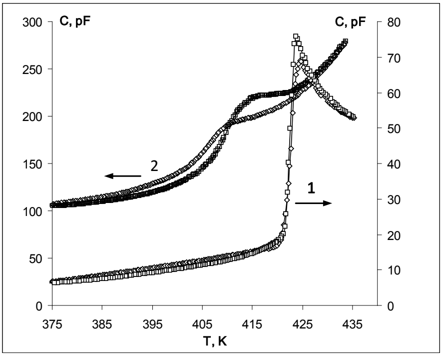

Fig.1. Dependence of the capacity on temperature for the bulk DIPAB sample (1) and DIPAB within nanopores (2) during heating and cooling.

It follows from Fig. 1 that the ferroelectric phase transition in confined DIPAB is strongly diffused compared to that in bulk, the thermal hysteresis broadens, and the Curie temperature decreases. The results obtained are treated within the framework of the Landau theory of size effects on structural phase transitions.

References

[1] S. Horiuchi, Y. Tokura. *Nat. Mater*. **7**, 357–366 (2008).
[2] J. Li, Y. Liu, Y. Zhang, et al. *Phys. Chem. Chem. Phys.* **15**, 20786–20796 (2013).
[3] M. Owczarek, K.A. Hujsak, D.P. Ferris, et al. *Nat. Commun*. **7**, 1–10 (2016).
[4] D.-W. Fu, H.-L. Cai, Y. Liu, Q. Ye, et al. Science **339**, 425–428 (2013).

Ferroelectric ordering of water molecules hosted by crystal lattice of cordierite and beryl

Z. Bedran[1*], M. Belyanchikov[1], E. Zhukova[1], V. Torgashev[2], V. Thomas[3], M. Savinov[4], P. Bednyakov[4], A. Dudka[5], A. Zhugayevych[6], S. Tretiak[6,7], F. Uhlig[8], J. Smiatek[8], M. Fyta[8], M. Dressel[1,8], B. Gorshunov[1]

[1]Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700 Russia
[2]Faculty of Physics, Southern Federal University, 344090 Rostov-on-Don, Russia
[3]Institute of Geology and Mineralogy, RAS, 630090 Novosibirsk, Russia
[4]Institute of Physics AS CR, Na Slovance 2, 18221 Praha 8, Czech Republic
[5]Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, 119333 Moscow, Russia
[6]Skolkovo Institute of Science and Technology, Moscow 143026, Russia
[7]Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
[8]1. Physikalisches Institut, Universität Stuttgart, 70569 Stuttgart, Germany
[*]Corresponding Author: zbedran@yandex.ru

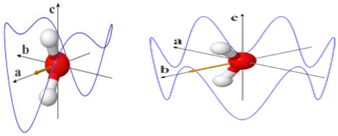

Fig.1 Water molecule in 6-well potential in beryl (left), and in 4-well potential in cordierite (right).

We have studied collective and single-particle excitations of an array of distinct water molecules hosted within a matrix of beryl and cordierite. During crystal growth process, the molecules enter the crystal lattice and end up localized in nano-sized cages formed by ions of beryl/cordierite crystal lattice to which they are coupled only weakly (*via* van der Waals forces) and can thus rotate around hexagonal (beryl) or rhombic (cordierite) c-axes experiencing, respectively, 6- or 4-well potential, as shown in Fig.1. In addition, having relatively large electrical dipole moment (1.85 D) and being regularly arranged at a distance 5-10 Å, the molecules are subject to intermolecular dipole-dipole interaction. Using radio-frequency, terahertz and infrared spectroscopy we have measured broad-band (1 – 10^{14} Hz) temperature-dependent (30 mK – 300 K) spectra of real and imaginary parts of dielectric permittivity and dynamical conductivity of water-containing beryl and cordierite. Measurements on dehydrates samples allowed us to extract the dielectric response caused exclusively by water molecular and phonon subsystems. In both crystals, translational and librational excitations of separate confined water molecules are studied. In beryl, we have discovered the emergence of an incipient ferroelectric state among H_2O molecules [1]. The different potential profile felt by H_2O molecule in cordierite, compared to beryl, leads to drastic qualitative changes of the dielectric response that we interpret basing on the librator/rotator model for terahertz excitations and ferroelectric relaxor-like [2] molecular dynamics for radio-frequency range.

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Reference

[1] B. Gorshunov, et al., *Nat. Comm.* 7:12842 doi: 10.1038/ncomms12842 (2016)
[2] L. E. Cross, *Ferroelectrics,* 76, 241-267 (1987)

Domain pattering in SBN crystals by microscopic methods

Ya.V. Bodnarchuk[1]*, T.R. Volk[1], L.S. Kokhanchik[2], R.V. Gainutdinov[1], L.I. Ivleva[3]

[1]Shubnikov Institute of Crystallography of Federal Scientific Research Centre
"Crystallography and Photonics" of Russian Academy of Sciences, Moscow 119333, Russia
[2]Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Science, Moscow 142432, Russia
[3]Prokhorov Institute for General Physics of the Russian Academy of Science,
119991, Moscow, Russia
*Corresponding Author: deuten@mail.ru

The fabrication of ferroelectric domain patterns of a specified configuration belongs to practically important problems of ferroelectricity owing to the potential of these structures for various applications. Writing by electron-beam (EB) irradiation in SEM and by dc-voltages of an AFM-tip provides a possibility to fabricate domain patterns with small spatial periods up to submicron scale. The elaboration of these techniques requires a deeper insight into the mechanism of domain formation under these specific conditions. We present the results of domain patterning by these techniques in uniaxial relaxor ferroelectric $Sr_xBa_{1-x}Nb_2O_6$ (SBN) crystals and compare these data to AFM and EB domain writing in $LiNbO_3$. Fig. 1 shows the results of domain writing on the nonpolar SBN surfaces.

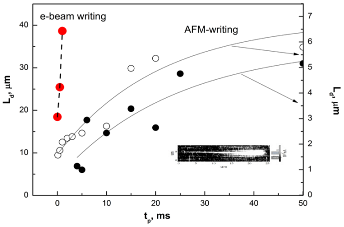

Fig.1 Domain length vs EB irradiation time (red circles) (accelerating voltage U = 25 kV, EB current I = 10 nA) and vs duration of the AFM-tip pulse voltage U_{DC} (black and bright circles correspond to U_{DC} = 20 and 40 V, respectively). In the inset –PFM image of a written domain.

The needle-like shape of domains written on the non-polar surfaces is identical in SBN and $LiNbO_3$ [1,2]. EB-written domains in SBN are completely stable and can be erased only by thermal annealing at T > Tc, whereas AFM –written domains are decaying within tens of hours. The characteristics of domain writing in SBN reveal a specificity related to the relaxor origin of this material. In particular, much longer times of domain formation with respect to LiNbO3 were found, which is accounted for by the domain pinning effects characteristic for relaxors. The formation of counter-propagating (head-to-head or tail-to-tail) domains in ZFC SBN crystals was observed and an enhanced stability of these patterns was shown.

This work was supported by the Russian Foundation for Basic Researches (projects Nos. 16–29–11777ofi-m and 16–0200439a).

References

[1] N.A. Pertsev, R.V. Gainutdinov, Ya.V. Bodnarchuk, T.R. Volk, *JAP*, 17, 034101 (2015)
[2] T.R. Volk, L.S. Kokhanchik, Ya.V. Bodnarchuk, R.V. Gainutdinov *JAP*, in press (2018)

DIELECTRIC AND ACOUSTIC PROPERTIES OF MODIFIED BARIUM TITANATE CERAMICS

K. Bormanis[1], A. Kalvane[1], A. I. Burkhanov[2], and R. V. Dikov[2]

[1]Institute of Solid State Physics, University of Latvia
[2] Volgograd Technical University, Russia
bormanis@cfi.lu.lv

The properties of ferroelectrics can be corrected by small amounts of admixtures. It is known that the elastic and dielectric properties of the $BaTiO_3$—based ceramics can be influenced by doping with the transition–metal ions [1]. A study of cobalt admixture effect on the elastic properties and dielectric response of $Ba_{0.95}Pb_{0.05}TiO_3$ solid solution within the range of 300–500 K is reported.

The studied ceramic solid solution samples of $(1–x)Ba_{0.95}Pb_{0.05}TiO_3+xCo_2O_3$ (x=0, 0.1, 0.3, 0.5, 1.0, 2.0 wt%) were obtained from high-purity oxides by conventional solid phase 2-stage synthesis and consecutive baking under atmospheric conditions and by hot-pressing technique.

Modifying by admixture of Co is found to change substantially the thermal anomalies of elastic and dielectric properties and shift the ferroelectric phase transition temperature.

Results of a study of the dielectric permittivity, dielectric loss and elastic parameters in samples of ceramic $(1–x)Ba_{0.95}Pb_{0.05}TiO_3+xCo_2O_3$ in the range of ferroelectric phase transition are presented. Dependence of the maximums of dielectric permittivity and loss on temperature, frequency and concentration are examined. The observed linearity of $e_{max}(x)$ points to being the "ideal" solutions. The dielectric permittivity on the curve e(T) depends on the history of the samples; it is strongly pronounced on the maximums in the range of the phase transition.

The diverse curves of longitudinal acoustic wave velocity v(T) was obtained for different Co concentrations. The observed features of the nonlinear behaviour of acoustic wave velocity v(T) depends on Co_2O_3 concentration and density of samples are discussed considering dynamics of domain boundaries at temperatures of coexisting phases.

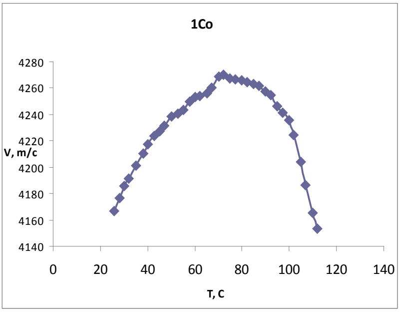

Figure 1. The temperature dependence of dielectric response (under weak E » 1 V/cm field intensities) and acoustic wave velocity v(T) of the $Ba_{0.95}Pb_{0.05}TiO_3+1wt\%Co_2O_3$ ceramics.

Reference

[1] H. J. Hagemann, H. Ihring. Phys. Rev. B20, 3871–3878 (1979).

DIELECTRIC RESPONSE OF COBALT DOPED (Ba, Pb)TiO_3 CERAMICS IN THE REGION OF PHASE TRANSITION

A. I. Burkhanov[1], K. Bormanis[2], R. V. Dikov[1], A. Kalvane[2],

[1]Volgograd Technical University, Volgograd, 400074 Russia
[2] Institute of Solid State Physics, University of Latvia Riga, LV-1063 Latvia
e-mail: burkhanov@inbox.ru

It is known that the dielectric properties of the $BaTiO_3$—based ceramics can be influenced by doping with the transition–metal ions [1].

A study of Co — doping effect on dielectric response and the elastic properties of $Ba_{0.95}Pb_{0.05}TiO_3$ solid solution within the range of 300–500 K is reported. The studied ceramic solid solution samples of $(1–x)Ba_{0.95}Pb_{0.05}TiO_3+xCo_2O_3$ (x=0, 0.1, 0.3, 0.5, 1.0, 2.0 wt%) was obtained from high-purity oxides by conventional solid phase 2-stage synthesis and consecutive baking under atmospheric conditions.

Modifying by admixture of Co is found to change substantially the nonlinear dielectric properties and of elastic properties and shift the ferroelectric phase transition temperature. The observed features of the dielectric nonlinearity at the ferroelectric phase transitions in the materials are described. The dielectric response data of the samples of different contents of the admixture in the $Ba_{0.95}Pb_{0.05}TiO_3$ ceramics are compared with the behaviour of their elastic properties. Figure 1 illustrate field dependences of effective permittivity $\varepsilon'_{eff}(E)$ at different temperature and temperature dependences of the velocity of longitudinal sound waves v(T) in $Ba_{0.95}Pb_{0.05}TiO_3$ + 1 wt% Co.

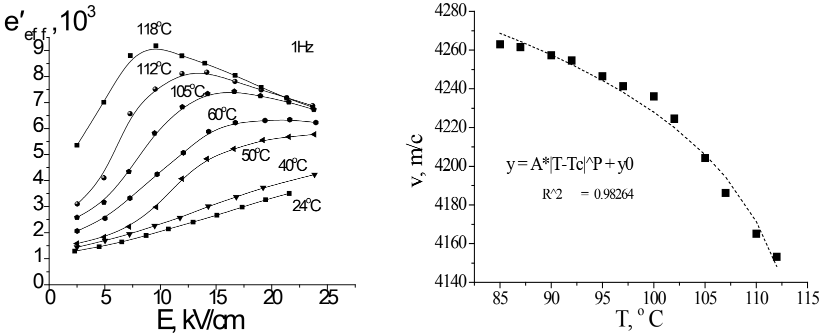

Figure 1.

Reference

[1] H. J. Hagemann, H. Ihring. Valence change and phase stability of 3d- doped $BaTiO_3$ annealed in oxygen and hydrogen. Phys. Rev. B20, 3871–3878 (1979).

Polymer Ferroelectrics-Graphene based composites

**V. S. Bystrov,[1,2,*] M. V. Silibin,[2] I. K. Bdikin,[3,2] D. V. Karpinsky,[4,2]
X. J. Meng,[5] B. B. Tian,[5] E. V. Paramonova[1]**

[1]Institute of Mathematical Problems of Biology, Keldysh Institute of Applied Mathematics
RAS, Pushchino, Russia
[2]National Research University «MIET», Moscow, Russia
[3]Department of Mechanical Eng. & TEMA, University of Aveiro, Aveiro, Portugal
[4]Scientific-Practical Materials Research Centre of NAS of Belarus, Minsk, Belarus
[5]National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, ChAS, Shanghai,
China
*Corresponding author: vsbys@mail.ru

The latest achievements in the field of experimental and theoretical computer numerical studies of new composite nanomaterials based on polymer ferroelectrics and graphene, as well as graphene oxide, are presented in this work. The main results of computer molecular modeling of the various nanostructures and piezoelectric properties of such nanocomposites constructed from thin films of polyvinylidene fluoride (PVDF)/poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) and graphene/graphene oxide (G/GO) were analyzed in comparison with experimental data at the nanoscale, in particular with the data of atomic force and piezo-response force microscopy (AFM/ PFM). The computer simulation of the polymer-based polymer composite nanostructures of graphene/graphene oxide (G/GO) and PVDF was studied by the different methods using the HyperChem software package: molecular mechanics (MM) (BIO CHARM), quantum mechanics (QM) using the semi-empirical PM3 approach. The piezoelectric response, the dielectric constant and the mechanical properties of the films were studied experimentally and found that they depend on the presence of the G/GO concentration. The experimental results correlate qualitatively with the results obtained in the calculations. In particular, the calculated data of the piezoelectric coefficients $d_{33} \sim 12–30$ pm/C for PVDF-G/GO models corresponding to their observed experimental behavior when the concentration (composition) of GO components is changed.

In addition, by molecular dynamics methods using the PM3 quantum method, calculations of the change in the polarization with increasing temperature were carried out and a P(T) dependence was constructed, which was in full agreement with the well-known thermodynamic theoretical dependence obtained from of Landau-Ginzburg-Devonshire approach. This dependence is also considered in the reduced dimensionless form, which is valid for any type of ferroelectric with a first-order phase transition (FP1). On the basis of this obtained relationship, the pyro-electric coefficients were also calculated, which were in good agreement with the known values — such as in the case of pure PVDF it value is ~ 40 $\mu C/(m^2 * K)$. For composite models with graphene it turned out that in the case of a single-layer graphene model the pyro coefficient increased by 3–4 times, and for the case of a two-layer model (sandwich model) it decreased by 2–3 times in comparison with a pure polymeric ferroelectric. To verify and properly evaluate these results, it is necessary to synthesize a thin film sample of such a composite by using the Langmuir-Blodgett method, applying PVDF layers to the substrate from graphene layers. Such work is now being carried out by our partners from China.

The obtained results give us the new important information about our understanding of the mechanisms of piezoelectricity and pyroelectricity in such new ferroelectric nanocomposites, give a new perspectives for their further creation, development and application of such new nanocomposites with the nanoscale polymer-graphene structures as a multifunctional nanomaterials.

Dielectric response function of the $Pb(Fe_{1-x}Sc_x)_{2/3}W_{1/3}O_3$ relaxor ceramics in a wide frequency range

**Sergey Chuchupal[1,*], Gennady Komandin[1], Alexander Bush[2],
Anastasia Koroleva[2], Oleg Porodinkov[1], Igor Spektor[1],
Yury Goncharov[1], Dmitry Seregin[2], and Victor Torgashev[3]**

[1]A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, Vavilova st., 38, Moscow, 119991, Russia
[2]Moscow Technological University (MIREA), Prospekt Vernadskogo st., 78, Moscow, 119454, Russia
[3]Southern Federal University, Bolshaya Sadovaya st., 105, Rostov-na-Donu, 344006, Russia
[*]Corresponding author: MirrorMan@yandex.ru

Solid solution of $Pb(Fe_{1-x}Sc_x)_{2/3}W_{1/3}O_3$ (PFSW) has a $Fm\bar{3}m$ cubic space group and belonging to a perovskite structural family. It possesses magnetic properties due to ordering in the Fe^{3+} sublattice. The Fe^{3+} to Sc^{3+} cation substitution allows to control of ordering degree in the B' position of $AB'_{2/3}B''_{1/3}O_3$ perovskite system [1]. The aim of this study is to investigate the evolution of the dielectric response function of the PFSW family in a wide frequency range of scandium concentrations and to determine of influence of Fe^{3+} substitution by Sc^{3+} on the vibrational and polar properties of this ceramics.

Experimental data were collected in a wide frequency range with use of the methods of immitance measurements, backward wave oscillator coherent spectroscopy and infrared Fourier spectroscopy. Factorized four-parameter semi-quantum dispersion model [2] was used for spectra fitting over measured spectral range. Complex dielectric functions $\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu)$ were calculated based on the determined parameters of experimental spectra simulations (Fig. 1).

In conclusion it was shown that in terahertz – infrared range spectral response has a diffusive type formed by a wide damped contours, reflected the high impact of disorder on vibrational characteristics of this solid solution.

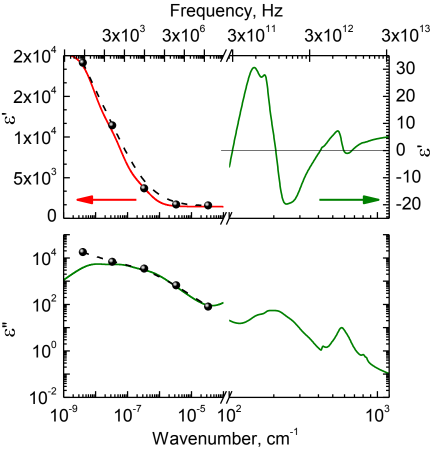

Figure 1. The spectra of $Pb(Fe_{0.8}Sc_{0.2})_{2/3}W_{1/3}O_3$ complex permittivity. Points are immitance measurements.

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References

[1] S.A. Ivanov et al., *Inorganic Chemistry*, Vol. 55, 2791-2805 (2016)
[2] F. Gervais, *Infrared and Millimeter Waves, ed. by K.J. Button*, Vol. 8, Academic Press, New York (1983)

Formation of the Dendrite Domain Structures in Lithium Niobate and Lithium Tantalate Single Crystals

M.A. Chuvakova,[1,*] A.R. Akhmatkhanov,[1] E.D. Saveliev[1], A.A. Esin,[1] D.S. Chezganov,[1] D.O. Alikin,[1] M.S. Nebogatikov,[1] A.I. Lobov,[1] and V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., Ekaterinburg, Russia
[*]Corresponding author: M.A. Chuvakova@urfu.ru

It was shown by us earlier that the domain wall shape instability leading to dendrite domain growth takes place under conditions of the stochastic nucleation domination and the bulk screening retardation [1–3]. These conditions can be realized during polarization reversal at high temperature with artificial dielectric layer.

In the present work the formation of the dendrite domain structures were studied in congruent lithium niobate and lithium tantalate single crystals covered by silicon dioxide film with thickness from 150 to 900 nm. The transparent ITO (indium tin oxide) electrodes were used for polarization reversal with simultaneous *in situ* visualization and recording of the switching current. The ITO electrodes were circular at Z+ polar surface and covered the whole Z- polar surface. The sample was placed in the temperature controlled microscope stage THMS600 (Linkam, UK) at 250 °C.

The main stages of domain structure evolution for polarization reversal in lithium niobate single crystals in the “middle” fields range (7–9 kV/mm) were revealed: (1) the appearance of domain nuclei, (2) the growth of the six main branches, (3) growth, splitting and branching of the main and secondary branches. The step-like velocity increase of the branch growth after splitting and increase of the branch diameter before tip splitting was revealed during polarization reversal in “middle” fields range. In the “low” fields range (5–7 kV/mm) the growth of only three main branches oriented along Y+ crystallographic directions with following splitting and branching was observed.

Analysis of the static domain structures allowed revealing of the strong dependence of envelop shape and filling ratio (ration of domain area to envelop area) on the value of the applied electric field. It was shown that the envelop shape changes from triangular to hexagonal and the filling ratio increase with field increase.

It was shown that the polarization reversal at high temperatures in congruent lithium tantalate with artificial dielectric layer leads to formation of the dendrite domains. The envelop shape of dendrite domains transformed from triangular to strongly rounded hexagonal shape with increase of the external field. The visualization of the domain structure in the bulk using Cherenkov second harmonic generation microscopy has shown that the depth of the dendrite structure is about 10 mm. The qualitative change of domain shape was revealed at the depth about 150 mm.

The phase-field simulation was used to verify the analogy between self-organized growth of domains and new phase during the first order phase transition [4]. The crystal symmetry C_{3v} was taken into account. The similarity of the simulated and experimentally observed shapes of isolated domains was achieved. The growth domain morphology phase diagram obtained by computer simulation was constructed.

The equipment of the Ural Center for Shared Use “Modern nanotechnology” UrFU was used. The research was made possible by Russian Science Foundation (Project № 14–12–00826).

References

[1] V. Ya. Shur, A.R. Akhmatkhanov, *Phil. Trans.R.Soc.A.*, 376, 20170204 (2017)
[2] V. Ya. Shur et al., *J. Appl. Phys.*, 121, 104101 (2017)
[3] V. Ya. Shur et al., *J. Appl. Phys.,* 112, 1–7 (2012)
[4] A.R. Akhmatkhanov et al., *IOP Conf. Ser.: Mater. Sci. Eng.,* 256, 012027 (2017)

The impact of technological conditions on dielectric and optical properties for $K_{0.5}Bi_{0.5}TiO_3$ ceramics

Piotr Czaja[a*], **Jan Suchanicz**[a], **Michał Piasecki**[b], **Wiktor Hudy**[a]

[a]Institute of Technology, Pedagogical University, ul. Podchorążych 2, 30–084 Kraków, Poland
[b]Institute of Physics, Jan Dlugosz University, Al. Armii Krajowej 13–15, 42–201 Częstochowa, Poland
* e-mail: piotr.czaja@up.krakow.pl

Lead-free ceramics type of $K_{0.5}Bi_{0.5}TiO_3$ (potassium bismuth titanate) were obtained by conventional sintering method under various technological conditions.

Samples were obtained at 1025 °C/7h or 1030 °C/5h and exhibit a single phase of the perovskite type. From the other hand, the samples obtained at 1035 °C/4h and 1040 °C /3.5h contain a small part of the second phase of the Aurivillius type $Bi_4Ti_3O_{12}$ (bismuth titanate).

The dielectric permittivity (ε) and dielectric loss (*tan(*δ*)*) measurements were carried out at the temperature range from 20 °C to 600 °C with the frequency range 0.1 kHz to 2 MHz.

The performed measurement shows the dielectric permittivity an increase when the sinter temperature rise. For 1040 °C and the sintering time of 3.5 hours, the value was about $5{\cdot}10^3$ which is twice as high as the value obtained for temperature 1025 °C and the sintering time of 7 hours. It was observed for all samples that the maximum value of dielectric permittivity is shifted towards higher temperatures with the frequency increment, which is the characteristic features of relaxor type materials. The dielectric properties of all materials were very similar, especially in the case of the dielectric loss. The values of the dielectric loss at room temperature was close to 0.07–0.08 for investigated range of frequencies.

The Raman studies were performed at room temperature for all samples. However, no significant changes were observed for different sintering temperatures or times.

Temperature dependences of the dielectric permittivity of nickel fluoroperovskites

R. M. Dubrovin,[*] S. A. Kizhaev, P. P. Syrnikov, and R. V. Pisarev

Ioffe Institute of the Russian academy of sciences, 194021, St. Petersburg, Russia
[*]Corresponding Author: dubrovin@mail.ioffe.ru

Perovskite materials exhibit an astonishing variety of ferroelectric, magnetic, multiferroic, and other properties and play important role in fundamental science and modern technology. In contrast to the widely studied oxide perovskites, the abilities of fluoroperovskites to exhibit multiferroic properties remains practically unexplored so far. Recent *ab initio* calculation aimed at the search of microscopic origin of multiferroicity in magnetic fluoroperovskites predict that at least some of them may possess ferroelectric instability in their high symmetry phase [1].

Our research is devoted to experimental study of temperature (5÷400 K) and frequency (10÷1000 kHz) dependences of the dielectric permittivity $\varepsilon(T)$ in a group of nickel fluoroperovskites with different tolerance factors t, and crystal and magnetic structures.

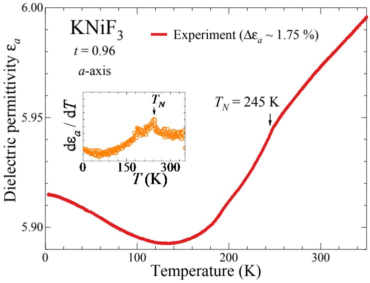

Figure 1. Dielectric permittivity in $KNiF_3$

In Fig. 1 we show the temperature dependence of $\varepsilon_a(T)$ in the cubic antiferromagnet $KNiF_3$ ($T_N = 245$ K) with $t = 0.96$ which demonstrates a complex behavior with three contributions. A wide minimum in the $\varepsilon_a(T)$ dependence is present at the temperature about 140 K. Above this temperature the lattice contribution is revealed in the growth of the permittivity with heating. Such behavior of $\varepsilon(T)$ is conventional for stable ionic crystals. Below 140 K the dielectric permittivity increases with cooling due to an instability contribution to the $\varepsilon_a(T)$. This growth of the dielectric permittivity is observed in other cubic fluoroperovskite and we associate it to the “hidden” structural instability. The kink on $\varepsilon_a(T)$ and a sharp peak on its temperature derivative (see inset in the Fig. 1) at the T_N are definitely related to magnetodielectric effect.

The temperature dependence of dielectric permittivity in the orthorhombic antiferromagnet $NaNiF_3$ ($T_N = 149$ K) showed only lattice contribution along the inequivalent *a*-, *b*- and *c*-axis directions, and the dielectric permittivity decreases at cooling with saturation at low temperatures. In hexagonal ferrimagnet $RbNiF_3$ ($T_C = 133$ K), the dielectric permittivity along the hexagonal *c*-axis $\varepsilon_c(T)$ linearly decreases with cooling, up to 70 K below which the increase of $\varepsilon_c(T)$ is observed similar to cubic $KNiF_3$. Along inequivalent direction normal to the ac-plane temperature dependence of the dielectric permittivity $\varepsilon_{ac}(T)$ has only lattice contribution. Spontaneous negative magnetodielectric effect is manifested in decreasing of the value of $\varepsilon(T)$ below magnetic phase transition temperature. It was observed in all studied crystals both in antiferromagnets and ferrimagnets due to spin-phonon interaction. Thus, our studies showed distinctly different behavior of the dielectric permittivity $\varepsilon(T)$ as a function of temperature in this group of materials which finds correlations with the tolerance factor t.

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References

[1] A. C. Garcia-Castro et al., Phys. Rev. B**89**, 104107 (2014).

Electrophysical and Mechanical Properties of PZT-Based Soft Ferroelectric Material in Wide Range of Temperatures

A. V. Skrylev,[1,*] G. M. Akbaeva,[2] and L. A. Dykina[1]

[1] Institute of High Technologies and Piezotechnics, Southern Federal University,
Milchakova st., 10, Rostov-on-Don, Russia
[2]Research Institute of Physics, Southern Federal University,
Stachki ave., 194, Rostov-on-Don, Russia
[*]Corresponding Author: skrylyov@sfedu.ru

The electrophysical and mechanical properties of a soft ferroelectric multicomponent piezoceramic material based on PZT with a coercive field and a Curie temperature have been studied.

As a result of the study of a number of soft ferroelectric materials, it was found that they exhibit properties characteristic of ferroelectric relaxors [1]. The disorder in the environment of different ions in crystallographically equivalent positions is characteristic of complex perovskites. It is this composite disorder that is the most important characteristic of relaxors, which contributes to the formation of dynamic polar nanoregions. Studies of electrophysical and mechanical properties indicate the presence of relaxation characteristics in the material under study.

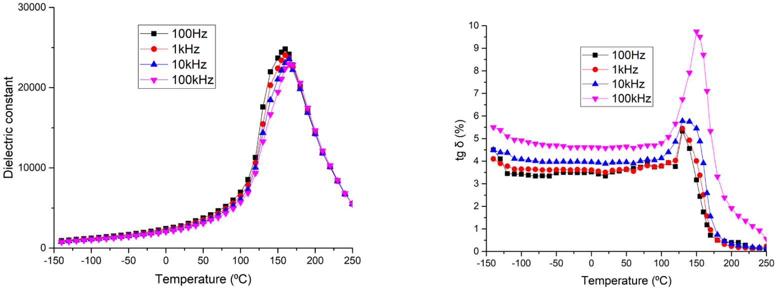

Figure 1. Temperature-frequency dependences of the relative permittivity and tangent of the dielectric loss angle of the material under study

The dielectric characteristics of the unpolarized material and the basic electrophysical parameters of the polarized material were measured over a wide temperature range from –150 to 250 °C and at frequencies from 100 Hz to 100 kHz. On the polarized samples electrophysical and mechanical characteristics were obtained according to the methods of the current industry standard [2], a set of which is necessary for modern modeling of converters over a wide range of temperatures.

References

[1] G. M. Akbaeva, V. G. Gavrilyachenko, A. F. Semenchev, Relaxor properties of multicomponent solid solutions based on PZT (Book of abstracts of International symposium «ODPO-13»), 111–113 (2010).

[2] Current industry standard 11 0444–87.

Grain growth in doped NBT

L. Eglite[1,2], M. Antonova[1], E. Birks[1], A. Sternberg[1], M. Knite[2]

[1]Institute of Solid State Physics, University of Latvia,
Ķengaraga Street 8, Riga, Latvia
[2]Institute of Technical Physics, Riga Technical University,
Paula Valdena Street 3, Riga, Latvia
*Corresponding Author: Laura.Eglite@outlook.lv

NBT ($Na_{0.5}Bi_{0.5}TiO_3$)-based solid solutions are among the most studied lead-free perovskites. Their microstructure and properties can be optimized by using different amounts of dopants and varying parameters of the sintering process [1]. Bi is frequently added in over-stoichiometric amounts to compensate the apparent loss of Bi ions during sintering. In this study we demonstrate how particular dopants and sintering parameters influence grain growth in NBT, comparing compositions with stoichiometric and over-stoichiometric content of Bi.

Microstructures of A-site Yb- and Er-substituted NBT solid solutions were studied. Small amounts of Yb noticeably increase grain size, while Bi over-stoichiometry suppresses grain growth as well as facilitates formation of unimodal grain size distribution in all cases. This can be attributed to presence of liquid phase in compositions with Bi over-stoichiometry, suppressing abnormal grain growth (AGG). No evidence on concentration increase of Bi has been found in compositions with Bi over-stoichiometry. Lanthanide concentration in final composition, as determined by EDS, is independent of Bi stoichiometry. Only minor loss of Bi during sintering has been observed.

$(1\text{-}x)Na_{0.5}Bi_{0.5}TiO_3\text{-}xCaTiO_3$ solid solutions follow an AGG mechanism which exhibits a bimodal grain size distribution with a small number of exceptionally large grains embedded in fine matrix grains [2].

In addition to different variations in types and concentrations of the dopant, using sintering methods such as hot pressing, two-step sintering and conventional sintering also leads to microstructural divergency. Two-step sintering, more specifically, Chen-Wang approach has shown to be successful in suppressing grain growth thus creating an appreciable unimodal grain size distribution with the maximum possible densification level which was also confirmed in the study [3].

Furthermore, sintering temperature and holding time were varied in an attempt to better understand grain growth mechanisms in ceramics and find optimal sintering parameters. It was found that by increasing holding time at $Na_{0.5}Bi_{0.5\text{-}x}Yb_xTiO_3$ sintering stage using the conventional sintering approach, grain size distribution becomes wider, and grains — less uniform.

References

[1] W. Jo, J.-B. Ollagnier, J.-L. Park, and E.-M. Anton, *J. Eur. Ceram. Soc.*, vol. 31, 2107–2117 (2011)

[2] Suk-Joong L. Kang, S.-Y. Ko, and S.-Y. Moon, *J. Ceram. Soc. Japan*, vol. 124, 259–267 (2016)

[3] N.J. Loh, L. Simao, and C.A. Faller, *Ceram. Int.*, vol. 42, 12556–12572 (2016)

Slow, Fast and Superfast Domain Wall Motion in KTP Single Crystals

A.A. Esin,[1,*] A.R. Akhmatkhanov,[1] E.M. Vaskina[1], M.A. Alam[1], and V. Ya. Shur[1].

[1]School of Natural Sciences and Mathematics, Ural Federal University,
Lenin Ave. 51, Ekaterinburg, Russia
[*]Corresponding Author: alexander.esin@urfu.ru

Potassium titanyl phosphate KTiOPO4 (KTP) crystals with periodical ferroelectric domain structures are one of the most promising materials for nonlinear optics. Despite the crucial importance of the understanding of the domains dynamics for creation of high quality periodical domain gratings, there are only a few works concerning in situ visualization of domain structure kinetics in KTP.

We present the results of *in situ* visualization of domain kinetics in KTP with high temporal resolution and simultaneous recording of the switching current data [1]. The wide range of domain wall velocities with two orders of magnitude difference was observed for switching in a uniform electric field. Distribution of the domain wall orientations and velocities was analyzed using "kinetic maps" (Fig. 1). The distinguished slow, fast, and superfast types of domain walls differed by their orientation. The mobility and the threshold fields for all domain walls were estimated. The revealed increase of the wall velocity with deviation from low-index crystallographic planes for slow and fast walls was considered in terms of determined step generation and anisotropic kink motion [2]. It was shown that the fast and slow domain walls provided the smooth input to the switching current. The appearance of superfast walls during domain merging resulted in short current peaks. The fitting of the measured double-maxima current peaks allowed extracting the information about change of the superfast wall orientation and velocity at the final stage of the merging process [3].

The obtained results are important for further development of domain engineering in KTP required for creation of high power, reliable, and effective coherent light sources.

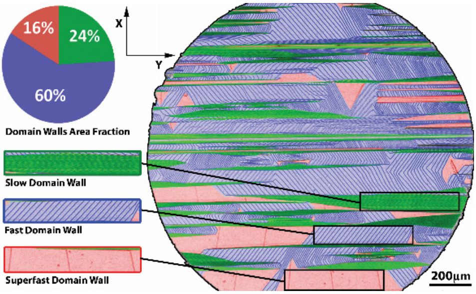

Figure 1. Kinetic map — overlapped set of instantaneous domain wall positions.
Electric field 6.75 kV/mm, frame rate 2000 fps.

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References

[1] V. Ya. Shur et al., *Appl. Phys. Lett.*, 111, 152907 (2017)
[2] V. Ya. Shur, *J. Mat. Sci*., 41, 199–210 (2006)
[3] A. R. Akhmatkhanov et al., *Ferroelectrics*, 525, in press (2018)

Latice dynamics in relaxor ferroelectric $PbNi_{1/3}Nb_{2/3}O_3$

A. I. Fedoseev,[1,*] V. G. Zalesskii,[1] S. G. Lushnikov,[1] N. Yu. Michaylin,[1] Ram S. Katyiar[2]

[1]Ioffe Institute, Politekhnicheskaya 26, St.-Petersburg, Russia
[2]Physics Department, University of Puerto Rico, San Juan, PR00931–3343 USA
[*]Corresponding Author: fedoseev@mail.ioffe.ru

$PbNi_{1/3}Nb_{2/3}O_3$ — (PNN) single crystals belong to the family of complex perovskites with the general formula $AB'_xB''_{1-x}O_3$. A wide frequency-dependent anomaly of the dielectric response observed in the vicinity of Tc ≈ 153 K in the studies of dielectric properties of PNN has shown that this crystal can be classified as belonging to a group of ferroelectrics with a diffuse phase transition (relaxor ferroelectrics) [1]. The physical properties of this family of perovskites are the subject of intense research (see, for example, [2]), but PNN crystals have been poorly studied, which can be explained by difficulties in synthesis of ceramics and growth of single crystals.

This report presents the results of studies of the lattice dynamics of PNN single crystals by Raman light scattering, dielectric spectroscopy and relaxation calorimetry. The investigations of the light scattering spectra were carried out in the backscattering geometry by using a T64000 spectrophotometer. The dielectric response was measured by a Good Will LCR-819 impedance meter in the frequency range from 12 Hz to 100 kHz in the temperature range 77–400 K. The temperature dependence of the specific heat *C(T)* was investigated with the help of PPMS in the temperature range 5 K — 400 K. As a result of measurements, the evolution of polarized spectra from those typical of cubic relaxor ferroelectrics (at high temperatures) to more complex spectra at low temperatures was observed. The processing of the scattering spectra allowed us to build temperature dependences of the integral intensity, half-width, and frequency of fundamental modes. The temperature dependences were found to exhibit anomalies which we attributed to possible instabilities of the PNN crystal lattice. The results of measurements of dielectric parameters, heat capacity, and Raman light scattering in PNN crystals are discussed in the framework of modern concepts of the physics of relaxor ferroelectrics.

References

[1]. V.A. Bokov and I.E. Mylnikova, *Sov. Phys. Solid State* vol 3, 613 (1961)

[2]. R.A. Cowley, S.N. Gvasaliya, S.G. Lushnikov, B. Roessli, and G.M. Rotaru, *Adv. in Physics*, vol 60, № 2, 229 (2011).

Local Switching in Relaxor SBN Single Crystals and PLZT Ceramics by Tip of Scanning Probe Microscope and Electron Beam

L. V. Gimadeeva,[1,*] V. A. Shikhova,[1] V. V. Fedorovyh,[1] D. S. Chezganov,[1] E. O. Vlasov,[1] A. S. Merzliakova,[1] A. L. Kholkin,[1,2] L. I. Ivleva,[3] B. Malič[4] and V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., 620000 Ekaterinburg, Russia
[2]Department of Physics & CICECO-Aveiro Institute of Materials, University of Aveiro, University Campus of Santiago, 3810–193 Aveiro, Portugal
[3]Prokhorov General Physics Institute, Russian Academy of Sciences,
38 Vavilov str., 119991 Moscow, Russia
[4]Ceramics Department, Jozef Stefan Institute, 39 Jamova str, 1000 Ljubljana, Slovenia
[*]Corresponding Author: lv.gimadeeva@urfu.ru

Stable interest to relaxor ferroelectrics is caused by a significant frequency dependence of their peak permittivity, diffused phase transition, and the origin of the nano-scale domain structure appearing after zero-field cooling [1,2]. Moreover the relaxor ferroelectrics are widely used in optical devices, actuators, sensors and modulators due to their outstanding electromechanical, piezoelectric and electrooptical properties [3].

We have studied the domain structure evolution in $Sr_xBa_{1-x}Nb_2O_6$ (SBNx) single crystals and $Pb_{1-x}La_x(Zn_{0.65}Ti_{0.35})_{1-x/4}O_3$ (PLZT x/65/35) ceramics by the biased tip of scanning probe microscope and electron beam irradiation. SBN61 undoped and Ni doped single crystals were grown in Institute for General Physics of the Russian Academy of Sciences. PLZT x/65/35 ceramics (x = 6–9 %) were sintered in Ceramics Department of Jozef Stefan Institute (Slovenia). The domain structures were visualized by piezoresponse force microscopy and scanning electron microscopy.

The studied as-grown self-similar (fractal-type) maze nanoscale domain structures obtained in both studied relaxors were quantitatively characterized by fractal dimension and average correlation radius.

The local switching in SBN crystals with various initial domain states by conductive tip of scanning probe microscope was studied. The domain growth was compared in as-grown domain structures and initial domain states created by: (1) scanning by biased tip, (2) in-field cooling, and (3) scanning by electron beam. The dependences of effective domain radius on the voltage and pulse duration were derived. The shape factor, domain wall mobility, and threshold voltage were delineated. We proposed using the shape factor of the domains formed by local switching for quantitative characterization of the initial domain states. The analysis of the obtained results allowed revealing the most effective method for the creation of a single domain state.

The correlation of the initial domain structure in PLZT ceramics and its evolution as a result of selective chemical etching and e-beam irradiation in single grains with different orientation have been studied. The considerable change of the initial fractal domain structure to the lamellar one was observed as a result of chemical etching. Different orientations of lamellar domains within single grain were revealed. It was shown that the e-beam irradiation led to formation of the lamellar domains in some grains and increase of the domain area (partial polarization reversal). The analysis of domain images as a result of e-beam irradiation with different doses allowed characterizing the domain structure evolution. The obtained knowledge will be used for development of the domain engineering in ferroelectrics.

The equipment of the Ural Center for Shared Use "Modern nanotechnology" Ural Federal University was used. The research was made possible by Russian Foundation of Basic Research (Grant16–02–00821-a).

References

[1] E. V. Nikolaeva et al., *Ferroelectrics,* 340, 137–143 (2006).
[2] J. Dec, V. V. Shvartsman, W. Kleemann, *Appl. Phys. Lett.,* 89, 212901 (2006).
[3] G. A. Samara, *J. Phys.: Condens. Matter,* 15, R367-R411 (2003).

Thermal Expansion, Polarization and Phase Diagram of (1-x)$PbNi_{1/3}Nb_{2/3}O_3$-x$PbTiO_3$ Solid Solutions

M. V. Gorev,[1,2,*] **I. N. Flerov,**[1,2] **K. Bormanis,**[3] **M. S. Molokeev,**[1,2] **and A. Kalvane,**[3]

[1]Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia
[2]Institute of Physics and Radioelectronics, Siberian Federal University, Krasnoyarsk, Russia
[3]Institute of Solid State Physics, University of Latvia, Riga, LV-1063, Latvia
[*]Corresponding Author: gorev@iph.krasn.ru

The PNN-PT solid solutions — (1-x)Pb($Ni_{1/3}Nb_{2/3}$) O_3-x$PbTiO_3$ — representing mixed ferroelectrics known for high dielectric permittivity, large piezoelectric and electrostriction coefficients are prospective for application. The PNN belong to multiferroic compounds of relaxor behaviour with $T_m \approx 153$ K and $T_N \approx 5$ K, respectively. Lead titanate is a well-studied typical ferroelectric with cubic-to-tetragonal phase transition at $T_c \approx 750$ K. A morphotropic region exists on the T-x phase diagram of the PNN-PT system around x ~ 0.35 where several phases may exist: the cubic, pseudo-cubic, tetragonal and rhombohedral [1].

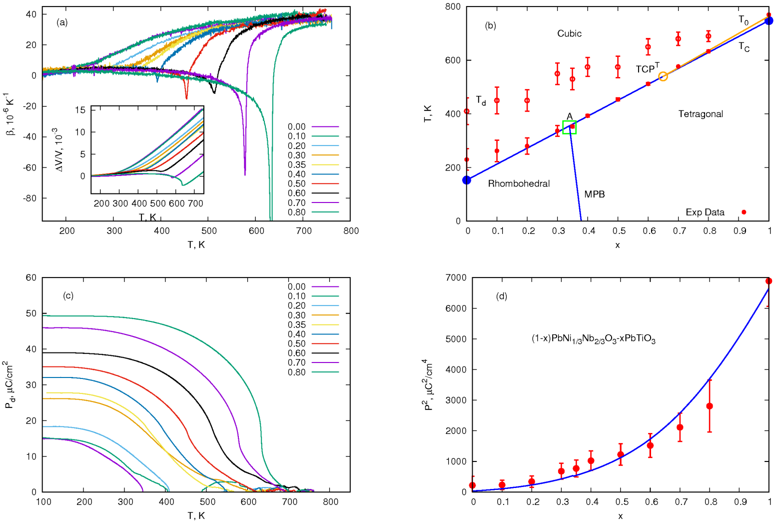


Figure 1. Thermal expansion (a), phase diagram (b) and polarization (c, d) of solid solutions (1-x) $PbNi_{1/3}Nb_{2/3}O_3$-x$PbTiO_3$

The features of the thermal expansion of the (1-x)PNN-xPT solid solution studied in the series of x= 0–0.8 in the temperature range from 100 to 750 K are reported. The obtained data and observed anomalies of thermal expansion are compared with dielectric properties, heat capacity, and the T-x phase diagram. The anomalous and lattice contributions of deformation and of the coefficient of thermal expansion are analysed; the data of deformation are used to estimate the Burns temperature and the mean square polarization of the samples found to decrease with the decrease of the $PbTiO_3$ concentration (Figure 1). The obtained results are discussed within thermodynamic theory [2] and coefficients 2–4–6 of Landau potential for solid solutions are determined.

References

[1] S. N. Kallaev, A. R. Bilalov, R. M. Ferzilaev, Z. M. Omarov, K. Bormanis, S. M. Sadykov, *Phys. Sol. State*, 54, 1829–1831 (2012)
[2] A. A. Heitmann, G. A. Rossetti, *J. Am. Ceram. Soc.*, 97, 1661–1685 (2014)

Dielectric properties of PVDF-based barium titanate and nickel zinc ferrite flexible multiferroics

R. Grigalaitis,[1,*] R. Salasevicius,[1] J. Banys,[1] M. A. Zaghete,[2] G. Teixeira,[2] M. Vijatovic Petrovic,[3] A. Dzunuzovic[3] and B. Stojanovic[3]

[1]Faculty of physics, Vilnius University, LT-10222 Vilnius, Lithuania
[2]Institute of Chemistry, Sao Paulo State University (Unesp), Araraquara, Brazil
[3]Institute for Multidisciplinary Research, Belgrade University, Belgrade, Serbia
[*]Corresponding Author: robertas.grigalaitis@ff.vu.lt

Flexible ceramic-polymer composites are perspective todays and future flexible electronic components due to the possibility to combine mechanical flexibility with the remarkable electrical and/or magnetic properties such as high dielectric permittivity, good magnetic and piezoelectric properties, etc. [1]. Polyvinylidene fluoride (PVDF) is one of the frequently used electroactive polymer for this purpose due to its excellent flexibility, chemical resistance and tunability abilities. Since the dielectric permittivity of PVDF is quite low, loading it with ferroelectric fillers like $BaTiO_3$ increases its dielectric permittivity but the dielectric dispersions remains mainly PVDF-based [2]. On the other hand, inclusion of ferrites in the PVDF might give rise to a multiferroic state. Coupled ferroelectric and ferromagnetic phenomena would be attractive for multifunctional devices.

Here we report the dielectric studies of PVDF-based composite with $BaTiO_3$ (BT) and $Ni_{1-x}Zn_xFe_2O_4$ (NF) obtained by hot pressing method. The BT and NF powders were prepared by the auto-combustion method and they have been further used for the preparation of composites by its mixing in different mass ratios. These composites were embedded into a PVDF matrix under the defined and optimized pressure and temperature. The thickness of the flexible films was around 50 microns. The electrical properties of all flexible composites were measured in the cooling regime from 420 K down to 120 K temperatures. Silver contacts were evaporated on the flat surfaces of flexible films and the complex dielectric permittivity was calculated form the measured capacitance and loss tangent employing the flat capacitor method.

Obtained results have shown that the main dispersion in all the samples originates from PVDF matrix but both $BaTiO_3$ and $NiZnFe_2O_4$ alters the strength of the dielectric dispersion. Also, the value of the dielectric permittivity in all measured composites is increased compared to pure PVDF.

References

[1]M. Arbatti, X. Shan and Z. Y. Cheng, Adv. Mater., 19, 1369–1372 (2007)
[2] Kułek, J., Szafraniak, I., Hilczer, B., and Połomska, M.J. Non-Cryst.Solids, 353, 4448 (2007).
[3] A.S. Dzunuzovic, M.M. Vijatovic Petrovic, B.S. Stojadinovic, N.I. Ilic, J.D. Bobic, C.R. Foschini, M.A. Zaghete, B.D. Stojanovic, Ceramics International, 41, 13189 (2015)

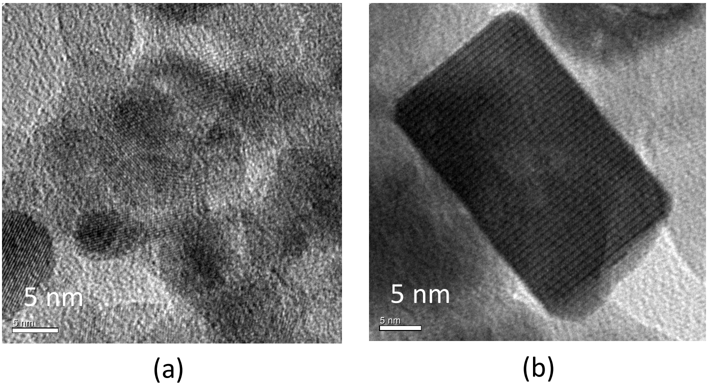
Hydrothermal synthesis of Perovskite metal oxide nanoparticles in supercritical water

Y. Hakuta[1*], H. Takashima[2], and M. Takesada[3]

[1]Advanced Operando-measurement Technology OIL,
AIST, Kashiwanoha 5–1–5, Kashiwa 277–8589, JAPAN
[2]AIST, Umezono 1–1–1, Tsukuba, JAPAN
[3] Department of Physics, Hokkaido University,
Kita 8, Nishi 5, Kita-ku, Sapporo 060–0808, JAPAN
[*]Corresponding Author: y-hakuta@aist.go.jp

Perovskite type metal oxide (ABO_3) are widely used on various electric devices such as capacitor, condenser, filter and memory, since it shows special properties involving high dielectric, ferroelectric, high thermal residence and chemical stability. Recently, scientific and academic interest of the physical-chemical property of the nano-sized perovskite metal oxide particles is growing more and more. Hydrothermal synthesis in supercritical water using a flow reaction system is well known as one method for making perovskite metal oxide particles. Here, the production of several dielectric Perovskite metal oxide particles using a supercritical water method is reviewed and a controlling factor of particle size are discussed

$BaTiO_3$ nanoparticles have been prepared by hydrothermal reaction of TiO_2 sols and $Ba(OH)_2$ aqueous solution under sub- and supercritical water conditions [1]. The size of BaTiO3 particles can adjust by reaction parameters such as reaction temperature, reaction time and concentrations. The $BaTiO_3$ particles with 8nm in diameter have been synthesized at 7 ms of the reaction time [2]. Other titanate perovskite metal oxide including $CaTiO_3$, $SrTiO_3$ and $PbTiO_3$ particles can be obtained under nearly same conditions as shown in Figure 1. The particle size of these titanate perovskite metal oxide has depended on A-site metal ions. Under same reaction condition of 400 C, 30Pa, 1 s of reaction time, the order of particle size was Sr < Ba < Ca < Pb. We will discuss the A-site metal ion dependence of particles size based on crystal form and reaction rate.



(a) (b)

Figure 1 TEM image of (a) $SrTiO_3$ and (b)$CaTiO_3$ nanoparticles obtained by supercritical water method

References

[1] Y. Hakuta et.al, Mater. Lett. 59, 1387–1390 (2005).
[2] K. Matusi et.al, J. Cryst. Growth, 310, 2584–2589 (2008).

Non-Linear Dielectric Spectroscopy of Mn-doped $PbMg_{1/3}Nb_{2/3}O_3$–0.1$PbTiO_3$

D. Jablonskas,[1,*] R. Katiliūte,[1] M. Ivanov,[1] R. Grigalaitis,[1] M. Vrabelj,[2] L. Fulanovic,[2,3] A. Bradeško,[2,3] Z. Kutnjak,[2,3] J. Banys[1] and B. Malič[2,3]

[1]Faculty of Physics, Vilnius University, Saulėtekio al. 9, 10222 Vilnius, Lithuania
[2]Jožef Stefan Institute, Jamova c. 39, 1000 Ljubljana, Slovenia
[3]Jožef Stefan International Postgraduate School, Jamova c. 39, Ljubljana, 1000 Slovenia
[*]Corresponding Author: dziugas.jablonskas@ff.vu.lt

Relaxor ferroelectrics (RFs) are a specific type of polar dielectrics. The definition of RFs is rather vague. However, it is usual to associate it with exceptional properties of this group of materials. That is, a broad and usually enormously large peak and a strong frequency dispersion of dielectric permittivity as a function of temperature. In contrast to ordinary ferroelectrics, the dielectric anomaly is not connected with any macroscopic structural change. Yet, solid solution of RF and ferroelectric may have an occurrence of actual structural phase transition. A good example is $PbMg_{1/3}Nb_{2/3}O_3$–0.1$PbTiO_3$ (PMN-0.1PT). However, the occurrence of structural phase transition in PMN-0.1PT is in debate. Either, the amount of ferroelectric compound, i.e. $PbTiO_3$ is not sufficient within the solid solution to drive it to structural phase transition or the structural changes are difficult to spot. Mn doping of PMN-0.1PT supposed to pin down the domains, which could be polarized with strong external electric field, below the temperature of phase transition. Pinning of polar nano regions (PNRs) of RF is probable, as well. A good tool to detect an occurrence of a phase transition is non-linear dielectric spectroscopy. According to the theory of Landau-Ginzburg-Devonshire, ferroelectric systems, which display continuous (2nd order) phase transition, have negative third order susceptibility (χ_3) in paraelectric state and, with decrease of temperature, χ_3 changes sign to positive at the temperature of the phase transition. In case of a discontinuous phase transition (1st order) the sign of χ_3 is positive and remains unchanged throughout the vicinity of temperature of the phase transition. In case of RFs, χ_3 have positive anomaly in temperature range of anomaly of χ_1.

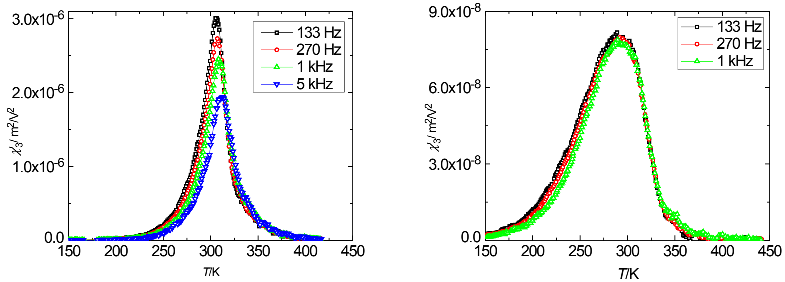


Figure 1. Temperature dependences of χ_3 of PMN-0.1PT (left) and PMN-0.1PT:1 %Mn ceramics

In this work we conducted non-linear dielectric spectroscopy on PMN-0.1PT undoped, doped by 0.5 % of Mn and 1 % of Mn ceramics. Figure 1 shows, that $\chi_3(T)$ of 1 % Mn-doped PMN-0.1PT has basically no temperature shift of maximum, as well as significantly decreased maximum value of χ_3.We speculate that such behavior is related to pinning of domains or PNRs by Mn-doping: pinned domains or PNRs are static and do not give contribution to collective motion of dipoles within the material. Further analysis and conclusions will be presented in poster presentation.

Elastic and anelastic properties of composites $(x)Mn_{0.4}Zn_{0.6}Fe_2O_4$ — $(1\text{-}x)PbZr_{0.53}Ti_{0.47}O_3$ near the ferroelectric Curie point

***A. V. Kalgin and S.A. Gridnev**

Department of solid state physics, Voronezh State Technical University,
Moskovskii pr., 14, Voronezh, Russia
*Corresponding author: kalgin_alexandr@mail.ru

Using the torsion pendulum method, elastic (the elastic compliance *s*) and anelastic (the internal friction Q^{-1}) properties of particulate magnetoelectric composites $(x)Mn_{0.4}Zn_{0.6}Fe_2O_4$ — $(1\text{-}x)PbZr_{0.53}Ti_{0.47}O_3$ [hereafter, (*x*)MZF — (1-*x*)PZT] at the frequency of 30 Hz over a temperature range including ferrimagnetic and ferroelectricphase transitions (PT) were studied.

Near the Curie point (T_C) of the ferroelectric phase, dependences of Q^{-1} on temperature *T* show a maximum that corresponds to the step-like decrease in *s*. Such a behavior of Q^{-1} and *s* is characteristic for the improper ferroelastic PT. At the same time, near the Neel point of the ferrimagnetic phase, dependences $Q^{-1}(T)$ do not show a maximum related to PT in MZF because it is by almost an order of magnitude lower than a maximum related to PT in PZT for all composite samples. Since PT in T_C is a first-order transition, anomalous mechanical lossescan be caused by the fluctuation formation of new phase nuclei and by the motion of interphase boundaries through a system of pinning centers. It was revealed that the Q^{-1}maximum is decreased in height, increased in width, and shifted to low temperatures with the increase in x from 0 to 0.6. The decrease in the Q^{-1} maximum is explained by the increase in the number of point defects preventing the motion of interphase boundaries in PZT under the external mechanical field as *x* is increased. Here, point defects in the PZT bulk are Fe atoms diffusively displaced from the MZF phase during the composite synthesis. The broadening of the Q^{-1} maximum follows from a wider spectrum of distribution of polar regions with local Curie temperatures that is associated with the increase in the number of point defects inhomogeneously distributed over the PZT bulk. The shift of the Q^{-1} maximum to low temperatures arises from the decrease in the chemical pressure because of the substitution of Ti atoms (with the ionic radius $R_{Ti} = 0.064$ nm) by Fe atoms (with $R_{Fe} = 0.067$ nm $> R_{Ti}$).

The smearing of PT also effects on *s*(*T*) curves: the step is decreased in height, smeared, and shifted to low temperatures testifying to the fact that PT loses features of a first-order phase transition.

Temperature dependences of the internal friction Q^{-1} near the ferroelectric Curie point can be presented as

$$Q^{-1}(\mathbf{T}) - Q^{-1}_{b}(\mathbf{T}) \sim (T_C - T)^m, \tag{1}$$

where $Q^{-1}_{b}(\mathbf{T})$ is the background of internal friction that weakly depends on temperature at the sufficient distance from T_C, *m* is the exponent.

A similar dependence can be also used to approximate temperature dependences of the elastic compliance

$$s(\mathrm{T}) \sim (T - T_C)^{-n}, \tag{2}$$

where *n* is the exponent.

In our experiments, the exponents of *m* and *n* are decreased with *x*. Such a behavior of the exponents enables us to use them as indicators reflecting the variation of the ferroelectric phase composition of composites near the ferroelectric Curie point.

The work was executed with the financial support of RFBR (grant no. 18–32–00017).

Thermal Diffusion and Thermal Conductivity of Multiferroic $Bi_{1-x}Gd_xFeO_3$ ceramics

S. N. Kallaev[1,2], A. G. Bakmaev[1], L. A. Reznichenko[3]

[1] Institute of Physics, Dagestan Science Centre, RAS, Makhachkala, 367003, Russia;
[2] Dagestan State University, Makhachkala, 367045, Russia;
[3]Southern Federal University, Rostov on Don, 344090, Russia;
e-mail: kallaev-s@rambler.ru

The bismuth ferrite $BiFeO_3$ compounds exhibiting a strong interrelation between the structure and the magnetic and electric properties are of growing interest for electromagnetic devices. Extremely high temperature of ferroelectric (T_c~1083K) and antiferromagnetic (T_N~643K) ordering is one of advantages of $BiFeO_3$.

The report on the studies of thermal diffusion ή and thermal conductivity λ of different compositions of the $Bi_{1-x}Gd_xFeO_3$(x=0–0.3) ceramics in the range of 130–1200 K is the main target of the present paper.

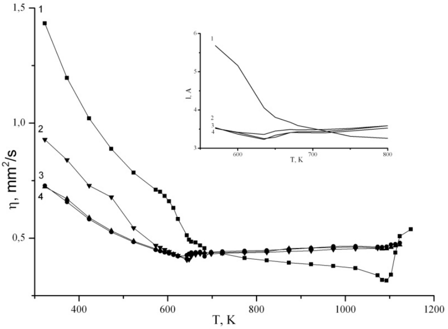


Figure 1. Thermal diffusion ήas functions of temperature in $Bi_{1-x}Gd_xFeO_3$: 1–x = 0, 2–0.1, 3–0.2, 4–0.3.On the inset: the dependence of the mean free path of phonons l on the temperature.

The ceramic samples of $Bi_{1-x}Gd_xFeO_3$ obtained from high-purity oxides by conventional solid phase 2-stage synthesis with intermediate grinding and granulation of the powder and consecutive baking under ambient conditions were chosen to be within the x = 0–0.30 range of doping concentrations.

Thermal diffusion and thermal conductivity were measuredfor 1 mm thick sample plates of 12.5 mm in diameter by laser flash techniques, employing a NETZSCH LFA-457 Micro Flash instrument.

The results of the present study together with available structural and acoustic data, testify that local distortions of the lattice, raised by deformations of the FeO_6 octahedrons and polar displacements of Bi^{3+} and Fe^{3+} ions, pose as the main centres of phonon scattering. The Gd doping is found to cause considerable change of the thermal diffusion and thermal conductivity anomalies during phase transitions — the appearance of a minimum at the antiferromagnetic transition around T_N and a broadening of the ferroelectric transition around T_c. The mechanisms of dominating thermal transfer of phonons at the phase transition and the dependence of the mean free path of phonons on the temperature are determined. The results are discussed to get her with research on structural data.

Phase transition and crystal structure of perovskite-type oxyfluorides, (1-x)$KNbO_3$-$x$$KMgF_3$

T. Katsumata,[1,*] N. Sawada,[1] R. Kuraya,[1] T. Hamagaki,[1] Y. Inaguma,[2] A. Aimi,[3] D. Mori,[4] R. P. Wang[5]

[1] School of Science, Tokai University, Kanagawa, Japan
[2]Faculty of Science, Gakushuin University, Tokyo, Japan
[3]Faculty of Science and Technology, Tokyo University of Science, Chiba, Japan
[4]Department of Chemistry for Materials, Mie University, Japan
[5]National Institute of Advanced Industrial and Technology, Ibaraki, Japan
[*]Corresponding Author: katsumata@tokai-u.jp

(1-x)$KNbO_3$-$x$$KMgF_3$ was synthesized using a sealed silica tube with an oxygen generator (KNMOF-O_2) or a high-pressure and high-temperature apparatus (KNMOF-hp) and the variations in phase transition temperature and crystal structure were investigated. The structure varied from orthorhombic to rhombohedral for both types of samples with increasing x. The rhombohedral structure was stable at room temperature above x=0.01 and x=0.03 for KNMOF-O_2 and KNMOF-hp, respectively. Figure 1 shows the variation of phase transition temperatures with x. The phase transition temperatures of these samples varied more drastically with x comparing with previous study[1], suggesting that these synthesis methods are very effective for this solid solution. However, these were almost constant for $x \geq 0.03$ and $x \geq 0.05$ for KNMOF-O_2 and KNMOF-hp, respectively. While a tetragonal-to-cubic phase transition, $T_{\text{T-C}}$, and an orthorhombic-to-tetragonal phase transition, $T_{\text{O-T}}$, decreased and a rhombohedral-to-orthorhombic phase transition, $T_{\text{R-O}}$, increased continuously with the increase in x for $x \leq 0.05$, these phase transition temperatures did not merge into one. According to the structure refinement for x=0.04 (KNMOF-hp), the polarization calculated from the displacement from the center of mass along the ferroelectric axis was reduced compared with that for $KNbO_3$ in tetragonal and orthorhombic phase. This result indicates the stabilization of the cubic structure by doping with Mg and/or F ions, which is in good agreement with the observed decrease in $T_{\text{T-C}}$.

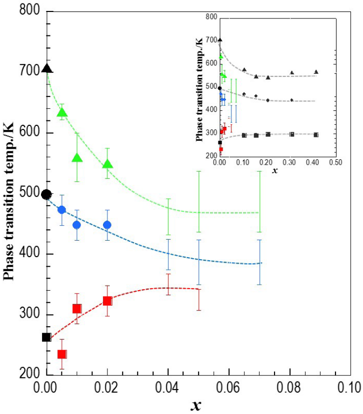


Figure 1. Variation in the phase transition temperatures, $T_{\text{T-C}}$, $T_{\text{O-T}}$ and $T_{\text{R-O}}$ with x. The inset shows the comparison of these results with those reported in previous works (black symbols) [1].

References

[1] M. Meyar, L. Taibi-Benziada, *J. Euro. Ceram. Soc.*, **27**, 1097 (2006)

Research and development of high temperature multilayer piezo stack based on $Na_{0,5}Bi_{4,5}Ti_4O_{15}$ lead-free ceramic system produced by tape-casting slurry technology

A. I. Spicin[1*], A. M. Khramtsov[1*], A. G. Segalla[1], A. A. Bush[2], K. E. Kamentsev[2]

[1]Research institute Elpa, Moscow
[2]Moscow Technological University (MIREA), Moscow
[*]Corresponding Author: opt@elpapiezo.ru

Piezoelectric materials that can function at high temperatures without failure are desired in the field of science and technology. However, the piezoelectric properties of high temperature ceramics are not enough for most practical uses. $Na_{0,5}Bi_{4,5}Ti_4O_{15}$ (NBT) lead-free ceramic system is one of the compounds within the Aurivillius, bismuth based layer structure ferroelectric (BLSF) family [1–4]. Major disadvantages of current NBT based ceramics are increased porosity (8–25 %) [2] and low piezoelectric constant (d_{33}) on the order 20 pC/N [3].

Continuing efforts are focused on the development and investigation of high temperature multilayer piezo stack based on NBT ceramic with the Curie temperature (Tc), 645 °C. Specimens were produced by tape casting slurry technology provides NBT ceramic material with the density ratios of 90–95 % to the theoretical density due to grain orientation by tape-casting process [4]. Formation of multilayer structure allowed to obtain specimens with high effective piezoelectric constant (d_{33}*) depending on the number of layers. The crystal structure of the ceramic was investigated by X-ray diffraction method. In addition this paper reviews the temperature dependence of the effective piezoelectric constant (Fig. 1), dielectric loss and dielectric constant.

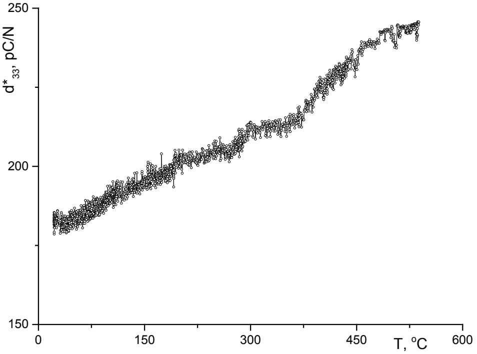


Figure 1. The measured effective piezoelectric constant (d_{33}*) as a function of temperature up to 600

References

[1] B. Aurivillius, Arkiv Kemi. Bd.1. No54, p. 463–480 (1949)
[2] A. Moure, L. Pardo, Journal of Applied Physics, V.97, p. 1–11 (2005)
[3] Wang, Chun–Ming, Physica status solidi (RRL)-Rapid Research Letters 3.1, p. 7–9 (2009)
[4] D. Maurya, Y. Zhou, Y. Yan, Journal of Materials Chemistry C. V.1. No11, p. 2102–2111, (2013)

Preparation and ferroelectric properties of BaxSr1-xTiO3 thin film by RF magnetron sputtering

M. S. Afanasiev[1], G. V. Chucheva[1], D. A. Kiselev[1,2,*], S. A. Levashov[1] and A. A. Sivov[1]

[1]Fryazino branch of the Kotel'nikov Institute of Radioengineering and Electronics of Russian Academy of Sciences, Vvedensky Square 1, Fryazino, Moscow region, Russia
[2]Department of Materials Science of Semiconductors and Dielectrics, NUST "MISiS",
Leninskiy pr. 4, Moscow, Russia
[*]Corresponding Author: dm.kiselev@gmail.com

The combination of functional properties of bulk materials and nanoscale samples allows creating structures with specified characteristics. Thin ferroelectric layers embedded into heterostructures are of interest both to fundamental research and to electronic applications. Barium titanate doped with strontium (BST) having perovskite structure is a common ferroelectric material with a high dielectric constant. It is an attractive material for applications such as multilayer capacitor, pyroelectric detectors, dynamic random access memory device, non-volatile memories, integrated circuit technology, energy storage devices, field-effect transistors, and energy harvesters [1]. Several novel devices have been fabricated based on Sr doped $BaTiO_3$ thin films, which include phase shifter, thin film capacitors, photovoltaic devices, optoelectronic devices and humidity sensors. Due to desirable properties and applications, over last few decades, synthesis of BST nanoparticles and thin film has attracted great attention. Properties of film structures strongly depend on their fabrication, electrode materials and substrate [2–4]. Polarization ordering and switching dynamics are among the most important issues in the physics of ferroelectrics. They should be addressed before considering any practical applications.

In this work, we have systematically studied electrical, dielectric, ferro- and piezoelectric properties of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST 80/20) films in order to understand its functional properties for future flash memory applications. The choice of the composition of ferroelectric BST material is conditioned by the fact that this composition has a pronounced hysteresis of polarization by an applied voltage. Ferroelectric BST 80/20 films with thickness in the range 150–550 nm were prepared by the high-frequency reactive sputtering on different substrate materials (SiOx/Si and $Pt/TiO_2/SiO_2/Si$). For measurements of electrical and dielectric characteristics on the automated experimental setup [5], dot-shaped Ni top electrodes with an area of $\sim 2.7\times10^{-4}$ cm^2 were deposited on the surface of BST films using a shadow mask by the vacuum evaporation. The surface morphology, local piezoelectric response and surface potential images of BST 80/20 films were measured by the scanning probe microscopy MFP-3D SA (Asylum Research, USA) in the Piezoresponse and Kelvin Probe modes. The obtained results point to the fact that the BST ferroelectric thin films are promising materials for using as memory elements.

The study was supported in part by the Russian Foundation for Basic Researches (projects 16–07–00665 and 16–07–00666).

References

[1] R. Sengodan, B. Chandar Shekar, S. Sathish, *J. Optoelectron. Adv. Mater.*, 14, 653–657 (2012).
[2] A. N. Kuskova, R. V. Gainutdinov, O. M. Zhigalina, *Journal of Surface Investigation*, 8(4), 761–766 (2014).
[3] D. A. Kiselev et al., *Thin Solid Films*, 619, 214–219 (2016).
[4] A. V. Tumarkin et al., *Technical Physics*, 62(10), 1592–1598 (2017).
[5] E. I. Gol'dman, A. G. Zhdan, G. V. Chucheva, *Instruments and Experimental Techniques*, 40(6), 841–846 (1997).

Intermediate phases of lead hafnate in pressure — temperature space

M.A. Kniazeva,[1,*] **R.G. Burkovsky,**[1] **D.A. Andronikova,** [1, 2] **Iu.A. Bronwald,** [1, 2]
A.V. Filimonov [1] **and S.B. Vakhrushev**[2]

[1] Peter the Great St. Petersburg Polytechnic University, 195251, Polytechnicheskaya 29, St.-Petersburg, Russia
[2] Ioffe Institute, 194021, Polytechnicheskaya 26, St.-Petersburg, Russia
[*]Corresponding Author: kniazeva.maria225@yandex.ru

The purpose of this work is to study the structure of unexplored intermediate phases of lead hafnate ($PbHfO_3$) and refine its phase diagram in the pressure region above 10 kbar. In the course of the study, the method of diffraction of synchrotron radiation in $PbHfO_3$ single crystals was implemented with simultaneous application of temperature and pressure. The experiment was carried out using the experimental equipment of The European Synchrotron (ESRF), ID27 beamline.

3-dimensional reconstructions of the reciprocal space for different phases of $PbHfO_3$ were obtained, and a refined phase diagram of $PbHfO_3$ was constructed (Fig. 1). The

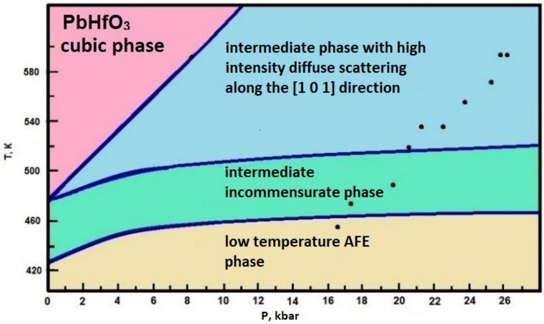


Figure 1. Refined phase diagram of $PbHfO_3$ in the temperature-pressure space: the points on the diagram correspond to the measurements made.

The incommensurate modulations in the lead sublattice observed at temperatures above 180 °C can be realized with a different modulation period of q ≈4.55 r.l.u. and ≈5.88 r.l.u. There are reflections at M positions, which have systematic extinction in the highly symmetric direction [H+ ½, 0, H+ ½]. That extinction indicates a rotation of the oxygen octahedra [3]. For the phase, that is observed only at non ambient pressures, diffuse scattering qualitatively differs from diffuse scattering in lead zirconate in the paraelectric phase by the presence of maxima at the points of the reciprocal space located in the [1 0 1] direction. The authors are grateful for the support of the Grant of the President of the Russian Federation for the state support of young scientists of Russia MK-5685.2016.2 and also the support of RFBR (16–52–48016, 16–02–01162).

References

[1] Samara G.A. Phys. Rev. B, 1:3777–3786, May 1970.— № . 1.— C. 277–289. (1971).
[2] Tagantsev A.K. et al. Nature Communications, 4:2229 (2013).
[3] Glazer A.M. Acta Crystallographica Section B: Structural Crystallography and Crystal Chemistry T. 28.— № . 11.— C. 3384–3392. (1972).

Wide-band dielectric spectroscopy of high-k ceramics.

Gennady Komandin[1,*], Oleg Porodinkov[1], Igor Spector[1], Sergey Chuchupal[1], Alexander Bush[2], and Dmitry Seregin[2]

[1]A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, Vavilova st. 38, Moscow, 119991, Russia
[2]Moscow Technological University (MIREA), Prospekt Vernadskogo, 78, Moscow, 119454, Russia
[*]Corresponding Author: gakomandin@mail.ru

Cation substitution in A and B positions of the perovskite structural family ABO_3 is an effective way to control the electrodynamic and thermodynamic parameters of these materials and, in particular, the dielectric permittivity [1]. The result of the investigation of both traditional $CaTiO_3$ and $SrTiO_3$ ceramics doped with Pb, Mg, Nb ions and comparatively new and scantily studied solid solution based on lead ferrotungstate are presented. Application the method of wideband dielectric spectroscopy with use of impedance, coherent submillimeter and Fourier infrared techniques, it was possible to obtain a set of experimental data in the range from one hundred Hertz to one hundred Terahertz. This made it possible to analyze all the electrodipole dispersion mechanisms that are responsible for the formation of high values of dielectric permittivity. The complex response functions of the single-phase solid solutions, heterophase systems with a ferroelectric and non-polar phases, and ceramic samples with a magnetoelectric interaction are investigated.

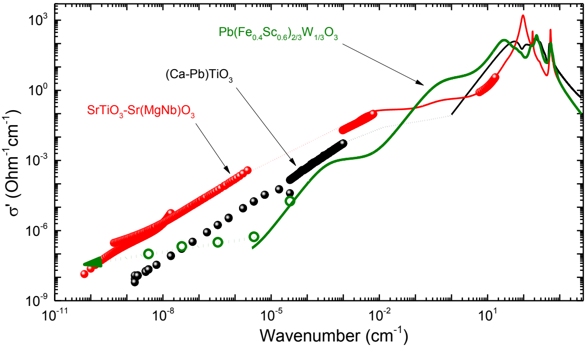


Figure 1. Wide band spectra of optical conductivity of high-k ceramics.

Figure 1 shows the spectra of dynamic conductivity in sample of three compositions. The range and nature of the dispersion, related to electrodipole absorption, in the region of the formation of dielectric permittivity high values are determined from these spectra.

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References

[1] V.V. Lemanov, A.V. Sotnikov, E.P. Smirnova, M. Weihnacht. Physics of the Solid State, vol. 44(11), 1948 (2002)

Diphenylalanine Peptide Nanotubes with Different Chirality: Structure and Properties

S. Kopyl,[1,*] V. S. Bystrov,[2] A. Nuraeva[3], P. Zelenovskiy[3], S. Vasilev[3], S. G. Arkhipov[4], V. Ya. Shur[3] and A. L. Kholkin[1,3]

[1]Department of Physics & CICECO–Aveiro Institute of Materials, University of Aveiro, 3810–193 Aveiro, Portugal
[2]Insititute of Mathematical Problems of Biology, Keldysh Institute of Applied Mathematics, RAS, 142290 Pushchino, Russia
[3]School of Natural Sciences and Mathematics, Ural Federal University, 620000 Ekaterinburg, Russia
[4]Institute of Solid State Chemistry & Mechanochemistry SB RAS, 630128, Novosibirsk, Russia
[*]Corresponding Author: svitlanakopyl@ua.pt

Self-organizing macromolecules tend to form hierarchical structures with an alternation of the sign of chirality in the transition to a higher hierarchical level. Depending on the conformation of the primary structure (L or D), the properties of the material also change. One example of such macromolecules is diphenylalanine peptide nanotubes (PNTs). Diphenylalanine (FF) is one of the self-assembling peptides which have recently become a focus of intense research in nanotechnology due to unique assembly characteristics [1]. Based on the detailed X-ray diffraction study, Gorbitz [2] was the first who found that the phenyl rings in the FF structure can stack into fascinating tubular arrangements with the hydrophilic internal cavity and hydrophobic exterior surface. FF structures possess unique physical and chemical properties such as high rigidity, unique optical properties related to quantum confinement of electrons and holes, appreciable thermal stability as well as exceptional piezoelectric effect and ferroelectricity. FF structures have shown great potential to be employed in nano- and micro devices [1, 3]. The main objective of this work was the investigation of physical properties of FF nanotubes with different chirality (L-FF and D-FF) experimentally and using molecular modelling approaches.

Both types of PNTs were fabricated by standard method [4]. Simulation showed that the L-FF has a stronger dipole moment and polarization in both conformations compared to D-FF. However, experimental studies have not yet shown any difference in properties of L-FF and D-FF, so, further research is needed. Besides, the developed models can be used for further studies of the hexagonal water confinement in FF PNTs to explain recent experimental data. One of the main structural differences of these FF PNTs is that, in the case of alfa-helix, conformation inside PNT cavity is mostly empty and, therefore, it is preferable to take more water molecules. Experimentally observed FF PNT structures (L and D) also show their origin from FF in alfa-helix, but not from beta-sheet. Models proposed for FF PNT with water molecules inside the tube based on hexagonal clusters need further study. The main issue is to obtain the best agreement between the modelling results and experimental data.

References

[1] L. Adler-Abramovich, E. Gazit, *Chem. Soc. Rev*, vol. 43, 6881 (2014)
[2] CH. Görbitz, Chem, vol, 7, 5153 (2001)
[3] ED. Bosne, A. Heredia, S. Kopyl et al, *Appl. Phys. Lett*, vol. 102, 073504 (2013)
[4] M Reches, E Gazit *Science*, vol. 300, 625 (2003)

Acknowledgments

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Electric-Field Dependence of Broadband Light-scattering in PZN-PT

A. Koreeda[1]*, K. Abe[1], Y. Fujii[1], Y. Kaiden[2], M. Iwata[2]

[1]Dept. of Physical Sciences, Ritsumeikan University, Kusatsu 525-8577, Japan
[2]Dept. of Physical Science and Engineering, Nagoya Inst. of Tech., Nagoya 466-8555, Japan
*Corresponding Author: kore@fc.ritsumei.ac.jp

Relaxors exhibit a broad peak in the temperature dependence of the dielectric constant, and the peak temperature shifts depending on the frequency of the applied electric field. Many studies suggest that the polar nano-regions (PNRs) formed in relaxors are deeply involved in such behaviors. In addition, mixed crystals consisting of Pb-based relaxors and ferroelectric $PbTiO_3$ show large dielectric response near the morphotropic phase boundary (MPB). It is reported that the physical properties near the MPB are sensitive to external electric fields. For $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PZN-xPT), it is known that the MPB is located at x=8-9% at room temperature [1]. Under dc bias, however, it has been reported that a sharp peak appears in the temperature dependence of the dielectric constant just like normal ferroelectrics, instead of exhibiting a broad peak characteristic of relaxors [2].

We have reported a self-similar, or power-law quasi-elastic light-scattering (QELS) spectrum in single crystals of relaxor such as PMN and PMN-xPT, and pointed out the possible existence of a fractal cluster formed by the PNRs in the single crystals [3]. The temperature dependence of the power exponent of the QELS implies that the spatial dimension (fractal dimension) of the PNR-clusters be closely related to the relaxor behavior.

In the present study, we conducted broad-band light-scattering spectroscopy from 100 K to 700 K under zero and dc biases on PZN-8%PT. As a result, under zero bias, it was confirmed that PZN-8%PT also exhibited a power-law QELS similarly to PMN and PMN-xPT (Figure1), which is considered to be typical of a relaxor. We will show the temperature dependence of the QELS under zero and dc biases, and discuss the relationship between the applied electric field and the power-law QELS.

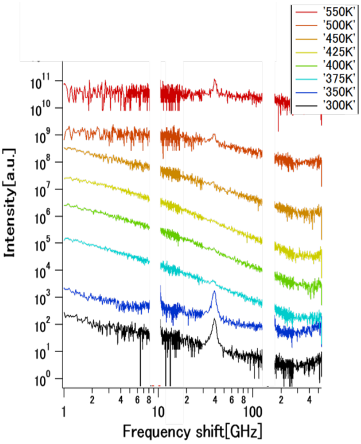


Figure 1. Broad-band light scattering spectrum of PZN-8PT under zero bias.

References

[1] J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys.* **21,** 1298-1302. (1982),
[2] M. Iwata and Y. Ishibashi, *Phase Transition* **84** (9-10), 753 - 759 (2011)
[3] A. Koreeda, H. Taniguchi, S. Saikan, and M. Itoh, *Phys. Rev. Lett.* **109**, 197601 (2012);
A. Koreeda, T. Ogawa, D. Katayama, Y. Fujii, and M. Tachibana, *Jpn. J. Appl. Phys*. **55**, 10TC06 (2016)

THE EFFECT OF THE CONCENTRATION OF IRON IMPURITIES ON THE THERMAL CONDUCTIVITY OF LITHIUM NIOBATE

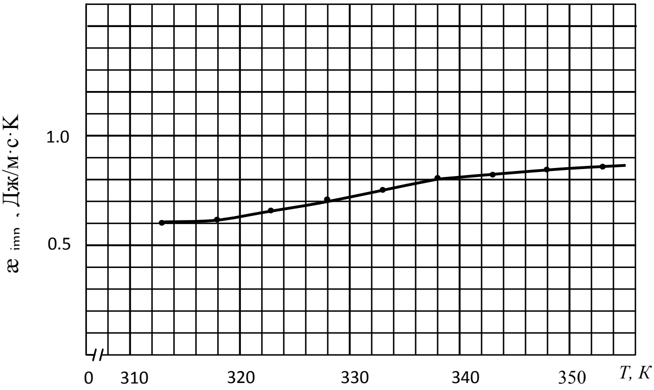
R. M. Magomadov, T. S. Chalaev

Chechen state University.
Grozny, 364907, 33 Kievskaya str. Russia
E-mail: Rukman20031@yandex.ru

Research of physical properties of lithium niobate crystals is connected with the fact that lithium niobate crystal is widely used in piezoelectric engineering, quantum, opto — and acoustoelectronics [1]. This is a high-resistance ferroelectric, its resistivity at T=300 K is equal to p =3.7 · 10^{15} Ohms · cm, which means that the mechanism of thermal conductivity of a pure crystal $LiNbO_3$ is phonon[2]. In the impurity crystal of lithium niobate, the thermal conductivity will be caused by phonons and impurities. The total coefficient of thermal conductivity of lithium niobate impurity crystal will be equal to:

$$æ = æ_{ph} + æ_{imp}, \tag{1}$$

where $æ_{ph}$ — this characterizes the contribution of phonons to the coefficient of thermal conductivity, and $æ_{imp}$ — the contribution of impurities.



Rice.1. The temperature dependence of the easy clad ænp. the thermal conductivity coefficient of lithium niobate with simple (weight. 0.06.%)

From the temperature dependence of the thermal conductivity coefficient of pure crystal and crystal with an admixture of iron (0.06 weight.%) the impurity contribution to the thermal conductivity of the crystal was calculated. As can be seen from Fig. No. 1, the contribution of impurities to the conductivity of $LiNbO_3$: Fe increases with increasing temperature, and strive to saturation. This dependence is most likely due to an increase in the frequency of vibration of the impurity with an increase in temperature.

References

[1] H. P. Kochanczyk, T. R. Wolk. Features of formation of domains in crystals of lithium niobate under the action of electron beam. The collection of works. XXI all-Russian conference on physics of ferroelectrics (VKS — XXI), June 25–30, Kazan, Russia, 2017, p. 83.

[2] R. Berman. The thermal conductivity of solids. M., 1979, 286 p.

Influence of Low-Dimensional Conductive Components on the Properties of Digital Piezo-Materials of the “Piezoceramic-Polymer-Metal” System

D.I. Makarev[1],*, M.A. Lugovaya[1], A.N. Rybyanets[1]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
*e-mail: dmakarev@rambler.ru

One of the possible solutions for the problem of making piezoelements using 3-D printing methods is the adaptation of the existing technology of layer-by-layer gluing of powders. The essence of this technology consists in gluing the layers of piezoceramic particles with polymer glue. The glue is applied from the cartridge, which is positioned to the target location using a programmable three-axis mechanical system. The main problem of this technology is the huge difference in dielectric permittivities of piezoceramics and polymer glue reaching three orders of magnitude. The encapsulation of piezoceramic particles having high dielectric permittivity with polymer glue does not allow the electric field to properly influence the piezoceramic particles, which are the main active part of such composites. This problem can be circumvented in several ways, for example, by creating single-layer composites [1, 2], or by using a substance with a relatively high conductivity as a binder component.

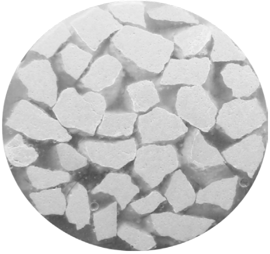


Figure 1. Photograph of the single-layered piezoceramic-polymer composite

This can be achieved, in particular, by introduction metal particles into the composite matrix. In this case, the dimensions and concentration of the metal particles are selected to ensure high matrix conductivity in a thin layers between the piezoceramic particles and a low one in a thick layer comparable to the dimensions of the piezoelements made from this composite. We have considered the possibility of replacing three-dimensional metal particles with quasi-one-dimensional thin conducting rods with linear dimensions comparable with the characteristic distances between the piezoceramic particles in the composite. It was shown that in this case the number of conducting contacts between particles can be substantially increased. In this case, the total conductivity of the piezoelement and their dielectric losses tangent remains within the technical norm. The increased number of point conductive contacts between the piezoceramic particles through the thin conducting rods allows more efficient polarization of the piezoelements made from these composites, and, therefore, substantially increase their active properties. This makes it possible to create digital piezoelectric materials based on the composites of the “piezoceramic-polymer-metal” system with improved characteristics.

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References

[1] D.I. Makarev, A.N. Rybyanets, G.M. Mayak, *Tech. Phys. Lett.*, vol. 41, N4, P. 317–319 (2015).
[2] D.I. Makarev, A.N. Rybyanets, *Journal of Nano- and Electronic Physics*, vol. 8, N4, P. 04089–1–04089–3 (2016).

Properties of CSBN single crystals after the action of electrons

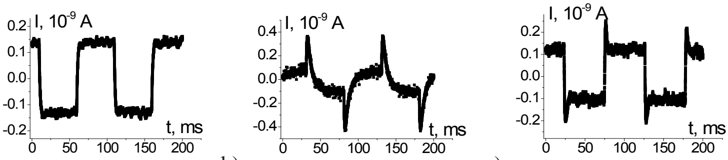
O. Malyshkina[1,*], E. Barabanova[1], J. Dec[2]

[1]Tver State University, Sadovij per. 35. 170002 Tver, Russia.
[2]University of Silesia, Institute of Materials Science, PL-40–007 Katowice, Poland
[*]Corresponding Author: Olga.Malyshkina@mail.ru

In the present work, we studied the mixed compounds based of the calcium-barium niobate, $Ca_{0.28}Ba_{0.72}Nb_2O_6$ (CBN28), and strontium-barium niobate, $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN61), single crystals with the following nominal concentrations of SBN61 and CBN28 in the melt:

$(Ca_{0.28}Ba_{0.72})_{0.25}(Sr_{0.61}Ba_{0.39})_{0.75}Nb_2O_6$ (CSBN25);
$(Ca_{0.28}Ba_{0.72})_{0.50}(Sr_{0.61}Ba_{0.39})_{0.50}Nb_2O_6$ (CSBN50);
$(Ca_{0.28}Ba_{0.72})_{0.75}(Sr_{0.61}Ba_{0.39})_{0.25}Nb_2O_6$ (CSBN75).

The investigated CSBN single crystals were pulled from the melt along [001] crystallographic direction as described in [1]. The primary measurement of the temperature dependence of the permittivity showed that CSBN crystals have a sharp maximum on the temperature dependence of the permittivity [2]. Action of an electron beam of an electron microscope (with an accelerating voltage of 15 kV) during the scanning process led to an enhanced DC conductivity of the samples, and consequently the dielectric loss greatly increased, as evidenced by the absence of a maximum on the temperature dependence of the permittivity at frequencies below 10 kHz (Fig. 1). Pyroelectric studies in a dynamic mode have shown that the poling of samples leads to the formation of a space charge near the surface induced by the conductivity (Fig. 2). The pyroelectric response, similar to the initial one, was obtained only after annealing the samples in a vacuum at a temperature of 600 K for 4 hours. But even in this case, a space charge remains near the surface, as evidenced by the "peak" observed at the initial moment of the pyroelectric response.



a) b) c)

Fig. 2. Pyroelectric responses poled CSBN25 crystals. Before (a) and after (b, c) the action of electrons. c — crystal was poled after vacuum annealing.

This work was done under the government assignment of Russian Ministry of Science and Education No 3.8032.2017/BCh. The CSBN single crystals were grown at the Institute of Electronic Materials Technology (Poland) under the guidance of Prof. T. Lukasiewicz.

References

T. Łukasiewicz, M. A. Swirkowicz, J. Dec, W. Hofman, W. Szyrski. *J. Crystal Growth*. 310, 1464 (2008).

O. Malyshkina, A. Ivanova, Y. Malyshkin, A. Folomeeva, M. Shashkov, J. Dec *Ferroelectrics*. 511:1, 76 (2017).

Phononic Band Gap and Wave Propagation on multiferroic based acoustic metamaterials

Zafer Ozer[1], Oral Oltulu[2], Amirullah M. Mamedov,[3,4,*] Ekmel Ozbay[3]

[1]Electronic Technology, Mersin Vocational School, Mersin University, 33335, Mersin, Turkey [2]Department of Physics, Faculty of Science and Letters, Harran University, 63000, Sanliurfa, Turkey
[3]Nanotechnology Research Center, Bilkent University, 06800, Ankara, Turkey
[4]International Scientific Center, Baku State University, Baku, Azerbaijan
[*]Corresponding Author: mamedov@bilkent.edu.tr

Keywords: phononic crystals; acoustic band gaps; topological insulator; multiferroic

In the present work, the acoustic band structure of a two-dimensional phononic crystal (PC) containing an multiferroic materials ($LiCu_2O_4$) and topological insulator (TI) was investigated by the plane-wave-expansion (PWE) method. Two-dimensional PC with square lattices composed of TI cylindrical rods embedded in the PVDF matrix is studied to find the allowed and stop bands for the waves of certain energy. Phononic band diagram $\omega = \omega(k)$ for a 2D PC, in which non-dimensional frequencies $\omega a/2\pi c$ (c-velocity of wave) were plotted versus the wavevector k along the Γ–X–M–Γ path in the square Brillouin zone shows six stop bands in the frequency range between 24 and 340 kHz. The multiferroic properties of $LiCu_2O_4$ and the unusual properties of TI give us the ability to control the wave propagation through the PC over a wide frequency range.

Properties of the Quasi-Two-dimensional Electron Gas at the Interface between Ferroelectric and Antiferromagnetic

D. P. Pavlov[1], I. I. Piyanzina[1,2], V. I. Muhortov[3], D. A. Tauyrskii[2],
I. A. Garifullin[1], R. F. Mamin[1,2,*]

[1]Zavoisky Physical-Technical Institute of FIC KazanSC RAS,
Sibirskii tract 10/7, Kazan 420029, Russia
[2]Institute of Physics, Kazan Federal University,
Kremlevskaya 16, Kazan 420008, Russia
[3]Southern Scientific Center, Russian Academy of Sciences,
Rostov-on-Don 344006 Russia
*Corresponding Author: mamin@kfti.knc.ru

A high-mobility electron gas was first observed in 2004 [1] at the interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO). After that, such heterointerfaces involving two insulating nonmagnetic oxides were comprehensively studied. In particular, it was found that the metallic phase (two-dimensional electron gas, 2DEG) is formed in the STO layers at the LAO/STO interface when the number of LAO layers is larger than three [2]. Such a system undergoes a transition to a superconducting state at temperatures below 300 mK [3].

We investigate the properties of 2DEG at the interface between ferroelectric oxide and insulating oxide in heterostructures, isostructural to $BaTiO_3/LaMnO_3$. The temperature dependence of the electrical resistance has been studied for heterostructures formed by antiferromagnetic $LaMnO_3$ single crystals of different orientations with epitaxial films of ferroelectric $Ba_{0.8}Sr_{0.2}TiO_3$ (BSTO) deposited onto them. The measured electrical resistance is compared to that exhibited by $LaMnO_3$ (LMO) single crystals without the films. It is found that, in the samples with the film, for which the axis of polarization in the ferroelectric is directed along the perpendicular to the surface of the single crystal, the electrical resistance decreases significantly with temperature, exhibiting metallic behavior below 160 K [4]. The numerical simulations of the optical, structural and electronic characteristics of the $BaTiO_3/LaMnO_3$ ferroelectric– antiferromagnetic heterostructure have been performed. The transition to the state with two-dimensional electron gas at the interface is demonstrated. The effect of a magnetic field on heterostructure BSTO/LMO haves been investigated. It is sown that magnetic field change the resistivity properties of the interface BSTO/LMO very strong. The new properties of the interfaces of some other heterostroctures will have been presented.

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References

[1] A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004);
[2] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science **313**, 1942 (2006).
[3] N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Ruetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, Science **317**, 1196 (2007).
[4] D. P. Pavlov, I. I. Piyanzina, V. I. Muhortov, A. I. Balbashov, D. A. Tauyrskii, I. A. Garifullin, R. F. Mamin, JETP Letters, том 106, вып. 7, 440–444 (2017).

Dielectric response of $BaTiO_3$ thin film under AC electric field studied by time-resolved X-ray absorption spectroscopy

N. Nakajima,[1,*] S. Kato,[1] J. Adachi[2], Y. Niwa[2], and S. Yasui3

[1]Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan
[2]Photon Factory, KEK, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
[3]Materials and Structures Laboratory, Tokyo Institute of Technology,
4529 Nagatsuta, Midori, Yokohama 226-8502, Japan
[*]Corresponding Author: nobuo@hiroshima-u.ac.jp

Ti K-edge X-ray absorption spectra (XAS) of a *c*-axis oriented $BaTiO_3$ thin film were observed to elucidate the dielectric response under AC field from an electronic point of view. A $BaTiO_3(001)$ 100 nm/$SrRuO_3$ (001) 50 nm film on a $(LaAlO_3)_{0.3}$-$(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}(001)$ substrate was prepared by pulsed laser deposition method. 50-nm-thick Pt was evaporated on the surface of the film, and it served as an upper electrode. The triangular electric field of ±1000 kV/cm at 50 kHz was applied parallel to the spontaneous polarization (*c*-axis) of $BaTiO_3$. Time-resolved measurements were performed at 8 characteristic points of the ferroelectric hysteresis loop. The shoulder structure just below the main edge in XAS, which is indicative of the influence of hybridization between the A-site cation and the TiO_6 octahedron [1], showed a gradual change in response to the magnitude of polarization (***P***). On the other hand, the pre-edge Ti-3*d* e_g peak increased in intensity according to ***P*** [2], especially showing a slight enhancement only at the instant of maximum polarization. From these results together with theoretical calculations based on the multiple scattering theory, it was revealed that the shoulder structure and the pre-edge Ti-3*d* e_g peak have different electronic origins, hence that these features reflect different aspects of dielectric properties of $BaTiO_3$.

References

[1] N. M. Novikovskii, E. S. Nazarenko, A. A. Novakovich, R. V. Vedrinskii, *Bull. Russ. Acad. Sci.: Phys.*, **72**, 431-433 (2008).

[2] R. V. Vedrinskii, V. L. Kraizman, A. A. Novakovich, Ph. V. Demekhin, and S. V. Urazhdin, *J. Phys: Condens. Matter*, **10**, 9561-9580 (1998).

Mechanical and Piezoelectric Properties of Composites Based on Diphenylalanine Microtubes

**A. S. Nuraeva,[1,*] P. S. Zelenovskiy,[1] T. A. Koryukova,[1] V. V. Yuzhakov,[1]
S. G. Vasilev,[1] E. V. Gunina,[1] D. S. Chezganov,[1] A. L. Kholkin,[1,2] V. Ya. Shur[1]**

[1]School of Natural Sciences and Mathematics, Ural Federal University,
620000 Ekaterinburg, Russia
[2]Physics Department & CICECO — Materials Institute of Aveiro, 3810–193 Aveiro, Portugal
[*]Corresponding Author: alla.nuraeva@urfu.ru

Self-assembling supramolecular peptide structures are a class of organic piezoelectrics capable for biomedical applications and devices [1,2], nanoelectronics [3], etc. Functionalization of peptide nanostructures by nanoparticles (NPs) leads to formation of new organo-inorganic composites. Interaction between NPs and biological macromolecules via weak hydrogen bonds and van-der-Waals forces represents fundamental interest, since NPs act on the formation and structural stability of the supramolecular structures [4]. Diphenylalanine (FF) is a model material for investigation of NPs influence on the structure and physical properties of peptide nanostructures. Although physical properties of FF nanostructures are well known, the properties of their composites with NPs are insufficiently studied.

In this work, we studied the influence of piezoelectric ZnO (diameter 30±11 nm) and non-piezoelectric SiO_2 (diameter 43±11 nm) and TiO_2 (diameter 26±7 nm) NPs on growth kinetics, structure, mechanical and piezoelectric properties of new organo-inorganic composites based on FF microtubes. These composite structures were obtained by mixing FF powder dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol with stable NPs water suspensions (concentration 0.5 mg/mL). The final concentration of FF monomers was 2 mg/mL.

The growth kinetics study showed that all types of NPs did not affect noticeably the self-assembly kinetics of FF microtubes. However, it was shown that voids and cavities in FF microtubes were formed due to embedding of NPs. The effective transverse Young's modulus of the composites was slightly reduced due to these defects while their lateral piezoelectric coefficients were decreased almost twice. At the same time, insertion of ZnO NPs provided noticeable vertical piezoresponse which is absent in pure FF microtubes. The obtained results demonstrate the ability to control the properties of self-assembling composite biomaterials by NPs.

The research was carried out using equipment of Ural Center for Shared Use "Modern Nanotechnologies" Ural Federal University with the financial support by the grant of the President of the Russian Federation for young scientists (Contract 14.Y30.17.2294-MK) and the Government of the Russian Federation (Resolution 211, Contract 02.A03.21.0006). Part of this work was developed in the scope of project CICECO-Aveiro Institute of Materials (ref FCT UID/CTM/50011/2013), financed by national funds through the FCT/MEC and, when applicable, cofinanced by FEDER under the PT2020 Partnership.

References

[1] E. Gazit, *Chemical Society Reviews*, 36, 1263–1269 (2007)
[2] A. B. Seabra, N. Duran, *Peptides*, 39, 47–54 (2013)
[3] G. Rosenman, et al., *Journal of Peptide Science*, 17, 75–87 (2011)
[4] A. D. Pomogailo, *Russian Chemical Reviews*, 69, 53–80 (2000)

Inhomogeneous deformation induced by an external electric field and its hysteresis in single crystals $KTaO_3$

E. D. Obozova*, V. G. Zalesskii, P. P. Syrnikov

Physico-Technical Institute. AF Ioffe of the Russian Academy of Sciences
Polytechnicheskaya 26, St. Petersburg, 194021, Russia
*Corresponding Author: oed1990@gmail.com

The electromechanical effect, in which an inhomogeneous deformation is induced by an external electric field, is called the converse flexoelectrical effect (CFE) [1]. The effect is largely manifested in crystals and films of submicron and nanoscopic scale, which is relevant for integrated electronics and development of micro electromechanical systems. Despite the developed phenomenological theory of flexoelectricity, a known deficit in experimental data is observed, even in basic model materials [1]. The main tasks of the flexoelectricity are to establish the type of inhomogeneous deformation (torsion deformations, cylindrical (cantilever) and spherical bending) and thermodynamic characteristics of the flexoelectric parameters of dielectric materials.

Potassium tantalate $KTaO_3$ (KT) belongs to the family of ferroelectrics-perovskites, in which the direct flexoelectrical effect reaches the greatest values [1]. Moreover, KT is a cubic paraelectric that excludes the influence of the piezoelectric effect on the overall induced deformation of the crystal. The flexoelectric coefficients for KT have not yet been determined and there is no experimental evidence of converse effect [1].

The inhomogeneous deformation of thin single-crystal KT plates was measured using optical interferometry [2]. The method also made it possible to scan the surface of the plates to determine their bending profile.

As a result, induced deformation of the spherical bending type (spherical sagging) is observed. The curvature radius for KT plates with a thickness of 140 μm in a field of 11 kV/cm reaches 50 m. The hysteresis is observed in the dependence of the inhomogeneous deformation on the external field and it is much lesser than in $SrTiO_3$. It is shown that the hysteresis is associated with stress relaxation with a characteristic time $\tau = 2–4$ s.

References

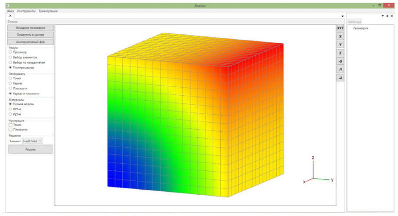
[1] P. Zubko, G. Catalan and A. Tagantsev. *Annu. Rev. Mater. Res*. 43, 387 (2013)
[2] E. D. Obozova, V. G. Zalesskii. *JETP Letters,* 103:11, 699–701 (2016)

Estimation of Piezo-Magneto Composites Properties using ACELAN COMPOS Package

A. N. Soloviev[1,2,*], N. V. Kurbatova[2], D. K. Nadolin[2], A. V. Nasedkin[2], P. A. Oganesyan[2]

[1] Theoretical and Applied Mechanics Department, Don State Technical University,
Rostov-on-Don, Russia
[2] Mathematical Modeling Department, Southern Federal University, Rostov-on-Don, Russia
*Corresponding Author: solovievarc@gmail.com

Material properties of composite depend on coherence type and material properties of components. Finite element package ACELAN COMPOS (figure 1) is designed to model representative volumes with pores [1] or granules inclusions and 3–3 coherence materials. Such composites are widely used in science and manufacturing. FEM modules of the package are based on schemes presented in [2]. Representative volumes are generated as finite element meshes by custom generation algorithms [3]. Package is capable of solving problems with electric, magnet and elastic properties, including coupling. Any subset of these properties can be set for each component of the composite. Material properties identification is based on homogenization process. Package includes material library with initial materials and calculated properties of composites. Main FEM module is available as part of desktop application or via WEB interface that allows to perform computations o server side. Program interfaces of ACELAN COMPOS allows to export meshes in different CAD/CAE formats to perform analysis in other FEM packages.



Режим
○ Просмотр
○ Выбор элементов
○ Выбор по координатам
● Постпроцессор

Отображать
○ Точки
○ Каркас
○ Плоскости
● Каркас и плоскости

Материалы
● Полная модель
○ PZT-4
○ PZT-4

Нумерация
☐ Точки
☐ Плоскости

Решение
Элемент Hex8 Solid

Figure 1. Package desktop user interface

Series of numerical example with different boundary conditions can be performed using scripting tool, included in package. Most common usage case is a set of load cases that allows to evaluated basic physical properties of the composite. Variating mesh properties and generating random distribution of material with given type of coherence allows to increase precision of experiments. Further development of the package can be based on inverse problems analysis for composite materials.

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References

[1] A. Nasedkin, A. Nasedkina & A. Rybyanets. Finite element simulation of effective properties of microporous piezoceramic material with metallized pore surfaces. Ferroelectrics Vol. 508, Iss. 1, 2017

[2] Belokon AV, Eremeyev VA, Nasedkin AV, Solov'yev AN (2000) Partitioned schemes of the finite element method for dynamic problems of acoustoelectroelasticity. Journal of Applied Mathematics and Mechanics 64(3):367–377Elsevier. p 133

[3] N. V. Kurbatova, D. K. Nadolin, A. V. Nasedkin, P. A. Oganesyan, A. N. Soloviev. Finite element approach for composite magneto-piezoelectric materials modeling in ACELAN-COMPOS package. Advanced Structured Materials. 2018. 69–88. DOI: 10.1007/978–981–10–6895–9_5

Taking into account conductivity in describing electrocaloric effect in ferroelectrics

A. S. Starkov,[1,*] O. V. Pakhomov,[1] and I. A. Starkov[2]

[1]National Research University of Information Technologies, Mechanics and Optics,
Kronverksky pr. 49, 197101 St. Petersburg, Russiae
[2]Nanotechnology Center, St. Petersburg Academic University,
Khlopin st.8/3, 194021 St. Petersburg, Russia
[*]Corresponding Author: starkov@spbau.ru

Electrocaloric effect (ECE) consists in changing entropy or temperature of the sample when applying or removing the electric field. FOR average dielectrics ECE is rather small, and noticeable changes in temperature occur in materials which dielectric permeability strongly depends on temperature. These materials include ferroelectrics. Almost all the ferroelectric materials possessing ECE have finite conductivity σ. Thus, conductivity contribution to ECE can be only a few percent and can have an appreciable effect in thermodynamic cycles. The presence of electrocaloric material conductivity leads to the appearance of conductivity current. In addition, there still exists bias current caused by the change in polarization over time. The current presence leads to the existence of Joule heat proportional to the current square and, consequently, to the electric field intensity square.

Since ECE is proportional to the second degree of intensity only at its low values, and at high values the degree decreases, with the growth in intensity, the influence of Joule heat increases. In addition, the current presence leads to the magnetic field appearance. Considering the current to be approximately constant over the entire volume of the sample, one comes to conclusion that the arising magnetic field depends on the sample shape and size. Hence, the conductivity influence will increase with the growth of the sample size. The simultaneous presence of two fields (electric and magnetic) indicates that taking into account the conductivity current leads to the expansion of ECE concept. This effect actually becomes multicoloric. [1]. Calculations based on free energy of Landau type lead to the following formula for adiabatic changing of temperature at ECE (1).

$$dT = -\frac{T}{C}\left(\frac{\partial P}{\partial T} + \sigma\frac{\partial \sigma}{\partial T}Ea^2\right) \qquad (1)$$

Here, *a* is the characteristic size of the sample. Formula (1) is generalization of the known formula for ECE that takes into account the effect of conductivity.

References

[1] A. S. Starkov, I. A. Starkov, *JETF*, 119(2), 258–263 (2014)

Evolution of domain structure of $LiNbO_3$: ZnO crystals during high temperature annealing

M. N. Palatnikov, V. A. Sandler, N. V. Sidorov, O. V. Makarova

Tananaev Institute of Chemistry — Subdivision of the Federal Research Centre "Kola Science Centre of the Russian Academy of Sciences" Science Centre of Russian Academy of Sciences,
184209, Akademgorodok, 26a, Apatity, Russia
Corresponding Author: palat_mn@chemy.kolasc.net.ru

Lithium niobate ($LiNbO_3$) attracts attention of scientists in integral and nonlinear optics. Researches of $LiNbO_3$: ZnO crystals are caused by their optical damage resistance [1]. Paper [2] has reported anomalous behavior of s(T) dependences in $LiNbO_3$: ZnO crystals doped in the concentration range (~ $5.4 < C_m \leq 6.8$ mol% in the melt. Jump-like increase in s is observed at temperature $T^*\approx 800\pm10$K. Piezoelectric coefficient d_{333} value of originally polydomain $LiNbO_3$: ZnO crystal increases to ~ $16.2 \cdot 10^{-12}$ C/N. This value exceeds the maximum values of $LiNbO_3$ crystals artificially brought to single-domain state [2]. The piezoelectric coefficient d_{333} jump value linearly increases with increase in conduction jump $\Delta\sigma$ near temperature T* ≈ 800 К [3]. This paper compares conduction of crystals $LiNbO_3$: ZnO and congruent $LiNbO_3$ and researches evolution of $LiNbO_3$: ZnO crystals domain structure caused by the conduction jump in the temperature range ~ 800K. Increase in the $LiNbO_3$: ZnO crystals unipolarity range is accompanied by vanishing of domain structure. Such structure reveals in $LiNbO_3$: ZnO crystals by chemical etching. After annealing in short circuit we have observed drastic increase in unipolarity degree. Piezoelectric coefficient d_{333} value also increased. Etching figures were only separate hexagonal microdomains ~ 1–3 µm in diameter. At the same time temperature behavior of conductivity and unipolarity degree is usual for nominally pure congruent $LiNbO_3$ crystals at T < ~ 900 K annealing at short circuit. Existence of anomalies on s(T) dependences in $LiNbO_3$: ZnO crystals at quite certain temperature (~ 800±10K) confirms that evolution of domain structure starts by thermal decomposition of charged clusters that stabilize domain walls. This leads jump-like injection of extra charge carriers. Anomalous increase in conductivity in $LiNbO_3$ crystals at T* ≈ 800 К leads to the following: At T<800К conductivities of $LiNbO_3$: ZnO and congruent $LiNbO_3$ are comparable, at T>800K conductivity of crystal $LiNbO_3$: ZnO one order of magnitude higher than that of congruent $LiNbO_3$. This is apparently the explanation of changes in domain behavior of $LiNbO_3$: ZnO and congruent $LiNbO_3$ at high temperatures.

References

[1] Sidorov, N. V., Volk T. R., Mavrin B. N., Kalinnikov, V. T. Lithium niobate: defects, photorefraction, vibrational spectra, polaritons. Moscow: Nauka, 2003, P. 255

[2] Palatnikov M.N., Sandler V.A., Sidorov N.V., Makarova O.V., Biryukova I.V., Efremov I.N., ivanenko D.V. Spontaneous unipolarity and anomalies of the dielectric and piezoelectric properties and electrical conductivity of initially heavily doped polydomain LINBO3: ZN crystals. Phys. Solid State. 2015, V 57, # 8 P. 1541–1546. DOI: 10.1134/S1063783415080235

[3] Palatnikov M.N., Sandler V.A., Sidorov N.V., Biryukova I.V., Makarova O.V. Dielectric and piezoelectric properties and electrical conductivity of LiNbO3: ZnO crystals in a wide range of dopant concentrations. Inorg. Mater. 2016. V. 52. № 12. P. 1291–1296. DOI: 10.1134/S0020168516120086

Classification of phenomenological models of phase transitions with a three-component order parameter by catastrophe theory methods

S. V. Pavlov

Physics Department, Moscow State University, Lenin Hills, 1, Moscow, Russia
e-mail: swcusp@mail.ru

Is it possible to construct a structurally stable phenomenological model of phase transitions (PT), which describes the experimental data, by simple series expansion in powers of the order parameters (OPs)? Yes, but only for one single-component OP. In the case of a multicomponent OP or several interacting OPs, this method can lead to the appearance on the phase diagram of a model of structurally unstable regions. Usually this issue is solved by taking into account in the expansion of the thermodynamic potential of higher terms, thereby increasing the number of phenomenological coefficients and increasing the degree of nonlinearity of the model. This complicates studying the model and comparing it with experimental results. However, there is a method to avoid these difficulties. The use of catastrophe theory, which takes into account symmetry of the OPs, leads to construction of structurally stable and compact models that adequately describe anomalies of the physical properties of substances near the PT. In this case, the initial data are only knowledge of the symmetry of the OP and the number of thermodynamic control parameters that are varied in the experiment (temperature, pressure, chemical potentials of impurities, etc.). Moreover, this approach makes it possible to classify phenomenological models for a given OP symmetry based on the number of control parameters. Such a classification has already been carried out for two interacting one-component OPs [1] and for two-component OPs [2]. In this work we present the results of the classification of phenomenological models with a three-component OP, with the symmetry of the PP corresponding to the groups $L = T_d$ ($J_1 = \sum_{i=1}^{3}\eta_i^2, J_2 = \prod_{i=1}^{3}\eta_i, J_3 = \sum_{i,j=1}^{3}\eta_i^2\eta_j^2$) and $L = O_h$ ($J_1 = \sum_{i=1}^{3}\eta_i^2, J_2 = \sum_{i,j=1}^{3}\eta_i^2\eta_j^2, J_3 = \prod_{i=1}^{3}\eta_i^2$) (Tables 1 and 2).

Table 1. Models with L=T_d ($\bar{4}3m$)

c	F	μ
1	$a_1J_1+J_2+b_1J_1^2$	3
2	$a_1J_1+a_2J_2+J_3+b_1J_1^2+b_2J_1^3+b_3J_2^2$	6
3	$a_1J_1+a_2J_2+a_3J_3+J_1^2+b_1J_2^2+b_2J_3^2+b_3J_2J_3$	7
4	$a_1J_1+a_2J_2+a_3J_1^2+a_4J_3+J_1J_2+b_1J_1^3+b_2J_1^4+b_3J_1^5+b_4J_2^2+b_5J_3^2$	1

Table 2. Models with L=T_d ($m\bar{3}m$)

c	F	μ
1	$a_1J_1+J_1^2+b_1J_2+b_2J_3+b_3J_1^3$	5
2	$a_1J_1+a_2J_2+J_1^2+b_1J_2^2+b_2J_3+b_3J_1^3+b_4J_2J_3$	7
3	$a_1J_1+a_2J_2+a_3J_1^2+J_1^3+b_1J_3+b_2J_1J_2+b_3J_1^4+b_4J_1J_3+b_5J_1^5+b_6J_2J_3+b_7J_1^6+b_8J_1^4J_2+b_9J_2^3+b_{10}J_3^2$	14

Models with such symmetry of the OP describe sequences of the PT in superionic conductors, Laves phases, boracites, in PZT ceramics and in PMN-PT and PZN-PT single crystals. The first columns of the tables indicates the number of control parameters c, the second column contains phenomenological models in dimensionless mathematical form F, the third column shows multiplicity of critical points μ, namely, the number of nondegenerate critical points obtained from splitting of multicritical degenerate points when changing control parameters. Analysis of the phase diagrams shows that the model with L=T_d and with three control parameters describes all possible low-symmetry phases, whereas for L=O_h all phases are described in a model with two control parameters.

References

[1] S. V. Pavlov, *Moscow University Phys. Bull.,* vol. 71, P. 508, (2016).

[2] T. M. Izotova et al., www.ivtn.ru/2004/physmath/enter/r_pdf/dp04_30.pdf. (2004)

Anomalies in the Complex Parameters of the Transparent Ferroelectric Piezoceramics PLZT in the Vicinity of the Diffused Phase Transition

E. I. Petrova,[1,*] M.A. Lugovaya,[1] A.N. Reznichenko,[1] N.A. Shvetsova,[1] A.N. Rybyanets

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
[*]e-mail: harigamypeople@gmail.com

Ferroelectrics with a diffuse phase transition (PT) are promising materials for applications in various fields of modern technics due to their special properties. The interest grows in the development and study of ferroelectrics with diffuse PT is caused not only by the search for answers to fundamental questions regarding the physical nature of the glass-dipole state and processes occurring in ferroelectrics with diffuse PT, but also by the possibility of their practical application. Among the known ferroelectrics with diffuse PT, the highest practical and theoretical interest has the piezoceramics of the PLZT (X/65/35) system, which demonstrate a wide range of electrophysical parameters and represent a unique object of modeling processes occurring in ferroelectrics with diffuse PT [1]. However, despite the long history of studies, the complex elastic, dielectric and piezoelectric parameters of ferroelectric piezoceramics of the PLZT (X/65/35) system and the parameters of surface acoustic waves propagation in the vicinity of the diffuse PT, have not been investigated and published to date.

The main objective of the papers was to study the anomalies in the electrophysical parameters of the ferroelectric piezoceramics of the PLZT (X/65/35) system in the vicinity of the diffuse phase transition, and also to measure the sets of complex set of electrophysical parameters over a wide frequency range.

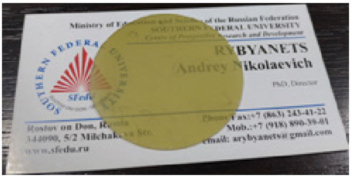

Figure 1. Hot pressed transparent ceramics PLZT (8.5/65/35)

The ferroelectric piezoceramics of the system $(Pb_{1-x}La_x)(Zr_{0,65}Ti_{0,35})\,O_3$ with lanthanum content x = 7,5–8,5 % were chosen as the object of the study. The experimental samples of piezoceramics were prepared by the hot pressing method. The complex parameters of the experimental samples were determined by the piezoelectric resonance analysis method using the software package PRAP. As a result of the study, a set of complex elastic, dielectric and piezoelectric parameters of transparent ferroelectric piezoceramics $(Pb_{1-x}La_x)(Zr_{0,65}Ti_{0,35})\,O_3$ was obtained. The frequency dependences of these parameters were measured in the frequency range up to 20 MHz. The anomalies in the behavior of surface acoustic waves velocity and attenuation in the vicinity of temperature T_d located below the Curie point and corresponding to the additional maxima of the dielectric constant and the dielectric loss tangent were found. In accordance with the common view on the diffuse PT in PLZT, the observed anomalies in the surface acoustic wave parameters in the PLZT (X/65/35) piezoceramics were interpreted as a result of the disappearance of the long-range ferroelectric order and the destruction of the macro domain state induced by polarization.

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References

[1] V. Bobnar, Z. Kutnjak, R. Pirc, A. Levstik, Physical Review B, vol. 60, N9, P. 6420–6427 (1999).

Phase formation, phase transitions, ferroelectric and relaxor properties of nonstoichiometric NBT ceramics

A.V. Mosunov[1], E.D. Politova[1*], D.A. Strebkov[2], N.V. Golubko[1], G.M. Kaleva[1], B.A. Loginov[3], A.B. Loginov[3], S. Yu. Stefanovich[1,2]

[1]L.Ya.Karpov Institute of Physical Chemistry; Vorontsovo pole, 10, Moscow 105064 Russia,
[2]M.V. Lomonosov Moscow State University, Leninskie gory, 1, Moscow, 119992, Russia,
[3]National Research University "MIET", 124498, Moscow, Zelenograd, Shokin sq., 1, Russia
*Corresponding Author: politova@nifhi.ru

Lead-free ferroelectric materials on the base of relaxor rhombohedral perovskite $(Na_{0.5}Bi_{0.5})TiO_3$ (NBT) are being intensively studied in order to replace widely used Pb-based ones [1–3]. Presence of polar nanoclusters leading to high mobility of boundaries "domain walls/polar clusters" comprise peculiarity and advantage of the NBT-based compositions [4].

In this work, phase formation, crystal structure parameters, microstructure, dielectric, relaxor and ferroelectric properties of nonstoichiometric ceramics $(Na_{0.5-x}Bi_{0.5})TiO_3$ (I) and $(Na_{0.5}Bi_{0.5+x})TiO_3$ (II) with ratio Na/Bi<1 and with $x = 0$–0.1 have been studied.

Ceramic samples were prepared by the two-step solid-state reaction method at temperatures $T_1 = 1073$ K (6 h), and $T_2 = 1370$–1450 K (1–2 h). The samples were characterized using the X-ray Diffraction, Scanning Electron Microscopy, Second Harmonic Generation (SHG), and Dielectric Spectroscopy methods.

The pseudocubic unit cell parameter decreased in the system I, while increased in the system II in accordance with the ionic radii changes. Main size of grains decreased with x increasing in both systems.

Ferroelectric phase transitions were revealed as steps at ~ 400 K and at ~ 600 K in the dielectric permittivity versus temperature curves. Phase transitions near 350–400 K revealed typical relaxor-type behavior attributed to the presence of polar nanoregions in a nonpolar matrix. In the samples II with $x>0.05$ additional anomalies in the $\varepsilon(T)$ dependences were revealed near 900 K, evidently related to the presence of the admixture ferroelectric $Bi_4Ti_3O_{12}$ phase. Accordingly, increase in the spontaneous polarization value was observed in ceramics II using the SHG method. At the room temperature, non monotonous changes of the dielectric parameters were observed in modified compositions studied. The results obtained confirmed prospects of new lead-free materials development by modification of NBT-based compositions close to the MPB with aliovalent cation substitutions, and influence of the A-sublattice stoichiometry changes in $(Na_{0.5}Bi_{0.5})TiO_3$ compositions with Na/Bi<1 on phase content, structure parameters and functional properties of ceramics was proved.

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References

[1] Y.S. Sung, J.M. Kim, J.H. Cho, T.K. Song, M.N. Kim, H.H. Chong, T.G. Park, D. Do, and S.S. Kim, Effects of Na nonstoichiometry in $Bi_{0.5}Na_{0.5+x}TiO_3$ ceramics. *Appl. Phys. Lett.* V. **96**, 022901 (2010).

[2] Li Ming, H. Zhang, S.N. Cook, Li Linhao, J.A. Kilner, J.M. Reaney, and D.C. Sinclair, The dramatic influence of A-site non-stoichiometry on the electrical conductivity and conduction mechanisms in the perovskite oxide $Na_{0.5}Bi_{0.5}TiO_3$, *Chem. Mater*. V. **27**, pp. 629–634 (2015).

[3] V.V. Shvartsman, and D.C. Lupascu, Lead-Free Relaxor Ferroelectrics, *J. Amer. Ceram. Soc.* V. **95**, pp. 1–26 (2012).

[4] W. Kleemann, Random-field induced antiferromagnetic, ferroelectric and structural domain states, *Int. J. Mod. Phys. B*. V. **7,** pp. 2469–2507 (1993).

Effect of powder grain size on the microstructural, dielectric, ferroelectric and piezoelectric properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics

S. G. Ponomarev,[1]* V. P. Tarasovskii,[1] and A. V. Reznichenko [1]

[1]The Moscow Polytechnic University, B.Semenovskaya 38,
Moscow, Russian Federation
*Corresponding Author: s.ponomarev@mami.ru

Piezoceramic materials based on solid solutions of potassium and sodium niobates are considered to be the most promising substitutes for materials containing lead [1]. Moreover these materials possess a unique combination of dielectric parameters such as relatively low dielectric constant ε, high speed of sound, etc. Typically, researchers try to obtain samples of the piezoelectric ceramics with the highest bulk density and the lowest value of dielectric loss tangent tgδ [2]. However, in some cases it is advisable to use the porous piezoelectric ceramics. In this case, as compared with high-density ceramics, dielectric permeability decreases, the quality increases, and the values of piezo modules vary slightly. The piezoelectric ceramics with different porosity and pore sizes may be obtained using piezoceramic powders with different particle size.. This paper deals with the dependence of the sintered ceramic properties upon the average particle size of piezoceramic powders.

The material with composition $K_{0.49}Na_{0.49}Sr_{0.02}NbO_3$ has been received by conventional solid state reaction method from the mixture of sodium carbonate Na_2CO_3, potassium carbonate K_2CO_3, strontium carbonate $SrCO_3$ and niobium oxide Nb_2O_5 powders. The samples of the piezoelectric ceramics have been shaped out by dry pressing at a pressure of 100МПа. The charge has been prepared from synthesized powders of two fractions with the average particle size of 0.7 microns (F1 powder) and 1.2 microns (F2 powder) respectively. After roasting and mechanical treatment the samples obtained the shape of discs with a diameter of 12mm and a thickness of 1.2 mm. Table 1 shows the characteristics of the samples obtained where P is the open porosity, ρ is the density of samples related to its theoretical value, d_{33} is the value of the piezo constant.

Table 1. Dielectric and piezoelectric properties of samples.

Charges	P, %	ρ, %	ε	tgδ, %	d_{33}, pC/N
F1	37	60	350	3	80
F2	34	65	400	3	80
F1+F2	4	92	600	2.5	90

As can be seen from the table, the d_{33} value for three groups of samples is practically the same. At the same time, monotonous decrease of ceramics dielectric permeability with increasing porosity is observed. It should be also noted that practically the same values of d_{33}, ε, tgδ for dense ceramics were earlier obtained in [3].

Thus, by varying the granulometric composition of the charge, one can control the dielectric properties of piezoceramics.

References

[1] Y.Saito, H.Takao, T.Tani et al. Natur, 432, 84 – 87 (2004).
[2] B.Jaffe W. R. Cook, H. Jaffe Piezoelectric ceramics (1971).
[3] B.Malic, J. Bernard, J. Holc et al. Ferroelectrics, 314, 149–156 (2005).

Anomalous diffraction patterns in $PbFe_{1/2}Nb_{1/2}O_3$ single crystals

E.A. Popova[1,*], A.I. Berskrovnyi[2], D. Neov[2], S.V. Krivovichev[3,4], S.G. Lushnikov[1,3]

[1]Ioffe Institute, 26 Politekhnicheskaya, St Petersburg 194021, Russia
[2]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia
[3]Department of Crystallography, St. Petersburg State University, St. Petersburg, Russia
[4]Kola Science Centre, Russian Academy of Sciences, Apatity, Russia
[*]Corresponding Author: elena.popova566@gmail.com

Single crystals of $PbFe_{1/2}Nb_{1/2}O_3$ (PFN) belong to the family of complex perovskites with atomic disorder in the B sublattice. The attention of researchers to this compound is due to the fact that a number of successive structural transitions occur in PFN above room temperature and include formation of ferroelectric and antiferromagnetic phases. Even the room-temperature crystal structure of PFN remains a subject of discussion, since the models presented in the literature cannot fully explain the experimental results. The monoclinic (*Cm*), rhombohedral (*R*3*m*) and tetragonal (*P*4*mm*) models are discussed [1–3]. This motivated our detailed study of the crystal structure of PFN single crystals at room temperature.

The work presents the results of X-ray and neutron diffraction experiments done on PFN single crystals. The X-ray diffraction experiments were carried out at a Bruker SMART APEX II single crystal X-ray diffractometer equipped with a CCD detector. The diffraction data obtained were processed by using the Bruker SAINT (2009) software package. Neutron diffraction experiments were performed at the Real-Time Neutron Diffractometer (RTD) [4] at the IBR-2 reactor in the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia.

The main sections of the reciprocal space were found to exhibit splitting of the main Bragg reflections. The position of two peaks in each split "pair" correspond to different scattering angles (according to the X-Ray data), i.e., to the different *d*-spacings. It is shown that these sections of the reciprocal space cannot be explained within the framework of a simple model of the crystal structure, even with allowance for a possible twining effect. A model of phase coexistence is considered, possible physical mechanisms of the effect observed are discussed.

References

[1] Singh S P, Pandey D, Yoon S, Baik S and Shin N2007 Appl.Phys. Lett. 90 242915
[2] Ivanov S A, Tellgren R, Rundlof H, Thomas N W and Ananta S2000 J. Phys.: Condens. Matter 12 2393
[3] V. Bonny, M. Bonin, P. Sciau, K.J. Schenk, and G. Chapuis. Solid State Communications, 102(5): 347–352, 1997
[4] A.M. Balagurov, A.I. Beskrovnyy, V.V. Zhuravlev, G.M. Mironova, I.A. Bobrikov, D. Neov, S.G. Sheverev, Journal of Surface Investigation "X-ray, Synchrotron and Neutron Techniques", ISSN1027–4510, 10 (2016), No. 3, pp. 467–479.

Dynamic particularities of the coefficients determination in the crystal Rb_2ZnCl_4 free energy decomposition according to the polarization by the harmonic analysis method

V. V. Gorbatenko[1,*], B. N. Prasolov[2], and S. A. Gorbatenko[2]

[1] Voronezh State Technical University, 394026, Moskovski pr., 14, Voronezh, Russia
[2] Scientific and production firm “Sensor”, 394061, pr. Truda, 24, Voronezh, Russia
*Corresponding Author: vlgorbatenko@rambler.ru

According to the theory of Landau-Devonshire [1,2] it is possible to decompose the free energy W_C in powers of the polarization P_C only component in the case of an uniaxial ferroelectric. Using the theory of Landau-Devonshire for quantitative evaluations of the measurement results of the unit A_2BX_4 model crystal — chlorinate rubidium Rb_2ZnCl_4 polarization properties is applicable in the case of the W_C free energy sorting in powers of the polarization only component limited to members to the fourteenth power [3]. Limited to members to the fourteenth power of polarization we can get:

$$W_C=\frac{1}{2}aP_C^2+\frac{1}{4}bP_C^4+\frac{1}{6}cP_C^6+\frac{1}{8}dP_C^8+\frac{1}{10}eP_C^{10}\frac{1}{12}fP_C^{12}+\frac{1}{14}gP_C^{14}-EP_C, \quad (1)$$

where a, b, c, d, e, f, g — the coefficients having a certain physical meaning [4], E — electric field strength.

It is known that the equilibrium configuration ($d(EP_C)/dP_C=E$) is determined by the minimum $W_C(P_C)$ finding. This equation in Landau-Devonshire theory gives an expression for the electric field E as a polarization function P_C. In the case of seven members using in the decomposition we have:

$$E=aP_C+bP_C^3+cP_C^5+dP_C^7+eP_C^9+fP_C^{11}+gP_C^{13}. \quad (2)$$

The theory of Landau-Devonshire assumes that the coefficient a changes with temperature in the vicinity of the Curie point ($T \approx T_C$). Other coefficients in the free energy decomposition do not depend on temperature[1,2,4].

In the process of the P_C measuring in the dynamic, for example, using the Sawyer-Tower scheme, it is necessary to take into account the dynamic features of the P_C measurement because of $d(EP_C)/dP_C=E+P_C dE/dP_C$.

In [3] the prepolarization process of A_2BX_4 group model crystal — chlorinate rubidium Rb_2ZnCl_4 under the action of harmonic electric field of the amplitude that above the coercive field tension by the method of harmonic analysis was investigated. The time dependence of the current density $J_X(t)$ that appears in the sample under the action of harmonic fields has a complex periodic form. The dependence $J_X(t)$ includes two components — capacitive $J_C(t)$ and the conduction current $J_G(t)$ density.

In the present work the study of the current density $J_C(t)$ harmonics allowed to create the dependences of the test sample volume unit free energy W_C and the electric field intensity E from its polarization P_C that was measured in the dynamic, to determine the coefficients a, b, c, d, e, f and g values (expression 1), and to trace their temperature evolution near the temperature T_C in the crystal Rb_2ZnCl_4 ferroelectric phase.

References

[1] L.D. Landau, E. M. Livshiz, *Statistical physics* (M.: Nauka), 486 (1976).
[2] A.F. Devonshire, *Theory of Ferroelectrics* (ADV. Phys.) 3, 85 (1954).
[3] V.V. Gorbatenko, B. N. Prasolov, *Izv. RAN. Ser. Fis* T. 80, № 9, 1255 (2016).
[4] K.M. Rabe, C. G. Ana, J.-M. Triscona, *Physics of ferroelectrics* (M.: BINOM), 85 (2011).

Lattice and spin dynamics of the polar incommensurate antiferromagnet Ni_2InSbO_6

M. A. Prosnikov[1,*], V. Yu. Davydov[1], A. N. Smirnov[1], and R. V. Pisarev[1]
T. Sato[2] and T. Arima[2]

[1]Ioffe Institute, Russian Academy of Sciences, St. Petersburg, Russia
[2]Department of Advanced Materials Science, University of Tokyo, Japan
*Corresponding Author: yotungh@gmail.com

Trigonal plate-like single crystals of Ni_2InSbO_6 (NISO) were successfully grown with the use of chemical vapor transport method. They are crystallizing in a non-centrosymmetric corundum-like R3 (#146) space group [1] with interlocked polar domains (P || *c*-axis ~ 6 μC/cm [2]). Magnetic Ni^{2+} ($3d^8$, $S = 1$) ions occupy two non-equivalent 3*a* positions with octahedral oxygen coordination. Below $T_N = 76$ K a complex incommensurate long-range magnetic order with propagation vector **k** = (0, 0.029, 0) takes place.

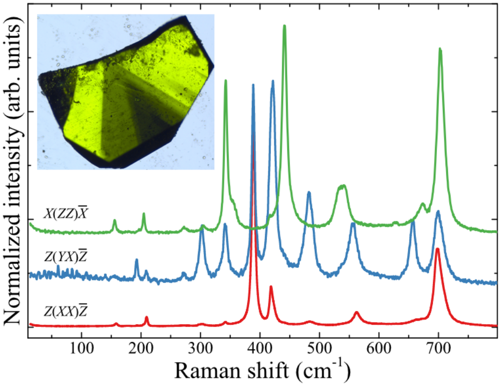


Figure 1. Room temperature normalized Raman scattering spectra for different polarizations. Inset shows polar domains on (001) plane observed with the polarized microscopy.

In this talk, we report on lattice and spin dynamics of Ni_2InSbO_6 in a wide temperature range, including the magnetic ordering temperature T_N=76 K, studied with the use of Raman spectroscopy for all informative polarizations/geometries. Most of the predicted by the group-theory phonons were observed in the energy range of 150–800 cm^{-1} and identified. Since NISO is non-centrosymmetric, LO-TO phonon splitting is expected; it was experimentally observed and studied through polarized scattering technique. The observed two-phonon scattering suggests high structural quality of the samples. Experimental observations are supported by the magnetic symmetry analysis and calculations within the linear spin-wave theory (LSWT).

Work is supported by the Russian Science Foundation grant No. 16–12–10456.

References

[1] Ivanov, S. A. *et al.* Spin and dipole ordering in Ni_2InSbO_6 and Ni_2ScSbO_6 with corundum-related structure. *Chemistry of Materials* **25,** 935–945 (2013).
[2] Weil, M., Mathieu, R., Nordblad, P. & Ivanov, S.A. Crystal growth experiments in the systems Ni_2MSbO_6 (M=Sc, In) using chemical vapour transport reactions: Ni_2InSbO_6 and $NiSb_2O_6$ crystals in the mm range. *Crystal Research and Technology* **49,** 142–151 (2014).

Charged Domain Walls in Lithium Tantalate with Spatially Nonuniform Stoichiometry Deviation

V. I. Pryakhina,[1,*] E. D. Greshnyakov,[1] B. I. Lisjikh,[1] A. R. Akhmatkhanov,[1] P. S. Zelenovskiy,[1] D. O. Alikin,[1] A. Bartasyte,[2] and V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., Ekaterinburg, Russia
[2]Time Frequency Department, FEMTO-ST Institute,
26 rue de l'Epitaphe, Besançon, France
[*]Corresponding Author: viktoria.pryahina@urfu.ru

The influence of nonuniform spatial distribution of stoichiometry deviation on as-grown domain structure has been studied in lithium tantalate (LT) single crystals. Vapor transport equilibration (VTE) method has been used to create nonuniform spatial distribution of Li concentration (c_{Li}).

Congruent LT 0.5-mm-thick Z-cut plates were annealed in Li-rich atmosphere at maximum temperature 1300 ºC during 24–100 h. The heating/cooling rate was 1 ºC/min. Confocal Raman spectroscopy was used for characterization of composition distribution. Visualization of domain structure in the crystal bulk was performed by Cherenkov-type second harmonic generation (CSHG) and confocal Raman microscopy, at the crystal surface after selective etching — by optical and scanning electron microscopies.

The nonuniform distribution was defined as the c_{Li} difference between surface and bulk (Δc) and had three types: (i) high nonuniformity with high c_{Li} (near stoichiometric) at the surfaces and low (congruent) in the bulk ($\Delta c > 1\%$), (ii) low nonuniformity with higher c_{Li} at the surfaces ($0\% < \Delta c < 1\%$), and (iii) reversed low nonuniformity with higher c_{Li} in the bulk ($-1\% < \Delta c < 0\%$).

The as-grown domain structure was formed during cooling after VTE process. Two mechanisms have been revealed: (a) formation of wide domain boundary in the bulk due to phase transition, (b) formation of isolated domains in pyroelectric field during subsequent cooling to room temperature [1].

The dependence of as-grown domain structure on composition distribution was investigated. The large nonuniformity (i) resulted in formation of wide charged domain boundary with width about 160 ± 10 μm along Z direction consisting of nanodomains. Visualization of domain structure at Y cross section revealed the tail-to-tail boundary with the zig-zag shape. The samples with small nonuniformity (ii) had layered domain structure with interlaced tail-to-tail and head-to-head domain boundaries. The CSHG visualization and following 3D reconstruction of domain structure allow revealing the continuous head-to-head domain boundary with roughness about 40 μm. The reversed low nonuniformity (iii) resulted in formation of a wide charged domain boundary with width 350 ± 20 μm along Z direction consisting of a great number of dense nanodomains.

The isolated domains formed between polar surfaces and charged domain boundary in all samples represented by both through cylindrical and non-through conical domains with diameter at the polar surface from 1 to 3 μm. The domain shape changed depending on local stoichiometry deviation from hexagonal for stoichiometric composition to trigonal for congruent one.

The equipment of Ural Center for Shared Use "Modern Nanotechnology" Ural Federal University was used.

References

[1] V. I. Pryakhina et al., *Ferroelectrics* 525 (2018) *in press*.

Lead-free porous and composite materials for ultrasonic transducers applications

A. N. Reznichenko,[1,*] M.A. Lugovaya,[1] E.I. Petrova,[1] N.A. Shvetsova,[1]
A. N. Rybyanets

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
[*]e-mail: reznichenkoan@yahoo.com

Lead-free ferroelectric ceramics is of great interest mainly due to the growing attention to environmental problems. Promising candidates among the lead-free systems are perovskites based on alkali metal niobates (Na, Li)NbO_3 and (Na, K)NbO_3, layered bismuth-containing compounds $Bi_4Ti_3O_{12}$, $(Na_{1-x}Bi_x)TiO_3$. $SrBi_2Nb_2O_9$ and tungsten bronzes (Sr, Ba)Nb_2O_6 [1, 2]. However, it seems very doubtful that any new lead-free piezoceramic system with piezoelectric properties close to the properties of the PZT system will be found in the nearest future. Therefore, the interest is currently concentrated on the known lead-free compositions in attempts to improve their properties and adapt to various applications. The use of alkali metal niobates in the form of 1–3 composites, ceramic matrix composites, and porous ceramics allows to increase the main functional parameters of these materials and makes them competitive with piezoceramics of the PZT system. Thus, the study of composites and porous ceramics based on lead-free compounds, is interesting both from scientific and practical points of view.

This paper describes the fabrication technology, as well as the results of systematic studies of the properties of "ceramics-polymer" composites with 1–3 connectivity type, ceramic matrix composites "ceramics/crystal", and porous ceramics based on lead-free sodium-lithium niobates (Na, Li)NbO_3 and sodium-potassium niobates (Na, K)NbO_3 compositions. Experimental samples of lead-free porous piezoelectric ceramics and composites were fabricated, and measurements of elastic, dielectric and piezoelectric parameters, as well as microstructural studies of experimental samples were performed. It was shown that the use of alkali metal niobates in the form of 1–3 composites, ceramic matrix composites, and porous ceramics allows to increase the main functional parameters of these materials and makes them competitive with piezoceramics of the PZT system. The developed lead-free porous and composite materials have a unique combination of parameters and can be used in the manufacture of ultrasonic transducers and devices for a wide range of applications, including medical and nondestructive testing equipment. The results of systematic studies allowed to develop manufacture technology of "ceramics-polymer" composites with 1–3 connectivity type, ceramic matrix composites "ceramics/crystal", and porous ceramics based on lead-free sodium-lithium niobates (Na, Li)NbO_3 and sodium-potassium niobates (Na, K)NbO_3 compositions. The developed lead-free porous and composite materials have a unique combination of parameters unachievable for standard PZT ceramic compositions fabricated by standard methods and can be used in the manufacture of ultrasonic transducers and devices for a wide range of applications, including medical diagnostic equipment, nondestructive testing, level and flowmetry, underwater acoustics, as well as power ultrasonic systems for medical and technological purposes.

This work was financially supported by the Ministry of Education and Science of the Russian Federation: the basic parts of the state task, themes № BP0110–11/2017–44 (12.5425.2017/8.9), № 3.8863.2017/ITW (3.8863.2017/7.8).

References

[1] Yi-Qing Lu, Yong-Xiang Li, *J. Adv. Dielect.*, vol. 01, P. 269 (2011).
[2] R. Machado, M. Sepliarsky, M.G. Stachiotti, *Applied Physics Letters*, vol. 103, N24, P. 242901 (2013).

Phase Transition induced by high pressure in a Hg_2F_2 ferroelastic crystals

E. M. Roginskii* and Yu.F. Markov

Spectroscopy of the solid state laboratory, Ioffe Institute, Politekhnicheskaya st. 26,
Saint-Petersburg, Russia
*Corresponding Author: e.roginskii@mail.ioffe.ru

Univalent mercury halide crystals Hg_2Hal_2 (Hal = Cl, Br, I) are the model objects in a study of general problems of the structural phase transitions. These crystals obtains unique physical properties, namely low sound speed, high birefringence and acousto-optics constants. However the Hg_2F_2 crystals are poorly studied. The structure of the crystal is still under discussion.

Using the X-Ray diffraction (XRD) data of the Hg_2F_2 powder the Ritvield Refinement method with Hg_2Cl_2 structure parameters as initial was applied to estimate lattice parameters and atomic positions. The significant reduce of parameter perpendicular to C_4 axes with respect to Hg_2Cl_2 data was found. X-Ray analysis reports on existing small amount of impurities namely HgF_2, HF, HgO etc. There is no significant difference (for instance no peak splitting and no new reflexes observed) in XRD for both room and low (7K) temperature revealed.

Then the set of *ab initio* calculations was performed to estimate the most stable phase at normal conditions. The different approximations was tested to find most adequate technique with good reproducing of the experimental data.

The calculations of electronic structure and dynamical properties was performed within Density Functional Theory (DFT) with electronic wavefunctions at each k-point expanded in terms of a discrete plane-wave basis set and by using pseudopotential approximation. The Local Density Approximation (LDA) and General Gradient Approximation with longrange dispersion corrections for density functional to account weak Van-der-Waals interaction of linear molecules Hg_2F_2 was found to reproduce experimental data with a good agreement.

The several initial structures (monoclinical $P2_1/m$ as suggested in paper[1], doubled orthorhombic unitcell Cmcm and tetragonal I4/mmm) in geometry optimization procedure is tested. As a result all initial structures is finally optimized in tetragonal unitcell with the single linear molecule Hg_2F_2 with the high accuracy (0.0001Å). The structure is stable as soon the calculated phonon spectra in all set of the high-symmetry points of the Brillouin Zone (BZ). Also the determinant of the stiffness tensor is positive. The tetragonal phase reveals the stability in a long range of hydrostatic and monoaxial applied pressure.

The baric dependence of phonon spectra is studied by DFT within LDA approximation. The soft modes which leads to ferroelastic phase transition (PT) is found. In case of hydrostatic pressure the phonon with irreducible representation X_3^+ (Stokes notation[2]) which is bound with libration vibration of the linear molecule softening at the boundary M-point of BZ with pressure increasing and freeze at P_c=9.3GPa, which induces the PT with unit cell doubling. The group theory predicts three isomorphic subgroups of the supergroup I4/mmm, namely face centered orthorhombic Cmce, orthorhombic $P4_2/ncm$ and orthorhombic Pccn. By applying the atomic displacements along eigenvector of the soft mode the final Cmce symmetry of the structure was discovered. In opposite in case of monoaxial applied pressure along C_4 axis the soft mode irreducible representation is X_3^- the mode is acoustical TO-branch at the boundary X-point of Brillouin zone. The phase transition induced by “freezing” of X_3^- phonon accompanied with doubling unitcell and lowering the symmetry to Cmcm.

References

[1] S.Emura, J. Phys.: Condens. Matter, **2**, 7877 (1990).

[2] H.T. Stokes, B.J. Campbell and Ryan Cordes, Acta Cryst. A. **69**(4), 388 (2013)

The structure and dielectric properties of $Bi_{1-x}Sm_xFeO_3$ (x = 0–0.20)

S.A. Sadykov, N.M.-R. Alikhanov, D.K. Palchaev, Zh. Kh. Murlieva

Dagestan State University, 367000 Makhachkala, Russia
ssadyk@yandex.ru

The reseach of the structure and the frequency and temperature dependences of $Bi_{1-x}Sm_xFeO_3$ ceramics dielectric properties are presented. $Bi_{1-x}Sm_xFeO_3$ ceramics were obtained by cold pressing of nanopowders thermally treated at 600 °C. It is shown that $Bi_{1-x}Sm_xFeO_3$ (x = 0; 0.05) crystallizes in rhombohedral structure with R3c space group. XRD analysis of the composition x = 0.1 indicates the presence of a new orthorhombic (space group: Pbam) phase. With a 15% bismuth's substitution, the crystal structure is completely transformed from rhombohedral to orthorhombic phase.

The measurements dielectric properties (electrical conductivity, dielectric constant, dielectric losses) were carried out in the frequency range 1 kHz — 10 MHz in the temperature range 25–600 °C. Both components of ε undergo strong frequency dispersion. The intense temperature growth of the real part ε' begins above 200 °C, reaches its maximum at 300 °C, and has a frequency-dependent character inherent to relaxors. With increasing samarium content, ε' increases. At room temperature and at a frequency of 1 kHz, ε' increases from 80 (x = 0) to 150 (x = 0.2).

As can be seen from Fig. 1, the dependence $\sigma_{ac}(T)$ for 10 MHz has two regions with a boundary temperature of ~ 250 °C, where the temperature conductivity factors are substantially different. In the temperature range of ~ 250–400 °C, a sharp increase in the conductivity almost by two orders of magnitude at all frequencies is observed. The further behavior of $\sigma_{ac}(T)$ depends on the frequency. At frequencies < 1MHz, $\sigma_{ac}(T)$ reaches to saturation, while at frequencies above 1MHz, conductivity passes through a maximum. Moreover, the conductivity maximum temperature is shifted to lower temperatures area with an increase in both the frequency and the percentage content of samarium.

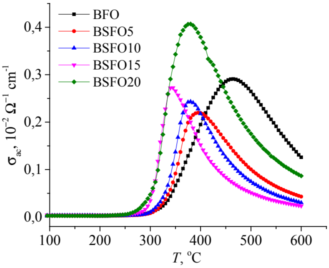


Figure 1. Plot of $\sigma_{ac}(T)$ at 10 MHz

The form of $\sigma_{ac}(\omega)$ curves for BSFO10 at different temperatures indicates its thermoactivation character, in which the activation energy E_A decreases with increasing frequency. In the investigated temperature range, this dependence is formed by four overlapping relaxation processes: from 25 to 160 °C with an activation energy $E_A = 0.35–0.016$ eV; from 160 to 250 °C $E_A = 0.74–0.11$ eV; from 250 to 380 °C for temperatures $E_A = 2.36–1.56$ eV. A significant decrease in conductivity in the fourth temperature region above 380 °C at frequencies > 1 MHz can be a consequence of a decrease in the mobility of charge carriers, since at these frequencies the charge carriers can not follow after the applied electric field.

Dielectric Response in Domain Engineered Rhombohedral phase of $BaTiO_3$ single crystals

M. Savinov*, P. Bednyakov, J. Pokorný, J. Hlinka

Institute of Physics CAS, Na Slovance 2, 182 21 Praha 8, Czech Republic
*Corresponding Author: savinov@fzu.cz

Unusual increase of dielectric permittivity of a $BaTiO_3$ single crystal in rhombohedral phase [1] has been a subject of substantial interest. The effect has been related to the appearance of nano-sized domains below 190 K [2] under a suitable electric field pre-treatment.

In this study the domain structure of $<111>_{pc}$-oriented single crystal plates of $BaTiO_3$ has been modified by combinations of in-plane and out-of-plane steady state electric poling at ambient temperature. It has been found that the annealed, in-plane and out-of-plane poled samples showed markedly different dielectric properties at low temperatures. The difference in low-temperature permittivity behavior is enhanced by an out-of-plane fast-decayed bipolar electric pulse treatment, even though there is no clear signature of differences in domain structure by optical microscopy [3].

We also report additional insights in the dynamics of this remarkable phenomenon. In particular, we have elucidated the role and the influence of the DC and AC electric field on the $<111>_{pc}$-oriented $BaTiO_3$ single-crystal in the rhombohedral phase. It is shown that the effect of the dielectric permittivity increase is strongly connected with the probing AC voltage while it does not depend on the value of the DC electric field. In addition, the frequency dependence has been studied in detail within the 10 Hz to 1 MHz range and for various amplitudes of the AC field. We also discuss a contribution of motion of ferroelastic domain walls and defects to the dielectric response of such a system.

This work was supported by the Czech Science Foundation (Project GACR 13-15110S)

References

[1] Y. L. Wang, Z. B. He, D. Damjanovic, A. K. Tagantsev, G. C. Deng, N. Setter, *J. Appl. Phys.* **110,** 014101 (2011).
[2] Y. L. Wang, A. K. Tagantsev, D. Damjanovic, N. Setter, *Appl. Phys.Lett* **91,** 062905 (2007).
[3] P Bednyakov, M. Savinov, J. Pokorny, J. Hlinka, submitted to *J. Appl. Phys.*

On the Phase Transitions of the Relaxor Ferroelectric Single Crystal of Strontium-Barium-Niobate

G. Shabbir,[1,*] and S. Kojima[2]

[1]Physics Division, PINSTECH, Nilore, Islamabad 45650, Pakistan
[2]Division of Materials Science, University of Tsukuba, Tsukuba 305–8573, Japan
[*]Corresponding Author: gshabbir@gmail.com

The tetragonal tungsten bronze (TTB) type ferroelectric material strontium-barium-niobate, $Sr_xBa_{1-x}Nb_2O_6$ (SBN-x, $0.25<x<0.80$), is an interesting candidate to understand the phenomena of relaxor ferroelectricity due to its strong anisotropic nature of local polarization besides its excellent physical properties [1]. The complex relaxor nature is relatively simplified in SBN-x single crystal because the local polarization is unidirectional (*i.*e., one-component order parameter) in contrast to pseudo-cubic perovskite-type relaxor oxides (*e.*g. $Pb(Mg_{1/3}Nb_{2/3})\,O_3$), which have a large number of possible orientation states of local polarization [2]. As to the composition of SBN-x crystals, it gradually changes from typical ferroelectric (for low values of x) to relaxor character with increasing strontium contents. In the present study, the investigations on the ferroelectric phase transitions in SBN-75 *c*-plate relaxor ferroelectric single crystal are briefly reported in broad temperature range.

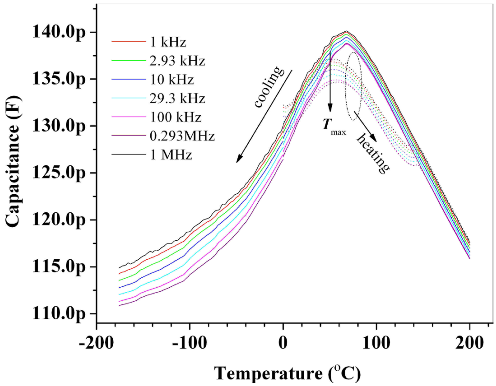


Figure 1. Measured capacitance of the SBN-75 crystal as a function of temperature.

The real part of the complex capacitance, $C^*(f, T) = C'(f, T)\text{-}iC''(f, T)$, as a function of temperature (T) at some selected frequencies, f, of the applied weak *ac*-field is shown in Fig. 1. It is clear that the SBN-75 crystal exhibits a strong frequency dispersion with a broad temperature maximum, $T_{max} \approx 58$ °C (for f=10 kHz) in heating the crystal from room temperature. During heating cycle, T_{max} and the measurement frequency obey well the Vogel-Fulcher (VF) law. In subsequent cooling the crystal (after heating cycle), a broad maximum at $T_{max} \approx 68$ °C, with no frequency dispersion and no additional anomaly down to the lowest measured temperature (~ -170 °C) was observed. The anomaly observed at T~140 °C disappeared during cooling cycle, whereas this anomaly completely disappeared upon poling the crystal at room temperature.

References

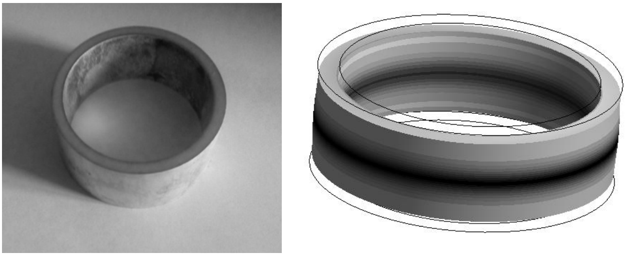
[1] A. M. Glass, J. Appl. Phys. 40, 4699 (1969).
[2] J. H. Ko and S. Kojima, Appl. Phys. Lett. 91, 082903 (2007).

Finite Element Simulations of Cylindrical Standing Waves inside Cylindrical Piezoelectric Transducer

S.A. Shcherbinin,[1,*] I.A. Shvetsov,[1] A.V. Nasedkin,[1] N.A. Shvetsova,[1] A.N. Rybyanets[1]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
[*]e-mail: step_scherbinin@list.ru

At the present work, we have studied high-intensity ultrasound fields of standing cylindrical waves, generated by cylindrical piezoelectric transducer with radial polarization in its internal volume filled by liquid (Fig. 1). Generating of such standing waves inside liquid volume seems to be promising for some purposes of different technology areas. For example, ultrasound exposure can be applied for reducing viscosity of heavy oils, for ultrasonic cosmetic procedures and so on [1, 2]. It is common to use focused or plane ultrasound but approaches based on the using of standing cylindrical waves, for the best of our knowledge, is poorly developed.



(a) (б)

Figure 1. Cylindrical piezoelectric transducer made of PZT-19 ceramics and its vibrational profile on resonant frequency 70 kHz

In our previous paper [1] we have shown, that for common piezomaterials and liquids it is impossible to create standing cylindrical waves inside cylindrical transducer operating on its radial mode of oscillations. Thus, present paper is focused on length-extensional and thickness vibrational modes of cylindrical piezoelectric transducer.

We have performed the finite-element simulations of standing cylindrical waves formation for different piezoelectric materials, liquids and vibration modes of piezoelectric cylinder using ANSYS software package [3].

To choose the most effective excitation regime, we have calculated nodal structure of cylindrical standing waves, acoustic pressure and ultrasound intensity for each vibrational mode and displacement profile of cylindrical piezoelectric transducer changing acoustic parameters of the liquid medium and properties of piezoelectric material.

This work was financially supported by the Ministry of Education and Science of the Russian Federation: the Basic parts of the State task, Themes № BP0110–11/2017–44 (12.5425.2017/8.9), № 3.8863.2017/ITW (3.8863.2017/7.8) and RFBR project № 16–01–00785.

References

[1] S.A. Scherbinin, I.A. Shvetsov, N.A. Shvetsova, D.I. Makarev, A.N. Rybyanets, Nova Science Publishers Inc., (in print).
[2] D.I. Makarev, A.N. Rybyanets, V.L. Sukhorukov, Indian Journal of Science and Technology, vol. 9, Issue 42, P. 168–174 (2016).
[3] ANSYS (http://www.ansys.com).

Electronic structure, magnetic, optical and polarization properties of the multiferroic $CaMnTi_2O_6$ by first principles

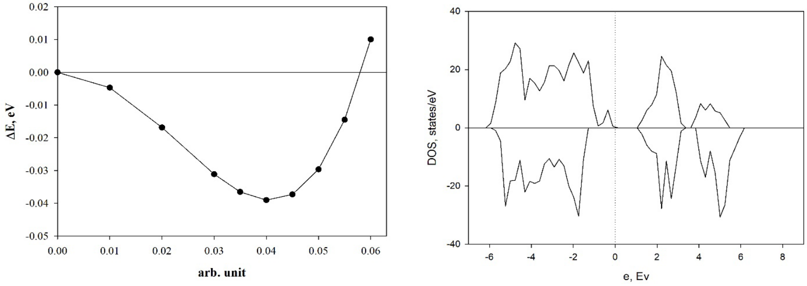
A. S. Shinkorenko, V. I. Zinenko, M. S. Pavlovskii

Kirensky Institute of Physics, Federal Research Center KSC SB RAS,
Akademgorodok 50, Krasnoyarsk, 660036, Russia
E-mail: shas@iph.krasn.ru

The scientific community is devoting considerable attention multiferroics because they have a practical value. One of these compounds is the recently discovered multiferroic $CaMnTi_2O_6$ [1]. Two phases are known ferroelectric with space group symmetry $P4_2mc$ and paraelectric with space group $P4_2/nmc$. The phase transition from $P4_2mc$ to $P4_2/nmc$ occurs at a pressure of 7 GPa [2] or a temperature of 630 K.

In this work, result of the calculations of the electronic structure, magnetic, optical and polarization properties is presented.

Calculation of lattice dynamics showed the presence of soft modes in center of the Brillouin zone in paraelectric phase. The softest mode with a frequency of 120i cm^{-1} is polar. Dependence of energy on magnitude of the displacement of the eigenvector of polar soft mode is shown in Fig.1(a). It is found that in the ferroelectric phase with space group $P4_2mc$ all modes are stable.



a) b)

Fig. 1. a) Dependence of energy on magnitude of displacement in ferroelectric phase b) calculated electron DOS in paraelecrtic phase

An estimate of the spontaneous polarization was made and it was $\Delta P = 40\ \mu C/cm^2$.

The electron structure and optical properties for two phases were calculated. In Fig. 1(b) densities of electron states in the paraelectric phase $P4_2/nmc$ is shown.

References

[1] Aimi et al., Chem. Mater., 26, p. 2601–2608 (2014).
[2] J. Ruiz-Fuertes et al., PHYSICAL REVIEW B96, 094101 (2017).

Forward Domain Growth in Uniaxial Ferroelectrics

V. Ya. Shur[1, *], **D. O. Alikin**[1] **A. P. Turygin**[1] **A. V. Ievlev**[2] **and S. V. Kalinin**[2]

[1]School of Natural Sciences and Mathematics, Ural Federal University, 51 Lenin Ave.,
620000 Ekaterinburg, Russia,
[2] The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory
37831 Oak Ridge, TN
[*]Corresponding Author: vladimir.shur@urfu.ru

The growth of single domain in polar direction ("forward domain growth") has been studied experimentally with high spatial resolution by local polarization reversal on non-polar surfaces of uniaxial ferroelectric lithium niobate $LiNbO_3$. The original mechanism of domain growth based on kinetic approach allowed explaining the domain growth in the areas with negligible value of applied external electric field.

The forward growth of the isolated domains with charged domain walls is one of the main stages of the domain structure evolution during polarization reversal from the single domain state in any ferroelectric [1], but it still was not studied systematically with high enough precision due to low spatial resolution of the used experimental methods. In our experiments the forward domain growth has been studied for the first time with high spatial resolution by local polarization reversal non-polar cuts (Y- and X-cuts) of $LiNbO_3$ single crystals by conductive tip of scanning probe microscope [2–4]. The obtained wedge-like domain shape and large domain length differ drastically from the theoretical prediction [5]. The domain patterns have been visualized by piezoresponse force microscopy, scanning electron microscopy (after selective chemical etching), and confocal Raman microscopy [6]. Formation of the metastable domains with charged walls contradicts to dielectric discharge model commonly used for explanation of the forward domain growth. It was proposed by M. Molotskii et al. that "the main driving force for ferroelectric domain breakdown is… rather internal force generated owing to the minimization of depolarization field energy when the domain elongates" [7]. Nevertheless the appearance of the domains with charged domain walls and high depolarization field energy is demonstrated in many experimental situations.

The obtained results have been discussed in the framework of the kinetic approach to the domain growth based on the analogy of the domain structure evolution with the first order phase transformation (crystal growth) [1]. We have attributed the domain growth in the area with negligible value of the applied electric field to the self-maintained domain wall motion as a result of propagation of the interacted charged kinks [8].

The obtained knowledge is very important for understanding of the domain structure evolution during polarization reversal. Moreover it can be used for development of the domain engineering and domain wall engineering [9]. The new information about domain growth mechanism will be applied successively for micro- and nano-domain patterning [10].

The equipment of the Ural Center for Shared Use "Modern Nanotechnology" UrFU was used. The research was made possible by Russian Scientific Foundation (grant 14–12–00826).

References

[1] V. Ya. Shur, *J. Mater. Sci.*, 41, 199–210 (2006)
[2] D. O. Alikin et al, *Appl. Phys. Lett.*, 106, 182902 (2015)
[3] A. V. Ievlev et al., *ACS Nano*, 9, 769–777 (2015)
[4] A. N. Morozovska et al., *Phys. Rev. B*, 93, 165439 (2016)
[5] N. A. Pertsev, A. L. Kholkin, *Phys. Rev. B*, 88, 174109 (2013)
[6] V. Ya. Shur, P. S. Zelenovskiy, *J. Appl. Phys.*, 116, 066802 (2014)
[7] M. Molotskii et al., *Phys. Rev. Lett.*, 90, 107601 (2003)
[8] V. Ya. Shur et al., *Appl. Phys. Lett.*, 109, 132901 (2016)
[9] V. Ya. Shur et al., *Appl. Phys. Rev.*, 2, 040604 (2015)
[10] A. P. Turygin et al., *Materials*, 10, 1143 (2017)

Experimental Study of Focused Acoustic Fields Generated by HIFU Piezocomposite Transducers

I.A. Shvetsov,[1,*] S.A. Shcherbinin,[1] N.A. Shvetsova,[1] E.I. Petrova,[1] A.N. Rybyanets[1]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
*e-mail: wbeg@mail.ru

Over the past several decades, ultrasonic impact methods by the high-intensity focused ultrasound (HIFU) are becoming more widely spread in medicine, because of high selectivity and intensity in the local region of body. A recent developments of transmitting systems, generating acoustic fields of different spatial configuration with a wide range of intensities, allows the use of ultrasonic energy, as for diagnostic purposes and for therapy and even surgery of soft biological tissues [1].

In this paper, ultrasonic fields of focused ultrasonic transducers were studied. Numerical algorithms, based on the nonlinear parabolic Khokhlov-Zabolotskaya-Kuznetsov (KZK) equation, have been developed and applied to the calculations of acoustic fields of HIFU ultrasonic transducers. The influence of ultrasonic transducers designs on acoustic fields generated in different acoustic media were measured using 3D ultrasonic measurement systems UMS (Precision Acoustics Ltd.). HIFU transducers designs based on focusing elements made from porous piezoelectric ceramics were developed. Measurement of focused acoustic fields of HIFU transducers were made in acoustic bath using calibrated hydrophones with various dimensions and sensitivity (Fig 1).

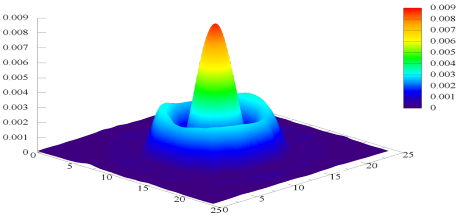


Figure 1. The intensity of focused ultrasound field in distilled water

It was shown, that any kind of irregularities in the shape and size of focused piezoelectric element as well as transducers design element peculiarities (housing, membrane, connecting wires and soldering points) strongly influence acoustic field distribution (intensity, side lobs level etc.).

The results of theoretical modeling, ex vivo experiments on tissues and vascular phantoms, as well as in vivo experiments in lamb's femoral artery proved the efficacy, safety and selectivity of developed HIFU transducers and combinational treatment methods that can be used for various therapeutic, surgical and cosmetic applications.

This work was financially supported by the Ministry of Education and Science of the Russian Federation: the basic parts of the state task, themes № BP0110–11/2017–44 (12.5425.2017/8.9), № 3.8863.2017/ITW (3.8863.2017/7.8).

References

[1] A.N. Rybyanets, N.A. Shvetsova, I.A. Shvetsov, O.A. Sapozhnikov, V.A. Khokhlova, Indian *Journal of Science and Technology*, vol. 9, Issue 42, P. 342–354 (2016).

Ultrasonic Transducer Designs for Combinational Treatment of Biological Tissues

**N.A. Shvetsova,[1,*] I.A. Shvetsov,[1] M.A. Lugovaya,[1] A.N. Reznichenko,[1]
A.N. Rybyanets[1]**

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
*e-mail: yfnfif_71@bk.ru

New methods and apparatus for ultrasonic therapeutic treatment, diagnostics and body aesthetics as well as a new application fields based on the advances in piezoelectric materials and ultrasonic transducer designing, visualization technologies and physical acoustics have appeared during a few past decades. Recently, multidimensional scientific researches directed to development of new medical and recovery technologies with application of physiotherapeutic methods as well as to identification of opportunity and expediency of a combination of various physical and medicaments factors were conducted [1]. However obvious is that fact that application of separate narrowly targeted therapeutic methods is ineffective and does not solve all range of the problems facing recovery and regenerative medicine.

The paper presents novel methods of complex therapeutic treatment of biological tissues of a patient. The methods are based on synergetic combination of different physical factors such as ultrasonic shear and standing waves impact, ultrasonic hating and cavitation, radio-frequency heating (RF), vacuum massage, as well as ultrasonically assisted delivery and activation of drags.

a) b)

Figure 1. Universal therapeutic module for the complex therapeutic treatment of superficial tissues (a) and HIFU transducer for tissue ablation (b)

Theoretical and numerical models of ultrasonic transducers along with the results of acoustic fields modeling and technological aspects of the ultrasonic transducer designing were discussed. The efficacy, safety and selectivity of developed methods and ultrasonic transducers for various therapeutic, surgical and cosmetic applications were proved by the results of ex vivo experiments with different biological tissues. The main advantages of new methods are: reduced treatment time, bigger treated tissue volume treatment of arbitrary body part, high selectivity and safety, continuous control of the treatment process and tissue condition, and wide range of applications. New ultrasonic transducers and methods can be used in the field of regenerative and aesthetic medicine for the accelerated healing of wounds and burns, scars removal, rejuvenation and tightening of skin, treatment of cellulitis, elimination of consequences of the disfiguring cosmetic procedures, as well as for surgical treatments of oncological diseases of a skin. The methods can be used also for ultrasonic ablation and surgical treatment of various tumors in vital organs of a patient.

This work was financially supported by the Ministry of Education and Science of the Russian Federation: the basic parts of the state task, themes № BP0110–11/2017–44 (12.5425.2017/8.9), № 3.8863.2017/ITW (3.8863.2017/7.8).

References

[1] A.N. Rybyanets, N.A. Shvetsova, I.A. Shvetsov, O.A. Sapozhnikov, V.A. Khokhlova, I*ndian Journal of Science and Technology*, vol. 9, Issue 42, P. 342–354 (2016).

Photonic Band Gap of Multiferroic-Dielectric Materials in IR region: FDTD method

Selami Palaz,[1] Sevket Simsek,[2*] Zafer Ozer,[3] Amirullah M. Mamedov,[4,5] Ekmel Ozbay[4]

[1]Department of Physics, Faculty of Science and Letters, Harran University, 63000, Sanliurfa, Turkey
[2]Department of Material Science and Engineering, Faculty of Engineering, Hakkari University, 3000, Hakkari, Turkey
[3]Electronic Technology, Mersin Vocational School, Mersin University, 33335, Mersin, Turkey
[4] Nanotechnology Research Center, Bilkent University, 06800, Ankara, Turkey
[5] International Scientific Center, Baku State University, Baku, Azerbaijan
*Corresponding Author: ssimsek_001@hotmail.com

Keywords: multiferroic, optical band gap, photonic crystals

In present investigation, the photonic band gap (PBG) is numerically analyzed in the infrared frequency region from the transmittance and reflectance, calculated by Finite-Difference Time-Domain (FDTD) method, from the number of the periods in the photonic crystal and the nature/ geometry of the existing materials. Out of the various photonic materials, the main work is focused on multiferroic material $V_2Mn_3O_8$, which have been alternately arranged with dielectric materials like $BaTiO_3$ or $KNbO_3$. The tunable characteristics are studied by changing with the replacement of Mn^{+3} from $V_2Mn_3O_8$ lattice with Fe^{+3}. The substitution of Fe^{+3} at the place of Mn^{+3} forms a solid solution with the parent $V_2Mn_3O_8$ — host lattice. The absorption response of the mixed metal solid solutions is approximately a linear combination of the characteristics of the two end members; as a result that demonstrates straightforward band gap tunability in oxides. The tunability is observed in a red-shift by varying the percentage of Fe^{+3} in the $V_2Mn_3O_8$ lattice. The effect of the number of periods with different dielectric material on the photonic band gap is illustrated. Using FDTD, the reflectivity of one dimensional periodic structure for TE and TM-modes at different angles of incidence has also been calculated.

Structural, Electronic, and Mechanical Properties of $A_3Mn_2O_7$ (A = Sr, Ca): *ab initio* calculation

Sevket Simsek*[1], Husnu Koc[2] Amirullah M. Mamedov[3,4], Ekmel Ozbay[3]

[1]Hakkari University, Faculty of Engineering, Department of Material Science and Engineering,
3000, Hakkari, Turkey
[2]Siirt University, Faculty of Sciences, Department of Physics, Siirt, Turkey
[3]Bilkent University, Nanotechnology Research Center, 06800, Ankara, Turkey
[4]Baku State University, International Scientific Center, Baku, Azerbaijan
*e-mail: ssimsek_001@hotmail.com

Keywords: Ruddlesden-Popper, Electronic Structure, Elastic Constants, First principles calculation

In present study, the structural, electronic, optical and mechanical properties of the Ruddlesden-Popper type oxide compounds are investigated by means of density functional theory based on pseudopotantial arpproximation. In our calculation, spin polarized electron band structures and density of the state were identified by adding to the spin contribution of the Mn-atom. For $A_3Mn_2O_7$ compounds, the real and imaginary parts of the dielectric function and other optical properties such as refractive index, energy loss function, effective number of valence electrons and effective optical dielectric constant were calculated accordingly. In addition, the bulk modules, shear modules, Young's modulus and Poisson ratios, anisotropy factors, sound velocities and Debye temperatures for these compunds were calculated too.

Modeling of the Flexoelectric Effect in the Bending of Unpolarized Ceramic Beam

A. N. Soloviev[1, 3*], V. A. Chebanenko[2] and I. A. Parinov[3]

[1]Don State Technical University, 344000, Gagarin sq., 1, Rostov-on-Don, Russia
[2]Southern scientific center of RAS, 344022, str. Chekhova, 41, Rostov-on-Don, Russia
[3]Vorovich Mathematics, Mechanics and Computer Science Institute, Southern Federal University, 344090, str. Milchakova, 8a, Rostov-on-Don, Russia
*Corresponding Author: solovievarc@gmail.com

In this study, modeling of the flexoelectric effect in unpolarized piezoceramics is considered. The sample under study made on the basis of the PZT-19, clamped at both ends, is loaded by the attached mass in the middle. The excitation of harmonic mechanical vibrations occurs by moving the base of the clamps. The output voltage is measured at the load resistance connected to the sample electrodes. On the basis of the Hamiltonian variational principle, in which the potential density has the form (1), by introducing the Euler-Bernoulli hypotheses and Kantorovich method a system of differential equations is derived [1].

$$U^L\left(\varepsilon_{ij},\varepsilon_{ij,k},P_i\right)=\frac{1}{2}a_{ij}P_iP_j+\frac{1}{2}c_{ijkl}\varepsilon_{ij}\varepsilon_{kl}+d_{ijk}P_i\varepsilon_{jk}+f_{ijkl}P_i\varepsilon_{jk,l}+\frac{1}{2}g_{ijklmn}\varepsilon_{ij,k}\varepsilon_{lm,n}, \qquad (1)$$

where P_i is the polarization vector, a_{ij} is the inverse dielectric susceptibility, ε_{ij} is the strain, c_{ijkl} is the elastic moduli tensor, d_{ijk} is the piezoelectric moduli tensor, f_{ijkl} is the flexoelectric moduli tensor, g_{ijklmn} is the tensor describing pure nonlocal elastic effects, $\varepsilon_{ij,k}$ is the strain gradient.

The results of the study of the amplitude-frequency characteristics of the output voltage for various load resistances for the model under study are shown in Fig. 1.

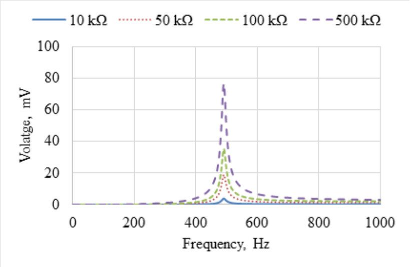


Figure 1. The frequency response of the voltage across the resistor with different values of the load resistance obtained from the numerical experiment

During the research it was shown that the output electric potential can arise in unpolarized samples, and its values can serve to determine the flexoelectric constants. In addition, the variation of such constants is possible only up to a certain point, when the effective rigidity of the beam becomes negative, and the results lose physical meaning.

The work was supported by the RFBR projects 16–08–00740_a and 16–58–52013 MHT_a

References

[1] A. N. Soloviev, V. A. Chebanenko, Yu. N. Zakharov, E. V. Rozhkov, I. A. Parinov, V. K. Gupta, *Advanced Materials — Techniques, Physics, Mechanics and Applications*, vol 193, 485–500 (2017)

Domain wall motion in the electric field of a piezoforce microscope probe: the effect of curvature and geometry of the domain wall

A. S. Starkov[1,*] **and I. A. Starkov**[2]

[1]Department of Advanced Mathematics, National Research University of Information Technologies,
Mechanics and Optics, Kronverksky pr. 49, St. Petersburg, Russia
[2]Nanotechnology center, St. Petersburg National Research Academic University RAS,
Khlopin st.8/3, 194021 St. Petersburg, Russia
*Corresponding Author: ferroelectrics@ya.ru

The description of the domain wall (DW) motion is very important in the development of devices that use the physical properties of ferroelectrics. One of the possibilities is based on the Landau-Khalatnikov (LK) equation [1], which is also known as the time-dependent Landau-Ginzburg-Devonshire equation

$$g\Delta P-\gamma\frac{\partial P}{\partial t}=aP+bP^3-E.$$

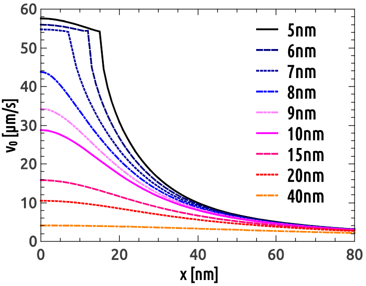


Figure 1. The dependence of the domain wall velocity on a distance from the axis of the microscope tip. The numbers to the right correspond to the span between the tip and the sample.

The equation (1), for constant material coefficients, has a solution depending on one coordinate x

$$P(x)=P_1+\frac{P_3-P_1}{1+\exp ks},$$

where $P_1<P_2<P_3$ are the roots of the stationary Landau- Ginzburg equation, and

$$s=x-v_0t,\quad k=(P_3-P_1)\sqrt{\frac{b}{2g}},\quad v_0=\frac{1}{\gamma}\sqrt{\frac{gb}{2}}(P_1+P_3-2P_2).$$

The solution of (3) describes a 180° domain wall moving with velocity v_0, which in the theory of nonlinear equations is called a "kink" [2]. In our study, the equations (2),(3) are generalized to the case of a slowly varying electric field and a curved DW. As an example, the motion of DW in lithium niobate ($LiNbO_3$) is considered under the electric field of the piezoresponse force microscope tip. When calculating the field distribution, piezoelectric characteristics of $LiNbO_3$ were taken into account [3].

References

[1] L. D. Landau, I. M. Khalatnikov, *Dokl Akad Nauk SSSR*, 96, 469–473 (1954)
[2] V. G. Danilov, V. P. Maslov, K. A. Volosov, Mathematical modelling of heat and mass transfer processes (Vol. 348). *Springer Science & Business Media*, (2012)
[3] A. S. Starkov, O. V. Pakhomov, I. A. Starkov, *Ferroelectrics*, 442, 10–17 (2013)

The multicaloric effect in bilayer magnetostriction-piezoelectric structure

A. S. Starkov[1,*] **and I. A. Starkov**[2]

[1]Department of Advanced Mathematics, National Research University of Information Technologies,
Mechanics and Optics, Kronverksky pr. 49, St. Petersburg, Russia
[2]Nanotechnology center, St. Petersburg National Research Academic University RAS,
Khlopin st.8/3, 194021 St. Petersburg, Russia
[*]Corresponding Author: ferroelectrics@ya.ru

The multicaloric effect (μCE) consists of a change in the entropy or in temperature with a simultaneous change in the electric, magnetic, and/or elastic fields [1]. The most significant μCEs can be observed in multiferroics, where the interaction of various fields is the greatest and interaction coefficients strongly depend on temperature. These coefficients include magnetoelectric, piezoelectric, and piezomagnetic/magnetostrictive constants. In natural materials, the electric and elastic fields interact (piezoelectric effect) most strongly, while the electric and magnetic fields (magnetoelectric effect) demonstrate weak coupling. Such a peculiarity of natural materials is due to a small value of the magnetoelectric susceptibility α. Therefore, composite structures are used to increase it. The simplest are laminate composites for which a significant increase in α is possible. For instance, the magnetoelectric susceptibility is $1.6 \cdot 10^{-5}$ sm^{-1} for a two-layer $Fe_{50}Rh_{50}/BaTiO_3$ system. This is five orders of magnitude greater than in the best natural materials [2]. In view of this, it is of undoubted interest to investigate μCE in a two-layer composite made of magnetocaloric and electrocaloric materials. Caloric effects are noticeable near the phase transitions. Elasticity plays an important role at these points and all three of the above fields may interact in such structures. This kind of interaction has never been considered elsewhere, and its study is the main objective of this work.

As an example of the model, we examine the μCE in the composite composed of the magnetic $Fe_{48}Rh_{52}$ and piezoelectric $PbZr_{0.53}Ti_{0.47}O_3$ layers. Based on the Landau-Ginzburg model, it is demonstrated that the presence of an electric field results in a μCE shift in temperature, but not its increase. A similar shift occurs when a uniaxial pressure is applied to the composite. The results predicted by the theory are in good agreement with the reported experimental data [3].

The reported study was supported by the Global Energy Association (grant no. МГ-2017/04/2) and the Ministry of Education and Science of the Russian Federation (project no. 074-U01).

References

[1] I. A. Starkov, A. S. Starkov, *International Journal of Solids and Structures*, 100, 187–194 (2016)

[2] R. O. Cherifi, V. Ivanovskaya, L. C. Phillips, A. Zobelli, I. C. Infante, E. Jacquet, V. Garcia, S. Fusil, P. R. Briddon, N. Guiblin, A. Mougin, *Nature materials*, 13, 345 (2014)

[3] A. A. Amirov, V. V. Rodionov, V. V. Rodionova, A. M. Aliev, "Electric-field Control of Magnetocaloric Effect in FeRh-based Composite", *IEEE7th International Conference on Nanomaterials: Applications and Properties (NAP)*, 04NESP24–1 04NESP24–4, (2017)

The role of disorder on the luminescence of Er^{3+} ions in $Na_{1/2}Bi_{1/2}TiO_3$

A. Sternberg*, M. Dunce, G. Krieke, E. Birks, L. Eglite, J. Grube, A. Sarakovskis

Institute of Solid State Physics, University of Latvia, 8 Kengaraga str., Riga, Latvia.
*Corresponding Author: stern@cfi.lu.lv

$Na_{1/2}Bi_{1/2}TiO_3$ (NBT)-based materials are widely studied as the potential candidates for the replacement of the lead-based materials, currently dominating in market of piezoelectric applications [1–2]. Recently lot of attempts are being devoted to the investigation of components which, added to NBT, could improve the properties important for particular applications. In this respect, rare-earth elements have also been tested.

In this research the photoluminescence spectroscopy is used for investigation of influence of poling on the luminescence efficiency of NBT and the analysis of the local environment of Er^{3+} ions in NBT.

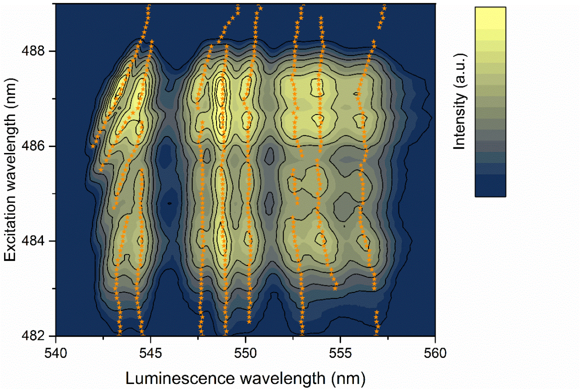


Figure 1. Contour plot of fixed luminescence intensity lines in dependence on emission and excitation wavelength of depoled, Er-doped NBT detected at 10 K. Positions of luminescence maxima are marked with stars.

The results suggested strong reduction of photoluminescence intensity in green spectral range after the poling of erbium-doped NBT. Considerably higher luminescence intensity of the depoled state was confirmed by the analysis of the temperature dependence of luminescence intensity on the heating of poled samples. In the photoluminescence spectra at low temperatures, which were studied to reveal the presence of various environments, where Er^{3+} ions reside, continuous shift of long wavelength luminescence maxima in dependence on the excitation wavelength was detected (see Fig. 1). This shift is explained by coexistence of large number of local environments around Er^{3+} ion reflecting large variety of Na/Bi configurations in A-sublattice of perovskite ABO_3 structure. The comparison of low temperature photoluminescence spectra of poled and depoled samples reveled less distorted state of poled state in comparison to depoled one.

References

[1] P. K. Panda, J. Mater. Sci., 44, 5049–5062 (2009).

[2] Chang-Hyo Hong, Hwang-Pill Kim, Byung-Yul Choi, Hyoung-Su Han, Jae Sung Son, Chang Won Ahn, Wook Jo, J. Mater., 2, 1–24 (2016).

Size effects in a ferroelectric NH_4IO_3

E. V. Stukova[1*], T.A. Meredelina[2], S. V. Baryshnikov[2], A. Yu. Milinskiy[2]

[1]Amur State University, Blagoveshchensk
[2]Blagoveschensk State Pedagogical University, Blagoveshchensk,
Corresponding author: lenast@bk.ru

Many efforts are now focused on studies of nanocomposites which consist of mesoporous matrices loaded with ferroelectric materials. When ferroelectrics are embedded into pores, they form an array of nanoparticles which size and layout are governed by geometry of the pore network. Properties of confined particles can differ remarkably from those of relevant bulk ferroelectrics due to the influence of size effects, changes in structure, coupling with pore surface and between nanoparticles [1,2]. In this paper, we present the results of dielectric studies of nanocomposites based on ammonium iodate embedded in Al_2O_3 matrices with pore sizes of 60 nm.

Ferroelectric properties in NH_4IO_3 were discovered by Oka, Mitsui, Shiroishi and Sawada in 1976 [3]. Above 393 K, ammonium iodate is in the cubic α-phase. Below 393 K, the crystal passes into the orthorhombic piezoelectric b-phase ($Pc2_1n$). With a further decrease in temperature in the region of T ~ 358 K, a transformation occurs in the ferroelectric γ phase ($Pm2_1b$). The introduction of ammonium iodate into the pores was carried out from a saturated aqueous solution. In the experiment, the dielectric properties and the third harmonic coefficient were measured.

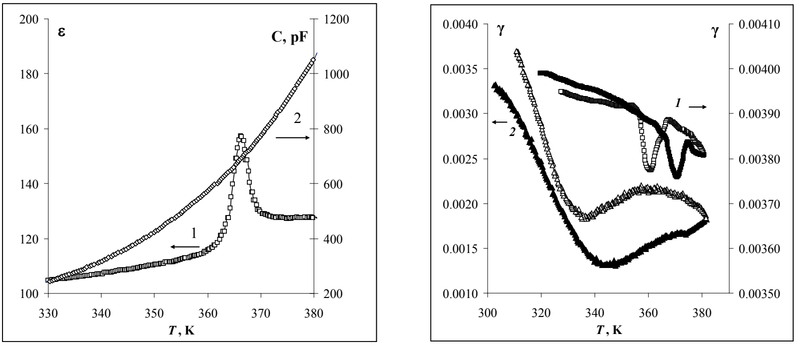


Fig.1 The temperature dependences ε '(*a*), $\gamma_{3\omega}$ (*b*) for the bulk sample (*1*) and the nanocomposite (*2*).

As follows from the graphs, the dielectric anomaly at the phase transition for NH_4IO_3 in the pores is absent. However, it follows from the third harmonic coefficient that the phase transition is smeared out and the Curie temperature shifts to a low-temperature region of ~ 13 K. The results obtained are discussed within the framework of the Landau-Ginzburg theory.

References

[1] S. V. Baryshnikov, E. V. Charnaya, A. Y. Milinskiy, et al. J. Phys.: Conden. Matter **21**, 325902 (2009).

[2] S. V. Baryshnikov, E. V. Charnaya, A. Y. Milinskiy, et al. Physica B. **405**, 3299 (2010).

[3] T. Oka, T. Mitsui, Y. Shiroishi, S. Sawada. Journal of the Physical Society of Japan. **40**, 913 (1976).

Thermal conductivity of (1-x)$BaTiO_3$-x$Pb(Zn_{1/3}Nb_{2/3})\ O_3$ ceramics (x=0, 0.025, 0.05, 0.075, 0.1, 0.125 and 0.15)

J. Suchanicz[1*], H. Czternastek[2], K. Kluczewska[1], P. Czaja[1], D. Sitko[2], K. Konieczny[1], M. Sokolowski[3], A. Węgrzyn[1]

[1]Institute of Technology, Pedagogical University, ul.Podchorazych 2, 30–084 Krakow, Poland
[2]Institute of Physics, Pedagogical University, ul.Podchorazych 2, 30–084 Krakow, Poland
[3]Faculty of Computer Science, Electronics and Telecommunications, AGH University of Science & Technology, ave. Mickiewicza 30, 30–059 Krakow, Poland
*Corresponding Author: sfsuchan@up.krakow.pl

Barium titanate $BaTiO_3$ (BT) is one of the widely applied lead-free ferroelectric materials due to relatively high permittivity and low cost. Lead zinc-niobate $Pb(Zn_{1/3}Nb_{2/3})\ O_3$ (PZN) belongs to a class of disordered and inhomogeneous materials, i.e. is the relaxor. Low-lead (1-x)BT-xPZN ceramics (x=0, 0.025, 0.05, 0.075, 0.1, 0.125 and 0.15) were prepared by two-step conventional oxide mixed sintering process [1]. Thermal conductivity (κ) of these ceramics was measured for the first time from room temperature to 200 °C. It was shown that the thermal conductivity decreases with both decreasing temperature and with increasing of PZN content. κ(T) curves show anomaly at Curie temperature, which is connected with change of specific heat. Obtained results indicated that thermal conductivity of investigated samples is mainly related to phonons scattering by lattice defects and by atomic mass fluctuation resulted from PZN incorporation to BT [2].

References

[1] J. Suchanicz, K. Świerczek, D. Sitko, P. Czaja, P. Marchet, H. Czternastek, D. Majda, *J. Appl. Phys*, 122, 124105 (1–7), (2017)

[2] M. Tachibana, T. Kolodiazhnyi, E. Takayama-Muromachi, *Appl.Phys.Lett*., 93, 092902 (1–3), (2008)

Domain Structure Evolution in PMN-33PT during Field and Zero-field Temperature Treatments

A. D. Ushakov[1,*], A. A. Esin[1], Q. Hu[2], D. S. Chezganov[1], E. O. Vlasov[1], A. P. Turygin[1], X. Wei[2], A. R. Akhmatkhanov,[1] and V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., Ekaterinburg, Russia
[2]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University,
28 Xianning West Rd., Xi'an, China
[*]Corresponding Author: andrey.ushakov@urfu.ru

Relaxor ferroelectric single crystals, such as $(1\text{-}x)\mathrm{Pb(Mg_{1/3}Nb_{2/3})\ O_3}\text{-}x\mathrm{PbTiO_3}$ (PMN-PT) and $\mathrm{Pb(Zn_{1/3}Nb_{2/3})\ O_3\text{-}PbTiO_3}$ (PZN-PT), have attracted extensive attention over the last twenty years due to their superior piezoelectric properties leaving far behind polycrystalline ceramics $\mathrm{Pb(Zr_xTi_{1\text{-}x})O_3}$ (PZT) [1,2]. PMN-PT is the most widely used relaxor single crystal due to its broad morphotropic phase boundary (MPB) and comparatively simple growth procedure [4]. Comprehensive studies have been focused on the piezoelectric response of the domain engineered crystals.

In this work the typical MPB composition single crystal 0.67PMN-0.33PT [9] was investigated. We carried out an experimental observation of the domain structure evolution during the field and zero-field cooling using *in situ* optical microscopy and separated the main stages of the process. The static domain structures before and after temperature and field treatments (Fig. 1) were visualized using piezoresponse force microscopy (PFM) and scanning electron microscopy (SEM). The complementary combination of the used experimental methods allowed studying the domain structure evolution in multiaxial relaxor ferroelectric.

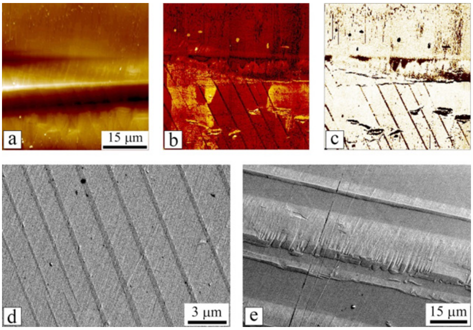


Figure 1. PFM images after field treatment: (a) topography, (b) amplitude, (c) phase. SEM images of (d) stripe and needle-like domains, (e) wide stripe domains.

The equipment of the Ural Center for Shared Use "Modern nanotechnology" Ural Federal University was used. The research was made possible in part by Government of the Russian Federation (Act 211, Agreement 02.A03.21.0006) and by RFBR (grant 17–52–80116-BRICS_a).

References

[1] S. E. Park, T. R. Shrout, *J. Appl. Phys.,* 82, 1804–1811 (1997)
[2] S. Zhang, F. Li, *J. Appl. Phys.* 111, 031301 (2012)
[3] R. Wang et al., *Appl. Phys. Lett.,* 108, 152905 (2016)
[4] H. Fu, R. E. Cohen, *Nature,* 403, 281–283 (2000)

NMR studies of organic ferroelectric DIPAC

N. I. Uskova,[1,*] E. V. Charnaya,[1] D. Yu. Podorozhkin,[1] S. V. Baryshnikov,[2]
A. Yu. Milinskiy,[2] I. V. Egorova[2]

[1]Physics Department, Ulianovskaya Street 3, St. Petersburg State University, St. Petersburg, Russia
[2]Department of Physics and Mathematics, Blagoveschensk State Pedagogical University,
Lenina Street 104, Blagoveschensk, Russia
*natalyauskova.spbu@gmail.com

Diisopropylammonium chloride (DIPAC) is an organic salt, which belongs to a family of organic ferroelectrics [1]. It has a molecular formula $C_6H_{16}NCl$, exhibits the spontaneous polarization $P_s = 8.9$ µC/cm^2 at room temperature and the Curie temperature $T_c = 440$ K. No NMR studies of this compound were reported until now.

We present results of first NMR studies of DIPAC within a large temperature range which covers the Curie point. The measurements were carried out on a Bruker Avance400 pulse spectrometer equipped with a cross-polarization magic angle spinning (CP MAS) probehead. The spinning rate was 4 kHz. The pulse sequence used for acquiring the spectrum was a standard (from proton to ^{13}C) MAS pulse sequence.

The ^{13}C CP MAS NMR spectrum of DIPAC at room temperature is presented in Fig. 1.The spectrum shows the presence of five well-resolved lines corresponding to two crystallographically equivalent –CH — carbon positions (line 1) and four crystallographically non-equivalent $-CH_3$ carbon positions (lines 2–5) in agreement with the crystal structure.

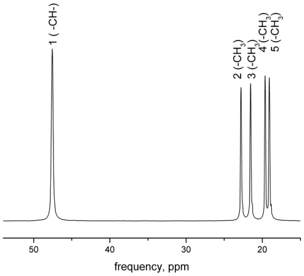


Figure 1. ^{13}C CP MAS NMR spectrum for DIPAC at room temperature.

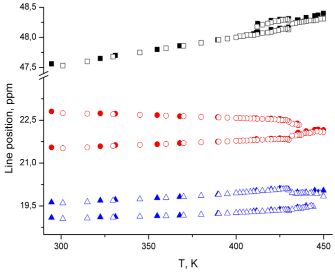


Figure 2. Temperature dependences of line positions for DIPAC. Closed and open symbols correspond to warming and cooling, respectively.

When the temperature increases, the positions of all the lines first shift monotonically. At a temperature above 411 K, the splitting of the high-frequency line into two components is observed, which corresponds to two non-equivalent –CH- carbons. Near 430 K the two components of line 1 merge together. Some anomalies are seen on lines 2–4 at the same temperature. Above 435 K the lines 2, 3 and 4, 5 approach each other in pairs and merge into two single lines finally. The difference between the spectra at room temperature and near 450 K agrees with the symmetry change at the ferroelectric phase transition. However, the total temperature evolution of the spectra reveals more complicate structural changes in DIPAC than it was claimed previously.

References

[1] D. W. Fu, W. Zhang, H. L. Cai, J. Z. Ge, Y. Zhang, R. G. Xiong, *Adv. Mater.* 23, 5658–5662 (2011).

Implementation of spectroscopic contact Kelvin probe force microscopy

A. F. Vakulenko

Peter the Great Saint-Petersburg Polytechnic University,
Polytechnicheskaya 29, SaintPetersburg, Russia
vakulenko705@gmail.com

Piezoresponse force microscopy (PFM) is a great method to measure the ferroelectric hysteresis loops but if it is used to determine is the sample a ferroelectric or not it could give a false positives loops on a nonferroelectric samples [1].

One of possible way to solve this problem is to use spectroscopy cKPFM (contact Kelvin probe force microscopy) and PFM methods simultaneously [2]. Usually PFM hysteresis loop are measured in following scheme: firstly the writing pulse applied to the sample (to change it's state), after this the zero voltage read pulse applied to the sample to measure the remnant polarization. To obtain a surface potential dependence on the write voltages PFM loop measured many times with different levels of read voltages and A·cos(φ) (PFM_X) component measured with respect to read voltage level like in a classic open-loop Kelvin probe microscopy.

We this work used a LabView for implementation of cKPFM and PFM methods. The experiment was carried out using a cryogenic atomic force microscope Attocube Systems AttoAFM I equipped with an external lock-in amplifier SR844 (Stanford Research Systems) and a functional generator Yokogawa FC120. All applied methods were created in the LabView 13, external devices were connected to PC with GPIB-USB interface. Object of study is epitaxial $PbZr_{0.3}Ti_{0.7}O_3$ thin film with thickness about 60 nm.

Figure 1A shows obtained hysteresis loop (phase of PFM signal with respect to write voltage) and figure 1B shows the corresponding cKPFM dependencies, each line was obtained at some point on the graph A and for each line it's intersections with voltage axes corresponds to surface potential. Where are two dense cluster of points on graph B (in red rectangles) which express two states of polarization direction and a few points between this clusters corresponds to fast moments of polarization direction changing. Following the conclusions of [3], our results indicate that the obtained hysteresis loop has truly ferroelectric nature (as it should be for PZT film). The obtained results are in complete agreement with [3].

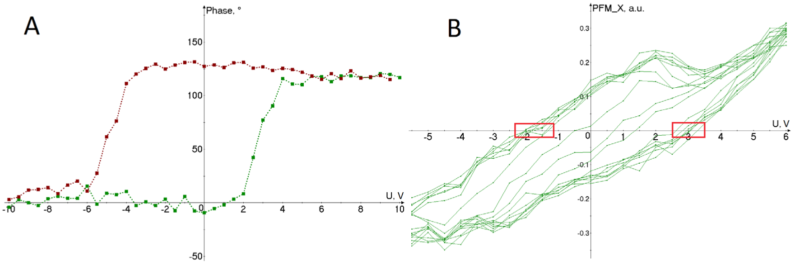


Figure 1. A — PFM hysteresis loop measured on $PbZr_{0.3}Ti_{0.7}O_3$ thin film; B — measured cKPFM dependencies of PFM_X component with respect to read voltage.

References

1. **Hongchen, Miao.** More ferroelectrics discovered by switching spectroscopy piezoresponse force microscopy? / Hongchen Miao, Chi Tan, Xilong Zhou [et al.] // Europhysics Letters — 2014. — Vol. 108. — P. 27010.
2. **Balke, N.** Exploring local electrostatic effects with scanning probe microscopy: implications for piezoresponse force microscopy and triboelectricity. / N. Balke, P. Maksymovych, S. Jesse [et al.] // ACS Nano. — 2014. — Vol. 8(10). — P. 10229–36.
3. **Balke, N.** Differentiating Ferroelectric and Nonferroelectric Electromechanical Effects with Scanning Probe Microscopy / N. Balke, P. Maksymovych, S. Jesse [et al.] // ACS Nano. — 2015 — Vol. 9(6) — P. 6484.

Design and testing of ferroelectric hysteresis loop analyzer

A. F. Vakulenko

Peter the Great Saint-Petersburg Polytechnic University,
Polytechnicheskaya 29, SaintPetersburg, Russia

vakulenko705@gmail.com

The measurement of the hysteresis loop is important in the study of ferroelectric materials. This is usually done by using the Sawyer-Tower circuit and in this case it is possible to obtain an incorrect results related to some parasitic effects like RC phase rotation of leakage currents [1].

In this work we describe the homemade ferroelectric hysteresis loop analyzer based on a classic Sawyer-Tower circuit. The core of the system is an Arduino Uno microcontroller equipped with external digital to analog converter, it allows to generate a sine wave and read the Sawyer-Tower signal up to 150 Hz with 192 points per period. To obtain a high voltage output signal we use a 2 kV output transformer amplifier with frequency band from 20 Hz to 150 Hz. The main purpose of designing this system is to use a double wave method, which is very useful for the separation of negative effects of RC phase rotation or sample conductivity effects [2]. In this method two half-sine waves of the same polarity subsequently applied to the sample, only first of this waves changes the direction of polarization and the output signal have a “step” at coercive field E_c. The second wave does not change the direction of polarization, thus the output signal during the second wave expresses only parasitic effects.

A single crystal of $BaTiO_3$ was used as a test sample. Thickness of the crystal is about 600 μm. To create electrodes a conductive silver paste was painted on the sample surface. The area of electrodes is about 4 mm^2.

Figure 1 shows obtained hysteresis loops (red) and signal of secondary waves (blue). So much difference between the signals of the first and second waves means that the steps are caused by change of the polarization direction, which switches in a certain direction only at first wave. Positive and negative parts of the loop is offset due to the fact that after each wave the capacitor relaxes to 0 V. The obtained hysteresis loop is in good agreement with the results of [3].

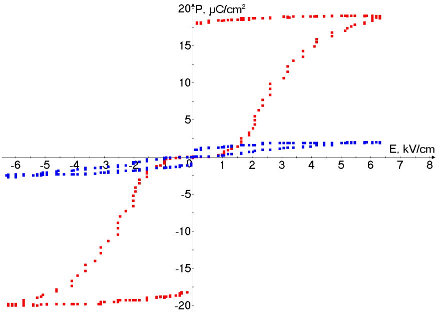


Figure 1. Hysteresis loop measured on $BaTiO_3$ crystal; amplitude and frequency of applied voltage is 400 V and 50 Hz respectively; red dots is a first wave signal and blue dots corresponding to second waves.

Ferroelectric hysteresis loop analyzer with maximum output voltage of 2 kV and frequency band 20 - 150 Hz was successfully designed and tested. Double wave method was used to obtain ferroelectric hysteresis loop on $BaTiO_3$ single crystal.

References

[1] Scott, J.F. Ferroelectrics go bananas / J.F. Scott // J. Phys.: Condens. Matter – 2008. – Vol. 20 - P. 021001.

[2] Fukunaga, M. New Technique for Measuring Ferroelectric and Antiferroelectric Hysteresis Loops / M. Fukunaga, Y. Noda // Journal of the Physical Society of Japan – 2008. – Vol. 77. – 064706.

[3] Wongdamnern, N. Dynamic ferroelectric hysteresis scaling of $BaTiO_3$ single crystals / N. Wongdamnern, A. Ngamjarurojana, Y. Laosiritaworn [et al] // Journal of Applied Physics – 2009. – Vol. 105. – P. 044109.

Peculiarities of local ordering in single crystal $Sr_{0.6}Ba_{0.4}Nb_2O_6$

P. Yu. Vanina,[1,*] **A.A. Bosak,**[2] **and A.A. Naberezhnov**[3]

[1]Research and Education Center “Physics of nanocomposite materials for electronics”,
Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya, 29, St. Petersburg, Russia
[2]European synchrotron radiation facility, avenue des Martyrs, 71, Grenoble, France
[3] Ioffe Institute, Polytechnicheskaya, 26, St. Petersburg, Russia
[*]Corresponding Author: p.yu.vanina@gmail.com

The structure and diffuse scattering were studied in a single crystal of a uniaxial relaxor $Sr_{0.6}Ba_{0.4}Nb_2O_6$ with synchrotron radiation at room temperature and in the temperature range 90–370 K on heating. At room temperature, two different types of local ordering were found with different correlation lengths and different types of correlation functions in reciprocal space. The first type characterizes by squared Lorentzian function and probably associated with correlated displacement waves of oxygen atoms in NbO_6-octahedra. The second type is described by Lorentzian and possibly corresponds to ordering of Sr and Ba atoms in the pentagonal cross-section channels. These types of ordering are related to the internal structure of the crystal and can affect the relaxor properties. The values of the correlation lengths at room temperature and their temperature evolution in the 90–370 K region are estimated (Fig. 1).

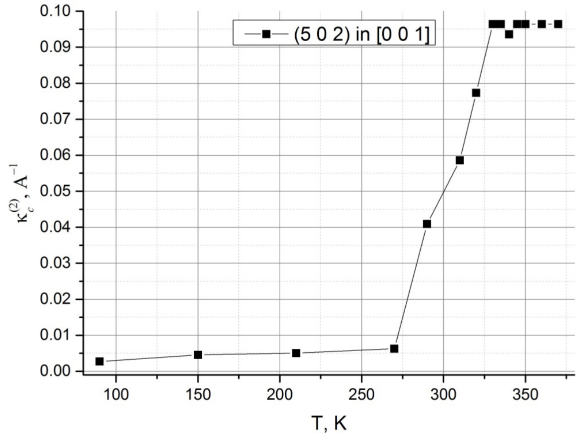


Figure 1. The temperature dependence of the inverse correlation length obtained in the vicinity of the reflection (5 0 2) in the [0 0 1] direction in the temperature range 90–370 K

It can be seen that the inverse correlation length gradually reaching saturation in a given direction at heating when it approaches the transition to the paraelectric phase. So the correlation length itself decreases sharply and becomes small in the paraelectric phase (above 340 K). The values of the correlation lengths calculated from these data (at room temperature) and from the data obtained at room temperature earlier [1] are in good agreement: in both cases, $x^{(2)}_{c} = 1 / k^{(2)}_{c}$ c is ≈ 25 nm along the [0 0 1] direction.

References

[1] A.A. Bosak, Vakhrushev S.B., Naberezhnov A.A., Vanina P. Yu., *St. Petersburg Polytechnic university journal: Physics and mathematics*, 1 (3), 235–238 (2015)

Formation of Self-Organized Ferroelectric β-Glycine Films by Evaporative Dewetting

D. S. Vasileva,[1,*] E. Seyedhosseini,[2] K. Romanyuk,[1,2] P. S. Zelenovskiy,[1]
A. S. Nuraeva,[1] S. G. Vasilev,[1] S. A. M. Tofail,[3]
V. Ya. Shur[1] and A. L. Kholkin[1,2]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
620000 Ekaterinburg, Russia
[2]Physics Department & CICECO — Materials Institute of Aveiro, 3810–193 Aveiro, Portugal
[3]Bernal Institute, University of Limerick, V94 T9PX, Ireland
[*]Corresponding Author: daria.vasileva@urfu.ru

Crystalline structures based on vital biological molecules (amino acids, peptides, DNAs) demonstrate nonlinear optical, piezoelectric, and ferroelectric properties similar to their inorganic counterparts [1–4]. Recently observed room-temperature ferroelectricity [5] and high shear piezoelectricity [6] in β-glycine opens up new perspectives of using this material in biocompatible non-volatile memories, optical switches, transistor gates, nonlinear optical and piezoelectric devices. With the continuing demand for miniaturization of ferroelectrics it is becoming extremely important to scale down their dimensions and to form arrays of self-organized micro- and nanocrystals.

In this work spin-coating formation of self-organized β-glycine films is presented. The morphology of the obtained films varied from feather-like structures to quasi-regular arrays of individual micro- and nanoislands and nanowires. Micro- and nanoislands are oriented in a radial direction from the center of "grains" formed during evaporative dewetting. The kinetics of the dewetting follows the $t^{-1/2}$ law, which is responsible for the observed polygon shape of the grain boundaries [7]. It was confirmed by confocal Raman microscopy that all the structures belonged to ferroelectric β-phase and possess high stability.

Piezoelectric properties and domain structure of the films were studied by piezoresponse force microscopy. It was shown that ferroelectric polarization in β-glycine islands is parallel to the substrate and switchable under a relatively small bias applied by the conducting tip of piezoresponse force microscope.

The research was carried out using equipment of Ural Center for Shared Use "Modern Nanotechnologies" Ural Federal University with the financial support by the Government of the Russian Federation (Resolution 211, Contract 02.A03.21.0006). Part of this work was developed during mobility visit in University of Limerick with financial support of the Erasmus+ International Credit Mobility Programme.

References

[1] V. V. Lemanov, et al., *Ferroelectrics*, 285, 207–216 (2003)
[2] V. V. Lemanov, *Phys. Solid State*, 54, 1841–1842 (2012)
[3] A. Kholkin, et al., *ACS Nano*, 4, 610–614 (2010)
[4] N. Vijayan, et al., *Cryst. Growth. Des.*, 6, 2441–2445 (2006)
[5] A. Heredia, et al., *Adv. Funct. Mater.*, 22, 2996–3003 (2012)
[6] S. Guerin, et al., *Nature Materials*, 17, 180–186 (2018)
[7] E. Seyedhosseini, et al., *ACS Appl. Mater. Interfaces*, 9, 20029–20037 (2017)

Photorefractive Effect in Composite Based on a Ferroelectric Polymer

K.A. Verkhovskaya[a]*, **V.V. Savel'ev**[b], **T.V. Krivenko**[b]

[a] A.V. Shubnikov Institute of Crystallography of Federal Scientific Research Centre "Crystallography and Photonics" of Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119333 Russia
[b] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119071 Russia
*E-mail: vkira123@gmail.com

The photorefractive effect is demonstrated for the composite consisting of a ferroelectric material (polyvinylidenefluoride–trifluoroethylene) and single_walled carbon nanotubes that serve as nonlinear optical chromophores and, simultaneously, spectral sensitizers for the laser radiation with a wavelength of 1064 nm. The PVDF–TrFE films exhibit the spontaneous polarization $P_s \sim 0.065$ C/m^2 in the polar orthorhombic phase 2 mm [1]. For the PVDF–TrFE ferroelectric copolymer (70: 30) internal electric field E_{in} related to the spontaneous polarization is estimated as [2]

$$E_{in} = (P_{ind} + P_s) / 3\varepsilon_0 = 2.5\times10^9 \text{ V/m}. \quad (1)$$

The thickness of the composite is 8 μm. In the experiments, the laser beam is split into two beams *1* and *2* that intersect in the polymer layer and generate the interference pattern.The spatial period of the interference pattern at $\lambda = 1064$ nm is $\Lambda = \lambda/(2n_0\sin\theta) = 2.56$ μm, since $\theta=7.5°$ and the refractive index of PVDF–TrFE is 1.42. The initial stage of the PR effect involves the formation of free charges due to the photoexcitation of the spectral sensitizer in the regions of bright interference fringes, apparently, owing to the reaction

$$\text{SWCNT* + SWCNT} \rightarrow \text{SWCNT}^- \ldots \text{SWCNT}^+.$$

Here, SWCNT* is the photoexcited nanotube that is located in the region of the bright interference fringe and SWCNT$^-$…SWCNT$^+$ is the electron–hole pair. In the presence of internal dc electric field E_{in} the charge separation takes place: holes and electrons drift along opposite directions and are trapped by deep traps.Trapped opposite charges generate periodic electric field of space charge E_{sc} Periodic field E_{sc} provides the periodic modulation of refractive index Δn:

$$\Delta n = (2\pi/n_0)\, \chi^{(3)} (E_{in} + E_{sc})^2, \quad (2)$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility. Thus, a phase diffraction grating emerges in the polymer layer. The PR effect is measured under two conditions. (i) A voltage of 1000 V is applied to the composite, and input and output electrodes serve as a cathode and anode, respectively. Then the external field is switched off and the measurements are performed in the absence of the external field. When the sample is polarized by the external field, the dipoles of the copolymer are oriented along the normal to the film plane and the internal electric field leads to the directional transport of the photogenerated carriers. (ii) The external field is reversed. After repolarization of ferroelectric material the internal electric field is opposite. We obtain the coefficient of two-beam amplification Γ=16.5см$^{-1}$. Thus, the presence of the internal electric field in the ferroelectric material allows one to measure the photorefractive effect in the absence of the external field. This circumstance makes it possible to avoid the destruction of the diffraction grating due to the dark current that is injected from the electrodes.

References

[1] T. Furukawa, Phase Transit. **18**, 143 (1989).
[2] M. Blinov, K.A. Verkhovskaya, and S.P. Palto, Crystallogr. Rep. **41**, 310 (1996).

Second Harmonic Generation in PPLN Waveguides Poled by Electron Beam Irradiation

E. O. Vlasov,[1] D. S. Chezganov,[1,*] L. V. Gimadeeva,[1] M. M. Neradovskiy,[2]
E. A. Neradovskaya,[2] H. Tronche,[2] F. Doutre,[2] P. Baldi,[2] C. Montes,[2]
M. P. De Micheli,[2] and V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
51 Lenin Ave., 620000 Ekaterinburg, Russia
[2]Université Côte d'Azur, CNRS, InPhyNi, Parc Valrose, Nice, France
[*]Corresponding Author: chezganov.dmitry@urfu.ru

The second harmonic generation (SHG) has been studied in waveguides produced by soft proton exchange (SPE) method in congruent lithium niobate (CLN) with periodical domain structures poled by electron beam (e-beam) irradiation [1,2].

The studied samples represented the 0.5-mm-thick Z-cut CLN plates. The SPE process [3] was carried out in benzoic acid bath diluted by 3.1 % lithium benzoate (BL) at 300 °C for 72 hours, using a SiO_2 mask on Z– polar surfaces to fabricate the channel waveguides. The formation of domain structures has been made by irradiation of Z– polar surfaces by scanning electron microscope (Auriga Crossbeam, Carl Zeiss) attached with electron-beam lithography system (Elphy Multibeam, Raith). The domain patterns were visualized by piezoresponse force and optical microscopies. SHG experiments were done using a TUNICS T100S-HP tunable laser with a fiber amplifier delivering 100 mW within the wavelength range 1535–1570 nm.

The periodical poling by e-beam in LN crystals with SPE layers was elaborated. It has been shown that the use of a resist layer is mandatory for successful poling [1]. The dependences of domain size on dose and period have been obtained. The formation of arbitrary shaped domains has been demonstrated. We have produced by e-beam poling the high quality PPLN-channel SPE waveguides with different periods, an aspect ratio close to 0.4, and a PPLN section length that is an integral multiple of 1.5 mm, the maximum length that can be obtained without moving the sample. For 1.5-mm-long periodically poled structures, we obtained up to $48\,\%/\mathrm{W}\times\mathrm{cm}^2$ normalized nonlinear conversion efficiency at the quasi-phase-matched (QPM) resonant wavelength of 1555 nm. Longer domain patterns, obtained by joining up to four 1.5-mm-long periodically poled structures, present several finite stitching errors.

The detailed numerical study of the impact on the nonlinear performances of one or several stitching errors occurring during e-beam periodical poling was performed [2]. This study shows that a single finite stitching error does not simply decrease the nonlinear efficiency but splits the second harmonic signal into a double peak spectrum, where the position of the peaks and their width at half- maximum depend not only on the poling period, the total length of the grating, and the waveguide parameters, but also on the amplitude and the position of the stitching error. The numerical results were confirmed by SHG experiments where the nonlinear grating was composed of one to four e-beam-written 1.5-mm-long PPLN sections with pronounce important stitching errors. In this case the spectrum is quite complicated. It is clear that randomly distributed along the propagation path domain merging and missing can occur in e-field poling.

This study shows that it is possible to get state-of-the-art SHG efficiency by domain patterning after the waveguides fabrication and necessity to take stitching errors into account explaining experimental results and indicate the steps that have to be taken to improve the components quality.

The equipment of the Ural Center for Shared Use "Modern nanotechnology" Ural Federal University was used. The research was made possible by the Russian Science Foundation (Grant № 17–72–10152).

References

[1] D. S. Chezganov et al., *Appl. Phys. Lett.*, 108, 192903 (2016)
[2] M. Neradovskiy et al., *J. Opt. Soc. B.*, 35, 331–336 (2018)
[3] L. Chanvillard et al., *Appl. Phys. Lett.* 76, 1089–1091 (2000)

Hydrogen in $LiNbO_3$: New aspects

A.V. Yatsenko,[*] S.V. Yevdokimov, S.V. Yagupov and A.S. Pritulenko

Physics and Technology institute of Crimean Federal University,
Vernadsky av.,4, Simferopol, Russia
[*]Corresponding Author: yatsenkoav@cfuv.ru

It is well-known that hydrogen incorporation in LN lattice strongly influenced its physical properties which utilized in practical applications [1–3]. It is believed that hydrogen can be additionally introduced into LN lattice by annealing treatments in pure hydrogen or water-vapor atmosphere at temperatures above 400°C [1]. In contrast, hydrogen can be removed from LN lattice due to annealing in a vacuum chamber at temperatures above 400°C or in pure oxygen atmosphere at 700–900°C [2]. Despite of great attention paid to research of the state of hydrogen in LN crystals [4], the mechanisms of hydrogen incorporation and removing are not understood well.

Here we discuss some results, which were obtained during investigation of thermochemically modified LN single crystals by NMR, optical and impedance spectroscopy. Results of investigation of hydrogen volume concentration (n) by ^1H NMR method in a series of identical samples, which were cut from a one boule, after different heat treatments are listed in a table.

Heat treatment	n, 10^{18} cm^{-3}
"as grown" CLN	6.5 ± 1.0
annealing in pure H_2 atmosphere (873 K, 3 hrs)	6.2 ± 1.0
annealing in pure H_2 atmosphere (873 K, 6 hrs)	6.6 ± 1.0
annealing in saturated H_2O vapor (773 K, 6 hrs)	<4
proton exchange in H_2SO_4 (473 K, 6 hrs)	8.2 ± 1.0

So, despite the fact that increase in the n value in PELN sample corresponds to calculated one, the data presented above show that other regimes of the heat treatment are ineffective to increase the hydrogen concentration in the volume of LN crystal.

It is shown recently that heating above 380 K in the ambient atmosphere of the preliminary reduced in saturated H_2O vapor LN samples leads to the instability of their electrical conductivity and optical properties due to progressive oxidization of subsurface layers [5].

We investigate the electrical and optical properties of the series of preliminary reduced and unreduced LN samples after additional heat treatment in air at 873 K during 4 hrs and at 673 K during 72 hrs. Comparison of the optical absorption coefficients in visible area and the values of activation energy for dc electrical conductivity of these series of samples gives a reasons to believe that reducing of LN crystals in H_2O or D_2O saturated vapor at 773 K leads to reduction of OH^- groups concentration in their volume.

References

[1] W. Bollmann, H.J. Stöhr, *Phys. Stat. Sol. (a)*. **39** 477–484 (1977).
[2] J.M. Cabrera et al., *Adv. In Physics*. **45** 349–392 (1996).
[3] M. Wöhlecke, L. Kovács, *Critical Rev. Solid State Mat.* **25** 1–86 (2001).
[4] T. Volk, M. Wöhlecke, Lithium Niobate. Defects, photorefraction and ferroelectric switching. Springer. 2008.
[5] A.V. Yatsenko et al., *Phys. Solid State*. **60** 532–536 (2018).

Polar soft mode in substituted single crystalline M-type hexaferrite $BaTi_xFe_{12-x}O_{19}$ (x=0.6, 1)

S. R. Yegiyan[1,*], L. N. Alyabyeva[1], V. I. Torgashev[2], E. S. Zhukova[1], D. A. Vinnik[3], S. A. Gudkova[3,4], A. S. Prokhorov[1,5], B. P. Gorshunov[1]

[1]Laboratory of Terahertz Spectroscopy, Moscow institute of Physics and Technology
9 Institutskiy per., Dolgoprudny, Moscow
[2]Faculty of Physics, Southern Federal University (SFedU), 5 Zorge Str., Rostov-on-Don
[3]Laboratory of crystal growth, South Ural State University, 76 Lenin Prospect, Chelyabinsk
[4]SEC Nanotechnology, Moscow institute of Physics and Technology,
9 Institutskiy per., Dolgoprudny, Moscow
[5]A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 38 Vavilov Str., Moscow
*Corresponding Author: Samvel_y@mail.ru

The M-type hexaferrites attract interest of scientific research groups due to their exciting physical properties, such as high coercivity, significant absorption at microwave frequencies or anisotropic response [1]. However, practically unexplored remain their dielectric properties in the terahertz-infrared frequency region and especially for substituted compounds that reveal peculiarities not observed in pure crystals. Using terahertz-infrared spectroscopies, we have studied polarization dependent broad-band dielectric response of titan substituted barium hexaferrites, $BaTi_xFe_{12-x}O_{19}$, x=0.6, 1, in the frequency range from 4 to 8000 cm^{-1} and at temperatures from 5 to 300 K. In addition to a rich set of phonon resonances typical for pure $BaFe_{12}O_{19}$ observed in the range 100–1000 cm^{-1} [2], several damped absorption lines including a polar soft mode (fig. 1, [2]) were discovered at the terahertz frequencies, 10–90 cm^{-1}, for both compounds in the $E\|c$ polarization. The resonances were modeled using regular Lorentzian expressions. The observed absorption lines were associated with electron transitions between the fine-structure terms of Fe^{2+} ions that plays a role of a charge compensator for substitution of Fe^{3+} with Ti^{4+}. For the Ec polarization, the low-energy dynamics is generally determined by the dielectric relaxation process associated with the dynamics of the polar domain walls.

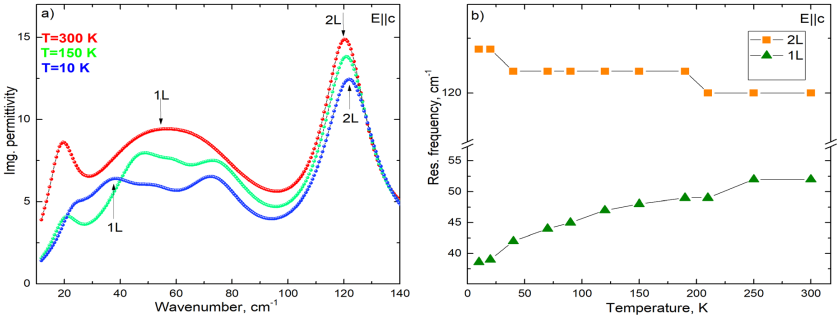


Figure 1. a) Spectra of imaginary part of dielectric permittivity of $BaTi_{0.6}Fe_{11.4}O_{19}$ ($E\|c$) measured at selected temperatures. b) Temperature dependences of the frequencies of the polar soft mode (1L) and of a phonon mode (2L).

This work was supported by Russian Ministry of Education and Science, Project 5–100.

References

[1] Kimura T. Ann. Rev. Condens. Matter Phys. V.3. P. 93–110. (2012)
[2] Mikheykin A. S. et al. The European Physical Journal. P. 1–2. (2014)

Local Structure Analysis of $PbTiO_3$ in High-Temperature Cubic Phase

Y. Yoneda,[1,*] H. Taniguchi,[2] Y. Kitanaka[3], and Y. Noguchi[3]

[1]Japan Atomic Energy Agency, Kouto, Sayo-cho, Sayo-gun, Hyogo, Japan
[2]Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan
[3]Research Center Advanced Science and Technology, The University of Tokyo, Komaba, Meguro-ku, Tokyo, Japan
[*]Corresponding Author: yoneda@spring8.or.jp

High-energy X-ray diffraction study was performed on lead titanate ($PbTiO_3$). Short-range order structure was revealed using atomic pair-distribution function (PDF) method. The crystal structure of ferroelectric tetragonal $PbTiO_3$ changes to paraelectric cubic phase at 766 K. We found a drastic change of the local structure of $PbTiO_3$. In the room-temperature tetragonal phase, Pb atoms shift along the [100] direction. The observed local structure of the tetragonal phase was similar to that estimated from the average structure. In the high-temperature cubic phase, there is a large deviation between local and average structure. Especially, Pb atoms deviated from the cubic lattice framework, but establish Pb-O-Pb random network. Figure 1 shows the comparison of PDFs for $PbTiO_3$ observed at 300 K and 1078 K. In the high-temperature cubic phase, PDF peak corresponding to Pb-O-Pb appeared around 3.6 Å, indicated by the dashed line. This PDF peak cannot be reproduced by assuming the cubic average structure.

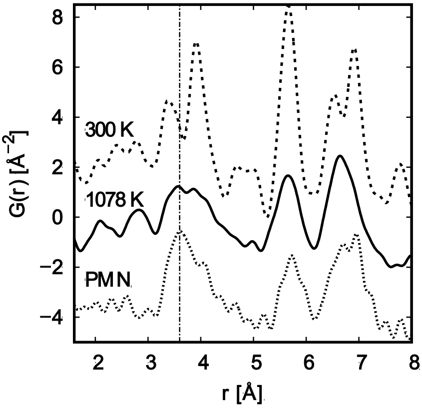


Figure 1. Observed PDFs of $PbTiO_3$ observed at 300 K and 1078 K, and that of $Pb(Mg_{1/3}Nb_{2/3})\,O_3$.

We also performed the PDF analysis of relaxor $Pb(Mg_{1/3}Nb_{2/3})\,O_3$ (PMN). The observed PDF of PMN was also shown in Fig. 1. The average structure of PMN is a cubic structure. The observed PDF of PMN is similar to that of $PbTiO_3$ in the high-temperature phase. Relaxor ferroelectrics is known as an inhomogeneous system [1]. From the view point of the local structure, the tetragonal-to-cubic phase transition of $PbTiO_3$ occurred when the Pb atoms deviated from the average structure.

References

[1] Y. Yoneda. H. Taniguchi, and D. Fu, *Ferroelectrics*, 513, 1–6 (2017)

Crystal Growth and Electric Properties of Ta doped $La_2Ti_2O_7$

Jianding Yu,[1]* Hui Wang,[1,2] and Jiayue Xu[2]
[1]Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, China
[2]School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai, China
*Correspondence Author: yujianding@mail.sic.ac.cn

$La_2Ti_2O_7$ (LTO) crystal, with the layered perovskite structure, is an excellent ferroelectric material for high temperature transducer and electro-optic devices[1-2].

High quality LTO and Ta doped LTO single crystals about 40 mm in length and 5 mm in diameter have been successfully grown by floating zone (FZ)technique. After annealing in the air, as-grown crystals become to transparent and the transmittance is up to 76% in visible and near-infrared region. The influence of sintering temperature on the synthesis of pure phase LTO powder has been studied systematically. The D-E hysteresis loop at room temperature shows Pr=5.0 μ C/cm^2 and Ec=40kV/cm. The temperature dependence of dielectric constant shows a dielectric anomaly at about 130℃, which may associated with a phase transition.

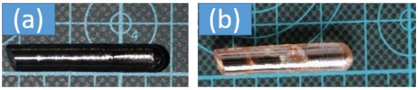


Fig. 1 Ta-LTO single crystal grown by FZ method; (a).as grown, (b) annealed at 1200℃

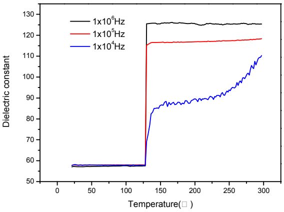


Fig.2 Temperature dependence of dielectric constant for LTO single crystal

References

[1]R. Turner, P. Fuierer, R. Newnham, T. Shrout. Appl. Acoustics, 41, 299–324(1994).
[2]Emilie Bruyer, Aslane Sayede. Journal of applied physics. 108, 053705(2010).

Modification of piezoelectric and elastic properties of diphenylalanine nano- and microtubes by water molecules

V.V. Yuzhakov,[1,*] **A.S. Nuraeva,**[1] **S.G. Vasilev,**[1] **P.S. Zelenovskiy,**[1]
D.S. Chezganov,[1] **V. Ya. Shur,**[1] **and A.L. Kholkin**[1,2]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
620000 Ekaterinburg, Russia
[2]Department of Physics & CICECO — Aveiro Institute of Materials, University of Aveiro, Aveiro,
3810–193 Portugal
[*]Corresponding Author: vladimir.yuzhakoff@mail.ru

Self-assembled micro- and nanotubes of diphenylalanine ($C_{18}H_{20}N_2O_3$, FF) represent advanced functional biomaterial for the developing of new medical equipment [1] due to its outstanding piezoelectric [2], pyroelectric [3] and ferroelectric [4] properties. But values of corresponding coefficients are lower than that of their inorganic analogues. Therefore practical applications require ways for improving their properties. Existence of water molecules captured inside the nanotube during the self-assembly is a requirement for stability of structure [5], whereas its concentration can lead to a change of physical properties [6].

In this work we present the results of systematic investigations of the effect of water concentration in nanochannels on piezoelectric and elastic properties of FF microtubes. The microtubes were grown from a solution of FF-monomer (Bachem AG, Switzerland) in a water with 1,1,1,3,3,3-Hexafluoro-2-propanol. Young's modulus was measured locally with using NanoScan-4D scanning nano-hardness tester (FSBI TISNCM, Russia). Average concentration of water in the microtubes was determined by confocal Raman microscope Alpha 300AR (WITEC GmbH, Germany) according to the procedure described in work [7]. Variation of water concentration in the nanochannels was carried out by controlled annealing and consequent hydration of the microtubes. The piezoelectric coefficient was measured using a scanning probe microscope MFP-3D (Asylum, USA).

FF microtubules in the initial state possess a bimodal distribution of Young's modulus with characteristic values of 10 GPa and 25 GPa. Controlled annealing at 80°C for 8 hours leads to water concentration decreasing and to unimodal distribution of the Young's modulus with characteristic value of 5 GPa. The piezoelectric coefficient d_{15} also decreases from 70 pm/V in initial state to 50 pm/V after annealing. Recovering of the annealed microtubes at atmosphere of high humidity leads to recovering of Young's modulus values to initial bimodal distribution with similar characteristic values. However, the values of the piezoelectric coefficient d_{15} of restored microtubes were not recovered. This phenomenon requires additional study.

Thus, our work demonstrates clear effect of water in the nanochannels on the physical properties of nanotubes. Whereas variations of annealing/restoring time allow managing the characteristic values of piezoelectric coefficient and Young's modulus.

The research was carried out using equipment of Ural Center for Shared Use "Modern Nanotechnologies", Ural Federal University with the financial support by the grant of the President of the Russian Federation for young scientists (Contract 14.Y30.17.2294-MK) and the Government of the Russian Federation (Resolution 211, Contract 02.A03.21.0006).

References

[1] A. Kholkin et al., *ACS Nano*, 4, 610 (2010).
[2] S. Vasilev et al., *J. Phys. Chem. Solids*, 93, 68 (2016).
[3] A. Esin et al., *Appl. Phys. Lett.*, 109, 142902 (2016).
[4] Z. Gan et al., *Angew. Chem. Int. Ed. Engl.*, 52, 2055 (2013).
[5] C.H. Görbitz, *Chem. Eur. J.*, 13, 1022 (2007).
[6] T. Andrade-Filho et al., *Theor. Chem. Acc.*, 135, 185 (2016).
[7] P. Zelenovskiy et al., *J. Raman Spectrosc.*, 48, 1401 (2017).

Studies of dielectric response of $PbCo_{1/3}Nb_{2/3}O_3$ crystals

L.A. Altynbayev[1,2], E.A. Popova [2,3] T.A. Smirnova[2], V.G. Zalesskii[2,*], S.G. Lushnikov[2]

[1] Peter the Great St. Petersburg Polytechnic University,
Polytechnicheskaya 29, St. Petersburg,195251, Russia
[2] AF Ioffe Physico-Technical Institute of the Russian Academy of Sciences,
Polytechnicheskaya 26, St. Petersburg, 194021, Russia
[3] St Petersburg State University,
Universitetskaya Emb. 7–9, St. Petersburg 199034, Russia
[*]Corresponding Author: nsh@mail.ioffe.ru

$PbCo_{1/3}Nb_{2/3}O_3$ (PCN) crystals belong to the family of perovskites ABO_3 with a complex substitution by valence ions in the B position. This family includes materials with unique physical properties: ferroelectrics and antiferroelectrics, relaxor ferroelectrics, and multiferroics. The PCN crystals are characterized by a diffuse maximum in the permittivity in the vicinity of 250 K [1,2]. It was reported in [1,2] that PCN can be classified as a relaxor. Its dielectric properties (dielectric spectrum, dielectric hysteresis loops, and character of conductivity) require detailed studies.

The polar state of the crystal was studied through observations of dielectric hysteresis and by the method of thermally stimulated depolarization (TSD). Measurements of the dielectric response $\varepsilon'(T)$ and $\varepsilon''(T)$ were carried out by a Good Will LCR-819 LCR meter in the frequency range 12 Hz — 100 kHz in the temperature range 78–400 K during heating and cooling at a rate of 1–3 K/min. In the same temperature range, the conductivity of the sample was measured by a E6–13 teraohmmeter, the dielectric hysteresis loop was investigated by an Aixacct EasyCheck meter at a frequency of 100 Hz, and the thermal depolarization current of the sample was measured by using an electrometer.

As a result of dielectric measurements, diffuse maxima in ε' with frequency-dependent positions were observed in the temperature range 240–250 K. In contrast to the known ferroelectrics-relaxors, the temperature dependence of the imaginary value of ε'' for PCN had two frequency-dependent maxima instead of one. In the vicinity of 150–170 K, an unusual distortion of the dielectric loops was observed. The TSD method revealed that the polar state in PCN was observed to a temperature of 181–184 K. The charge carrier activation energy obtained from the temperature dependence of conductivity was 0.43 eV. The results of studies were compared with the literature data of the model relaxor $PbMgNbO_3$.

References

[1] A.I. Agranovskaya et al., *Izvestiya, Akad. Nauk. Physical Ser.,* 24, 1275 (1960)
[2] E.A. Popova, et al, *Ferroelectrics,* v.412, 15 (2011)

The features of elastic coefficients in paraelectric phase of SBN crystals with different chemical composition probed by Brillouin spectroscopy

I. V. Zaytseva[1], A. M. Pugachev[1], N. V. Surovtsev[1], L. I. Ivleva[2], P. A. Lykov[2]

[1]Institute of Automation and Electrometry of SB RAS, 630090, Novosibirsk, Russia
[2]Prokhorov General Physics Institute, RAS, 119991, Moscow, Russia

ZaytsevaIV@iae.sbras.ru

The barium strontium niobate crystals (SBN-100x) can possess the properties of both conventional ferroelectrics and relaxors depending on chemical composition [1]. In present time, it is generally accepted that the main feature of ferroelectrics with diffuse phase transition and relaxors is local polar nanoregions (PNR) arising in paraelectric phase in certain temperature range [2]. On the other hand, the fluctuations in paraelectric phase are responsible for anomaly of acoustic coefficients [3].Thus, it seems important to study the influence of the PNR on the behavior of elastic coefficients in relaxor and ferroelectric states of SBN crystals.

The temperature dependences of elastic coefficients C_{11} и C_{33} in SBN-100x crystals of different chemical composition were investigated. Brillouin scattering spectra were measured using a 3+3 pass tandem Fabry-Perot in wide temperature range (93 K ÷ 900 K). The Brillouin scattering spectra were measured using both heating and cooling. To determine elastic coefficients and acoustic damping coefficients the position and width of the Brillouin doublet shapes were measured. The elastic coefficients C_{33} were calculated by formula $C_{33} = \rho(\frac{\lambda \nu_B}{2n})^2$ where $\lambda = 532$ nm, $n \approx n_0 = 2.35$, ρ - density of the crystal, ν_B- the position of the Brillouin doublet.

We detected thermal hysteresis in SBN-33, SBN-50, SBN-61 crystals. In SBN-75 crystal the thermal hysteresis was not detected. In paraelectric phase in SBN-33 and SBN-50 crystals (conventional ferroelectrics) the temperature behavior of elastic coefficients C_{33} was linear, while in SBN-61 and SBN-75 crystals (the ferroelectrics with diffuse phase transition) a strong deviations in the temperature dependence of C_{33} from linear law were occurred (Fig.1). The observed deviations were interpreted by the influence of local inhomogeneities.

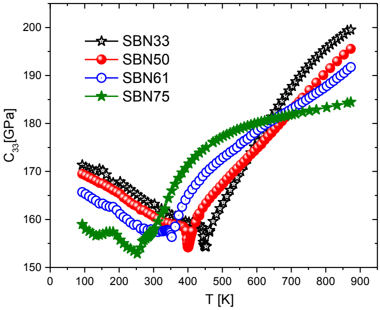


Figure 1. The temperature dependence of elastic coefficients C_{33} in SBN-100x.

References

[1] T. Lukasiewicz, M .A. Swirkowicz, J. Dec, W. Hofman, W. Szyrski, Ferroelectrics, J. Crystal Growth, Vol. 310, pp. 1464–1469 (2008).

[2] G. Burns, B. A. Scott, Solid State Comm., Vol.13, p. 423 (1973).

[3] M. E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford Univ. Press, Oxford, 1977; Mir, Moscow, 1981).

Magnetic, magnetoelectric and electronic properties of spinels Co_3O_4, $MnGa_2O_4$ and $CoAl_2O_4$.

V.S. Zhandun, A.V. Nemtsev and V.I. Zinenko

Kirensky Institute of Physics FRC “Krasnoyarsk Scientific Center of the SB RAS”,
Krasnoyarsk, 660036, Russia
Corresponding author: jvc@iph.krasn.ru

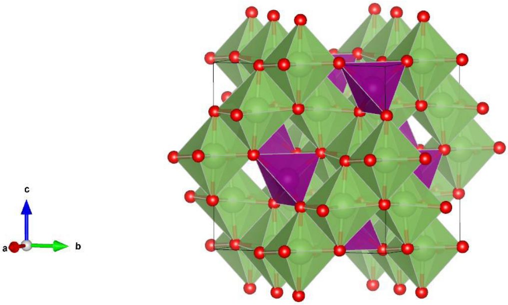


Fig. 1. Structure of the normal spinel

Compounds with a spinel structure with the general formula AB_2O_4 attract the attention of the scientific community in connection with the variety of physical properties arising in these compounds, depending on the chemical composition and ordering of the cations. One of the most promising and interesting is the presence of a magnetoelectric effect in spinels containing magnetic ions in the structure. In the structure of spinel there are 2 non-equivalent cationic positions A (tetrahedral) and B (octahedral), thus substitution of cations for these positions (nonmagnetic ion to magnetic and vice versa) can lead to changes in magnetic and magnetoelectric properties. We present a theoretical study of the magnetic, electronic, polarization, and magnetoelectric properties of Co_3O_4, $MnGa_2O_4$ and $CoAl_2O_4$ compounds with a normal and inverse spinel structures. All calculations were carried out within the framework of the DFT approach. The ground magnetic state and the exchange interaction constants are obtained. The experimentally established presence of spontaneous polarization [1] in these compounds was confirmed by first-principles calculations.

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Reference

[1] R. Saha, S. Ghara, E. Suard, D.H. Jang, K.H. Kim, N. Ter-Oganessian, and A. Sundaresan, *Magnetoelectric effect in simple collinear antiferromagnetic spinels*, Phys. Rev. B9**4**, 014428 (2016).

Evolution of the polarized state in rhomboedrical $Pb(Mg_{1/3}Nb_{1/3})\,O_3–PbTiO_3$ single crystal at elevated temperature

K. F. Zoteev[1,*], D. O. Alikin[1,4], A. P. Turygin[1],
P. S. Zelenovskiy[1], A. D. Ushakov[1], Q. Hu[1], V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics,
Kuibysheva str. 48, Ural Federal University, Ekaterinburg, Russia
[2]Department of Physics & CICECO — Aveiro Institute of Materials, 3810–193,
University of Aveiro, Aveiro, Portugal
[*]Corresponding Author: kirill.zoteev.lab@gmail.com

Single crystalline (1-x)$Pb(Mg_{1/3}Nb_{1/3})\,O_3$-x$PbTiO_3$ (PMN-xPT) exhibits classical ferroelectric behavior with PT content higher 30 % and typical relaxor behavior with PT below 30 % [1]. At present, the use of relaxors in optoelectronics, nonlinear optics and piezoelectricity is of special interest, therefore, attempts are being made to create regular micron and submicron domain structures, as well as to search for methods of these structures stabilization. The main advantages of PMN-xPT are extremely high piezoelectric, electro-optical and non-linear optical coefficients. The main issue is that the relaxor behavior hampered significantly creation of single domain state which could maximize the dielectric and piezoelectric responses and make possible realizing of the domain engineering in the material.

This contribution is devoted to the nanoscale study of the polarized state temporal and temperature evolution in PMN-0.26PT single crystals with relaxor properties by combined structural and functional methods. Piezoresponse force microscopy was used for the local polarization of the area, visualization of the created domain patterns and inspection of their temporal relaxation. Raman spectroscopy made in polarized by the tip area allowed to separate evolution of structural phases. The relaxation of domain patterns was dependent on temperature and was followed by the specific dynamics of surface charge screening highly dependent on temperature. We observed significant change of surface potential of poled area during monoclinic-tetragonal and tetragonal-cubic phase transitions. The relaxation of domain patterns and its different behavior on temperature is discussed in terms of backswitching. Local results supplemented by the data of macroscopic piezoelectric measurements gives further insight into stabilization of polarized states in relaxor ferroelectrics.

The equipment of the Ural Center for Shared Use “Modern nanotechnology” was used. The research was made possible in part by RFBR (grant 17–52–80116-BRICS_a).

References

[1] W. Kleemann, *J. Mater. Sci.*, 41, 129–136 (2006)
[2] S.-E. Park, T. R. Shrout, *J. Appl. Phys.,* 82, 1804 (1997)

Nanodomain Structures in nonlinear Crystal

S.V. Ivanova

P.N. Lebedev Physical Institute of RAS, Leninskii Pr. 53
*Corresponding Author: ivanova@sci.lebedev.ru

Thermal properties of barium sodium niobate crystal were investigated by means of light scattering methods in the temperature range of 20–600 °C. Three types of pictures, ellipses, rounds, stripes, have been observed on the screen in the far field depending on the temperature and polarization of the laser beam relatively to the crystallographic axes. It was observed that the changes of the type of scattering are correlated to the structural phase transitions at about 300 °C and 560 °C and with the evolution of the nanodomain structures at about 200 °C and 250 °C. Image analysis in the temperature region of 20–600 °C and comparison with the structural investigations below 300 °C allow to made conclusion that incommensurate phase in the temperature range of about 500–550 °C has the quasi-tetragonal symmetry.

Investigations were performed in the temperature range from 20 to 600 °C under illumination of crystals by incident laser beam ($\lambda = 514.5$ nm, P = 30–300 mW). The focused beam (F = 150 mm) was propagated through the sample and registered on the screen in far field on the distance about 250 cm from the sample. The direction of the laser beam in different experiments was parallel to the optical c-axis of the crystal with the polarization along a or b-axis. Samples (2 x 4 x 5 mm^3) oriented along the crystallographic axes were mounted inside an oven. Temperature was measured by means of thermocouple attached to the sample holder.

BSN undergoes a ferroelectric phase transition of first order at 550 °C — 585 °C (T_C) from the prototype nonpolar tetragonal 4/mmm phase to a tetragonal ferroelectric 4mm phase. Temperature of the transition is a function of composition of crystal. A ferroelastic transition occurs at T_I (300 °C) on cooling to orthorhombic structure with mm2 average point symmetry. Two orthogonal domains appear in this phase.

The incommensurate phase in structure of BSN was discovered by Schneck et al. in X-ray and neutron diffraction experiments [1, 2]. Two phases was observed on heating from room temperature: nearly commensurate stable up to 250 °C (T_{II}) and incommensurate phase elongated up to 300 °C (T_I). Kiat *et al* [3] and Mory *at al* [4] showed that the structure has a tetragonal symmetry in the range from 300 °C to 270 °C on cooling and consists of two type 1q and 2q ferroelastic microdomains with orthorhombic symmetry. The appearance of the 2q phase at during a thermal cycling at heating coincides with the transformation of large ferroelastic domains into microdomains. Pan Xiao-qing *et al* [5] in contradiction to previous structural data [1–4] by transmission electron microscopy method revealed that the incommensurate modulation of BSN disappears only near the ferroelectric to paraelectric phase transition point. The temperature of incommensurate phases and details of the phase transitions in this range unsettled.

In this work the incommensurate phase has been discovered by scattering light methods and defined of this boundaries and symmetry.

References

[1] J. Schneck, and F. Denoyer, Phys. Rev. B23, 383 (1981).
[2] J. Schneck, J.C. Toledano, C. Joffrin, J. Aubree, B. Joukoff, and A. Gabelotaud, Phys. Rev. B**2**5, 1766 (1982).
[3] Kiat, G. Calvarin, and J. Schneck, Phys. Rev. B49, 776 (1994
[4] S. Mori, N. Yamomoto, Y. Koyama, and Y. Uesu, Phys.Rev. B52, 6158 (1995).
[5] Pan Xiao-qing, Hu Mei-shen, Yao Ming-hui, and Feng Duan, Phys. Stat. Sol. 92, 57 (1985).

Kinetics of the crystallization of sodium niobate nanocrystals in alkali niobium silicate glasses

E. Koroleva[1,*], **A. Lipovskii**[2], **S. Petrunenkova**[3], **D. Tagantsev**[3]

[1] Ioffe Institute, Polytekhnicheskaya 26, St. Petersburg 194021, Russia
[2] St. Petersburg Academic University, Khlopina 8/3, St. Petersburg, 194021, Russia
[3] Peter The Great St. Petersburg Polytechnic University, Polytekhnicheskaya 29, St. Petersburg 195251, Russia
*Corresponding Author: e.yu.koroleva@mail.ioffe.ru

Alkali niobium silicate glasses have attracted special interest because their thermal processing allows precipitation of alkali niobate crystals which possess pronounced electrooptic, piezo- and pyroelectric properties. It is known that in the glasses with high Nb_2O_5 content, the crystallization upon heat treatment occurs in niobium-rich regions resulted from liquid-liquid phase decomposition of these glasses [1]. The crystallization leads to the formation of a heterogeneous structure consisting of $NaNbO_3$ nanocrystals surrounded by the residual silicate phase. The SAXS by the thermally processed glass corresponds to the scattering by a finely dispersed phase with effective grain radii of approximately 10Å. The high viscosity of the silicate phase provides temporal stability of the internal structure of alkali niobate phase regions [1].

The composition of glasses under study was $xNb_2O_5 \bullet (66 — x)SiO_2 \bullet 19Na_2O \bullet 11K_2O \bullet 2B_2O_3 \bullet 2BaO$ (mol%) with high Nb_2O_5 content x = 31 and 33 mol%. The glasses were produced by melting 180-g mix of proper reagent in a platinum crucible at 1450 °C for 2h with stirring. All measurements were performed with the ultrabroadband spectrometer Novocontrol BDS80 (Novocontrol, Germany) in a wide frequency (0.1 Hz-10 MHz) and temperature (150–850 K) ranges. For high-temperature measurements, the Novoterm furnace was used. The samples were plane-parallel plates with dimensions of ~1×1×0.1 cm^3 with sputtered platinum electrodes. We investigated the dielectric response of both the initial glasses and glasses subjected to the heat treatment at 610 °C for 4, 21, and 206 hours. We also studied the behavior of the dielectric response of the initial glasses in the course of annealing, which allowed us to observe for the first time the in-situ process of the glass crystallization and its effect on dielectric properties of the composite. It was found that the crystallization of sodium niobate nanocrystals in the glass matrix leads to a substantial increase in the dielectric constant of the sample and a decrease in losses due to decrease in the number of mobile sodium ions. Anomalies associated with phase transitions in sodium niobate were not revealed. This is possibly due to a clamping of the crystallites by the surrounding matrix.

References

[1] A.A. Zhilin, G.T. Petrovsky, V.V. Golubkov, A.A. Lipovskii, D.K. Tagantsev, B.V. Tatarintsev, J. Non-Cryst. Solids, 345–346, 182 (2004)

Relaxor behaviour of confined Rb_2ZnCl_4

L. S. Stekleneva[1], E. Rysiakiewicz-Pasek [2], I. N. Flerov[3], M. S. Molokeev[3], T. N. Korotkova,[4] L. N. Korotkov[1]

[1]Voronezh State Technical University, Moskovsky pr. 14, 394026, Voronezh,
Russian Federation
[2]Faculty of Fundamental Problems of Technology, Wroclaw University of Science and Technology,
50–370, Wroclaw, Poland
[3]Kirensky Institute of Physics, Federal Research Center KSC SB RAS,
660036, Krasnoyarsk, Russian Federation
[4]Voronezh Institute of the RF Ministry of Internal Affairs, pr. Patriotov 53,
394065, Voronezh, Russian Federation

The physical effects in conventional nanosized ferroelectrics have been studied to some extent at present. At the same time, the problems associated with the appearance of an incommensurate phase, its temperature evolution, and the transition to a commensurate polar phase under conditions of restricted geometry have not been practically investigated.

Suitable objects for such studies are nanocomposites based on Rb_2ZnCl_4, which in the bulk state undergoes transition from paraelectric to incommensurate phase near $T_i \approx 303$ K and transition from incommensurate to ferroelectric (FE) phase in the vicinity of $T_C \approx 194$ K. These transitions are accompanied by distinct anomalies of dielectric permittivity ε. Therefore, dielectric measurements are very informative when studying the effect of restricted geometry on the phase transitions in nanosized Rb_2ZnCl_4.

The purpose of present work is an experimental investigation of dielectric proprieties of Rb_2ZnCl_4 — SiO_2 nanocomposite.

The matrix nanocomposite of Rb_2ZnCl_4 — SiO_2 system was prepared by embedding the Rb_2ZnCl_4 salt from saturated aqueous solution into porous glass with average diameter of through pores 23 nm. X-ray analysis revealed that the crystallized in porous material and the bulk Rb_2ZnCl_4 possess identical crystalline structure at room temperature.

Comparative study of temperature dependences of dielectric permittivity ε for composite material and for the Rb_2ZnCl_4 single crystal were carried out within temperature range of 120–350 K at frequencies 5–500 kHz. For all samples under study, the characteristic maxima of dielectric permittivity were found in the vicinity of T_i and T_C. A small increase in T_i in the embedded Rb_2ZnCl_4 was observed in comparison with the bulk crystal. Transition from incommensurate to ferroelectric phase in confined Rb_2ZnCl_4 is diffused and its temperature is decreased considerably. The temperature dependence of ε in the vicinity of FE transition temperature is described by the so called “square Curie — Weiss law”: $\varepsilon \sim (T-T_m)^{-2}$, where the temperature T_m corresponds to the maximum of the dielectric permittivity.

Characteristic dispersion of ε due to dielectric relaxation is observed near T_m. It was found that average relaxation time is obeyed the Vogel-Fulcher law: $\tau = \tau_0 \exp[U/k(T - T_0)]$, where the k is the Boltzmann constant, the time τ_0 is the reciprocal frequency of attempts to overcome the potential barrier U and T_0 is the Vogel-Fulcher temperature interpreted as the “static freezing” temperature of electric dipoles.

Thus, we can conclude, that the confined Rb_2ZnCl_4 in opposite to the bulk crystal shows the features of relaxor ferroelectrics.

Pyroelectric response of x-cut $LiNbO_3$ electro-optic waveguide modulators

S.M. Kostritskii,[1,*] A.V. Yatsenko,[2] Yu.N. Korkishko,[1] and V.A. Fedorov[1]

[1]Optolink Ltd, Zelenograd, Sosnovaya al. 6A, Moscow, Russia
[2]Physics and Technology Institute, Vernadsky av.,4, Simferopol, Russia.
[*]Corresponding Author: skostritskii@optolink.ru

Experimental study of the pyroelectric effect has been made for x-cut $LiNbO_3$ modulators within multi-function integrated-optical chips (MIOC) used in fiber-optical gyroscopes [1]. The pyroelectric response was measured by the method which had been described in previous paper [2], i.e. the pyroelectric voltage *U* were directly recorded while changing the temperature *T* of the sample in the range from 295 to 380 K. The range of temperature scanning rate *V* covered the interval from 0.1 to 1.5 K/min. A measuring resistor (R_m = 91 MΩ) was wired in parallel to the MIOC's electrodes and amplifier input, thus *U* appeared on MIOC's electrodes and amplified by factor of 5 was measured with an electrometer, Fig. 1. Sharp pulses in the electrometer output are related to electric discharges over a MIOC's surface and within inter-electrodes gap.

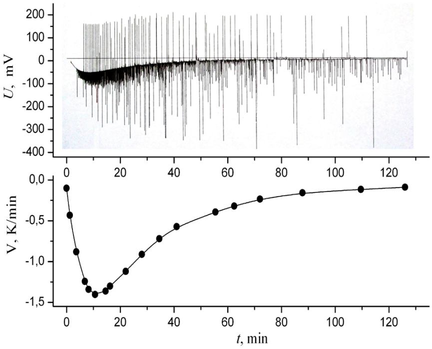

Figure 1. Pyroelectric voltage *U* (top part) and scanning rate *V* = d*T*/d*t* of temperature change (bottom part) as functions of scanning time *t* during cooling-down of MIOC.

A straight forward analysis shows that the observed thermally induced electric field exceeds the field due only to a uniform pyroelectric effect. We have used a two-component model [3] which accounts for the creation of electric field strengths in excess of the uniform pyroelectric field strength. The two components are (1) pyroelectric: un screened bound charge buildup occurs on *z* surfaces of lateral chip edges as the temperature is changed, and (2) electrostatic: capacitive loading of device electrodes causes the potential of the electrodes to change much less than the potential of the rest of the *x* surface, leading to a large potential difference between the electrode and the surrounding surface. Considering the close proximity of electrodes to bound charges on the surrounding surface, very large fields may be generated under electrodes well in excess of the uniform pyroelectric field strength. This transient field has pyroelectric origin and its strength will be limited by leakage and breakdown processes.

References

[1] S.M. Kostritskii, Yu.N. Korkishko, V.A. Fedorov, *Proc. SPIE*, 9065, 90650E (2013)
[2] S.V. Evdokimov, R.I. Shostak, A.V. Yatsenko, *Sol. State Phys.*, 49, 1866 (2007)
[3] P. Skeath et al., *Appl. Phys. Lett.*, 49, 1221 (1986)

Temperature Behavior Of BaBi$_2$Nb2O$_9$ Ceramics

S.N. Krylova, [1,*] A.S. Krylov, [1] M. Adamczyk, [2] L. Kozielski, [2] A.S. Oreshonkov, [1]
A.V. Shabanov, [1] A.N. Vtyurin [1]

[1] Kirensky Institute of Physics FRC KSC SB RAS, Academgorodok 50/38, Krasnoyarsk, Russia
[2] Department of Materials Science, University of Silesia, 41–200 Sosnowiec, s. Sniezna 2, Poland
[*] Corresponding Author: slanky@iph.krasn.ru

Ferroelectrics with their unique properties are used as active elements in functional devices applied in different fields of science and engineering. Some of these materials are layered ferroelectrics with a general Aurivillius formula $(A_2O_2)^{2+}(A'_{n-1}B_nX_{3n+1})^{2-}$, which are perovskite-like structures [1]. On the one hand, materials with the Aurivillius structure can be applied in ferroelectric memory devices [2, 3], capacitors, nonlinear variable resistors [4, 5]. On the other hand, the obvious advantage of these materials is the absence of lead ions in the structure. At present, designing electronic devices without lead is a challenge. The Raman scattering study of the $BaBi_2Nb_2O_9$ ceramics in the temperature range of 10–400 K is presented (Fig. 1). Raman rules in paraelectric I4/mmm and ferroelectric I4mm phases are shown. Raman spectrum of $BaBi_2Nb_2O_9$ ceramics in I4/mmm phase is calculated. Form and symmetry of vibrations are found. It was shown that significant changes of spectra with temperature decreasing occur in low wavenumber range up to 100 cm^{-1}. There are lattice vibrations and vibrations of bismuth ions and Bi–O layers in this part of the spectra. Evident changes of spectra in cooling occur in the range from 400 to 700 cm^{-1}. This part of spectra is related to vibrations of oxygen ions.

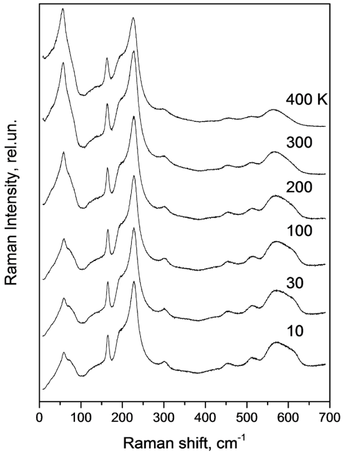

Figure 1. The temperature transformation of Raman spectrum

References

[1] B. Aurivillius, *Ark. Kemi*, 1, 463 (1950).

[2] C.A-Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, *Nature*, 374, 627–629 (1995)

[3] J.F. Scott, F.M. Ross, C.A. Paz de Araujo, M.C. Scott, M. Huffman, MRS Bull. 21, 33 (1996)

[4] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectric and Related Materials, *Clarendon*, Oxford, 1977.

[5] A.L. Kholkin, K.G. Brooks, N. Setter, *Appl. Phys. Lett.,* 71, 2044 (1997).

The Features of the structural phase transitions in Rb$_2$BReF$_6$ Crystals

A. S. Krylov,[1] A. N. Vtyurin,[1] V. N. Voronov[1] and S. N. Krylova[1,*]

[1] Kirensky Institute of Physics FRC KSC SB RAS, Akademgorodok 50/38, Krasnoyarsk, Russia
*Corresponding Author: slanky@iph.krasn.ru

Temperature and pressure changes in the perovskite like fluorides, cause a number of structural phase transitions, which are generally related to changes in the lattice of octahedral groups, such as small pivoting of CF$_6$ octahedra and displacement Rb atoms. In particular, these changes manifest themselves experimentally in substantial anomalies in the crystal lattice dynamics, including the condensation of soft phonon modes during displacive transitions. The soft mode condensation has been successfully observed before in other elpasolites [1–4]. Raman scattering spectra of Rb$_2$KHoF$_6$, Rb$_2$KDyF$_6$, Rb$_2$KTbF$_6$, Rb$_2$KLuF$_6$ crystals have been studied in temperature range from 7 K to 500 K. Raman spectra of Rb$_2$KHoF$_6$ crystal are distorted due to the fluorescence process. Parameters of Raman lines have been quantitatively analyzed. The investigation points to the considerable role of CF$_6$ groups in the temperature phase transition in Rb$_2$KReF$_6$ (Re: Ho, Dy, Tb, Lu) crystals. The anomaly of spectra changes with temperature testify to the first order phase transitions in these crystals. But in these experiments, one can clearly see the anomalous λ-shaped spike of the line position at the transition temperature (Fig.1). The abrupt changes of the mode positions indicate that the structural transitions in the crystals are of the first order. As contrasted to the double perovskite crystals with two temperature phase transitions [2–4] the significant changes in Raman spectra occur in the (Ho, Dy, Lu) –F stretching region.

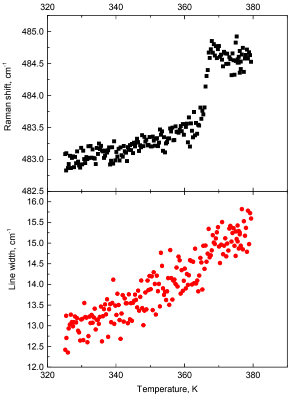

Figure 1. Dependencies of the position and linewidth on temperature of the Rb$_2$KLuF$_6$ crystal (Lu-F stretching mode).

This work was partly supported by Russian Foundation for Basic Research Grant no 16–02–00102.

References

[1] A. Vtyurin, A. Krylov, V. Voronov, S. Krylova, *Ferroelectrics*, 512, 58–64 (2017)

[2] A. S. Krylov, A. N. Vtyurin, A. S. Oreshonkov, V. N. Voronov and S. N. Krylova, *Journal of Raman Spectroscopy*, 44, Is.5,763–769 (2013)

[3] A. S. Krylov, S. N. Krylova, A. N. Vtyurin, V. N. Voronov, A. S. Oreshonkov, *Ferroelectrics*, 416, 95–100 (2011)

[4] A. S. Krylov, A. Bulou, S. N. Krylova, V. N. Voronov, A. N. Vtyurin and N. G. Zamkova, *Computational Materials Science*, 36, Iss. 1–2, 221–224 (2006)

Exchange mechanism in multiferroics

B. M. Darinskii[1], A. P. Lazarev[1], A. S. Sigov[2]

[1]Voronezh State University (VSU), [2]Moscow Technical University (MIREA)

Crystals being in spontaneous magnetization state within a wide range of the temperature phase transition of ferromagnetic-paramagnetic type are considered in the work. Crystalline structures are presented where applying of the external electric field results in the modification of the exchange energy that is proportional to the magnitude of this field. This effect is realized due to the reconstruction of the orbitals participating in formation of the exchange energy thus leading to the shift of the phase transition temperature and magnetization of a crystal. Equilibrium magnetization of the crystal in the field was calculated and a coefficient of the linear magnetoelectric coupling was found.

References

[1] A. P. Pyatakov, A. K. Zvezdin, Physics-Uspekhi, 182:6, 593–620, (2012)

Emergence of new structural distortions in epitaxial $PbZrO_3$ thin films

G. A. Lityagin,[1,*] R. G. Burkovsky,[1,2] D. A. Andronikova,[2] Iu. A. Bronwald,[1]
M. A. Kniazeva,[1] A. V. Filimonov[1] and S. B. Vakhrushev[2]

[1]Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya 29, Saint-Petersburg, Russia
[2]The Ioffe Physico-Technical Institute, Politekhnicheskaya 26, Saint-Petersburg, Russia
[*]Corresponding Author: georgiy.lityagin@gmail.com

Antiferroelectric crystals have energetically competing polar and anti-polar crystal structures among which the latter is stable in normal conditions and the former can be induced by the application of the external electric field. This switching between different structures is at the heart of a number of practical applications of antiferroelectrics [1-3]. In this paper, we present the experimental study of the phase transition sequence in PZO thin films with different thickness. We used synchrotron radiation scattering as a method of investigation. The experiment was carried out at the ID03 beamline of European Synchrotron Radiation Facility (ESRF).

We have measured temperature dependences of integral intensity for superstructure peaks, existed in PZO films. Apart from the superstructure reflections characteristic to the antiferroelectric phase, we identify the reflections with pseudocubic coordinates of the form (H+0.5, K+0.5, L). This indicates the presence of structures having orthorhombic symmetry as an effect of anti-phase Pb atoms displacements, which are apparently similar to the ones previously proposed for the rhombohedral high-temperature phase in $PbZr_xTi_{1-x}O_3$. For these structures, in the films only the domain orientations with displacements parallel to the surface are observed in contrast to the antiferroelectric domains where the parallel to surface Pb displacements are absent (Figure 1). Another intriguing observation is the smoothness of superstructure intensity evolution in the film, which is in contrast with the sharp appearance of antiferroelectric superstructures in the bulk PZO.

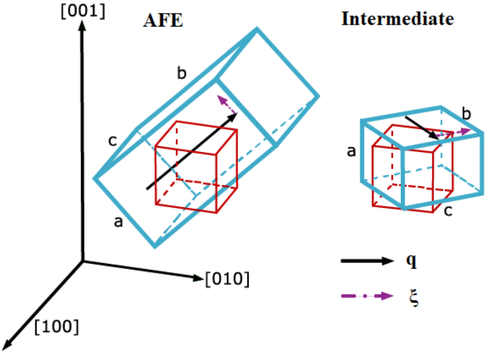

Figure 1. Depiction of AFE and intermediate orthorhombic structure illustrating their orientation with respect to the film normal. Solid black and dotted purple arrows here represent the vectors: **q** – modulation wavevector direction and ξ – displacement vector, respectively.

This study was supported by the Russian Science Foundation (project No. 17-72-20083).

References

[1] J.F. Scott, *Science*, 315, 954 (2007)
[2] M.H. Park, C.S. Hwang, *Springer Netherlands*, 295-310 (2016)
[3] E. Glazkova-Swedberg et al., *Comput. Mater. Sci.*, 129, 44-48 (2017)

Finite Difference Simulation and Experimental Study of Ultrasonic Waves Propagation in Inhomogeneous Piezoelectrically Active Composites

M.A. Lugovaya,[1,*] E.I. Petrova,[1] I.A. Shvetsov,[1] S.A. Shcherbinin,[1]
A.N. Rybyanets[1]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
[*]e-mail: lugovaya_maria@mail.ru

In recent years, inhomogeneous piezoelectrically active composites are widely used for industrial and ultrasonic transducers applications. The ultrasonic waves propagation in such composites are very complex process and these objects are very difficult for theoretical modeling and experimental study [1].

In this paper, a comprehensive study including computer 3D simulation and experimental measurements of different inhomogeneous composites was carried out. The Wave 3000 Pro finite differences software package was used for simulation [2]. The Wave 3000 Pro uses finite differences method for full time domain solution of the 3D viscoelastic wave equations. The program, besides simulating the complete spatial and time-dependent acoustic solution, allows to simulate ultrasound measurements in a variety of source and receiver configurations. The 3D composites objects for simulation were generated both internally using Wave3000 Pro "Geometry" routines and externally from optical and SEM slice data for real composites elements. Following types of ceramic matrix composites were studied: porous piezoelectric ceramics, ceramics/crystal, ceramics/polymer, ceramics/metal and ceramics/ceramics piezoelectrically active composites.

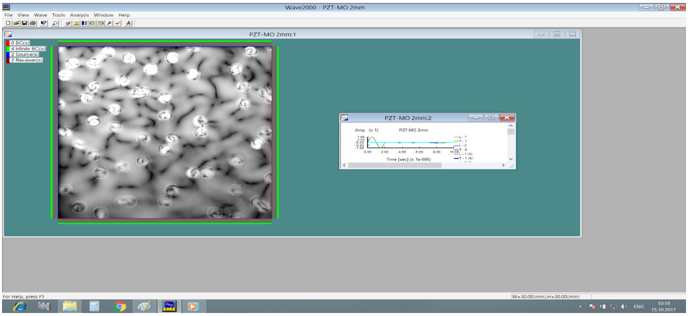

Figure 1. Wave 3000 Pro models of ceramics/polymer composites

The results of simulation of longitudinal ultrasonic waves propagation in different visco-elastic composites are presented. Anomalies of sound velocities and attenuation near corresponding elastic percolation thresholds were found out. The simulation results were compared with the experimental data obtained by ultrasonic pulse-echo and through-transmit methods.

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References

[1] A.A. Naumenko, M.A. Lugovaya, S.A. Shcherbinin, A.N. Rybyanets, *Ferroelectrics,* vol. 484, Issue 1, P. 69–77 (2015).

[2] Wave3000™ (www.cyberlogic.org).

Strong- and Small Dielectric Response of 2-Methylbenzimidazole Single Crystals

F. B. Svinarev[*]**, E.V. Balashova, and B.B. Krichevtsov**

Ioffe Institute, Politechnicheskaya 26, Saint Petersburg, Russia
[*]Corresponding Author: svinarev@mail.ioffe.ru

2-methylbenzimidazole (MBI) is organic molecular crystal with hydrogen bonds [1]. MBI has layered crystal structure which belongs to pseudotetragonal symmetry group $P4_2/n$ (Pn). Hydrogen bonds form chains along [110] axis within one layer, but along [1-10] axis in adjacent layer. Ferroelectric properties of MBI were demonstrated in 2012 [2]. Spontaneous polarization $P_s \cong 5$ μC/cm^2 includes two components, oriented along hydrogen bonds chains. With temperature increase the coercive field decreases from $E_c \cong 3$ V/μ at room temperature to $E_c \cong 1$ V/μ at $T = 400$ K. The purpose of the work was a detailed study of small- and strong-signal dielectric response in MBI single crystals.

The MBI specimens are rectangular parallelepipeds several millimeters in size elongated along (001) axis. As polarization microscopy and XRD analysis show, their side surfaces are perpendicular to (110) axis that allows us to perform dielectric measurements along hydrogen bonds chains.

The dielectric hysteresis loops were measured for different amplitudes and frequencies of the applied sinusoidal electric field in Sawyer Tower circuit in the temperature interval $T = 290$-390 K. Typical modification of hysteresis loop with amplitude of electric field is shown in Fig.1a. For small amplitudes of applied field $E_{max} \sim 1$ V/μ the unsaturated hysteresis loops with coercive field close to the applied field are observed. Increase of amplitude results in appearance of saturated loops. The saturation field E_s strongly depends on temperature. Modification of loops with frequency at $T = 381$ K is shown in Fig.1b.

Simulation of hysteresis loops is carried out in frames of Kolmogorov β-model. Fitting the experimental and calculated loops shows that the magnitude of the activation field in the Mertz law E_a decreases with increasing temperature from $E_a \sim 8$ V/μ at room temperature to $E_a \sim 2$ V/μ at $T = 380$ K.

The dielectric constant of MBI is characterized by frequency dispersion with non-symmetric distribution of relaxation times.

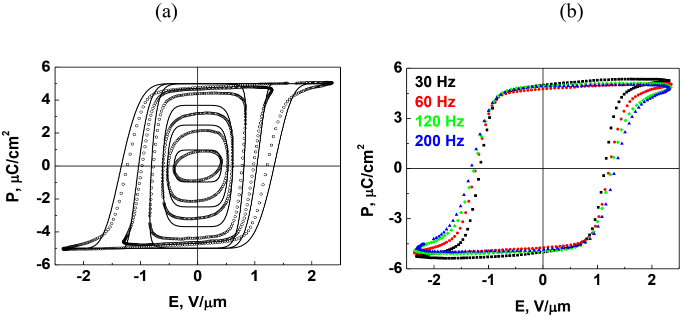

Figure 1. Dielectric hysteresis loops at $T = 381$ K for different values of the applied field amplitude E_{max} at $f = 60$ Hz (a), and for different frequencies at $E_{max} = 2.4$ V/μ (b). Lines - calculations, points – experiment.

The work was supported by RFBR grant N 16-02-00399

References

[1] A.E. Obodovskaya et al., *J. Struct. Chem*, 32, 421–422 (1991).
[2] S. Horiuchi et al., *Nature Communications*, Vol. 3, Art.2322 (2012).

Preparation and luminescence properties of Pr, Al doped $SrTiO_3$ thin films

Hiroshi Takashima[1], Yoshiyuki Inaguma[2]
[1]AIST, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
[2]Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan
E-mail: h-takashima@aist.go.jp

Perovskite $SrTiO_3$ showed many functionalities such as quantum paraelectricity. It is very interesting to develop a thin film device using its many functionalities. Among them, for developing electroluminescence devices with stacked thin films such as insulating/phosphor/insulating, we have prepared perovskite $(Pr_{0.002}Sr_{0.998})(Ti_{0.98}Al_{0.02})O_3$ (PSTAO) epitaxial thin films with red photoluminescence. The homoepitaxial growth can be expected, because the lattice constants of $SrTiO_3$ and PSTAO are very close. The films were grown on single-crystal $SrTiO_3$ (001) substrates by a conventional pulsed-laser deposition using a single-phase PSTAO polycrystalline target. The ArF excimer laser ($\lambda = 193$ nm) that we used had a repetition rate of 8 Hz and a fluence of ~1.2 $J \cdot cm^{-2} \cdot pulse^{-1}$ at the target surface. All the films in this study were approximately 300 nm thick. The crystal quality of the PSTAO grown on $SrTiO_3$ (100) substrate was examined by XRD and RHEED. In a sample of post-annealed 1000 °C after growing 700 °C, XRD pattern showed that the exclusive (00l) reflections appeared. Also, the clear streaky spot of RHEED was observed. This indicates that PSTAO layer was epitaxially grown on the single crystal substrate. The surface morphologies of as-grown PSTAO film, and post-annealed PSTAO film were characterized using AFM with a scan area of 2 μm × 2 μm. AFM images of as-grown PSTAO film reveals that the as-grown PSTAO film has a particle-type morphology, and the rms roughness was about 0.41 nm. However, after annealing, the morphology changed to a fairly clear and flat terrace structure. The width of the terrace is about 100 nm, and the step height is about 0.4 nm, corresponding to one-unit-cell of bulk PSTAO (a = 0.390 nm). The calculated misorientation angle of the post-annealed STO film was 0.126°, which is approximately the same as the general failure-cut-orientation angle of commercial substrates (less than 0.1°). The transmittance spectra of the double-side-polished $SrTiO_3$ (001) single-crystal substrate and a typical PSTAO (001) film showed as high as 70 % and 68 % at around 550 nm, respectively. The film shows a sharp emission line with around 30 nm of full width at half maximum (FWHM) at 610 nm, as is observed in powder samples. This emission line was assigned to the intra atomic transition from the $^1D_2$ state to $^3H_4$ in Pr^{3+} ions. The preparation of epitaxial thin films with strong luminescence and a high transparency may open up applications of light emitting device such as electroluminescence devices.

Scanning capacitance microscopy in the study of impurity distribution and domain structure of TGS — TGS + Cr ferroelectric crystals

R. V. Gainutdinov[1], N. V. Belugina[1], A. K. Lashkova[1], V. N. Shut[2], I. F. Kashevich[3], A. L. Tolstikhina[1*]

[1] Shubnikov Institute of Crystallography of Federal Scientific Research Centre “Crystallography and Photonics” of Russian Academy of Sciences, Leninsky pr. 59, Moscow, Russia
[2] Institute of Technical Acoustic NASB, 210027, Vitebsk, Belarus
[3] Vitebsk State University, 210032, Vitebsk, Belarus
*Corresponding Author: alla@ns.crys.ras.ru

Scanning capacitance microscopy (SCM) is known as a method for measuring spatial variations in capacitance with high resolution. It is mainly used for high-precision analysis of the dopant concentration in semiconductor structures, for the quantitative evaluation of the dielectric films thickness or for the dielectric constant [1]. To the ferroelectrics so far this method has been applied little, as one can see from the limited number of research papers [2, 3].

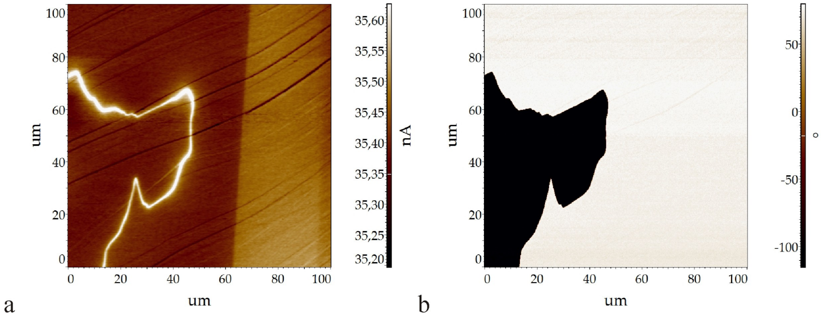

Figure 1. a — SCM image of the domain wall and boundary of TGS (left) and TGS + Cr (right) bands on the (010) surface of the TGS-TGS+Cr crystal, b — PFM image of the same region

The banded crystals TGS-TGS + Cr were studied in the work by SCM and PFM methods. A periodic change in the composition was achieved by growing the seed in solutions of a different composition (nominally pure and containing an admixture of Cr3 + (5–6 % by weight)). Figure 1a shows an SCM image, which clearly shows the contrast at the boundary of two bands: pure and impure, and the domain wall in the form of a brightly glowing line. On the PFM image, the contrast is formed only on the positive and negative domains. It is demonstrated that SCM is an effective method for controlling the spatial variation of the local permittivity and studying the relationship between the features of the domain structure and the impurity composition of local regions of ferroelectric crystals with a profile impurity distribution. Measurements with the help of the B2987A petaohmmeter at the Cascade Microtech Tesla probe station do indeed show 1.5–2 times larger current value for the impurity regions of the surface at ohmic regions of volt-ampere characteristics in comparison with the pure ones.

References

[1] Applied Scanning Probe Methods YIII: Scanning Probe Microscopy Techniques. B. Bhunshan, H. Fuchs, M. Tomitori. Springer-Verlag (2008)
[2] Ching-Chich Leu et al. *Electrochem. Solid-State Lett.* Vol.7, issue 10, A327-A330 (2004)
[3] Y. Naitou and H. Ogiso. *Jap. J. Appl. Phys.* Vol.45, Part 1. N.3B. P. 1922–1925 (2006)

Structure and microwave properties of film solid solutions of barium titanates, zirconates and stannates

A. V. Tumarkin,* A. G. Gagarin, A. A. Odinets, M. V. Zlygostov, E. N. Sapego

[1]Department of physical electronics and technology, Electrotechnical University, 5 prof.
Popov str., St. Petersburg, Russia
*Corresponding Author: avtumarkin@yandex.ru

Barium titanate based solid solutions are attractive ferroelectric materials for numerous applications. Recently it was demonstrated that $BaZr_xTi_{1-x}O_3$ (BZT) and $BaSn_xTi_{1-x}O_3$ (BTS) films in the paraelectric state may be considered as potential materials for applications in tunable devices in comparison with barium-strontium titanate (BST) [1,2]. The aim of the present work is to investigate the structure and dielectric properties of thin BZT and BTS films on sapphire (Al_2O_3) and silicon carbide (SiC) substrates, for their further utilization in microwave nonlinear elements.

Thin BZT and BTS films were obtained by RF ion-plasma sputtering of ceramic targets ($x = 0.5$) onto r-cut sapphire and 6H SiC (0001) substrates in oxygen atmosphere (1-2 Pa). The choice of the composition of sputtered targets with a high content of zirconium/stannum atoms was connected with the necessity to obtain thin films in the paraelectric state with low dielectric losses in the microwave band. The substrate temperature T_s was varied in the range of 700-880ºC. The layer thickness was about 500 nm. On the surface of films, upper electrodes were formed from 1-μm thick copper with a chromium adhesion layer.

The X-ray diffraction investigations have shown that BZT and BTS films both on sapphire and on SiC substrates are of pure perovskite structure. However, BZT and BTS solid solutions show a different growth behavior with the substrate temperature change. BZT films on sapphire demonstrate (100) texture at $T_s = 700°C$ and (110) one at 880°C, while the BZT layers on SiC reveal completely (100) orientation in temperature range investigated. BTS films both on sapphire and on SiC substrates possess (100) structure at $T_s = 700°C$ and become polycrystalline at increasing T_s up to 880ºC.

The dependence of the permittivity of BZT and BTS films on the applied field exhibits high degree of tunability under the action of an external field and practically total absence of hysteresis phenomena. The microwave measurements of BZT and BTS planar capacitors have shown the tunability of $n \cong 2$ on application of a field of 60 V/μm and dielectric losses less than 4% at a frequency of 1.5 GHz.

The results of presented investigations showed that BZT and BTS films grown on sapphire and SiC substrates possessed well-formed perovskite crystalline structure, which positively influenced their nonlinearity and dielectric microwave losses. A comparison of the obtained data to analogous values reported for thin BST layers showed that the proposed thin BTS and BZT films can be promising base materials for the creation of tunable microwave elements.

This work was supported by the RFBR, projects 16-07-00617, 16-29-05147 and the Ministry of Education and Science of the Russian Federation (3.3990.2017/4.6)

References

[1] A.V. Tumarkin, S.V. Razumov, at. al., *Technical Physics Letters*, vol. 42, 143–145, (2016)
[2] A.V. Tumarkin, V.M. Stozharov at. al., *Integrated Ferroelectrics,* vol. 173:1, 140-146, (2016)

Multilayered structures for ferroelectric tunnel junction applications

A.V. Tumarkin,* A.G. Gagarin, A.A. Odinets, M.V. Zlygostov, E.N. Sapego

Department of physical electronics and technology, Electrotechnical University, 5 prof.
Popov str., St. Petersburg, Russia
*Corresponding Author: avtumarkin@yandex.ru

The combination of ferroelectrics properties with the phenomenon of quantum mechanical tunneling enable to create conditions for non-destructive reading of information using ferroelectric tunnel junctions (FTJ). The basic device structure of a FTJ consists of an ultrathin ferroelectric (FE) barrier that separates two electrodes. Modulation of the tunnel transmission coefficient by the reversal of the polarization state of the FE layer leads to high and low resistance states.

The conductive materials used on both sides of the ferroelectric have a significant effect on the change value of the tunnel resistance. The magnitude of the conductivity of the contact layers in the FTJ structure directly affects the resistance switching coefficient, because it determines the uncontrolled series resistance. $La_{1-x}Sr_xMnO_3$ (LSMO) shows a great potential to make an electrode layer for the FTJ structures based on the low resistivity at room temperature in comparison with other oxide electrodes [1]. The usage of a high Sr content LSMO film significantly reduces the temperature dependence of the resistivity and increases the conductivity of the material [2], which is important for FTJ devices.

While the FTJ FE devices with LSMO electrodes using $SrTiO_3$ and MgO as the growth substrates have been described in detail, the BTO/LSMO/sapphire heterostructure has not yet been realized. So, the main goal of this work is to investigate the possibility to use a LSMO conductive layer with a low concentration of lanthanum for oriented growth of BTO film on r-cut sapphire for FTJ applications.

The LSMO films were deposited by radio frequency (RF) magnetron sputtering of a ceramic target onto r-cut sapphire substrates at a temperature of 700–880°C. The film thickness was ~300 nm. The BTO films were prepared by RF magnetron sputtering of a $BaTiO_3$ ceramic target on a LSMO buffered sapphire at a substrate temperature of 880°C. The BTO film thickness was ~15 nm.

According to the data of X-ray diffraction and atomic-force microscopy, the high-quality $La_{0.3}Sr_{0.7}MnO_3$ film, which combines an atomically smooth surface morphology with a fully (h00) oriented crystal lattice has been grown on r-cut sapphire by RF magnetron sputtering. The structure quality of LSMO films has been optimized by the proper choice of the deposition temperature. The XRD spectra of the LSMO film deposited at $T_s = 880^oC$ exhibit only (100) and (200) peaks, which means that the film was grown fully (h00) oriented without any secondary phases. The high (h00) growth of the BTO thin film on the LSMO-coated sapphire substrate was demonstrated and it has been attributed to the (h00) orientation of the LSMO layer. The lattice constant of LSMO film is about 3.96 Å, which is equal to the value of the sputtered target. The in-plane lattice constant of the BTO film is about 3.99 Å that corresponds to a non-stressed crystal of the barium titanate.

Analysis of piezoelectric images and histograms of the distribution of the piezoelectric response over the surface of thin BTO layers suggests that the vertical component of the piezo-response in films grown on a high-temperature sublayer is the most uniform in the film area, and the magnitude of the signal is much higher in comparison with BTO films on a low-temperature LSMO underlayer.

So, the incorporation of $La_{0.3}Sr_{0.7}MnO_3$ layer effectively suppresses the lattice mismatch and promotes oriented growth of the BTO thin films on r-cut sapphire substrate making this system more attractive for FTJ device fabrications

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References

[1] S. Majumdar, S. van Dijken, *J. Physics D: Applied Physics*, vol 47, 347 (2013)
[2] Prestgard, M.C., Siegel, G.P., Tiwari, A., *Advanced Materials Letters*, vol 5, 242 (2014)

Ferroelectric tunable capacitors on silicon carbide for high power microwave applications

A.V. Tumarkin,* A.G. Gagarin, A.A. Odinets, M.V. Zlygostov, E.N. Sapego, I.V. Kotelnikov

[1]Department of physical electronics and technology, Electrotechnical University, 5 prof. Popov str., St. Petersburg, Russia

*Corresponding Author: avtumarkin@yandex.ru

Ferroelectric (FE) films have received much attention as promising materials for the development of voltage controlled microwave (MW) tunable devices. One of the main parameters of MW devices is power handling capability (PHC) i.e. the capability to process the high power MW signal without the deviation of working parameters. This deviation can be divided to the electrical and thermal effects. The latter effect, caused by the overheating due to the dissipation of MW power remains a significant challenge for MW devices.

The problem of the overheating of the FE MW elements is partially caused by the poor thermal conductivity of the dielectric substrate. Therefore, the usage of the high thermal conducting substrate as a heat sink can effectively improve PHC of MW devices. In this context, the present work considers the possibility of creating FE microwave devices based on films of barium strontium titanate (BST) on semi-insulating silicon carbide (SiC) substrates.

Thin BST films were obtained by RF magnetron sputtering of a $Ba_{0.4}Sr_{0.6}TiO_3$ ceramic target. To get highly oriented films we used the structurization of the growing film by an intermediate annealing. Right after the deposition of the first layer, the discharge was turned off and the “in-situ” annealing under oxygen ambient was adopted. Then, the second layer was deposited on the first one at the same conditions [1]. On the surface of films, upper copper electrodes were formed.

According to X-ray diffraction analysis, the films structured by the intermediate annealing during the growth demonstrate the clear predominant orientation (h00), whereas the films deposited at conventional technological conditions had polycrystalline structure.

Fig. 1 shows capacitance C and quality factor $Q = 1/\tan\delta$ of varactors based on structured BST films vs. bias electric field. The tunability $K = C(U)/C(0)$ of the BST/SiC capacitor reaches the $K = 1.7$ at a quality factor of $Q \cong 50$ ($\tan\delta = 0.02$).

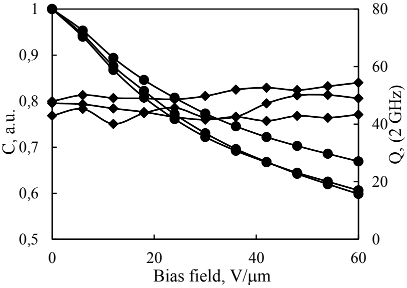


Figure 1. Capacitance and quality factor of BST film varactors on SiC substrate

The presented results showed that BST films grown on semi-insulating silicon carbide under structurization approach possessed well-formed perovskite crystalline structure, which positively influenced their nonlinearity and microwave losses. A comparison of the obtained data to analogous values reported for FE layers on alumina substrates showed that the BST films on semi-insulating silicon carbide can be promising base materials for the creation of high-power MW elements.

This work was supported by the RFBR, project 16-29-05147 ofi_m and the Ministry of Education and Science of the Russian Federation (3.3990.2017/4.6)

References

[1] A. Tumarkin, S. Razumov, at. al., *Integrated Ferroelectrics*, vol. 173:1, 38–45 (2016)

Local Switching and Domain Interaction on Non-polar Cuts of Lithium Niobate Crystals

A. P. Turygin[1,*], D. O. Alikin[1], Yu. M. Alikin[1], V. Ya. Shur[1]

[1]School of Natural Sciences and Mathematics, Ural Federal University,
Lenin Ave. 51, Ekaterinburg, Russia
*Corresponding Author: anton.turygin@urfu.ru

Scanning probe microscopy (SPM) is one of the important methods for investigation and modifying of ferroelectric domain structure. One of the key points of domain evolution is an electrostatic interaction of the charged domain walls during forward growth. The domain interaction during writing of the nanodomain arrays by local switching using SPM tip demonstrated by us at polar cut lithium niobate (LN) plates was studied by analysis of the domain size dependence on spacing [1]. The resent experimental study of the domain growth on LN nonpolar cuts revealed the modified domain interaction [2–4]. The detail study of the effect and formation of self-assembled nano-domain arrays on LN non-polar cuts will be presented.

The formation and interaction of isolated needle-like domains were studied experimentally on non-polar cuts of 5% MgO doped LN (MgO: LN). It has been found that the cycling of domain lengths in arrays produced by local switching strongly depend on the period (distance between neighboring domains). The domain sizes are differ for X and Y cuts and significantly dependent on relative humidity. Three main regimes of the domain length distribution in the array have been revealed: (1) uniform, (2) intermitted quasiperiodic, (3) chaotic. The measurement of the switching behavior for various pulse amplitudes (tip bias) and spacing between the points of bias application (domain spacing) allowed obtaining the phase diagram (Figure 1). It was shown that the effect is obtained for significantly higher voltages and spacing than previously observed effect on the polar cuts of LN [1].

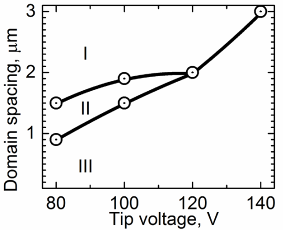


Figure 1. Phase diagram of the cycling of domain lengths in arrays as a function of bias and spacing between the points of bias application (domain spacing). Regions of various regimes of domain length distribution: (I) uniform, (II) intermittent quasiperiodic, (III) chaotic.

Obtained results give a new insight in the problem of the domain interaction during forward growth and can provide useful basis for application of the nanodomain engineering in development of non-linear optical frequency converters, data storage, and computing devices.

The equipment of the Ural Center for Shared Use “Modern Nanotechnology” UrFU was used. The research was made possible by Russian Science Foundation (Grant 14–12–00826).

References

[1] A. V. Ievlev et al., *Nature Phys.*, 10, 59–66 (2014)
[2] D. O. Alikin et al., *Appl. Phys. Lett.,* 106, 182902 (2015)
[3] A. V. Ievlev et al., *ACS Nano*, 9, 769–777 (2015)
[4] A. P. Turygin et al., *Materials*, 10, 1143 (2017)

Electric field effect on domain structure of PZT with low Ti content

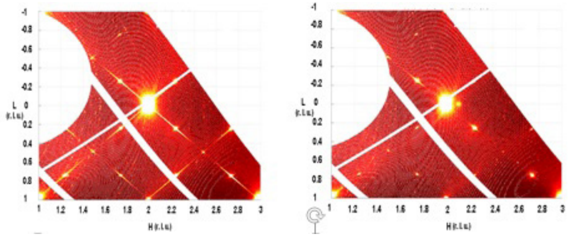
S.A. Udovenko[1,2*], D.A. Andronikova[1,2], A.V. Filimonov[1] and S.B. Vakhrushev[1,2]

1 Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya 29, Saint-Petersburg, Russia

2 The Ioffe Physico-Technical Institute, Politekhnicheskaya 26, Saint-Petersburg, Russia

*Corresponding Author: s_udovenko@mail.ru

One of the most commonly used commercial dielectrics is Lead Zirconate-Titanate (PZT). This material has a wide range of practical applications [1–3]. For Ti concentrations near 1 %, PZT single crystal undergoes two structural phase transitions: from cubic phase to intermediate ferroelectric phase and from intermediate ferroelectric to orthorombic antiferroelectric phase. We present experimental results demonstrating the influence of an electric field on phase transitions in PZT with 1.1 % Ti content over the temperature range 170–350 °C. The experiment was performed at the BM01 beamline of the European Synchrotron Radiation Facility (ESRF). We have measured the temperature dependences of components of diffuse scattering both parallel to and perpindicular to electric field direction. Our results show, that below 200 °C and in the absence of an applied electric field there are "strings" of diffuse scattering existing in two orthogonal directions. However, when a 5kV/cm field is applied, diffuse scattering "strings" are only observed in one direction(Fig.1).



References

[1] Fernandes, E. et.al., *SMART MATER STRUCT*, 27, 3 (2018)
[2] Zhang, H. et.al., *J APPL MECH-T ASME*, 85, 1 (2018)
[3] Sette, D. et.al., *MICROMACHINES*, 8, 10, (2017)

Young scientists school on the spectroscopic studies of critical dynamics at structural phase transitions

Atomic dynamics to large extend determines the microscopic mechanisms of the structural phase transition. Since the first observation by C. V. Raman the mode softening in quartz in 1940 theoretical approaches and experimental techniques had undergone. Nowadays it is possible to study dynamics in the broad range of characteristic times and spatial scales. In the frames of the "Young scientists school on the spectroscopic studies" that will be held as a satellite for the Russia/CIS/Baltic/Japan Symposium on Ferroelectricity (RCBJSF2018). Leading specialists in the field of the spectroscopic studies of ferroelectrics will present lectures on (but not limited to) the Ultrabroadband dielectric spectroscopy, THz spectroscopy, inelastic scattering of neutrons and X-rays (including the methods with μeV resolution). Dynamic extension of the Pair Distribution Function method — DPDF — will be described with the examples of the application of DPDF for the study of relaxors.

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Microwave and THz characterization of materials

D. Jablonskas, M. Ivanov, J. Macutkevic, S. Rudys, R. Grigalaitis, S. Lapinskas, J. Banys*

Faculty of Physics, Vilnius university, Vilnius, Lithuania
*Corresponding Author: juras.banys@ff.vu.lt

The dielectric response of materials provides information about the orientational adjustment of dipoles and the translational adjustment of mobile charges present in a dielectric medium in response to an applied electric field. Microwave and terahertz dielectric spectroscopy of ferroelectrics and related materials enables the independent determination of the dielectric permittivity and loss in the dispersion region, as well as the parameters of the soft modes related to phase transitions.

Besides scientific purposes, microwave dielectric measurements are of increasing importance in telecommunications related applications and the design of microwave circuit components. These applications include imaging radars, guidance systems, surveillance and secure communications. The magnetic properties are also of crucial importance. Dielectric and magnetic parameters fully characterize the manner in which electromagnetic waves propagate within the medium. The difficulties of making measurements on a wide range of materials over a wide frequency (and temperature) range have led to the development of various direct and indirect methods.

At microwave frequencies, the direct single-frequency methods were enriched in the recent years with more convenient broad band frequency domain dielectric spectroscopy (FDDS), time — domain spectroscopy (TDS), Fourier transform spectroscopy (FTS).

Computer controlled spectrometers are now the norm in dielectric spectroscopy. Computers allow the computation of electromagnetic fields in entirely new measurement geometries and the use of numerical analysis in the direct measurement process. The use of such spectrometers is now one of the most fruitful factors in new approaches to microwave dielectric spectroscopy. Each investigator employs the method adequate for the size and shape of a sample. The most important problem now is the rigorous mathematical solution of the microwave interaction with the samples in various geometries.

Although there is now complete overlap and coverage of the radio frequency to the infrared band, the different experimental methods based on coaxial, waveguide, resonator and free — space technique is still divided and will be presented.

Examples of various ferroelectric, relaxor, dipolar glass materials dielecric spectroscopy results will be presented.

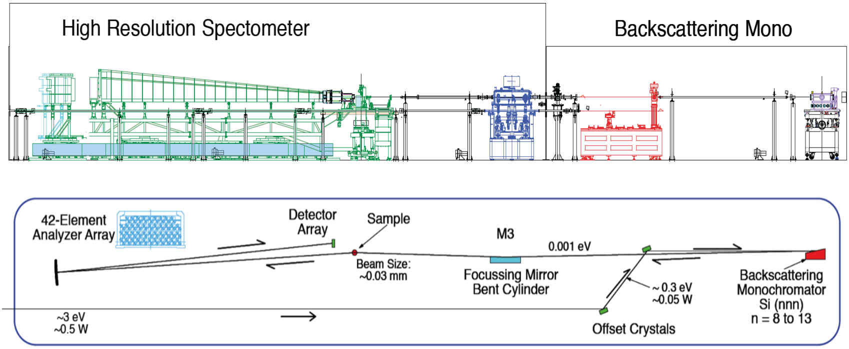
Introduction to meV-resolved Non-resonant Inelastic X-Ray Scattering

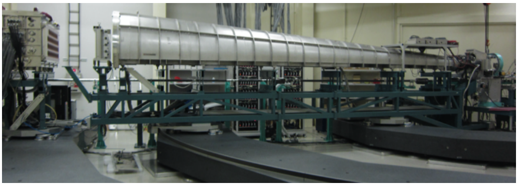
Alfred Q.R. Baron
Materials Dynamics Laboratory, RIKEN SPring-8 Center

This lecture will provide an introduction to high-resolution inelastic x-ray scattering (IXS), with an emphasis on aspects that are relevant for probing atomic dynamics in condensed matter and especially phonons in crystals (see [1] for an overview). Broadly speaking, IXS, as is now available at ~6 spectrometers worldwide, is similar to inelastic neutron scattering (INS), with access to ~meV energy transfers and ~angstrom scale correlation lengths. Advantages of IXS include access to small samples (2 mm is comfortable, 0.02 mm possible), relatively clean spectra, without backgrounds from incoherent or multiple scattering, sharp q-resolution, and easy access to large (>100 meV) energy transfers without degradation of resolution. Disadvantages compared to INS include limited energy resolution (generally not better than ~0.8 meV FWHM) and, usually, Lorentzian energy resolution, with, therefore, often non-negligible tails.

The lecture will cover the some of the scattering theory background, instrumentation, and some recent results. Some comparison will also be made with other methods, including some newer ones. The talk will emphasize issues relevant for investigating phonons in ferroelectric materials as is relevant to this school.

[1] A.Q.R. Baron, in *Synchrotron Light Sources and Free-electron Lasers SE - 41-1 and SE-52-1*, E. Jaeschke, *et al*. eds. (Springer International Publishing, 2015). Also: arXiv 1504.01098.





Above: Schematic of the BL43LXU phonon spectrometer including two hutches (about 25 m) on the experimental floor. Side view and beam path.
Left: Photograph of the 10m arm of the IXS spectrometer which scans to 55 deg. in tth (~10 Å^{-1})

DIFFUSE SCATTERING AND LATTICE DYNAMICS

Dmitry Chernyshov

Swiss-Norwegian Beam Lines at European Synchrotron Radiation Facility

First, a general introduction for diffuse scattering of X-ray and neutron radiations is given. Next, we focus of thermal diffuse diffuse scattering and see with examples how lattice vibrations contribute to the diffuse scattering; we also discuss information content of the diffuse scattering comparing to other probes of lattice dynamics, advantages and drawbacks of diffuse scattering experiments. Finally, we illustrate how phase transition phenomena manifest themselves in the diffuse scattering.

XPCS study of relaxation properties of Relaxors

Y. Chushkin*[1]

[1]ESRF,71 avenue des Martyrs, Grenoble, France
*Corresponding Author: chushkin@esrf.fr

X-ray photon correlation spectroscopy (XPCS) is a novel scattering technique that exploits a highly coherent and intense X-ray beam generated by modern synchrotron sources. When fairly coherent beam scatters from a sample one observes a characteristic speckle pattern in the far-field regime [1]. Speckle pattern results from a constructive and destructive interference of the waves and reflects instantaneous and exact distribution of the scatterers in a sample. Hence any motion of the scatterers causes speckle intensity fluctuation. XPCS quantifies the speckle intensity fluctuation by measuring intensity-intensity time correlation function. In this way the information about temporal and spatial density fluctuations is obtained. Therefore XPCS is used to probe slow dynamics in various systems including colloidal suspensions, gels, solid solutions, glasses etc [2]. It covers a wide range of length scales starting from submicron down to angstrom lengths and broad range of times from microsecond up to thousands seconds. Because XPCS operates in time domain it is a unique and powerful tool for studies of non-equllibrium phenomena such as ageing in glassy materials [3, 4].

The first and the largest part of the lecture will be focused on basic ideas of XPCS, including requirements for the X-ray beam properties, experimental setup and measurement strategy, data analysis and interpretation. The second part will cover application of XPCS for study of relaxation properties in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) relaxor. In particular we will show recent XPCS results on PMN and discuss tentative implication of our observations.

References

[1] M. Sutton, et. al., *Nature,* 532, 608-610 (1991)

[2] G. Grübel, A. Madsen and A. Robert, *Soft-Matter Characterization*, edited by R. Borsali & R. Pecoral, 935-995 (2008)

[3] A. Robert et al., *Europhys. Lett.*, 75, 764 (2006)

[4] B. Ruta et al., *Phys. Rev.Lett.*, 109, 165701 (2012)

Local dynamics observed by real-space inelastic scattering

T. Egami[1,2]

[1]Shull Wollan Center – Joint Institute for Neutron Sciences, University of Tennessee, Knoxville,
TN 37996 USA
[2]Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[*]Corresponding Author: egami@utk.edu

Functional materials studied today are more complex than early functional materials, because often competing forces in complex materials enhance the response, or susceptibility, of materials. The bond energies of regular solids are of the order of 1 eV, much larger than the thermal energy, kT, which is 1/40 eV at room temperature. Therefore most solids are "hard" and do not respond to our stimulus. However, by bringing down the energy scale to a fraction of eV the solid becomes more susceptible. Competing, or frustrated, forces in complex materials achieve this purpose. Relaxor ferroelectrics are an example of such frustrated systems. Liquids and glasses are also examples of frustrated systems, and they share many similarities in behavior of strongly temperature-dependent relaxation behavior. To study the atomic dynamics of these frustrated systems the conventional experimental approaches are often insufficient. Usually the atomic dynamics is studied by inelastic neutron or x-ray scattering to measure the dynamic structure factor, S(Q, E), where Q and E are the momentum and energy exchange in scattering. However, in frustrated systems dynamic fluctuations are local and strongly damped, so that it is difficult to observe them in S(Q, E). To capture such fluctuations we Fourier-transform S(Q, E) to the dynamic pair-density-function (DyPDF), g(r, E), or the Van Hove function (VHF), G(r, t). We show in Pb(Mg1/3Nb2/3)O3 (PMN) and Ba(Zr, Ti)O3 (BZT) DyPDF determined by inelastic neutron scattering can describe the local dynamics and elucidate their behavior. For water we show how the Van Hove function determined by inelastic x-ray scattering can depict the locally correlated dynamics and elucidate the molecular origin of viscosity. I predict that within 10 years nearly 1/3 of the results of the inelastic measurements will be presented in real space, in terms of the DyPDF or VHF.

Cold Neutron Scattering Studies of Photovoltaic Hybrid Organic Perovskites

Peter M. Gehring,[1,*] A. Gold-Parker,[2] I.C. Smith[2], H.I. Karunadasa[2], and M.F. Toney[3]

[1]NIST Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, USA
[2]Department of Chemistry, Stanford University, 333 Campus Drive, Palo Alto, USA
[3]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, USA
[*]Corresponding Author: peter.gehring@nist.gov

One of the most active areas of research in condensed matter physics today concerns the hybrid organic-inorganic perovskite $CH_3NH_3PbI_3$ (MAPI), a material that shows significant promise in photovoltaic applications. As device efficiencies continue to rise, there is growing interest in the fundamental physical properties of MAPI. The lattice dynamics are of special interest because they can provide information regarding two areas of active study: the dynamical coupling of electronic states to the lattice [1] and the vibrational coupling between PbI_6 octahedra and the MA+ cations [2]. Both couplings influence the opto-electronic properties. While there have been several theoretical efforts to calculate lattice dynamics [3], little work has been done on the critically important phonon lifetimes, and there is a scarcity of experimental data on the lattice dynamics [4].

Using cold neutron triple-axis spectroscopy, we have measured the momentum-resolved transverse acoustic (TA) and longitudinal acoustic (LA) phonon dispersions and lifetimes in the orthorhombic, tetragonal, and cubic phases of a single crystal of MAPI that was fully deuterated to minimize the incoherent scattering from hydrogen. We find that the TA phonon polarized along [100] becomes strongly damped with increasing wave vector, and on heating into the tetragonal phase the TA phonon lifetimes decrease by roughly a factor of two for wave vectors near the Brillouin zone boundary. The same effects are observed for the LA phonon polarized along [100]. This has major implications for the carrier scattering and cooling processes.

In addition, we observe strong diffuse quasi-elastic scattering (QES), absent in the orthorhombic phase, that appears abruptly upon heating into the tetragonal phase. This QES varies with the total scattering wave vector Q in a manner consistent with translational jump diffusion. We will discuss these observations in terms of the well-known Chudley-Elliot model.

References

[1] A.D. Wright et al., *Nature Communications*, 7, 11755 (2016)
[2] A.M. Leguy et al., *Nature Communications*, 6, 7124 (2015)
[3] F. Brivio et al., *Physical Review B*, 92, 144308 (2015)
[4] C. Stock et al., *Physical Review B*, 92, 100303 (2015)

Mapping excitations in single crystals using multi-analyzer spectrometers.

J. Kulda
Institut Laue-Langevin, CS 20156, 38042 Grenoble Cedex 9, France

Since the 1950's neutron triple-axis spectrometers (TAS) have been a traditional workhorse for investigations of structural and magnetic excitations in single crystals. They offer all the flexibility needed to access any chosen momentum point within their kinematic range and to investigate the inelastic scattering spectrum there. The resulting dispersion relations of phonons and magnons are found any textbook on condensed matter physics. In the last two decades the attention has shifted to more exotic excitations like continuum modes in low-dimensional quantum spin systems, fluctuations related to ordering processes and lattice vibrations in structurally disordered crystals. In such cases the data collection strategy does not need to rely any more on the traditional $\boldsymbol{Q}$ = const. scanning mode and can be accelerated by multiplexing the momentum and energy analysis of the scattered neutrons.

In this lecture we will first review different approaches to the multiplexing, which may target either an increased flexibility in detailed investigations of the dynamics in restricted regions of the $\boldsymbol{Q},\omega$ space within the *RITA* concept [1,2] or, on the contrary, aim to accelerate surveys of more extended ranges on the scale of several Brillouin zones like the *FlatCone* [3] or *CAMEA* [4] setups.

In the second part of the lecture we will concentrate on the experience with the *FlatCone* multianalyzer [3], developed more than a decade ago at the ILL and successfully exploited in the user experiments since then. Its combination of high incident monochromatic flux, characteristic of the ILL TAS instruments, with the flexibility of navigation in the $\boldsymbol{Q},\omega$ space and with the speed of data acquisition in its 31 parallel channels provide a highly efficient tool to gather an overview of static and dynamic response of structural and magnetic systems. Results from recent experiments (e.g. Refs. [5],[6]) will be used to demonstrate examples of data acquisition strategies, resolution calculations and data treatment.

[1] K. N. Clausen et al., Physica B 241 (1997) 50.
[2] O. Sobolev et al., Nucl. Instrum. Methods Phys. Res., Sect. A 772 (2015) 63
[3] M. Kempa, B. Janousova, J. Saroun et al., Physica B 385-386 (2006) 1080
[4] F. Groitl et al., Rev. Sci. Instruments 87 (2016) 035109
[5] Yao Shen et al., Nature 540 (2016) 559
[6] M.C. Rahn et al., Phys. Rev. B 95 (2017) 134405

Contact: kulda@ill.fr

Recent development of neutron backscattering spectrometer and its application to the study of ferroelectrics

M. Matsuura*

[1]Neutron Science and Technology Center, Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaraki 319-1106, Japan
*Corresponding Author: m_matsuura@cross.or.jp

Neutron backscattering spectrometer offers very high energy resolution (~μeV) by using high quality single crystal analyzer and large scattering angle. DNA is a recently developed time-of-flight type backscattering spectrometer at the pulsed spallation neutron source in Materials and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC) [1]. DNA has an extremely high signal-to-noise ratio ($\sim 10^5$) compared to that of conventional neutron backscattering spectrometer ($\sim 10^3$), which enables us to measure a weak signal of bio-molecules, soft-materials, spin dynamics of strongly correlated electron system, and lattice dynamics of ferroelectrics. In addition to the low noise, the most important new feature of DNA for the study of ferroelectrics is the wide dynamic range (~ 1 μeV $< E < \sim 1500$ μeV), which covers not only relaxational mode of ferroelectric domains but also low energy part of phonon modes. Furthermore, owing to the development of the position sensitive detectors and the improvement of neutron flux, the wave-vector (Q) resolution becomes nearly one order better. In this lecture, I will introduce new feature of neutron backscattering spectrometer DNA in comparison with the conventional neutron scattering technique, such as triple-axis spectrometer and conventional backscattering spectrometers.

References

[1] K. Shibata et al., *JPS Conference Proceedings*, 8, 030622 (2015)

Optical Harmonics Generation in Ferroelectrics and Multiferroics

R.V. Pisarev

[1]Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, Russia
*Corresponding Author: pisarev@mail.ioffe.ru

Invention of lasers in the year of 1960 stimulated very fast development of broad fields of fundamental and applied nonlinear optics, in which the coherent processes of frequency conversion, such as the second (SHG) and third (THG) harmonics generation, are the most interesting [1,2]. Being the lowest nonlinear processes in the light-matter interaction, the SHG and THG are characterized by relatively high susceptibility values. The strongest electric-dipole interaction allows the SHG process only in the non-centrosymmetric crystals, and therefore in ferroelectrics and multiferroics. In this sense, the THG process has a great advantage because it is allowed in crystals of any symmetry, as well as in amorphous materials, glasses, liquids, gases, and plasma. We must add that in particular cases the electric quadrupole and magnetic dipole processes can also contribute to the observed SHG and THG signals.

In ferroelectrics and multiferroics, SHG can be used for the studies of only non-centrosymmetric structures due to charge and spin ordering, whereas THG can be studied in all phases. We have to note, that up to now the THG studies are quite scarce in comparison to SHG, maybe because the former are more difficult to realize. In the recent years, important improvements were reached in increasing the abilities of the SHG and THG techniques concerning the sensitivity, the 2D and 3D resolution, the dynamics of phase transitions, domain switching, et al. At the early stages of the SHG and THG studies, the nanosecond-pulse lasers were widely used. However, the abilities of both these techniques were greatly expanded with the applications of the femtosecond-pulse lasers.

In many cases, SHG was applied for proving or disproving the presence or absence of the center of inversion in a material under study, first of all in single crystals, but also in polycrystalline and even powder samples. In the case of ferroelectrics, the SHG studies can provide a lot of information [3]. First of all, as a rule, the SHG intensity is proportional to the order parameter, or in other words, to the spontaneous or induced polarization. Another important property of SHG is its ability for visualizing and distinguishing ferroelectric domains, including 180^o domains. Visualization of domain walls exploring their spatial structure is possible due to the breaking of inversion between the centrosymmetric domains.

In the case of multiferroics and magnetoelectrics, the abilities of SHG are greatly expanded due to the presence of at least two order parameters, related not only to the charge, as in the ferroelectrics, but also to the spin ordering. Interference between these two contributions gives rise to many interesting phenomena, for example, to the interaction of ferroelectric and antiferromagnetic domain walls [4,5]. Another important extension of the SHG abilities in multiferroics and magnetoelectrics is the application of the spectroscopic studies as a function of the photon energy, due to the presence of electronic transitions in their absorption spectra.

This work is supported by the Russian Science Foundation, Grant # 16–12–10456.

References

[1] L.D. Landau and E.M. Lifshits, Electrodynamics of Continuous Media (Pergamon Press, 1984).
[2] Y.R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York,1984).
[3] S.A. Denev, T.T.A. Lummen, E. Barnes, et al, *Probing ferroelectrics using optical second harmonic generation*, J. Amer. Cer. Soc. 94, 2699 (2011).
[4] M. Fiebig, Th. Lottermoser, D. Fröhlich, A.V. Goltsev, and R.V. Pisarev, *Observation of coupled electric and magnetic domains*, Nature (London), 419, 818 (2002).
[5] M. Fiebig, V.V. Pavlov, and R.V. Pisarev, *Second-harmonic generation as a tool for studying electronic and magnetic structures of crystals: review,* J. Opt. Soc. Amer. 22, 96 (2005).

DYNAMIC RESPONSE FUNCTIONS FOR SYSTEMS WITH DEFECTS NEAR PHASE TRANSITIONS: PHENOMENOLOGICAL APPROACH

S. Sigov

Moscow Technological University (MIREA)

We consider here two types of dynamic response functions for systems near phase transitions. To the first type there belong the functions for those variables which can play the part of the *order parameter* η, and the second type concerns these functions for various *noncritical* variables ξ. The second type response functions are sensitive to phase transitions due to the nonlinear coupling between η and ξ. The most pronounced anomalies in these response functions appear when the coupling term in the Landau thermodynamic potential density is of the form $h^2\xi$. For the one-component order parameter such a term is allowed if ξ is a fully symmetrical variable (e.g., dilatation). The coupling term of the form h^2x^2 is allowed foe an arbitrary symmetry of ξ, it gives rise to far less pronounced anomalies in the response functions. To find a dynamic response function one begins with the equations of motion for η and for other variables coupled to η. The set of variables involved into consideration is different for different problems.

The presence of defects of various types gives rise to additional terms in the Landau thermodynamic potential density. For simplicity, we examine the systems with point defects of the so-called “random local field” and “random local transition temperature” types. Such defects are always present in a crystal, and thus are believed to determine normally the defect-induced anomalies. Due to an expansion of the space region distorted by the defect when approaching the phase transition temperature, the influence of defects increases and leads to sufficient anomalies of various properties of the system reflected by the soft mode and other noncritical modes behavior. The deviations from the results predicted by the Landau theory (for an ideal pure system free of defects) often look like these caused by thermal fluctuations in the order parameter but in most cases are much stronger in their value and temperature dependence. In such a way an explanation can be given for all kinetic coefficients anomalies including soft mode damping, sound dispersion and attenuation, neutron, X-ray, and light scattering, etc.

Mode coupling and phase transitions

S. B. Vakhrushev[1,2]

[1]Ioffe Institute, 26 Polytechnicheskaya, St Petersburg, Russia
[2]Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya, SPb, Russia
*Corresponding Author: s.vakhrushev@mail.ioffe.ru

The problem of the phonon mode coupling in the crystals is very old. Such coupling became especially important in the strongly anharmonic crystals undergoing structural phase transitions. For the review of the early papers see e.g. [1]. The mode coupling produces most pronounced effects of in the inelastic scattering of neutrons and X-rays. Already in the first review of the study of structural phase transitions by neutron scattering methods, the effect of mode coupling on the shape of phonon resonances was demonstrated [2]. Of course, the importance of mode coupling is not a distortion of the lineshape, but the physical effects caused by such coupling.

In this lecture, I will focus on a number of effects. After historic remarks and introducing of the basic ideas, we will discuss the results related to the mode coupling in ferroelectrics and atiferroelectrics. As shown in our paper [3], the mode coupling can be considered as the basis of the antiferroelectric transition in lead zirconate. The influence of the coupling between the TA and TO modes becomes even more pronounced when doping lead zirconate with titanium [4]. Possibility of the formation of complex modulated structures as the result of the mode coupling will be discussed also.

References

[1] J. F. Scott, Rev. Mod. Phys., 46, 83 (1974).
[2] G. Shirane, Rev. Mod. Phys., 46, 437 (1974).
[3] A. K. Tagantsev, et al., Nature Communications 4, 2229 (2013)
[4] D. A. Andronikova, DA; et al. J. Phys.: Conf. Ser., 769, 12070 (2016)

Raman Scattering Study of Structural Phase Transitions

A. N. Vtyurin[1,2]

[1]Kirensky Institute of Physics, Krasnoyarsk, 660036, Russia
[2]Siberian Federal University, Krasnoyarsk, 660041, Russia
vtyurin@iph.krasn.ru

For a long time Raman scattering are used for investigations of structural phase transitions in crystals, their mechanisms and connections with lattice dynamics[1–3]. Nowadays development of experimental equipment, both exciting light sources and registering spectrometers, transform this method from exotic experiments into routine approach widely used by numerous groups of physicists all over the world, that provides quantitative information on a phonon subsystem of a crystal under investigation and phonons role in lattice instabilities.

To obtain reliable quantitative data on lattice dynamics at phase transitions under some external influence (say, temperature, pressure, etc.) from Raman experiments first of all one should take into account “natural” changes of Raman spectra that are not induced by transition processes, like changes of population of vibrational levels, anharmonicity of vibrations, temperature induced lattice disorder. Manifestations of these effects in Raman spectra will be considered.

Nowadays spectroscopic equipment provide a possibility to register effects of phase transitions on Raman spectra with very high precision, and sometimes such measurements become more informative as compared to more traditional soft mode spectroscopy. Comparison of these two approaches will be presented in the report. Special attention will be paid to low frequency modes as well, like numerical treatment of spectral contours within central peak of scattering, effects of soft modes dumping and mode interactions near phase transitions.

Effects of phase transitions on electron-phonon interactions and their manifestations in Raman spectra will be considered. Some examples of magnetic phase transitions in multiferroic crystals will be considered as well.

References

[1] G. S. Landsberg, L. I. Mandelstam. *Ztschr. Phys.* 58, 250 (1929).

[2] V. L. Ginzburg, A. P. Levanyuk, A. A. Sobyanin. *Uspekhi Fiz. Nauk (Phys. Rep.)* 47, 151, (1980) (in Russian).

[3] Light Scattering near Phase Transition Points. Ed. H. Z. Cumminz, A. P. Levanyuk. Nauka Publishers, Moscow, 1990 (in Russian).

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