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Book of abstracts

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MONDAY
June 25, 2018

SECTIONS

Fundamentals of Ferroelectric and Related Materials

Domains

Thin Films and Nanostructures

New Studies of Ferroelectrics

J. F. Scott

School of Chemistry, University of St Andrews, St Andrews, United Kingdom

In this talk I will describe four things: First, the electrical measurements of the power spectrum of Barkhausen pulses in PZT [1], and the acoustic measurement in $BaTiO_3$, both giving an exponent of 1.65±0.04 (typical data in Fig.1 below), in excellent agreement with avalanche theory (1.66) and significantly greater than the mean field value of 4/3 (the parameter J is slew rate, which is a derivative of energy with respect to time); second, the achievement of domain wall currents in $BiFeO_3$ sufficiently large (300 nA) for commercial devices [2,3]; and third, the observation ferroelectric behavior in lead-free $SnTiO_3$[4] and multiferroic behavior in PZT:Pd [5,6].

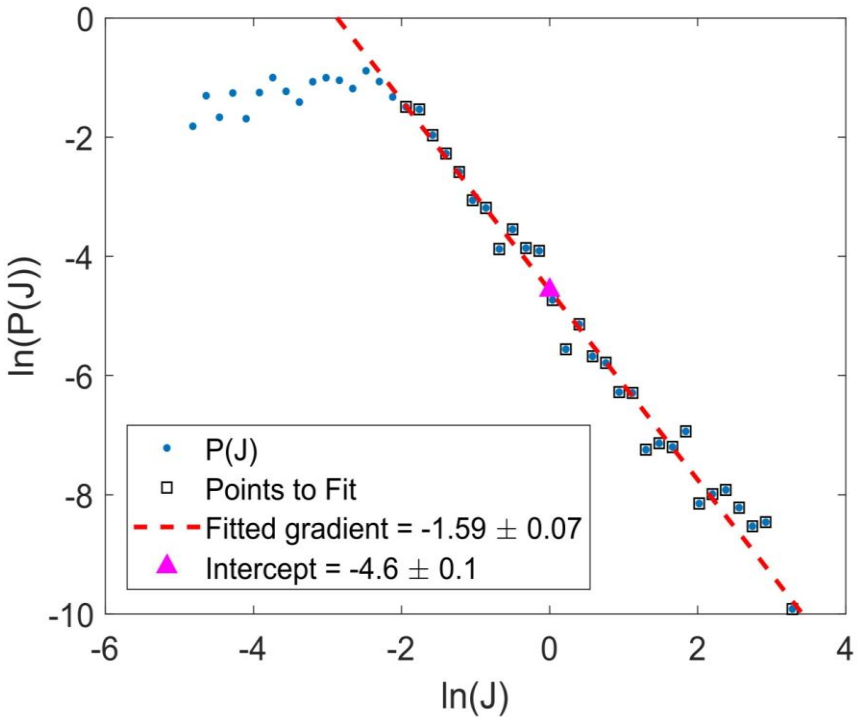

Fig. 1. Probability of Barkhausen voltage pulse of slew rate J = dI/dt versus slew rate (log-log) for PZT at T=293K [1]

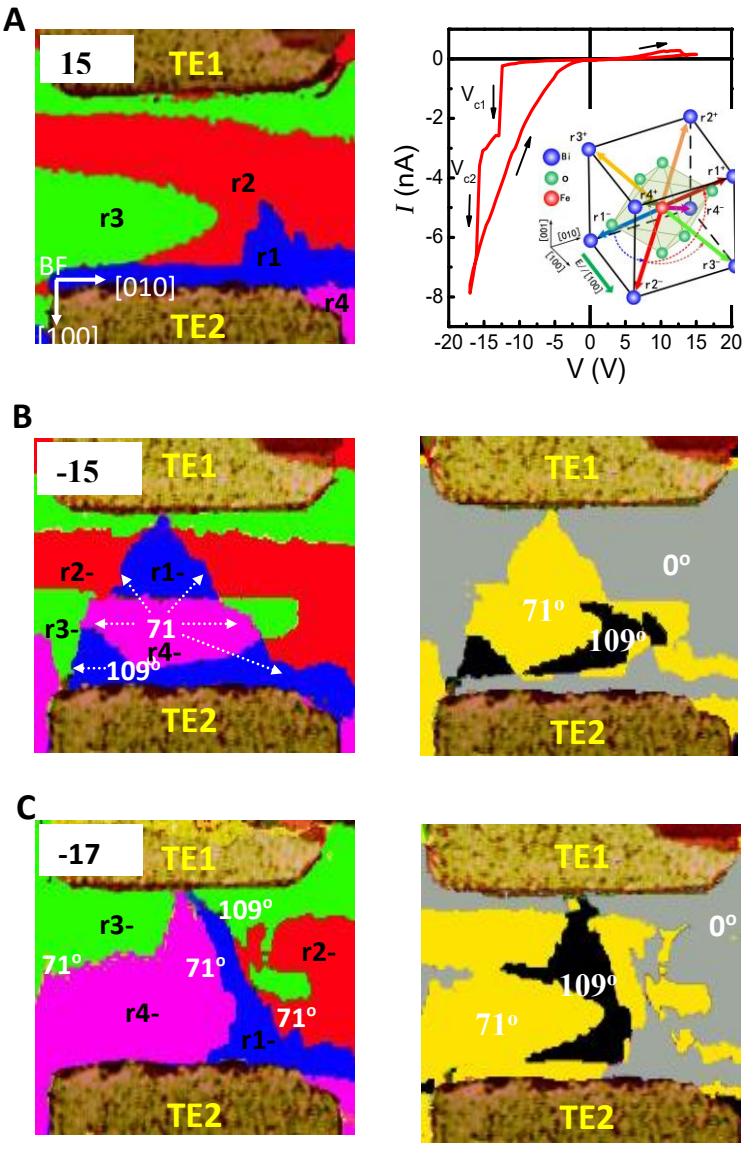

Fig. 2. Time sequence in establishing a domain wall current in $BiFeO_3$ via 71 and 109-degree domain walls [3]

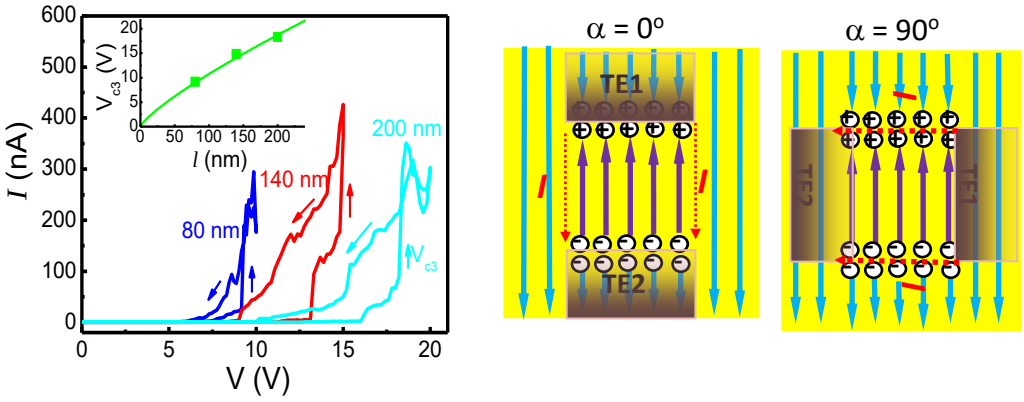

Fig. 3. Larger 300 mA domain wall currents in PZT [3]

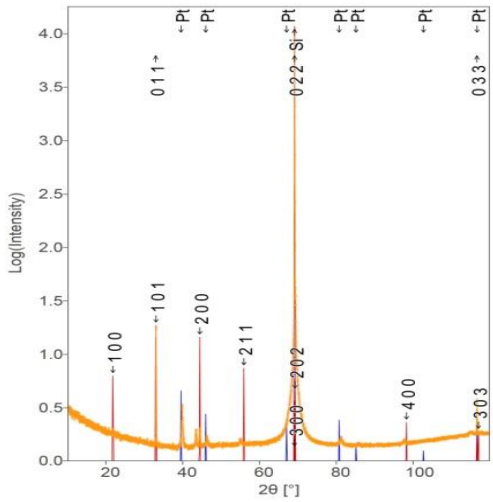

Fig. 4. XRD of SnTiO3 film deposited via ALD onto p-Si [4].

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The importance of being disordered: local versus long-range order in tetragonal tungsten bronzes

Elena Buixaderas

Department of Dielectrics, Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, buixader@fzu.cz

It is well known that disorder considerably affects the development of dielectric and ferroelectric properties in materials. One of the most striking effects of disorder is the ability to disrupt ferroelectricity, turning well-arranged ferroelectric domains into very small polar regions, and changing a ferroelectric phase transition with a sharp peak in permittivity into a diffuse transition, characterized by a broad peak in permittivity over a wide range of temperatures and frequencies. Disorder is mainly created by cationic substitution and the consequent distortions in the crystal lattice. Most of these material falls into the category of relaxors and, among them, many belong to the perovskite family.

Beside the perovskite family, the tetragonal tungsten bronze (TTB) structure is probably one of the most fruitful in developing tunable properties due to disorder. One of the main differences with respect to perovskites is its strongly anisotropic structure.. The oxygen octahedra network builds three different sorts of channels along the polar axis, which can allocate different types of cations. This creates anisotropy in almost all characteristics of the material, which is also an advantage for achieving directional properties. Moreover, the disordered structure, containing vacancies and cationic substitutional disorder in these channels influences many properties, like the dielectric response.

In this talk, the origin of disorder in TTBs will be analyzed, comparing the dielectric behaviour of several crystals with different compositions and cationic substitution, as well as its influence on the lattice dynamics. One of the main contributions to the permittivity arises from a very strong relaxation located in the MHz-GHz range which slows down on cooling. Its temperature dependence is one of the keys to understand the ferroelectric-relaxor transformation, in which different correlation lengths plays role [1]. Short range order, on the other hand, can be studied by diffuse scattering, and a proper analysis of the experimental and calculated patterns can help to understand the picture at the microscopic level. A combination of density functional-based calculations and large-scale molecular dynamics simulations allows to calculate short-range correlations, including polar distortions and oxygen octahedra tilts which are intimately associated with the ferroelectric/relaxor properties of TTBs.

Financial support from the Czech Science Foundation (project No. 16-09142S) is kindly acknowledged.

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Ferroelectric and piezoelectric properties of lead-free ceramics on the base of sodium-potassium niobate and sodium-bismuth titanate

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

[1]L.Ya.Karpov Institute of Physical Chemistry, Vorontsovo pole str. 10, Moscow 105064,
[2]National University of Science and Technology "MISiS", Leninskii pr. 4, Moscow 119991,
[3]Lomonosov Moscow State University, Leninskie gory 1, Moscow 119992, Russia,
E-mail: politova@nifhi.ru

During last decade, lead-free oxide materials were intensively studied with aim to replace widely used Pb-based ones. In this work we studied influence of cation substitutions and preparation conditions on structure parameters, microstructure, dielectric, ferroelectric, and piezoelectric properties of ceramics based on $(Na_{0..5}Bi_{0.5})TiO_3$ (NBT) and $(K_{0.5}Na_{0.5})NbO_3$ (KNN) perovskites.

The samples were characterized using the X-ray Diffraction, Scanning Electron Microscopy (SEM), Second Harmonic Generation (SHG), Dielectric Spectroscopy, and Atomic Force Microscopy in Piezorespone Force mode (PFM) methods.

Ceramic samples in systems $(Na_{0.5}Bi_{0.5})TiO_3$ - $BaTiO_3$ (NBT-BT) and $(K_{0.5}Na_{0.5})NbO_3$ – $BaTiO_3$ (KNN-BT) with compositions close to Morphotropic Phase Boundaries (MPB) additionally modified by Li^+, Mn^{3+}, Ni^{3+}, and Fe^{3+} cations were prepared by the two-step solid-state reaction method at temperatures of 900 – 1400 K. In order to improve density of ceramics the samples were modified by overstoichiometric KCl additives.

The unit cell volume changes observed in the KNN- and NBT-based ceramics correlate well with radii of substituting cations. Using dielectric spectroscopy method ferroelectric phase transitions as steps near ~ 400 K and peaks at ~ 550 K (in NBT-based) and at ~700 K (in KNN-based) were revealed. Phase transitions near ~ 400 K (NBT) revealed typical relaxor behavior related to the presence of polar nanoregions in a nonpolar matrix. At high temperatures > 700 K effects of dielectric relaxation caused by formation of oxygen vacancies in some compositions due to deficiency in the A-sites and/or presence of mixed valence B-site cations in the perovskite lattice were observed. With increasing BT content an increase in the spontaneous polarization value was proved for modified ceramics using the SHG method.

Local PFM hysteresis loops were observed for KNN-BT samples indicating ferroelectric polarization switching at nanoscale. In some KNN-BT samples effective d_{33} piezoelectric coefficient values reached 300 pm/V.

Finally, at the room temperature, non-monotonous changes in the dielectric permittivity and spontaneous polarization values were observed in the compositions studied thus confirming their prospects for new lead-free materials development.

Acknowledgement

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Electrocaloric effect and its relationship to other properties in relaxor lead magnesium niobate–lead scandium niobate solid solution

Elena Smirnova, Galina Sotnikova, Nina Zaitseva, Aleksandr Kapralov, Gennadiy Gavrilov and Andrey Sotnikov

Ioffe Institute, 26 Politekhnicheskaya, St Petersburg 194021, Russian Federation
Corresponding_author: esmirnoffa@gmail.com

Electrocaloric effect (ECE) is considered now as physical background for a promising solid-state cooling technology [1].

ECE is manifested in ability of material to change temperature by applying an electric field under adiabatic conditions and is characterized the temperature change δT, in particular.

ECE is inextricably linked with the accompanying effects that determine its magnitude, such as pyro- and piezoelectric ones, as well as with material parameters like thermal expansion, elastic constants and thermal capacity [2]. In ferroelectrics, the listed phenomena are functions of temperature and applied electric field. Among them, ferroelectric relaxors exhibit a particularly strong sensitivity to the external electric field. The extraordinary physical properties that underlie numerous applications of relaxors are determined by the existence of a natural nanostructure, namely, polar nanoregions in the paraelectric matrix.

Specific features of the ECE as well as its correlation with other electric field induced phenomena such as pyroelectric effect, dielectric nonlinearity, giant electroctriction and elasticity have been studied. A model solid solution lead magnesium niobate–lead scandium niobate (PMN-PSN) was selected for the study. The solid solution has been synthesized by conventional ceramic technique. An X-ray study has shown the ceramics to be of single-phase perovskite structure. The samples had 94% - 96% density of the theoretical value.

Both temperature dependences of the pyroelectric coefficient p and temperature change δT, characterizing ECE, were found to reveal diffused anomalies. The temperature of pyroelectric coefficient p as well as δT maxima were found to be shifted to higher temperatures with applied field increasing. Electric field dependence of δT demonstrates tendency to saturation at about 15 kV/cm in contrast to pyroelectric coefficient dependence which shows a diffuse maxima versus field at the same temperatures. The main contributions to ECE are examined and discussed. Vital importance of the electromechanical interaction is shown. The results obtained for relaxor are compared with ones for ferroelectrics undergoing the first-order phase transition.

The work was supported by the Russian Foundation of Basic Research, grant 18-02-00394.

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Brillouin light scattering in relaxor ferroelectric $PbNi_{1/3}Nb_{2/3}O_3$

A.I. Fedoseev[1], J.-T. Hong[2], S. H. Oh[2], J. W. Lee[2], J.-H. Ko[2], S.G. Lushnikov[1]

[1)]Ioffe Institute, 194021 Sankt-Petersburg, Russia

[2)]Hallym University, Chuncheon, Gangwondo 24252, South Korea

Sergey.lushnikov@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 $AB'_xB''_{1-x}O_3$. The first studies of the dielectric and optical properties of PNN single crystals have shown that a wide frequency-dependent anomaly of the dielectric response is observed in the vicinity of Tc ≈ 153 K [1]. This made it possible to classify this crystal as a family of ferroelectrics with a diffuse phase transition (relaxor ferroelectrics). The lattice dynamics of the PNN crystal was studied by Brillouin and Raman scattering [2, 3]. In the vicinity of the diffuse phase transition, anomalies in the behavior of longitudinal acoustic (LA) phonons and quasielastic scattering are observed. The broad anomaly of the velocity and damping of the LA phonon is characteristic of relaxor ferroelectrics. Experiments on Raman scattering have shown that the evolution of the scattering spectra with temperature change is of a complex nature and presupposes a sequence of phase transformations that are not trivial for classical relaxor ferroelectrics of the type considered. This motivated us to carry out detailed studies of the lattice dynamics of PNN crystals using Brillouin scattering. Single crystals of PNN were grown from the melt by the method of spontaneous crystallization. Oriented and polished plates with a surface of the (001) type and a thickness of 70 μm were used as objects. The Brillouin measurements were carried out with a high-resolution Fabry-Perot multipass interferometer at a 180° scattering geometry over the temperature range of 80-650 K. As a result of the measurements, the temperature dependences of the frequency shift and the half-width at half-maximum (HWHM) of the LA phonon with **q**II [100] in ~~a~~ cubic coordinates were obtained. The behavior of the frequency shift corresponds to the behavior of the elastic modulus C_{11}, and the behavior of the HWHM is associated to the damping of a long-wavelength acoustic phonon. At T_{c1} = 550 K, a jump in the C_{11} corresponding to the damping maximum is obtained, and in the vicinity of T_{c2} = 420 K the damping maximum is observed with a diffuse anomaly of C_{11}. Temperature of the frequency shift and the HWHM at lower temperatures demonstrates the relaxor behavior of the acoustic response, in which a wide maximum of a damping and a minimum of a C_{11} over several hundred degrees are observed. In the low-temperature region, at T = 130 K, another anomaly in the behavior of the acoustic response of PNN is observed. Thus, in the lattice dynamics of a PNN crystal, three instabilities can be identified, which we associate with a transition to a ferroelastic (below 550 K) and a relaxor ferroelectric phase. Possible mechanisms of the anomalies at 130 and 420 K are discussed.

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Recent achievements in micro- and nanodomain engineering. Periodical poling in $LiNbO_3$, $LiTaO_3$ and KTP

Vladimir Ya. Shur[1,2], Andrey Akhmatkhanov[1,2], Ivan Baturin[1,2], Dmitry Chezganov[1], Maria Chuvakova[1], Alexander Esin[1]

1-School of Natural Science and Mathematics, Ural Federal University, Russia
2- Labfer Ltd., Ekaterinburg, Russia
vladimir.shur@urfu.ru

The lithium niobate $LiNbO_3$ (LN), lithium tantalate $LiTaO_3$ (LT) and titanyl phosphate $KTiOPO_4$ (KTP) crystals with tailored periodically poled domain structure (PPLN, PPLT, PPKTP) created with nanoscale period reproducibility are used for second harmonic generation (SHG) and optical parametric oscillation (OPO) based on quasi-phase-matched (QPM) nonlinear optical wavelength conversion [1]. The study of the conductivity relaxation of charged domain walls allowed the poling optimization [2]. The domain-domain interaction has been investigated [3].

The poling process at room and elevated temperatures have been studied by *in situ* optical observation. The obtained knowledge was applied for producing high-fidelity patterns: (1) PPLN:MgO with period 6.95 and 4.3 μm for green and blue light SHG. (2) 1% MgO doped stoichiometric LT for green and yellow light SHG with output power above 14 W for CW. (3) Fan-out domain structures in 3 mm-thick MgO:LN for tunable OPO generation from 2.5 to 4.5 μm for 1.053 μm pump. The uniformity of SHG efficiency and QPM temperature was demonstrated.

The developed electron beam poling allowed to create the through domains with outstanding uniformity for green light generation and the domain walls with arbitrary orientation [4]. The high SHG efficiency was achieved in PPLN soft proton exchange waveguides.

The information obtained from the first *in situ* study of the domain kinetics with high temporal resolution allowed to obtain original important information about domain wall motion mechanism and to characterize KTP as the most appropriate for sub-micron periodical poling [5].

The equipment of the Ural Center for Shared Use “Modern nanotechnology” UrFU was used. The work was supported by Government of the RF (Act 211, Agreement 02.A03.21.0006).

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The influence of bulk screening retardation on domain kinetics in KTP single crystals

Andrei Akhmatkhanov[1], Ekaterina Vaskina[1], Maria Chuvakova[1], Elena Pelegova[1], Alexander Esin[1], Ekaterina Gachegova[1], Vladimir Shur[1]

1- School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
Andrey.Akhmatkhanov@urfu.ru

The periodically poled potassium titanyl phosphate ($KTiOPO_4$, KTP) crystals are one of the popular nonlinear optical materials. It was shown in lithium niobate and lithium tantalate that the domain kinetics is strongly dependent on the screening retardation [1]. Despite the interest to creation of tailored domain structures in KTP the systematical study of bulk screening retardation has not been published yet. We present the domain structure evolution and domain wall motion in KTP plates with artificial dielectric layer and in temperature range from - 70°C to 300°C.

The studied KTP Z-cut 1-mm-thick plates with bulk conductivity of $2 \cdot 10^{-7}$ $Ohm^{-1}cm^{-1}$ at room temperature were grown by top-seeded solution method. The photoresist film AZ nlof2020 (AZ Microchemicals) was spin-coated on Z+ polar surface. The polarization reversal with dielectric layer was carried out using liquid electrodes and in temperature range - using sputtered ITO electrodes.

In situ visualization of domain kinetics during polarization reversal allowed revealing the formation and growth of large number of narrow domain streamers oriented along [010] direction with about ten times higher velocity (6-60 mm/s) than the domain walls (2-5.5 mm/s). Study of the static domain structures demonstrated that the streamers are formed by [100] and [010]-oriented domain walls. The minimal streamer width was about 500 nm and minimal distance between the neighboring streamers – about 100 nm. The switching currents were approximated using the modified Kolmogorov-Avrami approach [2] taking into account the decrease of the growth dimensionality when the streamers reach the opposite electrode edge.

The polarization reversal in the temperature range has shown that temperature increase leads to increase of the input of fast and superfast domain walls [3] to the switching process and noticeable domain elongation. The domain wall velocities were measured and corresponding activation energies were extracted.

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.

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Study of domain formation after electron beam irradiation of lithium niobate single crystals

Dmitry Chezganov, Evgeny Vlasov, Lubov Gimadeeva, Maria Chuvakova, Vladimir Ya. Shur

School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
chezganov.dmitry@urfu.ru

We have studied the domain formation induced by 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 domain structures have produced 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^{o}C was carried out using thermal stage C1003 (Gatan Inc.). Both dot and stripe irradiations were used. The static domain structures were visualized by scanning electron microscopy (SEM) after selective chemical etching.

We have measured the dose dependence of shape and size of isolated domains, and the temperature dependence of the threshold dose value after dot irradiation. The hexagonal shape of domains appeared at room temperature. The temperature increase led to lack of domain shape stability and formation of self-assembled domain structures.

Four types of domain structures appeared after stripe irradiation at room temperature have been separated: (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 formation was characterized by dose dependences of domain density and length, 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.

The obtained results will be used for development of domain engineering methods.

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).

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Room temperature magnetoelectric control of ferroelectric domains in a chiral lanthanide complex

Maxim S. Ivanov[1], Jérôme Long[2], Vladimir A. Khomchenko[1], Jean-Marc Thibaud[2], Yannick Guari[2], Joulia Larionova[2] and Jose A. Paixão[1]

1-CFisUC, Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal
2-Institut Charles Gerhardt Montpellier, UMR 5253, Ingénierie Moléculaire et Nano-Objets, Université de Montpellier, ENSCM, CNRS, Place E. Bataillon, 34095 Montpellier Cedex , France

maxim.ivanov@uc.pt

Multiferroics are known as multifunctional materials that exhibit at least two ferroic orders such as ferromagnetism and ferroelectricity [1] and may provide a basis for developing high-density data storage, spintronics or low consumption devices [2, 3]. In natural materials, there are no examples of such association and designing of these systems is not straightforward owing to the phenomenological origin of both ferroic properties. On the other hand, magneto-electrical materials such as ferroelectric paramagnets are a more common class of materials that could also provide an interplay between magnetic and electrical properties [4]. In the present work, taking advantage of the flexibility of molecular chemistry, we describe a luminescent multiferroic consisting of molecular paramagnetic ferroelectric materials based on a chiral lanthanide complex that exhibits additionally a Near Infra-Red luminescence. Our molecular approach to design multifunctional multiferroics with strong coupling between the magnetic and ferroelectric features relies on the association of lanthanide ions, with a chiral diamagnetic zinc or nickel complexes in order to favor the crystallization in one of the ten polar point groups compatible with ferroelectricity. Thus, we give the experimental evidence of a room-temperature magneto-switching of the ferroelectric domains at the nanometric scale in multifunctional molecular ferroelectrics, opening tremendous perspectives for the generation of multiferroic materials.

The proof of concept of electrical polarization switchability at room temperature using a low magnetic field confirms that molecular materials can be competitive with pure inorganic materials and open new horizons in the design of multiferroics and magneto-electrical systems.

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Phase diagrams and dielectric properties of ferroelectric nanocomposites

Nikolay Pertsev[1,2], Andrei Nikitchenko[1,2], Andrei Azovtsev[1]
[1]*Ioffe Institute, St. Petersburg, Russia*
[2]*Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia*
pertsev.domain@mail.ioffe.ru

We report a nonlinear thermodynamic theory of particulate composites containing ferroelectric (FE) nanocrystals embedded into a dielectric (DE) matrix. The theory describes the mechanical effect of elastic matrix on the phase states of FE nanocrystals and evaluates the effective permittivities of considered FE-DE nanocomposites. The equilibrium polarization states of single-domain nanocrystals are determined by minimizing a special thermodynamic potential that describes the energetics of an ellipsoidal FE inclusion surrounded by a linear elastic medium [1]. To demonstrate the stability ranges of such states for a given material combination, we construct a phase diagram, where the inclusion's shape anisotropy and temperature are used as two parameters. The "shape-temperature" phase diagrams are calculated numerically for nanocomposites comprising spheroidal $PbTiO_3$, $BaTiO_3$, and $Pb(Zr_{1-x}Ti_x)O_3$ crystallites embedded into representative matrices generating tensile (silica glass) or compressive (potassium silicate glass) thermal stresses inside FE inclusions due to differences in the thermal expansion of the crystallites and the matrix. The developed phase maps demonstrate that the joint effect of thermal stresses and matrix-induced elastic clamping of FE inclusions gives rise to several important features in the polarization behavior of FE nanocrystals. In particular, the Curie temperature displays a nonmonotonic variation with the ellipsoid's aspect ratio, being minimal for spherical inclusions. Furthermore, the diagrams show that the polarization orientation with respect to the ellipsoid's symmetry axis is controlled by the shape anisotropy and the sign of thermal stresses. Under certain conditions, the mechanical inclusion-matrix interaction qualitatively alters the evolution of FE states on cooling, inducing a structural transition in $PbTiO_3$ nanocrystals and suppressing some transformations occurring in bulk $BaTiO_3$ crystals [2].

To describe the dielectric properties of FE-DE nanocomposites, we first calculate the intrinsic small-signal permittivities ε_{ii} (i = 1,2,3) of FE nanocrystals with the full account of the matrix mechanical effect on their polarization states. Next, analytical relations are derived for the effective permittivities of particulate composites in the Maxwell-Garnett approximation. These relations are distinguished by the account of both dielectric and shape anisotropies of FE inclusions, allowing to evaluate the effective permittivities of FE-DE nanocomposites as a function of the dielectric constants ε_{ii} of FE inclusions, their volume fraction $f << 1$, and the matrix permittivity ε_d. The numerical calculations show that, despite the lowering of macroscopic dielectric response by the glass matrix, the effective permittivity of the FE-DE nanocomposite remains rather high near the temperatures of phase transitions in FE inclusions. Importantly, in the nanocomposites involving spheroidal $BaTiO_3$ inclusions embedded into potassium silicate glass, a dielectric peak may be situated near the room temperature due to shifted phase transition between two polar states. Our theoretical results provide guidelines for the fabrication of FE-DE nanocomposites with enhanced dielectric responses.

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Multiferroic based 2D phononic crystal: band structure and wave propagations

Zafer Ozer[1], Cengiz Ahundov[2], Amirullah M.Mamedov[2,3], Ekmel Ozbay[3]

1-Mersin University, Mersin, Turkey
2- International Scientific Center, Baku State University, Baku, Azerbaijan
3- Nanotechnology Research Center (NANOTAM), Bilkent University, Ankara, Turkey
Corresponding_author_mamedov46@gmail.com

In the present work the acoustic band structure of a two-dimensional (2D) solid-solid phononic crystal (PC) containing multiferroic and dielectric was investigated theoretically and numerically by the plane-wave-expansion (PWE) method. Two-dimensional PC with square lattices composed of multiferroic cylindrical rods embedded in the organic/inorganic matrix is studied to find the existence of stop bands for the waves of certain energy. This phononic bandgap - forbidden frequency range - allows sound to be controlled in many useful ways in structures that can act as sonic filters, waveguides or resonant cavities. Phononic band diagram $\omega = \omega(k)$ for a 2D PC was plotted versus the wavevector k along the Γ-X-M-Γ path in the square Brillouin zone (BZ). The band diagram shows four stop bands in the wide frequency range. The unusual properties of matrix and multiferroic give us ability to control the wave propagation through the PC in over a wide frequency range. We study the 2D composites by solving the basic acoustic wave equation and use Bloch wave analysis to identify the band gaps.

Novel molecular crystals: nonlinear optical, piezo- and ferroelectric properties

Sergey Semin[1], Maxim Ivanov[2], Yulong Duan[1], Jialiang Xu[3] and Theo Rasing[1]

1-Institute for Molecules and Materials, Radboud University, Heyendaalseweg 135, 6525 AJ, Nijmegen, the Netherlands

2- Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Rua Larga, P-3004 516, Coimbra, Portugal

3- School of Chemical Engineering and Technology Tianjin University, Weijin Road 92, Nankai District, Tianjin, P.R. China

Corresponding_author: s.semin@science.ru.nl

Organic π-conjugated molecules, serving as light emitting materials in both the linear and nonlinear optical regimes, have attracted broad interest due to their tailor-made chemical structure, high optical susceptibility, band gap in the visible range and their high degree of fabrication flexibility and processability.

In this work we present results of the investigation of the optical, piezo- and ferroelectric properties of molecular crystals based on our newly synthesized 2,7-di([1,1′-biphenyl]-4-yl)-fluorenone (4DBpFO) molecule. The fluorenone moiety introduces a permanent dipole, oriented orthogonal to the long axis of the molecule, induced by the carbonyl group as an electron acceptor (D) and the biphenyl groups as electron donors (A) (see Fig 1a). The dipoles of the individual 4DBpFO molecules are oriented in the same direction as molecules assemble into a non-centrosymmetric crystal structure. Our results demonstrate that upon aggregation, the linear optical emission of the compound is greatly enhanced, together with the appearance of piezoelectric properties (see Fig. 1c) and nonlinear optical effects: second harmonic generation (SHG) and two-photon fluorescence (TPF) are observed from the self-assembled microcrystals, due to the non-centrosymmetric arrangement of the molecules (Fig. 1b).

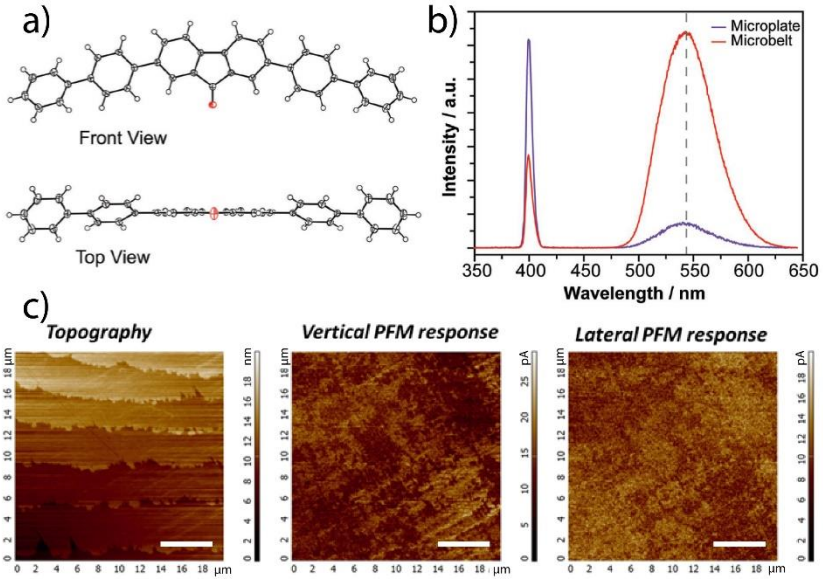

Fig.1. a) Structure of the 4DbPFO molecule, red spheres represent position of oxygen, grey spheres - positions of carbons; b) Nonlinear optical responses from two 4DbPFO molecular crystals aggregated as microplate (blue curve) or microfiber (red curve) demonstrating the presence of SHG around 400 nm) and TPF signal (around 550 nm); c) Topography and piezoresponse from the 4DbPFO microcrystal, revealing piezoelectric domains. Scale bar is 5 μm.

Dielectric properties of water molecules in nanoporous silicon oxide

S.D. Milovidova, O.V. Rogazinskaya, B.M. Darinskii, E.S. Nichugovskaya

Voronezh State University, Voronezh, Russia
darinskii@mail.ru

One of the problems in the manufacture of any composite with water-soluble crystals is the complete filling of the nanocannals with growing crystals in them. In the pores above the crystals there remain air nanostructures that can be filled with water molecules from the surrounding medium. This leads to a large effect of humidity on all properties of such nanocomposites, as indicated in studies of nanocomposites with ferroelectrics [1].

Therefore, the aim of this work was to study the effect of humidity on the dielectric properties of one of such amorphous nanoporous matrices obtained from the nanodisperse hydrosol of SiO_2 as described in [1]. Depending on the ambient humidity, the dielectric permittivity ε of such samples can vary from 10 to 10^4.

Figure 1 shows the characteristic dependence of ε and the dielectric loss tangent on temperature for all the samples studied under normal and high humidity conditions.

As the temperature increases from room temperature, the values of ε first increases, then a maximum is observed, after which a fairly sharp decrease of ε in the region of ~ 100 ÷ 110 ^{0}C to 10 ÷ 15 units is observed (curve 1 in Fig. 1).

When the sample was cooled, the values of ε remain small to a certain temperature, which depends strongly on the experimental conditions. In this case, the growth of ε begins at a relatively high temperature (~ 55 ^{0}C) and reaches large values at room temperature (curve 1 in Fig. 1).

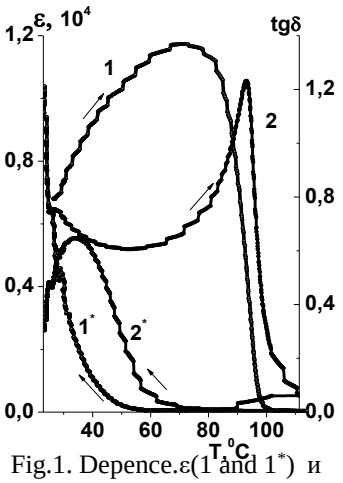

Fig.1. Depence.ε(1 and 1*) и tgδ(2 and 2*) on temperaturete SiO_2. with water molecule at when heating (1 and 2) and cooling (1*and 2*). f=1 kHz, E=5V / sm.

As the temperature increases from room temperature, the values of ε first increase, then a maximum is observed, after which a sharp decrease of ε in the region of ~ 100 ÷ 110 ^{0}C to 10 ÷ 15 units is observed (curve 1 in Fig. 1). Such anomalously large values of ε can be associated with the filling of nanopores by water molecules and the same orientation of their dipole moments. Water under such conditions becomes a kind of superparaelectric, similar to the existence of superparamagnets with a decrease in their size [2]. Or it is a manifestation of the ferroelectric properties of water, the possibility of which is discussed in [3].

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Structural and electronic properties of heterointerfaces composed of ferroelectric oxides

Irina Piyanzina[1,2], Rustem Zagidullin[1], Rinat Mamin[1,2]

1-Kazan E. K. Zavoisky Physical -Technical Institute (KPhTI), Russian Federation
2-Kazan Federal University, Russian Federation
Corresponding_author i.piyanzina@gmail.com

For the paradigmatic oxide heterostructure with $LaAlO_3$ (LAO) thin films grown on $SrTiO_3$ (STO) substrates, distinct electronic phases have been extensively characterized at the LAO/STO interface: for LAO films with more than three layers and LaO termination towards the TiO_2 interface, a two dimensional electronic system (2DES) is formed in the STO layers next to the interface which becomes superconducting below a temperature below 300 mK [1, 2]. Remarkably, the superconducting state coexists with a magnetic state being stable up to the room temperature. It was concluded, that the primary mechanism responsible for the 2DES formation is electronic reconstruction.

Analogous to the ionic polar discontinuity, the 2DES may be created at an interface due to electric polarization discontinuity [3,4]. An attractive materials for such purpose are ferroelectrics. They have a wide range of different distinctive properties, among them: spontaneous polarization switching, high dielectric permeability, dielectric nonlinearity, piezo- and pyro- activity, linear and quadratic electro-optical effects. Such a functionality can expand the scope of application in nanoelectronics.

In the present work based on first-principles band structure calculations, we demonstrate the possibility of a 2DES formation at the interface composed of perovskite ferroelectric ($KNbO_3$, $BaTiO_3$, $LiNbO_3$, $PbTiO_3$) and a wide band-gap insulator (STO, MgO). We analyze an impact of ferroelectric polarization onto the 2DES conducting properties, as well as a possibility of switchable and controllable metal-insulator transition in considered types of heterostructures.

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AFM Domain Writing and Domain Wall Conduction in $LiNbO_3$ Thin Films

Tatiana R. Volk and Radmir V. Gainutdinov

Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics" of RAS, Moscow, Russia

Corresponding author: volk-1234@yandex.ru

Domain patterns at the nanoscale have been the focus of researches over the past few years due to various practical potentials. In particular, the domain-wall conductance opens new ways for a number of novel applications.

We present the results on domain writing by atomic force microscopy (AFM) and measurements of a static domain-wall conductance (DWC) in single-crystal thin (300 – 500 nm thick) $LiNbO_3$ films fabricated by the ion-slicing method. A body of data was obtained on writing characteristics of single domains and specified 1D and 2D domain patterns. These results permit us the manipulation of the domain sizes and shapes in wide limits from nanosized domain dots to large (of tens of microns) arbitrarily-shaped patterns. Of special importance is the stability of created domain patterns, which persist with no degradation during observation times of months. .

The static conductance was found at domain-walls in the written patterns. DWC exceeds the conductance in the surrounding areas (in the switched and unswitched domains) not less than by five orders of magnitude. The current–voltage characteristics of DWC differ fundamentally from the I-U curves in the switched domains. DWC persists during observation times of about several months, i.e., its steadiness is determined by the stability of written domain patterns.

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.

This work was supported by the RFBR, projects Nos. 16-29-11777_ofi_m, 16-02-00439. The equipment of the Shared Research Center IC RAS supported by the Russian Ministry of Education and Science (project RFMEFI62114X0005) was used in experiments.

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Electron-beam domain writing in $LiNbO_3$ crystals of different compositions

L.S.Kokhanchik[1], T.R.Volk[2], R.V. Gainutdinov[2], and Ya.V.Bodnarchuk[2].

1- Institute of Microelectronics Technology and High Purity Materials RAS, Russia
2- Shubnikov Institute of Crystallography of FSRC "Crystallography and Photonics" RAS, Russia

mlk@iptm.ru

Periodical domain structures in ferroelectrics can serve for optical-frequency conversion on the basis of quasi-phase matching (QPM) principle. The most attractive material for nonlinear optical converters of this type is $LiNbO_3$. The non-contact method of electron-beam domain writing (EBDW) provides a possibility to fabricate domains both on the polar and non-polar surfaces of ferroelectrics.

We present a sum of our results on EBDW in $LiNbO_3$ crystals of different compositions. These results provide insight into the mechanism of EB induced ferroelectric switching and domain formation. $LiNbO_3$ is especially convenient for these investigations since the phenomena occurring under EB irradiation can be discussed in the framework of the $LiNbO_3$ intrinsic defect structure [1].

Our experiments were performed for the most part in domain patterns written by EB on the non-polar (X- or Y-)- crystal surfaces. The convenience of this geometry is due to possibility of 3D-characterization of written patterns using the combination of scanning force microscopy and nonlinear-optical techniques [2, 3]. The following compositions of $LiNbO_3$ were under study: the congruent (CLN) and stoichiometric (SLN) [4] crystals, optical damage-resistant Zn-doped $LiNbO_3$ [5], Ti-doped $LiNbO_3$ and chemically reduced (RLN) $LiNbO_3$ crystals [6]. A scope of data on the dependence of domain formation on the irradiation conditions (the accelerating voltage U and EB current I), the electron emission and conductivity was obtained and considered in the framework of EB charging of insulators. Effects of dopants of various types on the charge transport scheme, responsible for the space-charge field driving the domain motion, were discussed in terms of the modification of the intrinsic defect structure caused by different types of doping or external treatments.

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Charged domain walls in lithium tantalate with spatially nonuniform stoichiometry deviation

Victoria Pryakhina[1], Evgenii Greshnyakov[1], Boris Lisjikh[1], Andrei Akhmatkhanov[1], Pavel Zelenovskiy[1], Denis Alikin[1], Ausrine Bartasyte[2], Vladimir Shur[1]

1-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
2-Time Frequency Department, FEMTO-ST Institute, Besançon, France
viktoria.pryahina@urfu.ru

The as-grown domain structure with charged domain walls has been studied in lithium tantalate with nonuniform spatial distribution of stoichiometry deviation. The variations of stoichiometry distribution were obtained by vapor transport equilibration (VTE) process.

Congruent LT 0.5-mm-thick Z-cut plates were annealed in Li-rich atmosphere at 1300 ºC during 24-100 h with heating/cooling rate 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 and at the crystal surface after selective etching by optical and scanning electron microscopies.

The nonuniform distribution defined as the Li concentration difference (c_{Li}) between surface and bulk (Δc) 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 ($0 < \Delta c < 1\%$), (iii) reversed low nonuniformity with higher c_{Li} in the bulk ($-1\% < \Delta c < 0$). Two mechanisms of as-grown domain structure formation during cooling after VTE have been revealed: (a) formation of wide domain boundary in the bulk during 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 studied. (i) The large nonuniformity resulted in formation of wide charged domain boundary with width about 160 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. (ii) The samples with small nonuniformity 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. (iii) The reversed low nonuniformity resulted in formation of a wide charged domain boundary with width 350 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 1-3 μm.

The equipment of Ural Center for Shared Use “Modern Nanotechnology” UrFU was used.

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Orientation and velocity of the domain walls in KTP single crystals

Alexander Esin[1], Andrey Akhmatkhanov[1] Ekaterina Vaskina[1], Mohammad Aftab Alam[1,2], Vladimir Shur[1]

1- School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia

2- Center for Nanoscience & Nanotechnology, Jamia Millia Islamia, New Delhi, India

Alexander.Esin@urfu.ru

Periodically poled potassium titanyl phosphate $KTiOPO_4$ (KTP) crystals are one of the most promising materials for nonlinear optics. Although anisotropic domain growth facilitated the fabrication of fine domain gratings in KTP, deep understanding of the domains dynamics is prerequisite for reproducible production of nonlinear optical elements, due to uncontrollable broadening and merging of individual stripe domains. Despite these, there are only a few works with direct observation of domain structure kinetics in KTP.

We present the direct visualization of domain kinetics in KTP single crystals with high temporal resolution and simultaneous measurement of switching current [1]. Domain kinetics data was represented within the new concept of "kinetic maps" - overlapped set of instantaneous domain wall positions. Distribution of the domain wall orientations and velocities was extracted from the kinetic maps. The following types of domain walls were revealed: (i) the slow walls with velocities of 0.1–20 mm/s oriented along [010] direction, (ii) the fast walls with velocities of 25–105 mm/s oriented along [110] direction and (iii) the superfast walls with velocities of 450–1350 mm/s oriented along [100] directions. The mobility and the threshold fields for all domain walls were estimated. It was demonstrated that velocity of the slow and fast wall increases with deviation from corresponding low-index crystallographic planes. The effect was explained in terms of determined step generation and anisotropic kink motion [2]. It was shown that the fast and slow domain walls provide the smooth input to the switching current. The appearance of superfast walls during domain merging resulted in short current peaks referred also as Barkhausen jumps. 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 domain 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.

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.

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Are Water and Ice Normal Polar Dielectrics? Polarization Mechanism

Alexander Volkov

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

Water and ice are the universal fillers for many natural and artificial materials. They impact drastically the properties of materials, including electrical properties. Surprisingly, a detailed understanding of the polarization mechanisms in water and ice themselves is still opaque.

Liquid water is commonly thought to be composed of H_2O molecules linked by hydrogen bonds that continuously form and break [1]. The famous dielectric feature of water, the Debye relaxation, produces a peak in the dielectric loss spectrum $\varepsilon''(\nu)$ at ~ 1 GHz (Fig. 1b, red) and the large dielectric constant, $\varepsilon'(0)$ ~ 90 at freezing temperature (Fig. 1a, b, red). The phenomenon is interpreted as a collective relaxation of the microscopic dipole moments occurring on a time scale of ~ 10 ps [2]. The Debye relaxation takes place in ice, too (Fig. 1b, blue). In this case, however, it occurs at ~ 1 kHz and has a qualitatively different interpretation: instead of the molecular dipole reorientation «the dipole moment per O-O link seems to be a more pertinent take-off concept» [2]. Challenging is the common smooth temperature run of ε(0), Fig. 1a, red and blue.

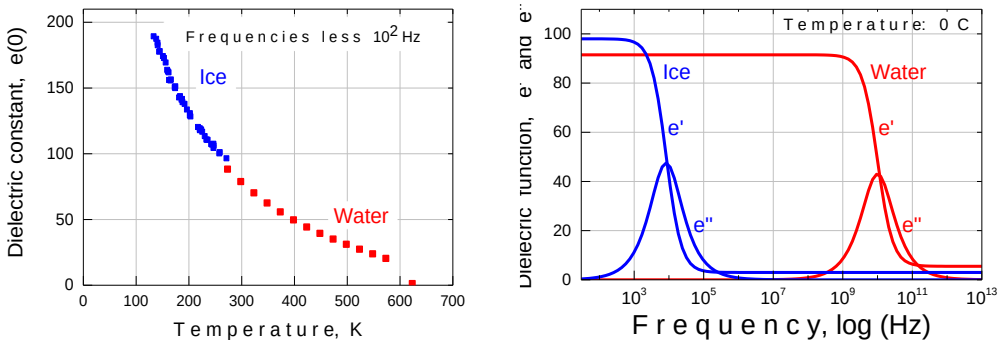

Fig. 1. a) Dielectric constant ε(0) of water and ice vs temperature, b) dielectric spectra ε'(ν) and ε''(ν) of water and ice at 0 C (the Debye relaxation).

We develop a unified approach to understanding the electrical properties of water and ice based on the model proposed by us in ref. [3]. The model implies the diffusion of molecules combined with their local movement in a cage of neighbors. ~1% of the molecules are marked by the charge (excess or missed proton) thus providing registered dielectric response.

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TUESDAY
June 26, 2018

SECTIONS

Fundamentals of Ferroelectric and Related Materials

Characterization & Properties of Ferroelectrics

Applications of Ferroelectric and Related Materials

Polar biomolecular materials and their applications

Andrei Kholkin[1,2]

1-Dept of Physics and CICECO – Aveiro Institute of Materials, University of Aveiro, Portugal
2-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
Corresponding_author_kholkin@ua.pt

Novel supramolecular biomaterials that mimic the structural peculiarities of living organisms and have significant pyro-, piezo- and ferroelectric properties have recently emerged because of the range of novel applications. One of these materials, diphenylalanine (FF) is one of the self-assembling peptides, which have recently become a focus of intensive research in the field of nanomaterials because they can spontaneously form fascinating discrete and well-ordered structures: nano- and microtubes, nanospheres, nanofibrils, and hydrogels [1]. FF peptide tubes (PTs) possess unique biological and physical properties such as inherent biocompatibility, high aspect ratio and remarkably rigid structure. Strong piezoelectricity and pyroelectricity found recently in FF [2,3] add a new important functionality useful for the development of sensors, actuators and micromechanical systems. Another biomolecular material that recently found to be strongly piezoelectric is amino acid β-glycine [4]. It is found to be relatively stable under ambient conditions and exhibit piezoelectric properties comparable to that of $BaTiO_3$ [4]. As such, these biocompatible materials are very attractive for the fabrication of future generation of resonance biosensors, energy harvesting elements [5], and other devices.

In this work, we report the results of our recent studies on the growth and characterization of FF PTs and amino acid glycine by piezoelectric, pyroelectric and dielectric techniques. A method of growth of large samples was developed and thus the crystals could be transferred and mounted on structured substrates. Piezoelectric properties were then evaluated by quantitative Piezoresponse Force Microscopy (PFM). We show that the entire piezoelectric matrix of FF PTs could be evaluated if the proper arrangement of the samples is constructed. Phase transitions were rigorously studied by the dielectric spectroscopy. Several anomalies were found in the temperature range 100-350 K accompanied by the strong dielectric relaxation. Unusual behavior of the piezoelectric and pyroelectric properties observed in this work was attested to the relaxation of water molecules in FF PTs nanochannels. Possible applications of polar biomaterials will be discussed.

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Ferroelectricity in the tungsten bronze structure families

Finlay D. Morrison

School of Chemistry, University of St Andrews, St Andrews, KY16 9ST
finlay.morrison@st-andrews.ac.uk

Oxides with the perovskite structure are arguably the most widely studied in solid-state/condensed matter science, and almost completely dominate the technologically important area ferroelectrics. However, the tungsten bronze–derived structures are closely related to perovskite in that they also consists of a network of corner-sharing BO_6 octahedra. After perovskite the largest family of oxide ferroelectrics adopt the tetragonal tungsten bronze (TTB) structure, general formula $A1_2A2_4B1_2B2_8C_4O_{30}$. The octahedra create three distinct channels: a large 15-coordinate A2 site; a slightly smaller 12-coordinate A1 (perovskite) site; and the relatively small 9-coordinate C site. The BO_6 octahedra are non-equivalent as denoted by B1 and B2. This additional crystallographic complexity affords TTBs more compositional flexibility than perovskites, but can result in large, complex unit cells and also incommensurate modulations leading to a range of electrical properties including dipole glass, relaxor ferroelectric (RFE) and classical (1st order displacive) ferroelectric (FE) behaviour – often in the same composition as a function of temperature. The hexagonal bronzes, by contrast, have been less widely studied, despite several reports of ferroelectricity in these materials.

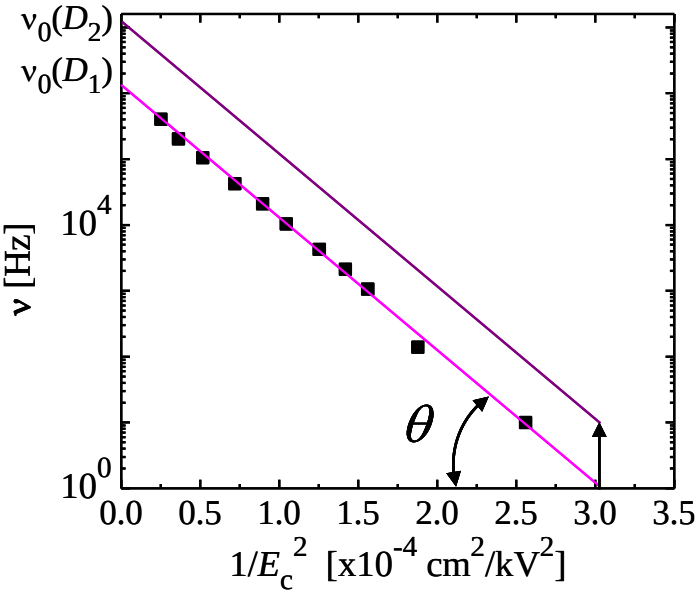
I will present recent data of two ferroelectric tungsten bronzes structural families: the tetragonal (TTB) and hexagonal (HTB) tungsten bronzes. In the TTBs conventional long-range, "average" structure, as determined by "conventional" synchrotron and neutron powder diffraction, was insufficient to rationalise the macroscopic properties and a combination of selected area electron diffraction and total neutron scattering was required to probe an order-disorder crossover and disruption of domains in these materials. I will also present a new improper ferroelectric with the HTB structure. Symmetry mode analysis and rationalisation of the crystal structure allowed us to predict that this material should produce the same topological domain structure as $YMnO_3$ and the rare earth manganites. This was then confirmed experimentally using piezo-force microscopy (PFM) measurements.

Fast polarization reversal in polycrystalline ferroelectric thin films: the origin of size effects

A. Yu. Belov

A.V. Shubnikov Institute of Crystallography RAS, Russian Federation
Corresponding_author_belov@crys.ras.ru

Polycrystalline ferroelectric PZT films with columnar grains at a certain thickness (typically about of 250 nm) show an unusual frequency dependence of the coercive field E_c: $ln(v/v_0) \sim 1/E_c^2$ [1]. A surprising feature of this law is not only the existence of the limiting frequency ν_0 (see Fig.1), but also its dependence on the top electrode diameter D: $\nu_0 = \nu_0(D)$. This effect can not be explained by the existing models of polarization reversal [2]. Here, a model of the Frank-Read type for a surface source emitting thin domains with reversed polarization is proposed to explain this unusual frequency dependence of polarization switching in polycrystalline PZT thin films in a wide range of frequencies. The model provides a solution to the coercivity paradox for polycrystalline thin films and in agreement with experiment predicts the existence of the limiting frequency for polarization switching. The model also predicts that the activation energy for domain nucleation increases with the source size, indicating an increase in the coercive field as minimum size sources deteriorate. The size of operating sources is assessed from the experimental values of the activation energy and can vary from 1 nm to the grain size (~100 nm), depending on the domain wall energy.



The proposed mechanism for the domain nucleation in polycrystalline PZT films can explain the electrode size dependence of the limiting frequency. This dependence is related with increasing role of the athermal domain growth in strongly inhomogeneous electric field near electrode edges. The athermal domain growth is shown to become possible for some types of the electric field decay with distance from the electrode edge. There is an analogy between this mechanism and Zener-Stroh model of the micro-crack formation from dislocation pile-ups in polycrystals.

Fig. 1. Semi-log plots *ln v* vs $1/E_c^2$ illustrating shift of the limiting frequency $\nu_0(D)$ with a change in the electrode diameter D ($D_2 < D_1$). Squares correspond to *RT* data and D_1 = 320 μm [1].

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Complex method of biological tissues treatment using synergetic combination of ultrasound, RF and vacuum massage

N.A. Shvetsova[1], I.A. Shvetsov[1], M.A. Lugovaya[1], N.A. Kolpacheva[2], A.N. Rybyanets[1]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
[2]Don State Technical University, Rostov-on-Don, 344000, Gagarin sq., 1, Russia
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.

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).

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Frequency doubling in electrostrictor-ferromagnet composite

Dmitri. Saveliev, Leonid Fetisov, Dmitri Chashin, Yuri Fetisov, Panich A.E.

Moscow Technological University (MIREA), Russia
dimsav94@gmail.com

In the composite structures containing mechanically coupled ferroelectric (FE) and ferromagnetic (FM) layers, the nonlinear phenomena of harmonics generation and frequency mixing, which arise due to nonlinear dependence of the FM layer magnetostriction on the magnetic field, were observed [1]. In the present paper it is shown for the first time that analogous phenomena can arise also due to nonlinear dependence of the FE layer strain on the applied electric voltage.

In the experiments we used a structure (see inset of Fig. 1) containing a layer of electrostrictive (ES) ceramics 6 mm x 20 mm in size and 0.4 mm thick and an amorphous FM layer of FeBSiC with a thickness of 30 μm, connected by glue. The ceramics was made on the basis of a solid solution of magnoniobate-titanate lead system, including PbO, MgO, Nb_2O_5, TiO_2, and La_2O_3 to increase the electrostriction.

Figure 1 shows the dependence of the ceramic layer strain S on the dc voltage U applied to the electrodes, measured with a strain gage. An excitation voltage $U\cos(2\pi ft)$ with a frequency of 1-100 kHz and an amplitude of up to 5 V was applied to the electrodes of the ES layer. A constant field H = 0 - 100 Oe was applied along the axis of the structure. The changes in the magnetization of the FM layer, arising due to deformations of the ceramic layer, were recorded using a coil.

Figure 2 shows the time dependence and the frequency spectrum of the excitation voltage (upper pictures), as well as the time dependence and frequency spectrum of the voltage from the coil (lower pictures). The frequency f_0 is chosen equal to half of the frequency 72 kHz of the acoustic resonance of the structure. It is seen that the symmetry of the $S(U)$ dependence leads to a doubling of the output signal frequency. It is shown that amplitude of the generated voltage $u \sim U^2$ and it strongly depends on H.

The work is supported by the Russian Foundation for Basic Research, grant 16-29-14017.

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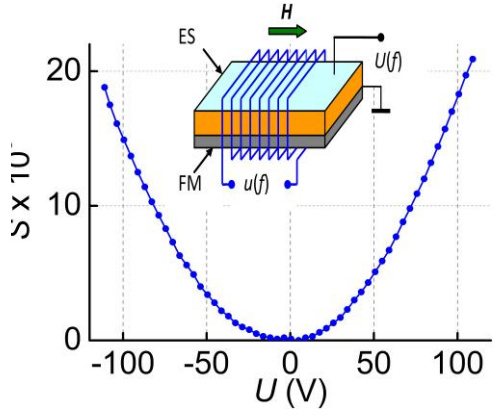

Fig. 1 Stress S vs. applied voltage U for the electrostrictive ceramics.

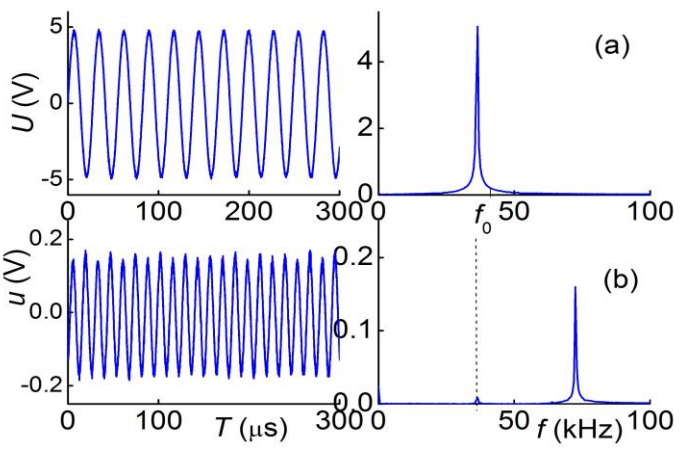

Fig. 2 Characteristics of input (a) and output (b) signals.

Surface analysis of piezoelectric materials

Mehtap Demir[1]

1-Faculty of Engineering, Department of Metallurgy and Material Engineering, Adiyaman University, Turkey

dmehtap@gmail.com

The usage of electrical devices increases energy needs significianlty. With the increase in energy consumption due to ever grown number of electrical devices, harvesting for reusable, clean, non-polluting energy source lot of mechanical motion and energy available at every second of human life in the work of converting mechanical energy into electrical energy. Piezoelectric crystals are the most advantage in this type of energy conversion its complete green energy process.

Piezoelectric materials are the first discovered piezoelectric crystals. For the piezoelectric behavior of these crystals, it is necessary to cut and shape the materials taking into account the crystallographic directions of the materials. There are different types of piezoelectric materials. Among all the piezoelectric materials, lead Zirconate Titanate(PZT) is by far the most performing one because of its high piezoelectric constant and large electromechanical coupling factor. Despite its properties, the presence of lead makes PZT a toxic material. Parliament and the European Council, on June 8th, 2011, approved a document (directive 2011/65/EU) regarding Chapter 1. Introduction 5 the restriction in using certain hazardous substances in electrical and electronic equipment. This has strongly motivated the world of the scientific research to consider and deeply study lead-free piezoelectric materials alternative to PZT.

Beside PZT, Zinc Oxide(ZnO) is one of the most investigated, because of its versatility, cost-effectiveness and easiness of fabrication. Piezoelectricity of ZnO has been widely exploited for the fabrication of surface acoustic wave devices.

AlN(Aluminum Nitride) is a piezoelectric crystal that is now being worked on. The aim of this work is to examine the synthesis and characterization of piezoelectric thin films and to find new nature-friendly syntheses in the future works.

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New generation of piezoactive and ultrasonic reverse osmosis, ultra- and microfiltration membranes

A.N. Rybyanets[1], N.A. Shvetsova[1], D.I. Makarev[1]

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

Baromembrane processes are used in many branches of industry and in laboratory practice for desalination of saline and wastewater treatment (reverse osmosis), separation and purification of biologically active substances (ultrafiltration), purification of technological solutions and water from finely dispersed substances (microfiltration) [1]. The main disadvantages of existing baromembrane technologies and devices are low selectivity and productivity and, in some cases, their high cost. In addition, all currently existing membranes used in baromembrane processes are fundamentally passive and, in some cases, ineffective for new promising applications.

The purpose of this work was to develop and study a new generation of piezoelectrically active and ultrasonic membranes for reverse osmosis, ultra- and microfiltration with improved selectivity and performance. As a result of the executed works were developed and studied:

1. New piezoelectric materials, including lead free biocompatible micro- and nanoporous ceramics, as well as piezoelectrically active and ultrasonic membranes on their base.
2. Designs of hybrid and composite piezoelectrically active and ultrasonic membranes and filters.
3. Prototypes of piezoelectrically active and ultrasonic membranes and filters with improved selectivity and performance.

The results of studies of micro- and nanoporous piezosubstrates, piezoelectrically active nanoporous selective layers, hybrid and composite piezoelectrically active and ultrasonic membranes are presented.

The developed piezoelectrically active and ultrasonic membranes for reverse osmosis, ultra- and microfiltration with increased selectivity and productivity, as well as filtration devices based on them, can be used for filtration of drinking water in water treatment systems, purification of sewage industrial waters and extraction of heavy metals and radionuclides from discharges of chemical and nuclear-fuel cycle factories, filtration of organic and food liquids, cleaning of petroleum products, biological media (hemodialysis), genetic analyzes and other 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).

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Second harmonic generation peculiarities induced by THz pulses in noncentrosymmetric thin film.

Vladislav Bilyk, Kirill Grishunin , Elena Mishina

1-Moscow Technological University, MIREA, Vernadsky Ave. 78, 119454, Moscow, Russia

Corresponding author: vrbilyk@mail.ru

Nearly single cycle intense THz pulses induce in Ba0.8Sr0.2TiO3/MgO generation of transient second harmonic from near-infrared pulse. The dynamics of the nonlinear optical signal is characterized by a step and oscillations at the frequency of about 1.67 THz. The step and oscillations can be mistakenly interpreted as a switching of ferroelectric polarization in Ba0.8Sr0.2TiO3 and coherent soft mode excitation, respectively. Here we demonstrate that the dynamics of the non-linear signal must be explained in terms of interference of static and relativistically moving sources of the second harmonic in the studied structure.

Here we demonstrate the importance of propagation effects in interpretation of results of nonlinear optical time-resolved experiments. Although Second Harmonic Generation is established as a powerful probe of ferroelectricity, time-resolved measurements of ultrafast dynamics in ferroics with the help of this effect can be hampered by the presence of several interfering sources of the detected radiation. In particular, the dynamics triggered by nearly single cycle THz pulse in BST/MgO structure can be mistakenly assigned to the dynamics of ferroelectric order parameter. Our experiments demonstrate that the observed non-linear signal must be explained in terms of interference of static and relativistically moving sources of the second harmonic in the studied structure.

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Quasi-two-dimensional electron gas at the ferroelectric/dielectric interface

R.F. Mamin[1,2,*]

[1]*Zavoisky Physical-Technical Institute of FIC KazanSC RAS, Sibirskii tract 10/7, Kazan, Russia*
[2]*Institute of Physics, Kazan Federal University, Kremlevskaya 16, Kazan 420008, Russia*
**Corresponding Author: mamin@kfti.knc.ru*

The creation of quasi-two-dimensional superconducting states at the interface and the ability to control such states by magnetic and electric fields is impossible without the use of new materials and without the development of new design interfaces. Unique properties of functional materials are achieved due to the effects associated with the complex composition of the interface structure. Such new materials include oxide heterointerfaces between two nonconducting oxides in which, owing to strong electronic correlations, unique transport properties are observed. A high-mobility electron gas was first observed in 2004 [1] at the interface of $LaAlO_3$ (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 (quasi-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 below 300 mK [3].

We investigate the optical properties of 2DEG at the interface between ferroelectric oxide and insulating oxide in heterostructures, isostructural to $BaTiO_3/LaMnO_3$. The numerical simulations of the structural and electronic characteristics of the $BaTiO_3/LaMnO_3$ ferroelectric-antiferromagnet heterostructure have been performed. 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 transition to the state with 2DEG 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 heterostrocture will have been presented.

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Electrocaloric effect in $BaTiO_3$ and $Ba(Ti,M)O_3$ (M = Sn, Zr) ceramics

Vladimir V. Shvartsman[1], Mehmet Sanlialp[1], Maksim O. Karabasov[1], Zhengdong Luo[2], Christian Molin[3], Brahim Dkhil[2], Sylvia Gebhardt[3], and Doru C. Lupascu[1]

1-Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany
2-Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupélec, CNRS-UMR8580,Université Paris-Saclay, France
3-Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany
vladimir.shvartsman@uni-due.de

The electrocaloric effect (ECE) is considered as a promising approach for developing compact solid-state environmentally-friendly cooling devices [1]. This has stimulated quest for materials showing a large ECE around room temperature. Solid solutions based on $BaTiO_3$ are among the promising systems. In this environmentally friendly compound substitution in either A- or B-site of the perovskite lattice allows to tune the ferroelectric-paraelectric phase transition, where the maximal ECE occurs, towards room temperature. In spite of intensive studies, there is still a lack of direct measurements of the ECE in such compositions. In this presentation we report on direct measurements of the ECE in $BaTiO_3$, $Ba(Ti_{1-x}Sn_x)O_3$ (BTSn), and $Ba(Ti_{1-x}Zr_x)O_3$ (BTZr) ceramics using both a modified differential scanning calorimeter and a specially built quasi-adiabatic calorimeter. All studied materials shows the maximal ECE slightly above the Curie temperature. The ECE peaks also at the orthorhombic-tetragonal phase transition. While in $BaTiO_3$ single crystal the sign of the ECE at the orthorhombic-tetragonal phase transition might be negative [2], it is positive in ceramics. For the BTSn and BTZr ceramics substitution of Ti results in a merger of different ferroelectric phases of parent $BaTiO_3$ at $x \approx 0.10$. These compositions show the largest ECE. On further reducing of the Ti content a cross-over to the relaxor behavior occurs. On the one hand, it is accompanied by a decreasing maximal value of the ECE. On the other hand, the peak of the ECE broadens and a large ECE is observed in a wider temperature range. Results of the direct measurements are compared with the indirect estimation of the ECE from temperature dependences of polarization. The discrepancy between the results of the two methods is discussed.

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Memristive behavior of ultrathin ferroelectric $Hf_xZr_{1-x}O_2$ - based junctions

Vitalii Mikheev*, Anastasia Chouprik, Yury Lebedinskii, Andrei Zenkevich, Dmitry Negrov
Moscow Institute of Physics and Technology, Moscow, Russia
vital1kamix93@gmail.com

Recent discovery of ferroelectricity in doped polycrystalline HfO_2 thin films stabilized in a non-centrosymmetric orthorhombic phase (o-HfO_2) [1] has attracted much attention, since this class of materials can solve most critical problems of ferroelectric (FE) memory technologies: the compatibility with Si and CMOS process as well as high leakage currents across perovskite ferroelectrics. Furthermore, it has been demonstrated that ferroelectricity persists in ultrathin $Hf_{0.5}Zr_{0.5}O_2$ layers [2], which paves the way for the design of HfO_2-based ferroelectric tunnel junction (FTJ) devices. Classic FTJ incorporates a potential barrier, which is thin enough to allow direct electron tunneling between two metal electrodes. The polarization reversal in the FE alters the electron tunneling resistance due to changes in the asymmetric potential profile [3].

The main challenge in HfO_2-based FTJ is to control the current across grain boundaries in polycrystalline films (Fig. 1). One of the promising approaches is the use of highly doped semiconductor as one of the electrodes. In this case, the modulation of the potential profile close to the interface occurs due to redistribution of space charge following the polarization reversal [4]. It has been shown previously [4] that the large fraction of non-FE monoclinic phase in 2.5 nm-thick $Hf_{0.5}Zr_{0.5}O_2$ films reduces the effect of polarization switching, since significant part of grain boundaries is located far from FE o-phase.

In this work, we have improved the effect of electroresistance change by optimization the parameters of FE layer in p^+-Si/$Hf_xZr_{1-x}O_2$/TiN junctions. Careful engineering of the device composition and processing has allowed to optimize the minimal thickness (5.5 nm) of FE layer which comprises FE o-phase only. For such optimized junctions the memristive property, i.e. continuous electroresistance change upon gradual polarization reversal in polycrystalline FE $Hf_xZr_{1-x}O_2$ films, has been demonstrated for the first time (Fig. 2).

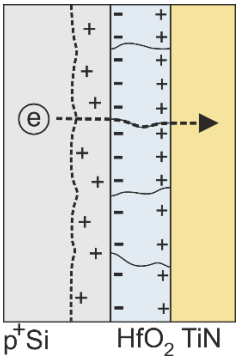

Fig. 1. Schematic representation of electron transport in polycrystalline FE HfO_2

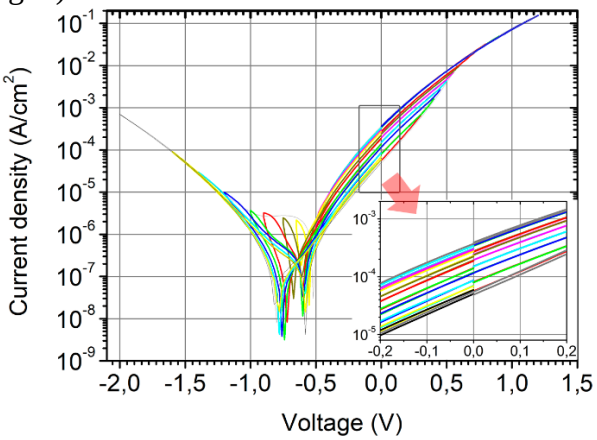

Fig. 2. Memristive effect at bias voltage U= -0.7 V applied to p^+-Si bottom electrode.

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Improved ferroelectric performance of La:$Hf_{0.5}Zr_{0.5}O_2$ thin films

M.G. Kozodaev[1*], A.G. Chernikova[1], R.R. Khakimov[1], C. S. Hwang[1,2] and A.M. Markeev[1]

[1]*Moscow Institute of physics and technology, 141700, Dolgoprudny, Moscow region, Russia*

[2]*Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Seoul 08826, Republic of Korea*

corresponding author: kozodaev.mg@mipt.ru

Ferroelectricity (FE) in doped HfO_2 thin films which was firstly reported in 2011 [1] is now a quite relevant topic due to the possibility of its implementation into ferroelectric memory (FeRAM) since it provides numerous advantages over perovskites, including CMOS and BEOL compatibility. However, different fundamental and technological tasks are upcoming.

The first one is suppression of parasitic m-phase stabilization in order to improve the ferroelectric response. The most effective way to solve this problem was doping by La, Y and Gd [2, 3]. However, the dopant concentration window in these cases is quite narrow; moreover, a high-T annealing (≈550 °C), exceeding the BEOL limit (400-450 °C), was required.

Secondly, HfO_2-based FE films are characterized by high coercive field (1.0-1.5 MV/cm) compared to PZT (0.1-0.2 MV/cm) [4], which requires 2.5-3.0 V of operating voltage to achieve the saturated polarization value. However, such field is very close to the breakdown one, which usually results in early hard breakdown. Consequently, the practical switching endurance of such films is limited by value ~10^9 which is significantly smaller than for PZT (~10^{12}). Therefore, decrease of the coercive field is highly desirable.

The aim of the present work was a deeper insights into phase transitions in ternary La:$Hf_{0.5}Zr_{0.5}O_2$ system. For such task four different La concentrations in the range 0.7-2.1 mol. % were utilized. It was shown that the crystallization temperature of these films did not exceed 400 °C. The detailed structural and electrical measurements were carried out to investigate such films. XRD data analysis allowed to expect t→o phase transition during La concentration variation, which was confirmed by small-signal CV measurements and DC-IV measurements which revealed a significant change in *k* value and leakage current density, respectively. In addition AFE-like to FE-like transition occurred during field cycling for two intermediate La concentrations. As a result of such detailed analysis rather promising ferroelectric response and long endurance following 5×10^{10} cycles with no breakdown was obtained.

This work was supported by Russian Science Foundation (Project. No 18-19-00527).

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WEDNESDAY
June 27, 2018

SECTIONS

Characterization & Properties of Ferroelectrics

Processing of Ferroelectric Crystals, Ceramics and Thin Films

Structural phase transitions in hybrid perovskites

Mantas Šimėnas[1], Sergejus Balčiūnas[1], Aneta Ciupa[2], Irina Anusca[3], Šarūnas Svirskas[1], Vytautas Samulionis[1], Maksim Ivanov[1], Vladimir V. Shvartsman[3], Doru C. Lupascu[3], Miroslaw Mączka[2], Georg Völkel[4], Andreas Pöppl[4], Jūras Banys[1]

1- Faculty of Physics, Vilnius University, Vilnius, Lithuania
2- Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland
3- Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany
4- Faculty of Physics and Earth Sciences, Universität Leipzig, Leipzig, Germany

juras.banys@ff.vu.lt

Recently, significant scientific attention has been concentrated on hybrid organic-inorganic perovskites. Highly attractive families of these compounds are metal-formate frameworks $[A][M(HCOO)_3]$ and methylammonium lead halides $CH_3NH_3PbX_3$ [1] (Figure 1). Here A^+ is a molecular cation such as dimethylammonium, M^{2+} denotes a transition metal ion and X = I, Br, Cl. The former perovskites are highly interesting as single phase multiferroic materials, while lead halides are extremely popular as efficient solar cell absorbers.

In both perovskites, the structural phase transitions occur due to the ordering of the central molecular cation and framework deformation. We present a comprehensive study of these transitions in selected members of both families. The compounds were characterized using various experimental techniques such as multifrequency electron paramagnetic resonance, broadband dielectric spectroscopy, ultrasonic measurements and others [2,3].

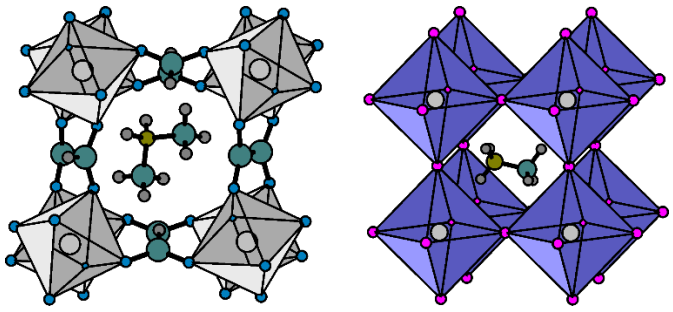

Figure 1. Structures of $[(CH_3)_2NH_2][Mn(HCOO)_3]$ and $CH_3NH_3PbI_3$ hybrid perovskites.

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Measurement Method of Depth Profile in Polarity-Inverted Layered Structure Using Scanning Nonlinear Dielectric Microscopy with Soft Probe tip

Hiroyuki Odagawa[1], Yohei Tanaka[1], Yasuo Cho[2]

1- National Institute of Technology, Kumamoto College, Japan
2- Research Institute of Electrical Communication, Tohoku University, Japan
odagawa@kumamoto-nct.ac.jp

Piezoelectric or ferroelectric materials such as ZnO, AlN, $LiNbO_3$, $LiTaO_3$, PZT are widely used in ultrasonic devices and optical devices including surface acoustic wave and bulk acoustic wave filters and sensors, actuators, optical devices and so on. Use of the polarity-inverted structure of them will be the important options to improve the device performance in the next stage.

Recently, it was reported that the polarity of ZnO and AlN piezoelectric thin film fabricated by radio frequency (RF) magnetron sputtering method can be switched by changing the growth condition, and polarity-inverted structure has been obtained [1]. That technique is applicable to piezoelectric MEMS devises so that small size and high performance piezoelectric devices will be realized.

On that background, we have proposed the quantitative measurement method for the thickness of a polarity inverted layer in ferroelectric or piezoelectric thin film [2, 3]. It is performed by surface measurement using scanning nonlinear dielectric microscopy (SNDM) non-destructively [4].

In this paper, we expand it to double-layered structure and measure the thickness of the two inverted layers by controlling depth profile of electric field inside the measurement materials using a soft probe tip. We will describe a principle for determining the thickness of two layers. Also, we will show experimental results of the thickness determination as well as well as the simulation results.

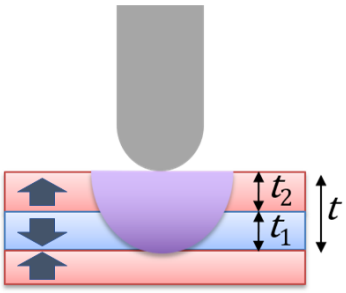

Fig. 1. Structure of the measurement sample.

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Atomic-scale Visualisation of Magnetic Cation Partitioning in Multiferroic Aurivillius Phase Thin Films

L. Keeney[1*], M. Schmidt[1], C. Downing[2], V. Nicolosi[2], M.E. Pemble[1,3], R. W. Whatmore[3,4]

1-Tyndall National Institute, University College Cork, 'Lee Maltings', Dyke Parade, Cork, Ireland.
2-School of Chemistry, CRANN, AMBER, Trinity College Dublin, Dublin 2, Ireland.
3-Department of Chemistry, University College Cork, Cork, Ireland.
4-Department of Materials, Faculty of Engineering, Imperial College London, SW7 2AZ, United Kingdom.
**Lynette.keeney@tyndall.ie*

Multiferroic materials, possessing simultaneous ferroelectric and ferromagnetic memory states, have been road-mapped as promising multi-state architectures for memory scaling beyond current technologies. The layered-structured Aurivillius phase, $Bi_6Ti_xFe_yMn_zO_{18}$ (B6TFMO), is a rare example of a single-phase multiferroic material demonstrating magnetoelectric switching at ambient temperature.[1, 2, 3] To produce samples with optimised and reliable magnetic response and to exploit this material for future data storage technologies, it is necessary to understand the origin of the room temperature magnetisation.

There are five perovskite layers per half-unit cell (m = 5) in the B6TFMO structure, giving three symmetrically-distinct *B*-site locations over which the magnetic cations (Mn and Fe) can be distributed. In this work we have used atomic resolution scanning transmission electron microscopy, EDX and EELS to discover how closely-packed Ti/Mn/Fe cations of similar atomic number are arranged within the 5- perovskite-layer Auivillius structure.

Direct evidence for partitioning of the magnetic cations (Mn and Fe) to the central three of the five perovskite layers within the Aurivillius phase structure is demonstrated at the atomic scale.[4] We infer that the clear preference for Mn cations to partition into the central perovskite layer is due to strain- and electrostatic-energy considerations. We reveal further changes in the relative proportions of magnetic ions in the region of stacking fault defects and out-of-phase boundaries. The observed increase (>8%) in magnetic cation content at the central perovskite layers provokes up to a 90% increase in potential FM spin alignments in the central layer and this could be key in terms of creating pathways to the long-range room temperature magnetic order and the unique room temperature multiferroic properties observed for B6TFMO.

Acknowledgements: This publication has emanated from research conducted with the financial support of the Royal Society and Science Foundation Ireland (SFI) University Research Fellowship UF 140263 and SFI funded centre AMBER (SFI/12/RC/2278).

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∂C/∂z-Mode Scanning Nonlinear Dielectric Microscopy for Local Permittivity Imaging

Yoshiomi Hiranaga, Yasuo Cho

Research Institute of Electrical Communication, Tohoku University, Japan
hiranaga@riec.tohoku.ac.jp

The importance of nanoscaled imaging or characterization of dielectric materials are growing up with miniaturization and performance enhancement of dielectric devices. Scanning nonlinear dielectric microscopy (SNDM) is a technique which can detect capacitance variation with high sensitivity. Conventional SNDM has mainly been used for observation of local electrical anisotropies through nonlinear permittivity measurement. Meanwhile, for liner permittivity imaging, a novel approach named ∂C/∂z-SNDM has been proposed recently. In this study, we discussed quantitative permittivity measurement using this technique.

Figure 1 presents a schematic diagram of the ∂C/∂z-SNDM instrumentation. The measurement probe consists of a free-running active LC oscillator and a conductive cantilever tip attached to an LC resonator, just as in conventional SNDM. This probe can detect the capacitance variation beneath the probe tip resulting from the cantilever vibration and determine the local permittivity of the measurement sample because the capacitance variation is dependent on the permittivity.

A cross-section of a multilayer oxide film was visualized using the ∂C/∂z-SNDM as a demonstration, as shown in Figure 2, and numerical simulations of the response signals were conducted to gain additional insights. The experimental signal intensities were found to be in a good agreement with the theoretical values, with the exception of the background components, demonstrating that absolute sample permittivity values could be determined. Additionally, the beneficial aspects of higher-harmonic response imaging were discussed, taking into account assessments of spatial resolution and quantitation.

Acknowledgments
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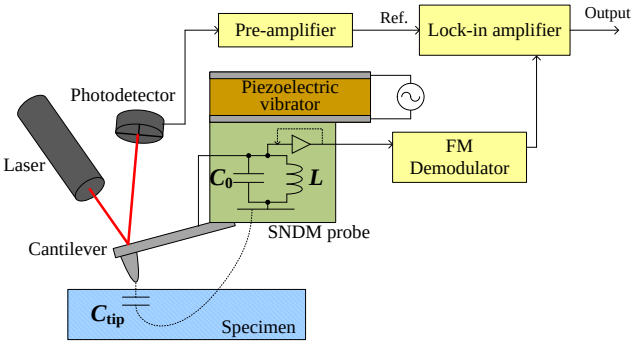

Figure 1. Schematic diagram of the ∂C/∂z-SNDM apparatus.

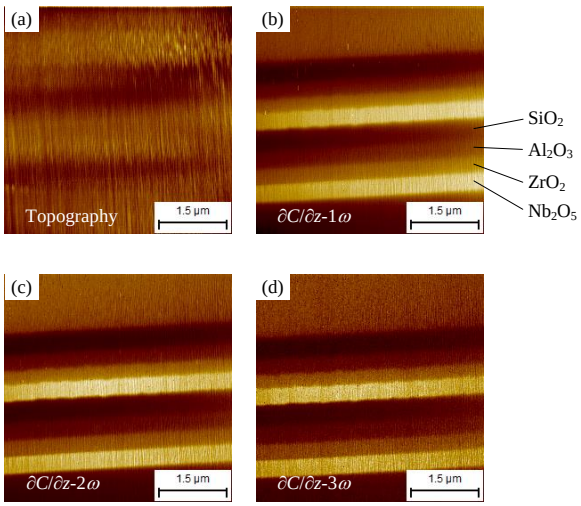

Figure 2. Topography and (b)-(d) permittivity images of a multilayer oxide sample acquired using the ∂C/∂z-SNDM technique with (b) 1ω, (c) 2ω, and (d) 3ω harmonic response signals.

Chemical Solution Deposition of Porous PZT Films

Dmitry Seregin[1], Nina Kotova[1], Liubov Delimova[2], Nina Zaitseva [2], Konstantin Vorotilov[1], Alexander Sigov[1]

*1- Moscow Technological University (MIREA), Vernadsky prosp., 78, Moscow, 119454, Russian Federation (*email: assigov@yandex.ru)*
2- Division of Solid State Electronics, Ioffe Institute RAS, Saint-Petersburg, 194021, Russian Federation

Corresponding_author_vorotilov@mirea.ru

Porous ferroelectric films with a random and regular pore structure are prospect media for different kinds of electronic devices: MEMS, pyroelectric detectors, memory, etc. They can also be used for creation of composite structures, for example ferroelectric/magnetic, ferroelectric/semiconductor, etc. In chemical solution deposition (CSD), porous structure is formed by addition of porogens – organic substances which are destroyed during a heat treatment, leaving empty pores, see e.g.[1]. Different precursor chemistries result in different porous structures.

Zirconium monosolvate isopropylate, titanium tetraisopropoxide, and anhydrous lead acetate produced by solid-state synthesis were used as precursors to prepare the film-forming solution. Polyvinylpyrrolidone (PVP) with different molecular weights and concentration was used as a porogen, and different kinds of surfactants as a template for evaporation induced self-assembly (EISA) process. The $PbZr_{0.48}Ti_{0.52}O_3$ films were formed on silicon wafers with a Pt (150 nm)/ TiO_2 (10 nm)/ SiO_2 (300 nm) /Si structure. X-ray diffraction, scanning electron microscopy, piezoelectric force microscopy, ellipsometry, dielectric hysteresis, capacitance-voltage and current-voltage dependences, photo induces currents are used for the characterization of films properties.

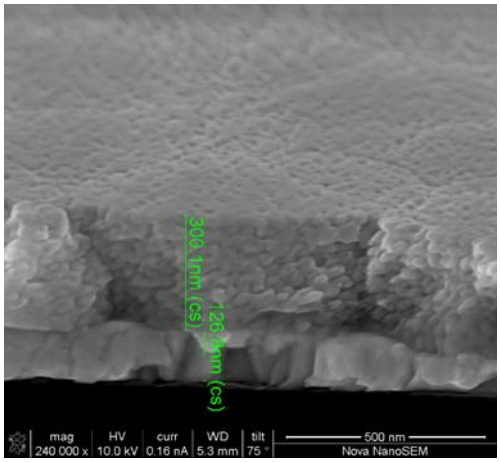

Fig1. SEM cross section view of porous PZT film

The film structure is dramatically changed with the kind and concentration of porogen: from separated voids in the body of perovskite column grains to spongy polycrystalline (see Figure 1). Dielectric constant is gradually decreased; however remanent polarization maintains sufficiently high value as a result of mechanical stress relaxation that is important, for instance, for application in infrared detectors. We discuss methods to control pore and crystalline structure of the films.

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Composition control of sputtered $Pb(Ti_xZr_{1-x})O_y$ films by oxygen pressure adjustment

V.G. Beshenkov, V.A. Marchenko, A.G. Znamenskii

Institute of Microelectronics Technology and High_Purity Materials, Russian Academy of Sciences, Chernogolovka, Russia

marchenk@iptm.ru

The report presents measured values of deposition rate, film relative concentration Pb/(Ti+Zr), substrate temperature in dependence on oxygen partial pressure P_{O2}, and radial distributions of thickness and concentration at different P_{O2}.

$Pb(Ti_xZr_{1-x})O_y$ (PZT) films were deposited by HF magnetron sputtering of $Pb(Ti_{0.48}Zr_{0.52})O_3$ target with identical discharge power (100 W) and argon pressure (P_{Ar}=2.5*10^{-3}mbar) in a gas mixture $Ar+O_2$ without intention substrate heating.

Important features of data obtained are strong fall of deposition rate and peak of Pb content in narrow P_{O2} range (fig.1) and local minimum of Pb content in the film area under the erosion groove at high P_{O2} (fig.2, profile 4 correspond to W=200W and smaller target to substrate distance).

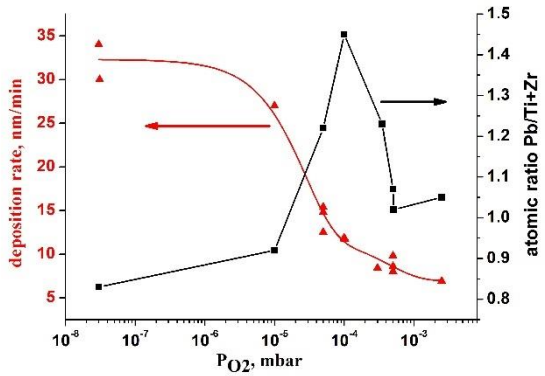

Fig.1 Deposition rate and Pb/(Ti+Zr) ratio in film center in dependence on P_{O2}.

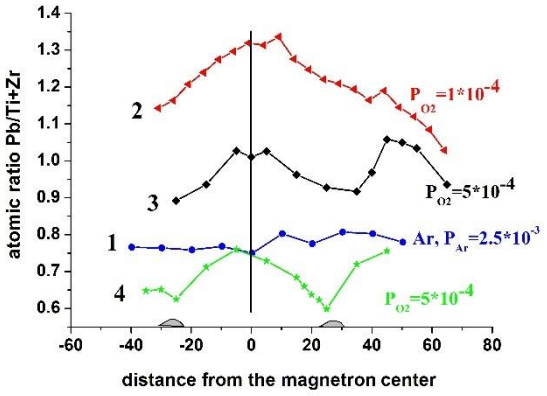

Fig.2 Pb/(Ti+Zr) ratio profiles. Profile 4 correspond to W=200 W and smaller target to substrate distance.

The data obtained are discussed in terms of redox reactions at target and film surfaces, film resputtering by reflected Ar ions, negative oxygen ions generation and reflection of lighter Ti, Zr atoms and its oxides from heavier Pb atoms at the film surface [1].

The practical value of the results is adjustment of PZT film composition by simple control of oxygen flow.

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Flexoelectricity as an additional mechanism of nonlinear response for two-beam coupling in photosensitive crystals

Stanislav Shandarov[1], Vasiliy Shepelevich[2], and Nikolai Burimov[1]

1-Department of Electronic Devices, Tomsk State University of Control Systems and Radioelectronics, Tomsk 634050, Russia
2-Department of Theoretical Physics and Applied Informatics, I.P. Shamyakin Mozyr State Pedagogical University, Mozyr 247760, Belarus
stanislavshandarov@gmail.com

We describe the main phenomena connected with elastic fields accompanied the non-uniform distributions of electric field in photosensitive crystals, which have been created by interference pattern at two-beam interaction. An occurrence of such elastic in photorefractive crystals is due to converse piezoelectric and flexoelectric effects (see, e.g., [1] and [2], and references therein).

Using the known approach [3] and the approximations of a one-dimensional space-charge field grating as well as the absence of spatial dispersion we have obtained the general expression for attendant elastic strains in the crystals with any symmetry. An elastic strain determined by converse piezoelectric effect is in-phase with electric field [3], whereas the converse flexoelectricity produces the distribution shifted by $\pi/2$. The magnitude of such nonshifted elastic component is independent on fringe spacing Λ of the grating and is determined by piezoelectric properties of the crystal [1, 3]. By contrast, the flexoelectrically induced elastic response varies inversely with Λ and can be different from zero in centrosymmetrical photosensitive media also [2].

We consider the contribution of converse flexoelectric and elasto-optic effects to the interaction between a strong stationary reference wave and a weak phase-modulated signal wave on the grating of the diffusion type in the cubic photorefractive crystals. It is shown that flexoelectricity provides the presence of linear component in phase-demodulation signal of adaptive holographic interferometer in the such cases: (i) contradirectional interaction in sillenite crystals for waves with circular polarizations of opposite signs; (ii) contradirectional interaction in crystals of symmetry group 43m for identical linear polarization of the waves; (iii) codirectional interaction in the (110)- and (111)-cut cubic photorefractive crystals for waves with identical polarizations.

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Strain Effects and Electronic Structures of Narrow Band Ruddlesden-Popper Ferroelectrics: First Principles Calculation

Nedim Bozdag[1], Husnu Koc[1], Sevket Simsek[2], Amirullah M. Mamedov[3,4], Ekmel Ozbay[3]

1-Siirt University, Faculty of Science and Letters, Department of Physics, Siirt, Turkey
2- Hakkari University, Faculty of Engineering, Department of Material Science and Engineering, 3000, Hakkari, Turkey
3-Nanotechnology Research Center, Bilkent University, Bilkent, Ankara, Turkey

4-Baku State University, International Scientific Center, Baku, Azerbaijan
Corresponding Author: husnu_01_12@hotmail.com

First-principles density functional theory is used to investigate the structural, mechanical, lectronic and optical properties of the Ruddlesden–Popper(RP)$Ba_3X_2S_7$ (X=Zr, Hf, Ti) compounds. The generalized gradiend approximation has been used for modeling exchange-correlation effects.It has been observed that the calculated lattice parameters are in good agreement with the experimental values. The tetragonal $Ba_3X_2S_7$ compounds with I4/mmm symmetry from the calculated formation energy (E_o) values are thermodynamically stable at the ground state. Bulk modulus (61.15 GPa, 63.38 GPa, and 51.30 GPa), shear modulus (33.09 GPa, 35.71 GPa, and 32.67 GPa), Young's modulus (81.44 GPa, 87.63 GPa, and 80.40 GPa), and Poisson's ratio (0.28, 0.27, and 80.40) fron the calculated elastic constants for $Ba_3Zr_2S_7$, $Ba_3Hf_2S_7$, and $Ba_3Ti_2S_7$ compounds, respectively have been obtained. For all three compounds from the obtained Poisson's ratio ($\upsilon = 0.25$) and G/B (covalent if the G/B≈1, ionic if the G/B≈0.6) ratio, The ionic character are dominant.We can say that these materials are almost stiffness materials when we consider the value of Young's modulus, which is a measure of stiffness;if the B/G ratio is less (high) than 1.75, a material is brittle (ductile). Therefore, $Ba_3Ti_2S_7$ is brittle while $Ba_3Zr_2S_7$ and $Ba_3Hf_2S_7$ compounds are ductile.The Debye temperature and sound velocity for these compounds have been also calculated.The Debye temperature is low for soft materials and high for rigid materials. The rigid order of these compounds: are $Ba_3Ti_2S_7$>$Ba_3Zr_2S_7$>$Ba_3Hf_2S_7$.The obtained electronic band structure for $Ba_3Zr_2S_7$and $Ba_3Hf_2S_7$ compounds are semiconductor in nature, and the $Ba_3Ti_2S_7$ compound also is semi-metal. Similar to ferroelectric oxides, there are pronounced hybridization of electronic states between X-site cations and anions in $A_3X_2S_7$. Based on the obtained electronic structures, we further calculate the frequency-dependent dielectric function and other optical functions in different phases.

Properties of ferroelectric perovskite superlattices

A.S.Sidorkin[1], L.P.Nesterenko[1], Y.Gagou[2], P.Saint-Gregoire[3], A.Yu.Pakhomov[1], N.G.Popravko[1]

[1]Voronezh State University, Russia
[2]Universite de Picardie Jules Verne, 80039 Amiens Cedex, France
[3]ICGM, C2M, 34095 Montpellier Cedex, France
University of Nimes, 30021 NIMES Cedex 01, France

sidorkin@phys.vsu.ru

The article presents the results of research of the structural, dielectric and repolarization properties of epitaxial ferroelectric superlattices (SL) in the form of 32 sequentially deposited layers of barium zirconate BaZrO3 (BZ) and barium titanate BaTiO3 (BT) with thicknesses of 6.65 nm and 6,672 nm, respectively. These superlattices were obtained by pulsed laser deposition on a substrate of monocrystalline magnesium oxide MgO with (001) orientation with the $La_{0.5}Sr_{0.5}CoO_3$ sublayer as a bottom electrode.

The structural reflex obtained from investigated structure indicates that the synthesized SLs are single-crystal. The temperature measurements of permittivity ε and dielectric hysteresis loops showed that at 393 °C the ferroelectric phase transition is observed in the SLs. The behavior of permittivity near the Curie point demonstrates the law of "two" and the absence of temperature hysteresis. With increasing of the applied field frequency the values of permittivity are decreased in the whole investigated temperature interval without changes of Curie point position. The values of spontaneous polarization and coercive field obtained by dielectric hysteresis loops at room temperature are P_s = 22 μC/cm^2 and E_c = 135 kV/cm. The investigated SLs have an internal displacement field E_{bs}, approximately equal to 30 kV/cm, directed from the superlattice to the substrate.

Study of the repolarization properties of BZ / BT superlattices with rectangular pulsed fields showed that the dependence of the maximum switching current on the applied field here, as in the case of conventional bulk and film of ferroelectric material, characterized by the presence of "activation" and the linear sections, separated by the so-called threshold field. The magnitude of said threshold field E_{th} approximately coincides with the value of the coercive field defined by dielectric hysteresis loops, and decreases with the approaching to the Curie point. For switching currents in weak fields there is a deviation from a simple exponential dependence of current on the inverse of the applied field, which can be approximated by introducing an addition exponent in said power dependence.

Hyperfine interactions and spatial spin-modulated structure of multiferroics $Bi_{1-x}Cr_xFeO_3$ (x = 0 - 0.20)

Vyacheslav Rusakov[1], Vyacheslav Pokatilov[2], Alexander Sigov[2]., Alexey Belik[3], Michael Matsnev[1], Alexey Gapochka[1], Kyrill Kulakov[1].

[1] Lomonosov Moscow State University, Moscow, Russia

[2] Moscow Technological University (MIREA), Moscow, Russia

[3] National Institute for Materials Science, Tsukuba, Japan

pokatilov@mirea.ru

It is known that a partial substitution of transition 3*d* atoms for Fe atoms in multiferroics based on $BiFeO_3$ markedly improves its electrical and magnetic properties. This effect is explained by perturbation and destruction of the spatial spin-modulated structure (SSMS) of the cycloid type existing in ferrite $BiFeO_3$. In order to establish the existence of SSMS and the influence of impurity atoms on SSMS in $BiFeO_3$, methods are needed that allow to observe and diagnose this structure. One such method is Mössbauer spectroscopy.

^{57}Fe Mössbauer study of the SSMS as well as electric and magnetic hyperfine interactions in multiferroics $BiFe_{1-x}Cr_xO_3$ with rhombohedral structure were carried out. The Mossbauer spectra have been analyzed in terms of the incommensurate anharmonic SSMS of cycloid type model. The synthesis of the samples with x = 0.05, 0.10, 0.20 was performed under a pressure of 6 GPa at a temperature of 1250 K for 1.5 h. Phase composition of samples was characterized by X-ray diffraction. All substituted ferrites contained the positions of the iron atoms in the first cation coordination sphere of which there are one, two, three, and four atoms of Cr depending on the composition of ferrites. The temperature ranges of existence of incommensurate anharmonic SSMS of the cycloid type were determined for these ferrites. The parameter of anharmonicity *m* increases with increasing concentration of chromium in ferrites. Based on the data obtained, a magnetic phase diagram was constructed (see figure).

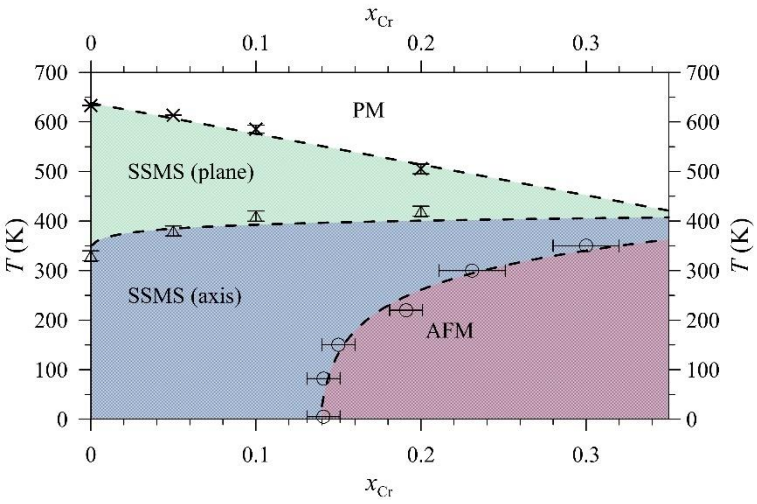

Figure. Magnetic phase diagram of the system of $Bi_{1-x}Cr_xFeO_3$ in the axes of "the impurity concentration x_{Cr}" – "temperature *T*": PM – region of the paramagnetic state, SSMS (axis) – area anharmonic SSMS (axis) with magnetic anisotropy of "easy axis", SSMS (plane) – anharmonic SSMS with magnetic anisotropy of "easy plane", the AFM – region of antiferromagnetic ordering.

In the framework of the model of SSMS, the temperature dependences of the hyperfine parameters of the ^{57}Fe Mössbauer spectrum – the isomer shift, the quadrupole shift of the spectral components, isotropic and anisotropic contributions to the hyperfine magnetic field – were obtained and analyzed.

This work was supported by the Russian Foundation for Basic Research (project no. 14-02-01109a) and the Ministry of Education and Science of the Russian Federation (project no. 3.5859.2017/BCh).

Comparison of ferroelectric properties in ALD vs. PVD deposited $Hf_{1-x}Zr_xO_2$ films

T. Mittmann,[1] M.H. Park,[1] C. Richter[1], T. Mikolajick[1,2], and U. Schroeder[1,*]

[1]*Namlab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany*
[2]*Chair of Nanoelectronic Materials, TU Dresden, 01062 Dresden, Germany*
Terence.Mittmann@namlab.com

The recently discovered orthorhombic phase in thin doped hafnium oxide films [1] enabled scaling of non-volatile ferroelectric random access memory cells in one-transistor-one-capacitor three-dimensional structures or ferroelectric field effect transistors. Various dopants were found to stabilize the ferroelectric orthorhombic phase in HfO_2. However, a solid state solution of hafnia and zirconia allows the widest known process window together with high remanent polarization values at reasonable semiconductor processing temperatures of 400-500°C [2].

This study analyses the structural (SEM, XRD) and electrical changes of ferroelectric HZO films deposited by atomic layer deposition (ALD) in comparison to physical vapor deposited (PVD) sputtered layers. Planar metal-ferroelectric-metal stacks of different composition and thickness are prepared in between TiN electrodes. An increase of the annealing temperature from 500 to 1000 °C results in a higher amount of the ferroelectric orthorhombic phase portion, but also a reduced field cycling endurance is caused for both deposition methods. For ALD based HZO an improved field cycling behavior is visible for higher ZrO_2 content compared to higher endurance for PVD deposited layers with low remanent polarization. Here, ALD films showed an appearance of the ferroelectric properties at lower temperatures. Clear differences were also seen for the composition dependence of the film in relation to the Hf:Zr ratio. Ferroelectric properties are confirmed in PVD deposited pure HfO_2 films, but not for ALD layers at the used condition. Impedance spectroscopy indicated the existence of an interfacial dead layer and its widening for higher anneal temperatures.

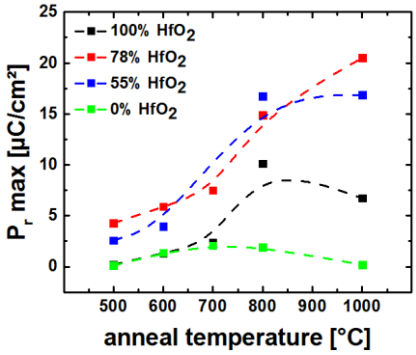

Fig. 1: Remanent polarization for PVD deposited $Hf_{1-x}Zr_xO_2$ films for different anneal temperatures.

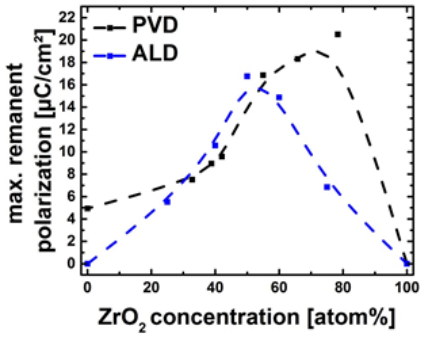

Fig. 2: Comparison of remanent polarization for different ZrO_2-concentrations of ALD and PVD deposited films.

As a result, ALD films are easier applicable to 3D capacitor structures and PVD layers for planar devices with higher thermal budget.

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Enhanced permittivity in $BaTiO_3$ composites as result of silver addition and critical grain size ~1μm

Ina Turcan, Vlad Alexandru Lukacs, Lavinia Curecheriu and Liliana Mitoseriu

Dielectrics, Ferroelectrics & Multiferroics Group, Faculty of Physics, "Alexandru Ioan Cuza" University of Iasi, Iasi, Romania
Corresponding_author_ina.turcan@yahoo.com

The effect of second phase additions into ferroelectrics or polar dielectrics matrix attracted high interest in searching for improved mechanical and electrical properties of composites. Finite element calculations demonstrated that both the linear and nonlinear dielectric properties in dielectric composites with conductive fillers can be tuned through inhomogeneous field distributions at the interfaces between di-similar materials, i.e. creating regions subjected to high fields and generating enhanced electrical response [1].

The present work aimed to optimize the sintering parameters in 5 vol% Ag-$BaTiO_3$ composite ceramics with in an attempt to increase permittivity through the synergy effect of high density, presence of metallic particles and preferred critical ceramic grain size of ~1μm, for which $BaTiO_3$ has a well-known maximum of its permittivity [2]. Ag-$BaTiO_3$ composite ceramics have been prepared by sintering the mixture of powders at temperatures above silver melting point (1000°C – 1300°C/2h) in open atmosphere. The resulting ceramics have relative densities of 76% – 94%, with ceramic grain sizes in the range of 350nm – 2800nm and bi-modal distribution of silver filler, with both fine Ag inclusions and large agglomerates embedded into the ceramic matrix. The frequency and temperature dependence of the dielectric properties have been investigated and discussed. As extracted from finite element computations, the addition of Ag particles in $BaTiO_3$ matrix results in field concentration in particular regions and therefore, in enhanced dielectric response with an increase of permittivity of about 7% with respect to pure $BaTiO_3$. The dispersion mechanisms and the role of oxygen vacancies on the dielectric relaxation responses has been also investigated.

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Compositional variation of lead zirconate titanate thin films near morphotropic phase boundary, formed by radio frequency magnetron method

Igor Pronin [1,2], Eugenii Kaptelov[1,2], Stanislav Senkevich[1,2], Dmitriy Dolgintsev[2], Vladimir Pronin[2], Dmitry Kiselev[2,3], Sergey Nemov[4]

1-Ioffe Institute, Russia
2-The Herzen State Pedagogical University of Russia
3-National University of Science and Technology "MISiS", Russia
4-Peter the Great St. Petersburg Polytechnic University, Russia
Corresponding_author_petrovich@mail.ioffe.ru

Thin ferroelectric films of lead zirconate titanate ($PbZr_{1-x}Ti_xO_3$ or PZT) are basic components for microelectromechanical systems (MEMS). Extreme dielectric and electromechanical properties of PZT as well known can be observed in narrow band of solid solutions with a composition corresponding to the region of morphotropic phase boundary (MPB) (at $x \approx 0.46 - 0.48$) [1]. The task of the work was the search for optimal compositions of self-poled PZT thin films [2-3] formed by RF magnetron sputtering of ceramic target (x = 0,46). The variation of the compositions (Zr and Ti proportion) was held by variation technological parameters of the sputtering such as the working gas pressure and the target - substrate distance.

The films were fabricated in two stage process on $Pt/TiO_2/SiO_2/Si$ substrate. At the first stage, PZT films were deposited at low substrate temperatures (~150°C) in vacuum camera. The two series of the samples were prepared. The first ones were deposited by varying the working gas ($Ar + O_2$) pressure in the range of 2-8 Pa at the target - substrate distance equal 50 mm. The second ones were made by varying the distance in the range 30-70 mm at the gas pressure equal 8 Pa. At the second stage, ones were annealed and crystallized into perovskite phase at 580-650°C in the conventional furnace. The films thickness was varied from 500 to 1000 nm. The structural, ferroelectric and piezoelectric properties of the films have been studied. Microstructure, composition and piezoelectric response of the films were studied using SEM EVO-40 (Zeiss) and AFM-PFM Ntegra (NT MDT, Zelenograd).

The results have shown the films composition ("x") may be changed up to 2-2.5% by varying the above mentioned technological parameters. The interpretation of the results was made on the base of the processes of thermalization and diffusion of streams of sputtered atoms of Pb, Zr and Ti in gas plazma. The change of structural, dielectric and piezoelectric properties depending on PZT composition are discussed.

The work was partly supported by the Ministry for Education and Science (Russian Federation) (Grant No 16.2811.2017/4.6) and Russian Fond for Basic Research (Grant No 16-02-00632).

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Optical vortices formation by controllable holographic diffraction structures in liquid crystal – photopolymer compositions

Artem Semkin[1], Sergey Sharangovich[1]

1-Tomsk state university of control systems and radioelectronics, Russia
a.o.semkin@gmail.com

Bessel-like laser radiation beams, in particular beams with a nonzero topological charge (or optical vortices), are widely used at present: from precision fiber-optic sensors to devices for nanoscale objects manipulating. To generate such beams, many methods have been developed: from magneto-optical diffraction [1] and optical wedge [2] to the most widely used method of Gauss or Laguerre-Gauss beam's diffraction on computer-generated holograms [3].

In this paper, a theoretical model of the light beams' diffraction on holographic structure formed in liquid crystal – photopolymer composition is developed. The structure makes it possible to transform the incident light fields into Bessel-like ones. Earlier in [4], a theoretical model of recording of such holograms was developed. The influence of an external electric field on the conversion efficiency of light beams is studied by numerical simulation.

To describe the problem of diffraction of extraordinary waves (the action of an external electric field does not affect the ordinary waves' diffraction), a system of coupled wave equations for the Bragg regime is compiled [5]. Its solution of this system is found in the approximation of a given field. Numerical simulations show, that the intensity distribution of the diffracted beam has a Bessel-like appearance, and the wave front has the form of a vortex. It is also shown, that with the external electric field's strength increasing the diffraction efficiency of hologram decreases, the amplitude of the diffracted beam falls. Thus this work shows that it is possible to create electrically controllable transformation elements in the liquid crystal – photopolymer compositions.

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Multifunctional phosphates and vanadates in the whitlockite family

Sergey Stefanovich, Bogdan Lazoryak

Lomonosov Moscow State University, Moscow, Russia
stefan@tech.chem.msu.ru

Polar dielectric tricalcium phosphate, $Ca_3(PO_4)_2$, is one of the main substances forming human bones and teethes. Much efforts are spending to make implants from $Ca_3(PO_4)_2$ for medicine purposes. However until very recently nobody was interested in fundamental properties of this composition entering in one of the most plural structural family of phosphates, vanadates, arsenates, and closely related to minerals whitlockite and cerite. Most of members of family are active dielectrics possessing ionic conductive, ferroelectric or antiferroelectric, luminescent, and optical nonlinear properties. Separately, or in various combinations, these properties are widely required in engineering. We correlate outstanding characteristics of $Ca_3(PO_4)_2$ and $Ca_3(VO_4)_2$ derivatives with structural peculiarities responsible for the properties:

- unique desorption of $Ca_3(PO_4)_2$ as bone implant may be related with typical for most of whitlockites the fast Ca^{2+} solid state mobility, as well as with ion-exchange substitution of some calcium to magnesium, iron, hydrogen, or other biologically active elements. We have shown that corresponding whitlockite-like compositions [1] may appear in hot water solutions;
- importance of whitlockites as promising luminescent materials arise from the rare-earth (RE) or transition metal cations distribution on 4 nonequivalent isolates positions in crystal lattice, thus providing minimal transfer of excitation and small fluorescence quenching [2];
- congruent melting of vanadate whitlockites $Ca_9R(VO_4)_2$, where R= RE, Y, Bi, allows to grow their large single crystals of stoichiometric or modified compositions assuring improvement of transparency, laser generation and optical nonlinearity parameters [3];
- dielectric dipoles order-disorder processes in whitlockites result in ferroelectric, anti-ferroelectric or paraelectric phases stabilization. The Curie temperatures (T_c) are in between 750-1600 K. They are controlled by two phase transition mechanisms, one of them displacive and other of order-disorder type. Latter mechanism involves re-orientation of one of PO_4 (VO_4) tetrahedra and is strongly influenced by nearest cation surrounding of the tetrahedra [4];
- guest atoms in Ca^{2+}-conductivity channels stimulate (Pb^{2+}) or prevent (Bi^{3+} *et.al.*) divalent cation mobility in whitlockites making level of the conductivity four or five orders different [5].

This research was supported by Russian Science Foundation (Grant 16-13-10340).

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THURSDAY
June 28, 2018

SECTION

Characterization & Properties of Ferroelectrics

Ferroelectrics in strong terahertz field

Elena Mishina

Moscow Technological University (MIREA), Russia
mishina_elena57@mail.ru

The unique feature of ferroelectrics is their ability to switch dielectric polarization allowing them to serve as key components in ferroelectric memories, actuators and electro-optical modulators. The speed of switching determines the maximum operational frequency of such devices. While for memories and actuators, polarization reversal and creation of remnant polarization is important, for modulators dynamic high frequency polarization modulations is the main operation parameter.

THz pump-probe techniques, along with characterization on ultrafast time scale give an instrument to operate dielectric polarization in a controlled manner. Electric filed can be applied to ferroelectric material in a contact-free fashion using freely propagating nearly single cycle THz pulse. The detection of the pulse-induced changes can be carried out by optical [1] or by X-Ray diffraction techniques [2]. In optical detection, time domain reflectivity (transmission) or polarization rotation are studied. For ferroelectrics, optical second harmonic generation (SHG) is widely used as optical probe as well. It is sensitive to spatial inversion (SI), and provides information on structural (ferroelectric) phase transition and polarization switching [3].

In this paper, we present the results of experimental and theoretical study of the dynamic switching of polarization in ferroelectrics and multiferroics, as well as the creation of quasi-remnant polarization (within and after action of THz field, respectively). Materials under the study were epitaxial ferroelectric (BaSr)TiO_3 film and multiferroic (BaSr)TiO_3/$BiFeO_3$ multilayers.

Sub-cycle terahertz field up to 1 MV/cm was generated by optical rectification in an organic crystal with the help of femtosecond optical pulse. As a measure of the dielectric polarization, the intensity of second harmonic generation (SHG) was recorded as a function of a delay time between THz pump and femtosecond optical probe. SHG parameters were used as measure of the order parameter (dielectric polarization).

Analysis of possible sources of SHG in the ferroelectric allows us to conclude that temporal dependence of the SHG intensity reveal a change of the polarization during the action of the THz pulse. After the action of the pulse, the system is brought to the initial state meaning that no ion transfer between the minima of potential well, i.e. true ferroelectric switching, in every unit cell occurred. Analysis also shows importance of propagation effects and dispersion of THz and optical pulses. The observed effect can be used in remotely controlled optoelectronic devices, in particular in ultrafast THz modulators.

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Piezoelectric softening at ferroelectric transitions: effect of doping in $BaTiO_{3-\delta}$

Francesco Cordero [1], Floriana Craciun[1], Francesco Trequattrini[2,1], Hans Theo Langhammer[3], Paulo Sergio da Silva Jr.[4], David A. Barbosa Quiroga[4]

1- Ist. di Struttura della Materia (ISM-CNR), Area della Ricerca di Roma-Tor Vergata, Italy
2- Dipartimento di Fisica, Università di Roma "La Sapienza", Roma, Italy
3- Inst. of Chemistry, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany
4- Department of Physics, Federal University of São Carlos, São Carlos/SP, Brazil.
Corresponding_author_francesco.cordero@cnr.it

The elastic softening occurring at pure ferroelectric transitions is of piezoelectric origin, and, neglecting fluctuations, can be written as the tensor product [1]

$$\Delta \boldsymbol{s}^{\text{piezo}} = \boldsymbol{d}^{+}.\boldsymbol{\varepsilon}^{-1}.\boldsymbol{d} \qquad (1)$$

where $\boldsymbol{s}$ is the compliance, $\boldsymbol{d}$ is the piezoelectric coefficient and $\boldsymbol{\varepsilon}$ the dielectric permittivity. Then, from elastic and dielectric measurements of an unpoled ceramic it is possible to obtain an angular average of $\boldsymbol{d}$, though different from the effective d_{33}, d_{31} and d_{15} measured on poled samples. Not all ferroelectric transitions produce simple steplike elastic softenings, but when this is the case, their amplitude is a useful measure of the local piezoelectric response in each domain of the unpoled ceramic, and hence of the potential intrinsic piezoelectric response that may be reached after full poling. This allows the piezoelectric response to be evaluated without the need of poling the sample. A quantitative test of the method has been made for the FE tetragonal phase of $BaTiO_3$ [2], and is successful sufficiently far from T_C and the next transition to the orthorhombic phase, possibly due the effect of the fluctuations, not included in Eq. (1).

The method may be useful when studying new materials, that are difficult to be fully poled for various reasons, or cannot be poled at all, for example due to excessive electrical conductivity. It can also be used to probe effects, otherwise difficult to probe, such as the effect of charge doping on the polar displacements. It has recently been shown by first-principle calculations [3], that the screening from doped electrons or holes can enhance, rather than suppress, the polar displacements. Indeed, we find that, introducing O vacancies in $BaTiO_{3-\delta}$ and therefore doping electrons, even though the Curie temperature is depressed, the amplitude of the step below T_C presents an initial increase of 17% and then stabilizes around the initial amplitude of the undoped sample, for δ up to 0.01. The microscopic state of O deficient $BaTiO_{3-\delta}$ is complicated, but the most obvious explanation of the effect is that the enhancement of the piezoelectric softening is related to the polar displacements P through $d = 2QP^2$, assuming a constant electrostrictive coupling Q, and constant ε, whose measurement is prevented by the free charges.

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Investigation of low-frequency phonon modes in $LiNbO_3$, $Mg:LiNbO_3$, and $Sn_2P_2S_6$ by active and passive methods of the terahertz wave spectroscopy

Galiya Kh. Kitaeva [1], Kirill A. Brekhov[2], Kirill A. Kuznetsov [1], Elena D. Mishina[2], Pavel A. Prudkovskii [1]

1-M.V. Lomonosov Moscow State University, Russia
2-Moscow Technological University (MIREA), Russia
Corresponding author gkitaeva@physics.msu.ru

Recent progress in the field of terahertz (THz) technologies led to the development of spectroscopic methods that provide previously inaccessible information about the behavior of the long-wave dispersion characteristics of crystal materials. We have measured and analyzed the THz-wave dispersion parameters of bulk ferroelectric crystals $Sn_2P_2S_6$, $LiNbO_3$, and $Mg:LiNbO_3$. The extraordinary dielectric function real and imaginary parts are determined for bulk $LiNbO_3$ and $Mg:LiNbO_3$ crystals in the wide spectral range of the lowest polariton branch using different methods of passive linear THz spectroscopy. At frequencies 0.1– 2.5 THz measurements were made by the method of pulsed terahertz time-domain spectroscopy (TDS), using two femtosecond laser-based schemes for generation and detection of the THz radiation. Advantages of each scheme are compared and analyzed. At higher frequencies up to 5.5 THz, the dielectric function real part is determined using a scheme of near-forward Raman scattering by phonon polaritons. A special approach is applied for measuring absorption coefficients at frequencies 1–3 THz, based on analysis of visibility of three-wave second-order interference under spontaneous parametric down-conversion. Imposing all the experimental data, for each crystal we determined the generalized approximate expression for dispersion of the complex dielectric function within the whole lower polariton branch. It is shown that the decrease in terahertz-wave absorption of lithium niobate crystals under Mg-doping is caused by changes in the defect structure and reduction of coupling of the terahertz-frequency polaritons with Debye relaxational mode [1].

THz spectroscopy studies of $Sn_2P_2S_6$ are of special interest due to the presence of previously detected ferroelectric soft mode in this spectral range [2]. Using the TDS method we studied evolution of the refractive index and the dielectric function dispersion of $Sn_2P_2S_6$ crystal in the frequency range 0.1 - 0.4 THz at temperatures before and after the ferroelectric phase transition at the Curie temperature $T_C = 64^0$C. For the waves polarized orthogonally to the vibrations of the soft mode, a break in the dependence of the refractive index near the phase-transition temperature was observed. It is shown that the imaginary part of the dielectric constant in this frequency range is well approximated by means of three vibration resonances. Dependence of the parameters of these excitations on temperature in the vicinity of the phase transition is analyzed. The ultrafast dynamics of the phonon excitation at the frequency of ferroelectric mode in $Sn_2P_2S_6$ has been investigated also using the two-color pump–probe active spectroscopy scheme [3]. Results, obtained for different temperatures of the crystal, before and after T_C, do not show effect of frequency softening.

The work was done under support of RFBR grant 16-02-00258 and RSF grant 16-12-10520.

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POSTER SESSION 1

Two-dimensional phononic band structure of Archimedean-logarithmic spiral-based slabs

Oral Oltulu [1], Selami Palaz [1], Amirullah Mamedov [2,3] , Ekmel Ozbay [2]

1-Department of Physics, Faculty of Science and Letters, Harran University, Sanliurfa, Turkey
2- Nanotechnology Research Center (NANOTAM), Bilkent University, Ankara, Turkey
3- International Scientific Center, Baku State University, Baku, Azerbaijan
Corresponding_author_mamedov46@gmail.com

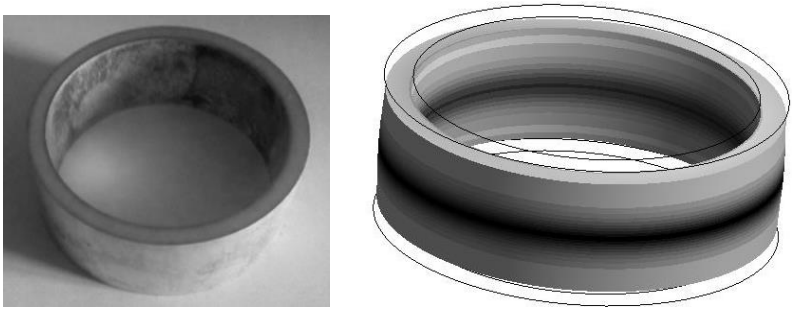
We present band structure results for elastic waves in periodic perovskite type composite materials consisting of a spiral scatterer shape embedded in a uniform matrix. The material of the scatterer is a high density material. The phononic band structure of two-dimensional solid phononic crystal is studied numerically by finite element method to obtain dispersion relations . We find full band gaps at relatively low frequencies for a low filling ratio. Due to spatial inhomogeneity, the unique structural characteristics of the spiral structure lead to localized modes. Hence, the proposed model geometry introduces a phononic crystal to cover a wide range of stopbands starting from low frequencies. The results could give a possibility to design effective filters for the low frequency range..

Finite element simulation and experimental study of cylindrical piezoelectric transducers

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
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]. 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.



(а) (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.

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.

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Focused acoustic fields of piezocomposite HIFU transducers: numerical modeling and experimental study

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
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).

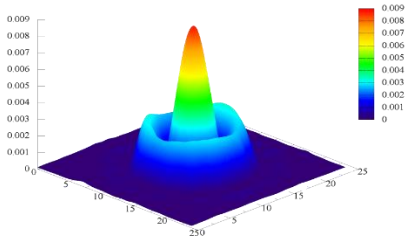

Figure 1. The intensity of focused ultrasound field in distilled water.

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).

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Dispersion features of elastic waves in phononic crystals: finite element analysis

Zafer OZER[1]

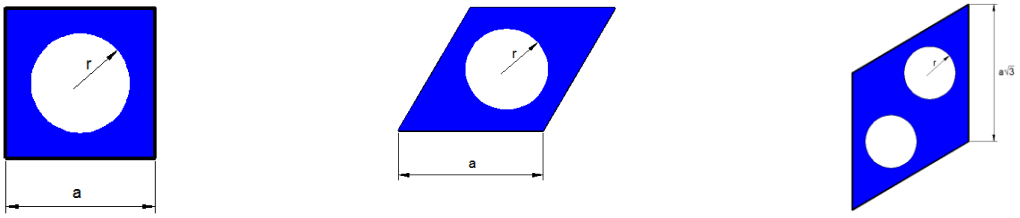
1- Mersin University, Mersin, Turkey
zaferozer@hotmail.com

Ferroelectric based phononic crystals (PnC's) are artificial materials that come into being from periodic sequencing of materials with different acoustic (sound velocity and density) properties or mechanical properties (elastic modulus, Poisson rate).

The increasing interest in such materials has also made interest in optimizing their band structures. Due to the Bragg scattering, these periodic structures has prohibited bands that certain frequencies cannot propagate. By using these structures, engineering designs can be realized in which mechanical waves at specific frequencies can be isolated. The solid (ferroelectric)-solid based PC is a 2D composite structure consisting of a square, hexagonal and honeycomb array of piezoelectric inclusions which has different cross-section (circle, square, triangle etc.) embedded in a host matrix of epoxy.

In order to find the band structure of the phononic crystals with different geometries and structures, Bloch periodic boundary conditions were applied to the unit cell of the periodic structure and numerical analysis was performed by the Finite Element method.

The stop phononic bands occurred between 15 kHz and 45 kHz for the different lattices (square, triangular and honey comb like).



a) b) c)

Figure 1. Unit cell of PnC a) square lattice, b) hexagonal lattice, c) honeycomb lattice

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Improved readout speed in ferroelectric probe data storage with large nonlinear permittivity media

Reshan Maduka Abeysinghe, Yoshiomi Hiranaga, Yasuo Cho

Research Institute of Electrical Communication, Tohoku University, Japan
hiranaga@riec.tohoku.ac.jp

Ferroelectric probe data storage is an unconventional data storage method, which uses ferroelectric materials as a recording layer.[1] In this method, digital data bits are recorded by nano-scaled polarization reversal. Extremely small domain dots (diameter of less than 10 nm) can be formed using ferroelectric thin films and nanoscale probe tip. Up to now, a domain dot array with an areal recording density of 4 Tbit/inch^2 has been written on a single-crystal $LiTaO_3$ recording medium to demonstrate its potential. Meanwhile the main drawback of this method is low readout speed. The readout speed that has been reported to date remains at 2 Mbps, and thus further and drastic improvement is strongly required.

Lead zirconate titanate (PZT) is one of promising candidates in this sense because of its large nonlinear permittivity ε_{333}. Figure 1 depicts the ε_{333} values of PZT films with various Zr/Ti composition ratios measured using a macroscopic quantitation approach called dynamic measuring method. The result shows different ε_{333} values depending on its composition, and the maximum value appears near Zr/(Zr+Ti) = 0.5. The ε_{333} for Zr/(Zr+Ti) = 0.52 was measured to be 50 aF/V, which was approximately 70 times as large as that of single-crystal $LiTaO_3$. To introduce recording media with large ε_{333} directly causes the improvement in signal-to-noise ratio of the readout signal because the SNDM signal intensity is proportional to the ε_{333} value. At the same time, this also means the improvement in readout speed for the data storage applications. In the conference, we will show some readout demonstrations using a hard-disk-drive-type data storage test system illustrated in Figure 2.

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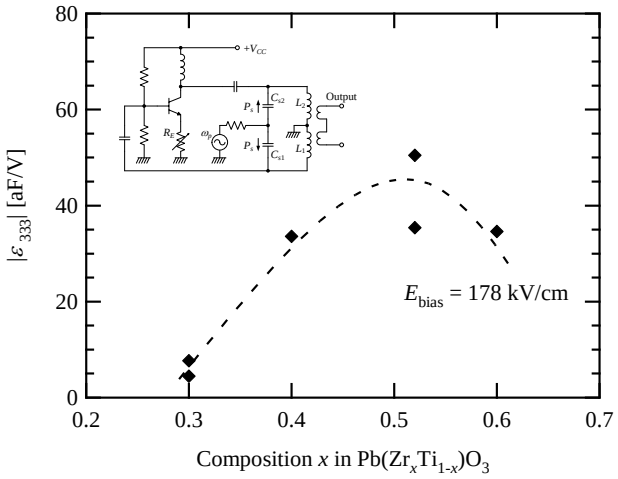

Figure 1. Nonlinear permittivity ε_{333} of $Pb(Zr_xTi_{1-x})O_3$ thin films.

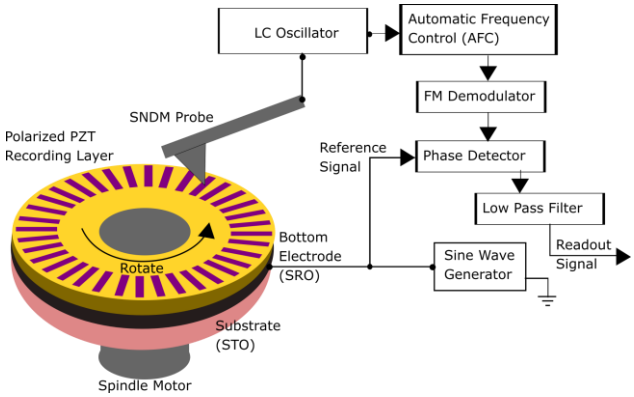

Figure 2. Schematic of HDD-type read/write test system for ferroelectric probe data storage.

Performance investigation of the electromechanical actuators based on Gd-doped ceria thin films

Andrei Ushakov[1], Eran Mishuk[2], Alexander Esin[1], Evgeniy Makagon[2], Denis Alikin[1], Sidney Cohen[3], Boris Slautin[1], Vladimir Shur[1], Andrei Kholkin[4], Igor Lubomirsky[2]

1-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
2-Department of Materials and Interfaces, Weizmann Institute of Science Rehovot, Israel
3-Department of Chemical Research Support, Weizmann Institute of Science Herzl St. Rehovot, Israel
4-Department of Physics and CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
andrey.ushakov@urfu.ru

Miniaturization and integration of functional oxide materials into microelectromechanical systems (MEMS) are among the most promising directions in expanding their functionality. Recently, several multifunctional materials based on the oxygen ionic conductors have been suggested as a substitution of lead containing piezoelectrics [1]. Such material, Gd-doped cerium oxide ($Ce_{0.8}Gd_{0.2}O_{1.95}$, CGO), showed to have a very large "non-classical" electrostriction response [2].

Here we present the results of the study of electromechanical performance of the self-supported CGO thin circular membranes with various electrode materials. The electromechanical performance of membranes was investigated using highly sensitive interferometric technique and showed two principal excitation mechanisms: common electrostriction and thermal contribution due to the Joule heating. Regardless of material used for contacts (Al, Ni or Ti) it was found that application of alternating electric field >100 kHz can produce lateral displacement at the membrane center of several microns (at 10 V) due to significant contribution of the thermal excitation (Joule heating, i.e., a thermoelectromechanical response) and large power dissipation (tens of mW at 10 V). Using of Ti contacts allows producing observable displacement in the presence of moderately high electric fields (~5 kV/mm). Built-in bias voltage of 1.5 V was found in the buckled actuators and it could not be attributed to a chemical inhomogeneity or to the contact potential differences. Complementary investigation using impedance spectroscopy, atomic force microscopy and interferometry provided the evidence that the apparent asymmetry leading to the first order response is related to the mechanical deformation of the buckled film.

The research was made possible by the Israeli Ministry of Science and Technology within the program of Israel-Russian Federation Scientific Collaboration, grant #12421-3 and by RFBR (Grant 15-52-06006 MNTI_a). The equipment of the Ural Center for Shared Use "Modern Nanotechnology" of Ural Federal University was used.

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Generation of OAM waves with lens antenna based on ferroelectric materials

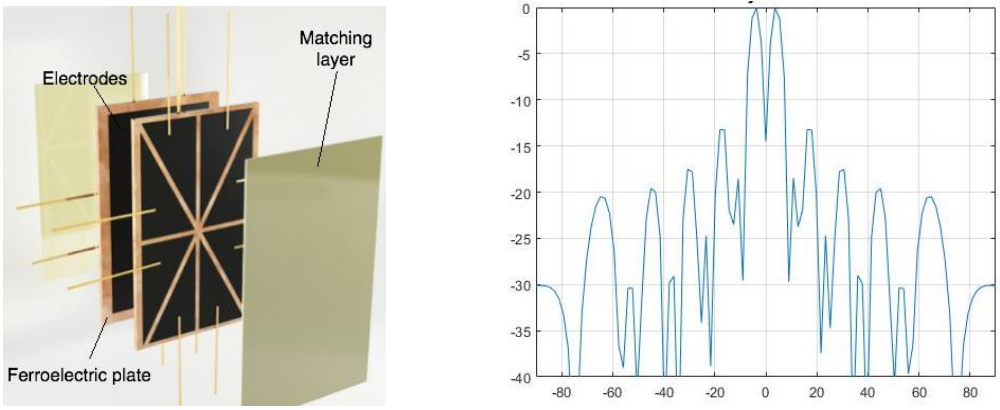
Andrey Altynnikov, Roman Platonov, Yuliana Ni and Andrey Tumarkin

Saint-Petersburg Electrotechnical University "LETI", Russia
avtumarkin@yandex.ru

Today there is an increasing interest in the desire to use orbital angular momentum (OAM) states in communication systems [1] OAM has been proposed to improve spectral efficiency [2,3] in communication systems by creating multiple sub-channels of propagation corresponding to the twisting degree of the electromagnetic wave. For realization of transmit systems with OAM, the spiral phase plates [4,5] are widely used due to simplicity of their structure and producing technology. Phase plate is a dielectric plate of complex shape thickness of which is change azimuthally. In such systems, the mechanical rotation of phase plate is needed for formation of OAM waves, that leads to decrease of transmit system reliability.

In this paper, we presented the construction of electrically tunable lens antenna based on ferroelectric materials for formation OAM waves. Lens consists of ferroelectric ceramic plates with highly resistive (transparent for microwaves) electrodes deposited on both sides (Figure 1a). Electrodes shape was designed to provide the specified distribution of dielectric constant along the plane of ferroelectric plate. Characteristics of proposed lens for 60 GHz were modeled. Simulation results of lens pattern presented in Figure 1b.

This work was supported by the RFBR, projects 16-29-05147 ofi_m, 16-07-00617 A and the Ministry of Education and Science of the Russian Federation (3.3990.2017/4.6).



a) b)

Figure 1. Construction of proposed ferroelectric lens (a); modelled pattern diagram of ferroelectric lens designed for 60 GHz (b).

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Characterization of $BaTiO_3/LaSrMnO_3$ heterostructures on sapphire for ferroelectric tunnel junctions

Alexander Gagarin, Andrey Tumarkin, Andrey Odinets, Evgeny Sapego
Saint-Petersburg Electrotechnical University, Russia
avtumarkin@yandex.ru

Currently, the new principle of realization of memory devices is developed using the influence of ferroelectric polarization on the tunnel current in nanoscale structures called ferroelectric tunnel junctions (FTJ). The basic FTJ device consists of a thin (several nanometers or less) ferroelectric (FE) barrier that separates two electrodes. The choice of materials is important for optimization of the FTJs performance and for CMOS compatibility of the FTJs fabrication process. The substrate and the bottom electrode layer influence directly on the microstructure of FE films, as well as the dielectric and ferroelectric properties of a whole device. Development of FTJ on sapphire substrate with bottom conductive layer of $LaSrMnO_3$ (LSMO) allows to combine the advantages of silicon-on-sapphire technology and FE-based components for the realization of high performance integrated circuits.

In this work, the $BaTiO_3/La_{0.3}Sr_{0.7}MnO_3$ (BTO/LSMO) heterostructures have been fabricated by radio-frequency deposition on a sapphire substrate for the first time. Structure properties of samples were characterized by x-ray diffraction and atomic force microscopy. Structure quality of LSMO layer was optimized by the proper choice of a substrate temperature during the deposition. The LSMO films deposited onto sapphire substrate at the deposition temperature of 880ºC revealed strong (h00) orientation. It was found that the highly oriented LSMO bottom layer with the surface morphology of 2.5 Å shows a marked effect on the structure properties of the BTO film. In comparison with BTO/sapphire heterostructure grown by similar process, the structure quality of the BTO film on LSMO buffered sapphire was significantly improved (see Fig.1).

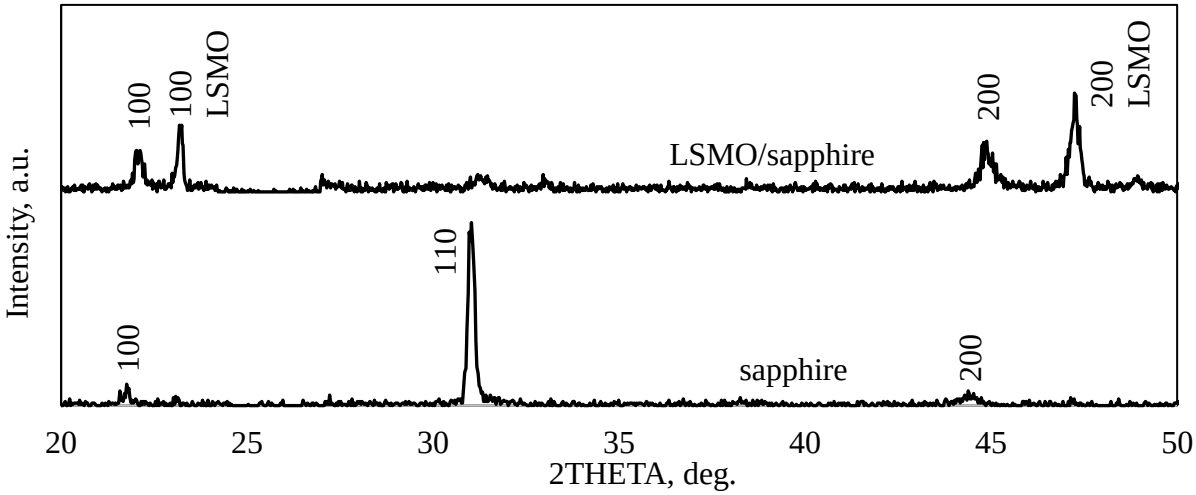

Fig. 1 XRD patterns of the BTO films

Piezo-force microscopy investigations of the BTO/LSMO/sapphire structure revealed the piezoelectric response and allows to calculate the polarization distribution across the FE film by Ginzburg-Devonshire theory.

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Optical formation of channel waveguide structures with different spatial parameters in surface-doped ferroelectric lithium niobate

A.D. Bezpaly, A.S. Perin, and V.M. Shandarov

Tomsk State University of Control Systems and Radioelectronics, Tomsk, 634050,Russia

id_alex@list.ru

Today, the rapid development of integrated optics and photonics requires intensive studies of methods to design and form the light control elements like channel waveguides and diffraction gratings based on ferroelectrics [1, 2]. One of the ways to form similar photonic elements is optical inducing, which allows to set and manage different topologies during the formation of such structures [2, 3].

The main aim of this work is experimental studies of methods to form different channel waveguides including those with spatial modulation of their parameters, optically induced in lithium niobate ($LiNbO_3$) sample with Cu-doped surface layer.

The channel waveguides have been formed via the point-by-point exposure at light wavelengths of 532 nm and 450 nm. Variation of distance between exposing light spot centers demonstrates the possibilities of optical inducing of longitudinally homogeneous (Fig. 1 a), inhomogeneous (Fig. 1 b) and curved (Fig. 1 c) channel waveguides with different width.

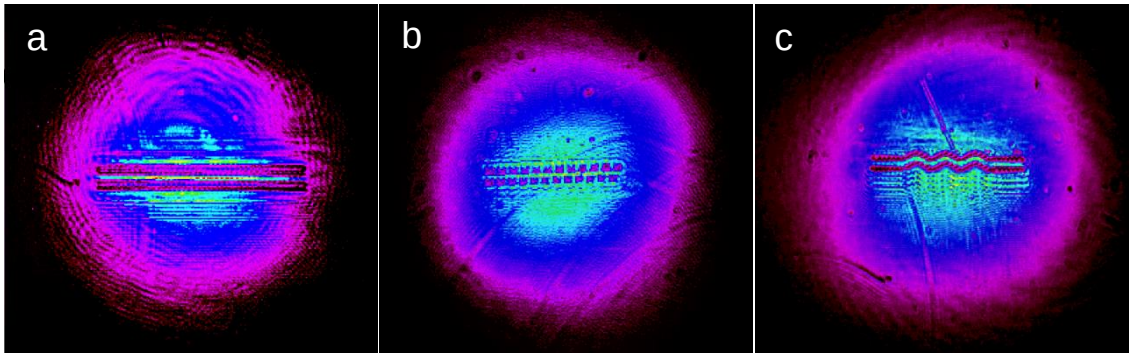

Figure 4. Near field light patterns at optical probing of the induced channel waveguides with different homogeneities and topologies.

This study was carried out with the financial support of Ministry of Education and Science of Russia (within the task N 3.1110.2017/PCh of the project part).

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Domain patterning of $LiTaO_3$ by electron and ion beams

Evgeny Vlasov, Dmitry Chezganov, Lubov Gimadeeva, Ekaterina Vaskina, Vladimir Ya. Shur

School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
evgeny.vlasov@urfu.ru

We have experimentally studied the domain formation induced by electron (e-beam) and ion beam (i-beam) irradiation in congruent lithium tantalate ($LiTaO_3$, CLT). All obtained results have been explained in terms of kinetic approach based on analogy with first order phase transitions [1].

The studied samples represented the 0.5-mm-thick Z-cut wafers of CLT single crystals. The irradiated polar surface was covered by artificial dielectric layer while opposite surface - by solid copper electrode. The samples were irradiated by means of the Auriga Crossbeam Workstation (Carl Zeiss) equipped with the electron-ion beam lithography system Elphy Multibeam (Raith GmbH). The domain structures were visualized by piezoresponse force microscopy and scanning electron microscopy (SEM) after etching in pure HF during 20 min at the room temperature.

The formation of circular domain arrays and domain wall shape instability induced by i-beam irradiation have been studied [2]. The dependences of domain radii on exposure dose and array period were obtained. The domain wall shape instability effect was revealed for doses above 20 pC (Fig. 1). The isotropic domain growth was attributed to stochastic nucleation due to prevailed isotropic screening mechanism. The domain wall shape instability is due to screening retardation in highly non-equilibrium switching conditions caused by existence of the surface dielectric layer.

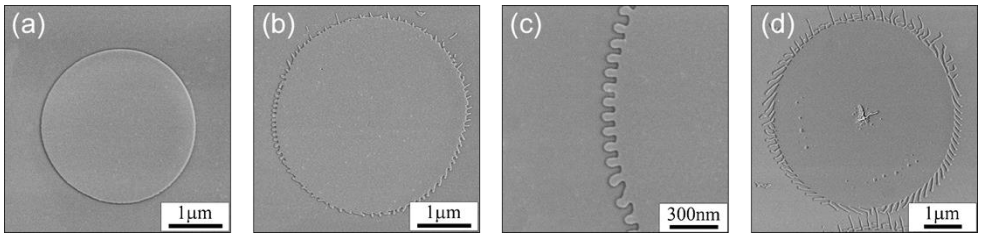

Figure 1. SEM domain images created at the charge doses, pC: (a) 10, (b), (c) 60, (d) 110.

We have studied the domain formation by e-beam and the influence of patterning parameters on domain morphology. The quasi-regular domain structures appeared at low charge doses and solid domains with dose increase. The dependences of domain structure parameters on irradiation conditions were extracted. The obtained knowledge was used for optimization of periodical poling (PP) process in CLT. The PPLT with a period down to 2 μm has been created.

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).

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Dependence of the ferroelectric properties of potassium sodium niobate ceramics on the synthesis method

Olga Malyshkina, Ekaterina Barabanova, Grigorij Shishkov, Egor Tsamtsurov

Tver State University, Russia

Olga.Malyshkina@mail.ru

In this paper we consider the structure and ferroelectric properties (pyroelectric effect, temperature dependences of dielectric permittivity) of samples of the ferroelectric sodium-potassium niobate ($NaKNb_2O_6$) ceramics was obtained by different methods of material synthesis. The reaction formula for synthesis in the first way is $Nb_2O_5 + K_2CO_3 + Na_2CO_3 \Rightarrow KNaNb_2O_6$. In the second method, sodium and potassium niobates were synthesized separately. The relevant reactions are $Nb_2O_5 + K_2CO_3 \Rightarrow KNbO_3$ and $Nb_2O_5 + Na_2CO_3 \Rightarrow NaNbO_3$. The examination of the samples with a scanning electron microscope showed that the samples obtained by the second method have a more compact grain structure (Fig. 1) and a uniform elemental composition.

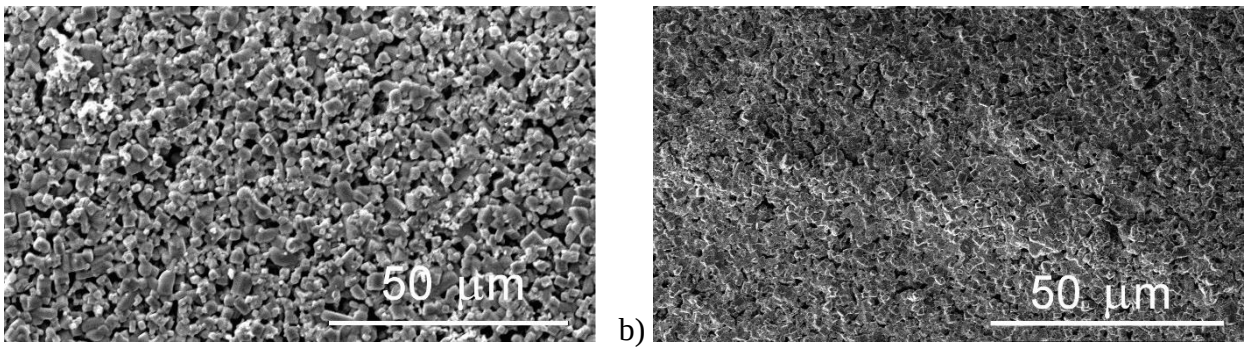

Figure 1. Image of $NaKNb_2O_6$ ceramic sample surfaces were synthesized by the first (a) and the second (b) methods.

The existence of the ferroelectric properties of the obtained samples was confirmed by the presence of sharp maximum in the temperature dependence of permittivity and pyroelectric response in samples poled by electric field 670 V/mm. At the same time, a sample whose material was synthesized by the first method had a pyroelectric response an order of value greater than that of another sample (Fig. 2).

This work was supported by the Ministry of Education and Science of the Russian Federation and performed at the Collective Usage Center of the Tver State University.

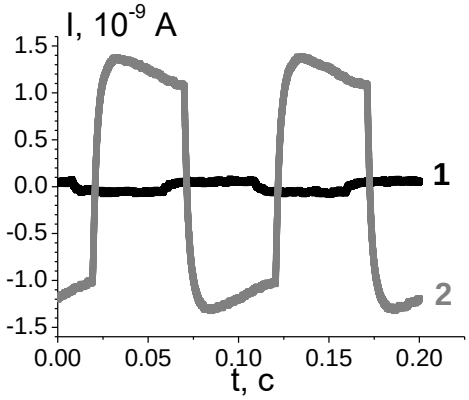

Figure 2. The pyroelectric response of $NaKNb_2O_6$ ceramic samples were synthesized by the first (curve 1) and the second (curve 2) methods

New semipolar aluminum nitride thin films: growth mechanisms, structure, dielectric and pyroelectric properties

Olga Sergeeva [1,4], Alexander Solnyshkin[1,4], Sergey Kukushkin[2,4], Andrey Osipov[2,4], Shukrillo Sharofidinov[3], Eugenii Kaptelov[3,4], Igor Pronin[3,4]

1-Tver State University, Russia
2-Institute of Problems of Mechanical Engineering RAS, Russia
3-Ioffe Institute, Russia
4-Herzen State Pedagogical University, Russia
Corresponding_author_o_n_sergeeva@mail.ru

In the work, the growth of AlN was carried out by hydride-chloride vapor phase epitaxy (HVPE) on hybrid SiC layers specially prepared for the growth of semipolar layers. SiC layers were grown on Si substrates of *p*-type (KDB) with (100) orientation and a deviation of 4 degrees from the normal to the substrate plane using the new method of the atomic substitution [1]. According to Ref. [2], on the vicinal face of the silicon substrate, this method produces a special structure of the SiC surface layer consisting of oblique hexagonal facets resembling "fish scales" with an hexagonal orientation $(1\bar{1}0\bar{2})$ and $(1\bar{2}00)$. Such facets permit to grow highly perfect epitaxial films of the semipolar hexagonal AlN phase on their surface.

A study of the microstructure showed that the angle between the direction of the hexagonal axis and the silicon substrate was 50-53°. Such a geometry allows reduce significantly the tensile stresses effecting on the AlN thin layer by the Si substrate, which are observed at the usual growth of the films along the hexagonal axis, and increase the polarization (dipole moment) oriented along the polar axis. A study of the microstructure showed that the semipolar films are not observed the cracking for the (0002) oriented films, and they have a smoother surface. This allows increasing the layer electric strength. The film thickness was varied in the range of 500 – 1000 nm. The size of top platinum electrodes was 1×1 mm^2. The Si substrates with electrical resistance of 20 Ω·cm with the SiC layer are bottom electrodes.

For a registration of pyroelectric response, the dynamic method was used. The laser module CLM – 1845 IR – 980 (λ = 980 nm) was a radiation source. Laser power was equal to 220 mW. The IR irradiation was modulated with rectangular shape pulses. Estimates of the pyroelectric coefficient showed that its value of 9-12 μC/(m^2K) nearly corresponds to the similar values typical to the textured hexagonal AlN films grown directly on Si substrates. The results obtained show the semipolar AlN thin films grown hybrid SiC/(100)Si substrates may be considered as promising materials for pyroelectric devices.

The work was partly supported by the Ministry for Education and Science (Russian Federation) (Grant No 16.2811.2017/4.6).

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Deposition and dielectric properties of the composite structure "poly(vinylidene fluoride-trifluoroethylene) in porous alumina matrix"

Alexey Belov[1], Inna Kislova[2], Evgeny Redichev[1], Anton Stroganov[1], Alexander Solnyshkin[1,2]

[1]National Research University of Electronic Technology, Zelenograd, Moscow, Russia
[2]Tver State University, Tver, Russia
nanointech@mail.ru

In this work, the study of dielectric properties of composite structures on the base of poly(vinylidene fluoride-triflouroethylene) copolymer P(VDF-TrFE) and porous aluminum oxide layers produced by the melt-impregnation is presented. For the composite structure preparation, the P(VDF-TrFE) copolymer powder with an TrFE content of about 28 % was used. Porous alumina grown by electrochemical method on an aluminum substrate with 100 μm thickness was used as a template for the melt-impregnation of P(VDF-TrFE). Porous alumina (AAO) grown by electrochemical method on an aluminum substrate with 100 μm thickness was used as a template for producing the composite structure. The porous alumina matrix thickness was equal to 10 μm. The electrical contact (the bottom electrode) was deposited on a surface of the porous oxide film by magnetron sputtering of copper with an adhesive titanium sublayer. To impart rigidity to the alumina structure, the copper layer additional to the sputtered Cu electrode was electrochemically grown. To fabricate the composite structure with 1-3 connectivity, P(VDF-TrFE) copolymer was melted on the anodic porous alumina matrix under vacuum. The pores in the Al_2O_3 layer were filled with the copolymer melt and, then, structure was cooled. The copolymer excesses on the porous oxide surface were removed both mechanically and chemically with its respective solvent. For electrical measurements, the top Cu electrode was also deposited by the magnetron sputtering on the adhesive Ti sublayer on the free surface of the composite structure.

Dielectric dispersion measurements in the frequency range between 10^{-1} and 10^7 Hz were carried out with a Novocontrol ALPHA High-Resolution Dielectric Analyzer. Hysteresis loops were observed using the Sawyer-Tower scheme. Generator produced a sinusoidal signal with a frequency from 20 to 100 Hz. Maximal value of the ac electric field applied to the samples was about 2000 kV/cm in peak-to-peak.

The comparative structure analysis revealed pore filling good enough. The electrical characterization of the composite samples was carried out. According to our data, the polarization of the entire composite structure is slightly less than one of the bulk copolymer films, since the oxide matrix is non-polar. The dielectric measurements have shown that the dielectric constant of the composite structures is lower than one of the bulk copolymer film. In frequency domain above 10^4 Hz, the dielectric loss of the composite sample is less than the one of the pure copolymer film. At lower frequencies of the measuring field, the dielectric loss tangent of the P(VDF-TrFE) in AAO structure increases more significantly as compared to the tan δ of the P(VDF-TrFE) film.

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Phase transition in triglycine sulfate by dielectric spectroscopy and piezoelectric response force microscopy

G.I. Ovchinnikova [1], N.V. Belugina [2], R.V.Gainutdinov [2], E.S. Ivanova [2], A.L.Tolstikhina [2]

1-Faculty of Physics, Moscow State University, Moscow, Russia
2- Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, Moscow, Russia
alla@ns.crys.ras.ru

Many studies were performed for a better understanding of the phase transition in triglycine sulfate (TGS) well know as ferroelectric organic compound. The material undergoes second – order phase transition at about 49 C. From the three glycine molecules (G1, GII, GIII) forming the unit cell the non – planar GI molecule is responsible for the polarization and shows a complex dynamics much faster than that performed by the other glycine molecules [1]. The phase transition in TGS has been studied in this work by means of dielectric spectroscopy and piezoelectric force microscopy (PFM). The TGS dielectric spectra measured in a wide frequency range have allowed us to tie the molecular dynamics with relaxation time τ characteristic for dielectric dispersions. The total dielectric spectra of TGS crystal measured near phase transition temperature is presented in the Fig.1. At least two characteristic times can be clearly revealed from this spectra; 300 kHz and 40 GHz. An attempt was made to combine the molecular dynamics data [1] in TGS near phase transition temperature with dielectric dispersion and observed in PFM structure transformation features.

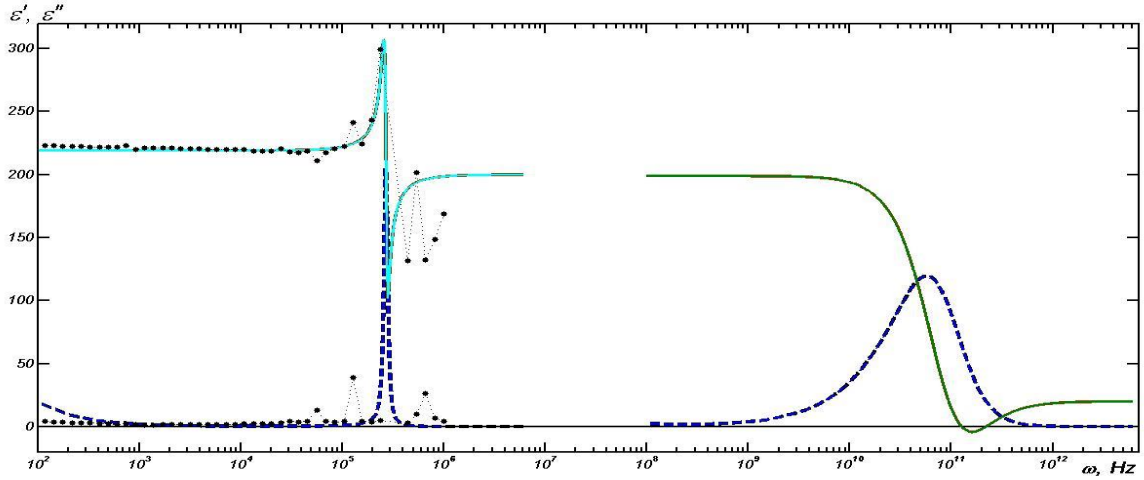

Fig.1 Dielectric spectra of TGS in the hole investigated frequency region

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Scanning capacitance microscopy and X-ray fluorescence of TGS−TGS+Cr crystals

R.V. Gainutdinov [1], A.L. Tolstikhina[1], B.S. Roshchin[1], V.E. Asadchikov[1], N.V. Belugina[1], A.K. Lashkova[1], V.N. Shut[2], I.F. Kashevich[3]

1- Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, Moscow, Russia
2- Institute of Technical Acoustic NASB, 210027, Vitebsk, Belarus
3- Vitebsk State University, 210032, Vitebsk, Belarus
alla@ns.crys.ras.ru

Scanning capacitance microscopy (SCM) is known as a method for measuring spatial variations in capacitance with high resolution. To the ferroelectrics so far this method has been applied little, as one can see from the limited number of research papers.

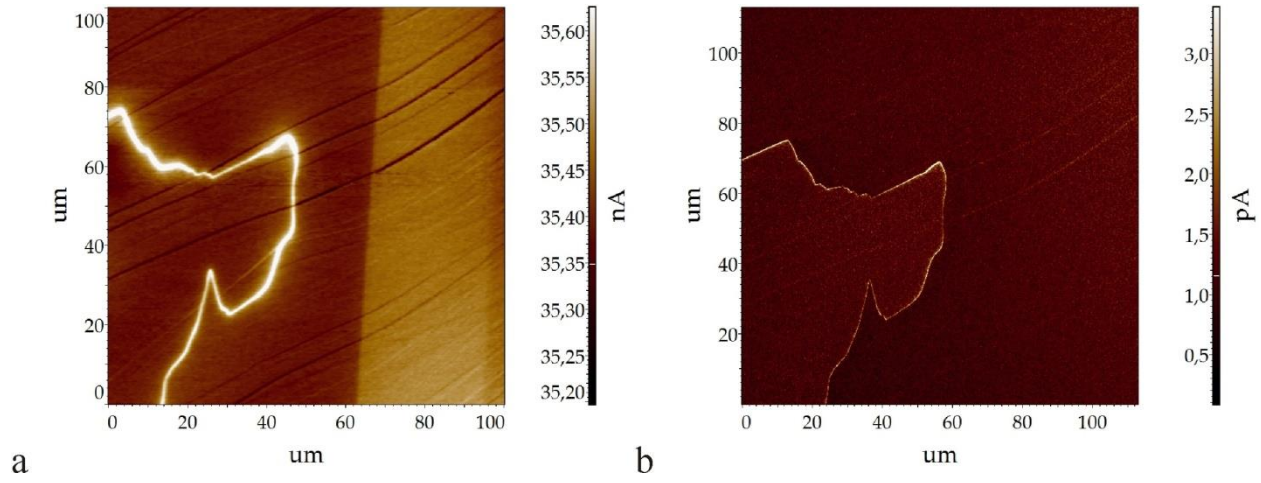

Figure 1. a – SCM image of the domain wall and boundary of TGS (left) and TGS + Cr (right) bands on the (010) surface of the TGS-TGS+Cr crystal, b – c-AFM image of the same region

The banded crystals TGS-TGS + Cr were studied in the work by SCM, conductive AFM (c-AFM) and X-Ray fluorescence (XRF) 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 Cr^{3+} (5-6% by weight)). Fig.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 bright line. On the c-AFM image, the contrast is formed only on the domain wall. 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. XRF allowed to determine the concentration of Cr^{3+} and to establish the periodic nature of the impurity distribution.

Bragg diffraction of light on periodically poled domain structure in lithium niobate under external sinusoidal voltage

Evgeny Savchenkov[1], Stanislav Shandarov[1], Andrei Akhmatkhanov[2], and Vladimir Shur[2]
1-Department of Electronic Devices,-Tomsk State University of Control Systems and Radioelectronics, Tomsk 634050, Russia
2-Institute of Natural Sciences, Ural Federal University, Ekaterinburg 620083, Russia
stanislavshandarov@gmail.com

We study theoretically and experimentally the time modulation of intensity for light beam produced at Bragg diffraction on periodically poled domain structure in lithium niobate crystal in presence of the external voltage with a frequency Ω.

The periodic domain structure (PDS) with alternating 180-degree Y domain walls and spatial period of 8.79 μm, which was developed in the $LiNbO_3$:5%MgO crystal by the electric-field poling, had been used in our experiments. Sinusoidal voltage having the frequency f = 1 kHz and amplitude from 0 to 136 V was applied along the Z axis of the sample with thickness of 1 mm. The incident light beam (λ = 655nm) polarized along the Z axis was focused by the cylindrical lens to the center of the sample. During propagation of this beam in XY plane at a Bragg angle to Y axis it is suffered diffraction on the PDS at the interaction length of 2 mm. It was established that time evolution of light intensity for diffracted beam is the superposition of spectral components with frequencies nf, where n = 0, 1 and 2.

The experimental dependences of the amplitudes of spectral components with frequencies nf on the applied voltage are shown in Fig. 1 by filled points. The solid lines in this Figure are the results of theoretical consideration tacking into account the summarized contribution into diffraction light field from isotropic diffraction on domain walls [1] as well as from electrically induced one on the PDS. It can be noted that the square-law behavior of second harmonic on the control voltage is liable to restrict the dynamic range of electro-optic Bragg modulators based on PDS in lithium niobate crystals.

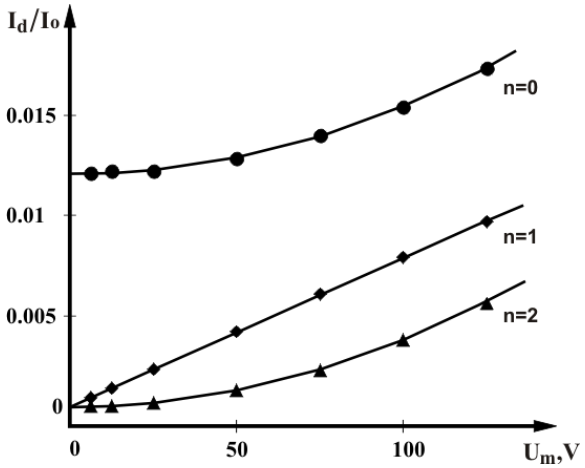

Fig.1. The amplitudes of the spectral components in the time dependences for diffracted-light intensity normalized to the intensity of incident beam vs. the voltage applied to the crystal. Symbols - experiment, lines – fits from a theoretical model.

This work was supported by the State Assignment of the Ministry of Education and Science of Russian Federation (within the tasks No. 3.8898.2017/8.9 and 3.1110.2017/PCh) and the RFBR (grant No. 16-29-14046-ofi_m).

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Optical writing of diffraction structures in photorefractive lithium niobate by Bessel-like optical fields

I.A. Trushnikov, A.V. Inyushov, A.S. Perin

Tomsk State University of Control Systems and Radioelectronics, Russia
trushnikov@mail.ru

Currently seen an increased interest in "diffraction-free" light fields, which include the Airy beams, Bessel and some others [1, 2]. With the help of experimental studies it was previously confirmed that light fields with bessel-like profiles have a high longitudinal homogeneity and concentration of the main part of the wave field in the central part. In this work, we study the possibility of formation Bessel-like light beams in the photorefractive crystal of lithium niobate. The geometrical dimensions of the crystal plate are $10\times2\times15$ mm^3 along X,Y and Z axes. It is doped with Cu while crystal growth. The light polarization corresponds to the crystal extraordinary wave. The idea of experiment is a study diffraction characteristics of the Bessel-like beams obtained by amplitude mask scheme and using tubular waveguides. The sourse of coherent radiation is a CW solid-state laser (Nd^{3+} YAG, light wavelength λ=532 nm, output power is near to 10mW). The $LiNbO_3$ sample is exposed to bessel-like light beam formed by optical fibers, amplitude transparencies and a focusing lens.

The spatial period of the light pattern is 80 μm. To investigate the light patterns at output plane, a BS-FW-FX33 laser beam analyzer is used. As the result exposure we observe the formation of interconnected photonic structures in a lithium niobate crystal. In conclusion, our experimental results confirm the possible creation of few-elements diffraction structures and photonics waveguide circuits within photosensitive materials like photorefractive crystals by light fields with Bessel-like shapes.

This study was carried out with the financial support of Ministry of Education and Science of Russia (within the task N 3.1110.2017/PCh of the project part).

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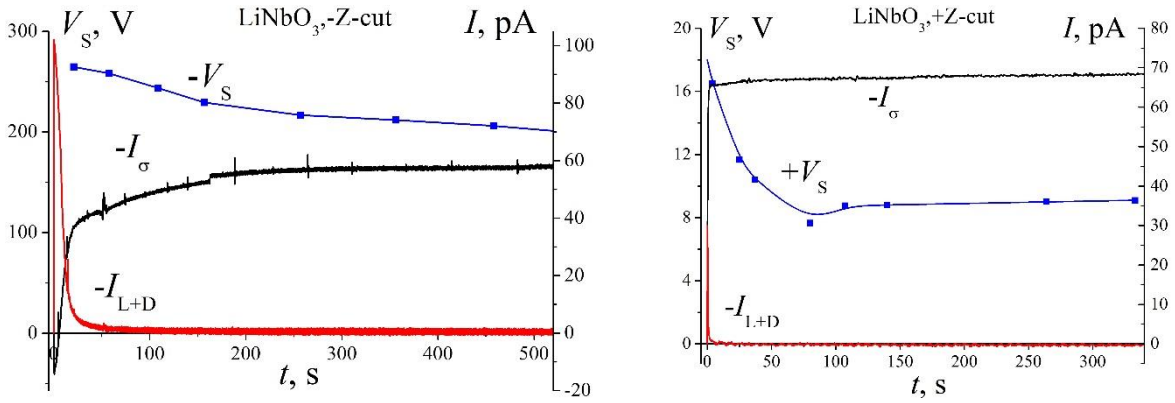
The features of polar dielectrics charging under electron beam irradiation

Eduard Rau[1], Andrey Tatarintsev[1,2], Kseniya Markovets[1]

1. Faculty of Physics of M.V. Lomonosov Moscow State University, Moscow, Russia.
2. Institute of Physics and Technology RAS, Moscow, Russia.
tatarintsev@ftian.ru

In recent years integration of polar dielectric materials such as ferroelectrics, piezoelectrics and pyroelectrics in microelectronic technology has been increased. Creating a regular domain structures (RDS) configuration required in ferroelectric crystals is a practically important problem. One of the most convenient ways to create the RDS of micron, submicron and (in very thin crystals) nanometer size is irradiation of a sample by focused electron beam in the electron beam lithography setup [1, 2]. However, the associated mechanism of ferroelectric charging under electron beam irradiation is not fully investigated and understood.

This work is aimed to a comprehensive study of all the main parameters of the charging process of ferroelectrics $LiTaO_3$ and $LiNbO_3$. Experiments were carried out on both sides of the Z-cuts: plus and minus. The main measured parameters versus time are: surface potential V_S, secondary electron emission I_σ, sum of displacement current (accumulated charge) and the leakage currents I_{L+D} (see Fig. 1). This complex approach [3] allows us to establish the main features of the process of charging ferroelectrics and the accompanying switching of the domain structure.



(a) (b)

Fig. 1. Surface potential V_S, secondary electron emission current I_σ, sum of displacement current and the leakage currents I_{L+D} versus time of ferroelectrics irradiation for –Z-cut (a) and +Z-cut of $LiNbO_3$. Charging parameters: primary electron beam energy E_0=1 keV and current density $j_0=10^{-6}$ A/cm^2.

The reported study was funded by RFBR according to the research project № 18-32-00254.

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Electronic and elastic properties of the multiferroic crystals with the Kagome type lattices -$Mn_3V_2O_8$ and $Ni_3V_2O_8$: First principle calculations

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 Sciences, 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: mamedov@bilkent.edu.tr

The electronic, mechanical, and optical properties of the Kagome staircase compounds, $Mn_3V_2O_8$ and $Ni_3V_2O_8$, have been investigated using the VASP (Vienna ab-initio Simulation Program) that was developed within the density functional theory (DFT). The spin polarized generalized gradient approximation has been used for modeling exchange-correlation effects. The electronic band structures for both compounds and total and partial density of states corresponding to the these band structures have been calculated. Spin up (spin down) E_g values for $Mn_3V_2O_8$ and $Ni_3V_2O_8$ compounds are 0.77 eV indirect (3.18 direct) and 1.58 eV indirect (0.62 eV) direct, respectively. It have been determined that the greatest contribution to the highest occupied valance bands and the lowest unoccupied conduction bands come from the Mn and V d states, but the contribution from the Mn d states are greater than the contribution from the V d states. Bulk modulus, shear modulus, Young's modulus, Poisson's ratio, sound velocity, Debye temperature have been obtained. when we consider the value (114.84 GPa for $Mn_3V_2O_8$ and 154.97 GPa for $Ni_3V_2O_8$) of Young's modulus, which is a measure of stiffness, we can say that $Ni_3V_2O_8$ is harder stiffness materialthan $Mn_3V_2O_8$. Since the B/G ratio (2.05 for $Mn_3V_2O_8$ and 2.20 for $Ni_3V_2O_8$) is high than 1.75, these compounds are ductile.The Debye temperature is low for soft materials and high for rigid materials. The rigid order of these compounds: are $Ni_3V_2O_8$>$Mn_3V_2O_8$.. Based on the obtained electronic structures, we further calculate the frequency-dependent dielectric function and other optical functions .

Dielectric response of the methylammonium lead halide solar cell absorbers

Sergejus Balčiūnas[1], Mantas Šimėnas[1], Šarūnas Svirskas[1], Jaroslavas Belovickis[1], Vytautas Samulionis[1], Maksim Ivanov[1], Jūras Banys[1], Irina Anusca [2], Mehmet Sanlialp [2], Gerhard Lackner [2], Christian Fettkenhauer [2], Vladimir V. Shvartsman [2], Doru C. Lupascu [2], Pascale Gemeiner [3], Brahim Dkhil [3].

1 Faculty of Physics, Vilnius University, Sauletekio 9/3 817k., LT10222 Vilnius, Lithuania
2 Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Essen, Germany
3 Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupélec, CNRS-UMR8580 Université Paris-Saclay, Châtenay-Malabry, France.
Corresponding_author_sergejus.balciunas@ff.vu.lt

Hybrid organic–inorganic perovskites have recently attracted overwhelming attention due to their excellent photovoltaic performance yielding efficiencies well exceeding 20%.This has been related to properties such as long charge carrier lifetime, the exceptionally large diffusion length, large absorption coefficient, high carrier mobilities, large opencircuit voltages, and direct band gap,The organo-lead trihalide perovskite compounds, $CH_3NH_3PbX_3$, are the forerunners in efficiency. The organic methylammonium (MA) cation, $CH_3NH_3^+$, occupies the cuboctahedron A-sites of the perovskite structure surrounded by 12 halogen anions (X = I, Br, Cl). Pb^{2+} resides on octahedron B-sites surrounded by six anions.

In this presentation dielectric and acoustic properties in wide temperature and broad frequency range of organic – inorganic perovskites $CH_3NH_3PbX_3$ (X = I, Br, Cl) will be shown. Figure 1 shows dielectric constant of the three MA – Pb – halides across wide frequency range at room temperature. Sections denote the dominant micromechanism contributing to dielectric response:

A) Ionic motion/Dirft,
B) MA –dipole relaxation
C) Anionic lattice dynamics (phonons),
D) Internal vibration of the MA molecule.

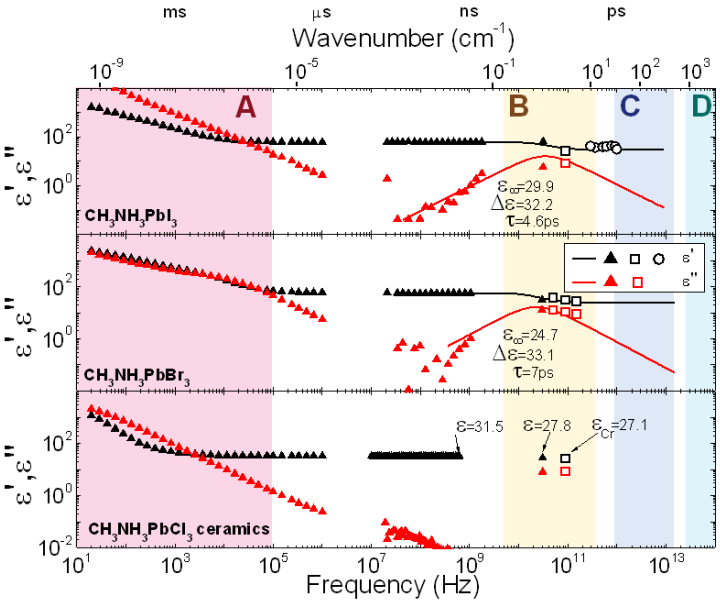

Figure 1 Frequency dependence of dielectric constant at room temperature for $MAPbX_3$ crystals.

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Delay time of phase transition to the polar phase in relaxors

S.A. Migachev[1], R.F. Mamin[1,2,*]

[1]Zavoisky Physical-Technical Institute of FIC KazanSC RAS,
Sibirskii tract 10/7, Kazan, Russia
[2]Institute of Physics, Kazan Federal University,
Kremlevskaya 16, Kazan 420008, 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 [2] developing 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. The delay time t_0 of the phase transition have been measured for different temperatures and applied electric field. The photoconductivity also has been investigate and correlation of observed results with developed model is discussed.

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Quasi-two-dimensional electron gas at the interface between $BaTiO_3$ and $LaMnO_3$

Irina Piyanzina[1,2], Yury Lysogorskiy[2], Rinat Mamin[1]

1-Kazan E. K. Zavoisky Physical -Technical Institute (KPhTI), Russian Federation
2-Kazan Federal University, Russian Federation
Corresponding_author mamin@kfti.knc.ru

For the paradigmatic oxide heterostructure with $LaAlO_3$ (LAO) thin films grown on $SrTiO_3$ (STO) substrates, distinct electronic phases have been extensively characterized at the LAO/STO interface: for LAO films with more than three layers and LaO termination towards the TiO_2 interface, a two dimensional electronic system (2DES) is formed in the STO layers next to the interface which becomes superconducting below a temperature below 300 mK [1, 2].

It has been shown that analogous to the ionic polar discontinuity, the 2DES may be created at an interface due to electric polarization discontinuity [3,4]. An attractive materials for such purpose are ferroelectrics. They have a wide range of different distinctive properties, among them: spontaneous polarization switching, high dielectric permeability, dielectric nonlinearity, piezo- and pyro- activity, linear and quadratic electro-optical effects. Obvious, such a functionality can expand the range of application in nanoelectronics.

One of the most important feature related to the 2DEG formation is the local polarity of layers inside the LAO slab. In the present work we have chosen the $BaTiO_3/LaMnO_3$ (BTO/LMO) heterostructure, where all layers in the simple electronic limit are neutral, but there is a ferroelectric polarization due to the Ti atoms displacements out of octahedron center in the BTO. The direction of such a polarization might be switched by an external electric field. Based on first-principles band structure calculations, we demonstrate the possibility of q-2DES formation at the interface composed of perovskite ferroelectric BTO and antiferromagnet manganite LMO. We present the results of structural, optical and electronic properties calculations of BTO/LMO heterostructure composed of varying number of layers. We analyze an impact of ferroelectric polarization onto the 2DES conducting properties by layer-resolved density of states calculations.

The reported study was funded by Russian Scientific Foundation, research project No. 18-12-00260.

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Evolution of domain structure in lithium niobate with nonuniform distribution of conductivity

Victoria Pryakhina, Denis Alikin, Vladimir Shur

School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
viktoria.pryahina@urfu.ru

Domain evolution during polarization reversal in non-equilibrium conditions undergoes an essential change due to bulk screening retardation [1]. The artificial dielectric ("dead") layer at the sample surface is prevalent method to create non-equilibrium conditions. We demonstrate features of domain evolution in lithium niobate after its surface layer modification by reduction treatments.

Plasma source ion irradiation of $+Z$ surface and vacuum annealing at temperatures 600-850 ºC were used to modify surface layer of 0.5-mm-plates of Z-cut $LiNbO_3$. Both treatments resulted in increase of surface conductivity, which led to inhomogeneous distribution of electric field during polarization reversal. Domain evolution was *in situ* visualized during polarization reversal using transparent liquid electrodes. Static domain structures were visualized by piezoresponse force microscopy (PFM) at the crystal surface and by confocal Raman microscopy in the crystal bulk.

The decrease of threshold field for formation of the first domains (E_{th}) has been revealed. Domain nucleation started from $-Z$ surface. The domain structure evolution is significantly depended on the applied voltage excess above E_{th} ($\Delta E = E_{ex} - E_{th}$) (Fig. 1). This is accounted for retardation of bulk screening. It was shown that the high-conductive surface layer prevented forward domain growth in polar direction that results in formation of the charged domain walls in the bulk localized in the vicinity of the high-conductive layer [2, 3].

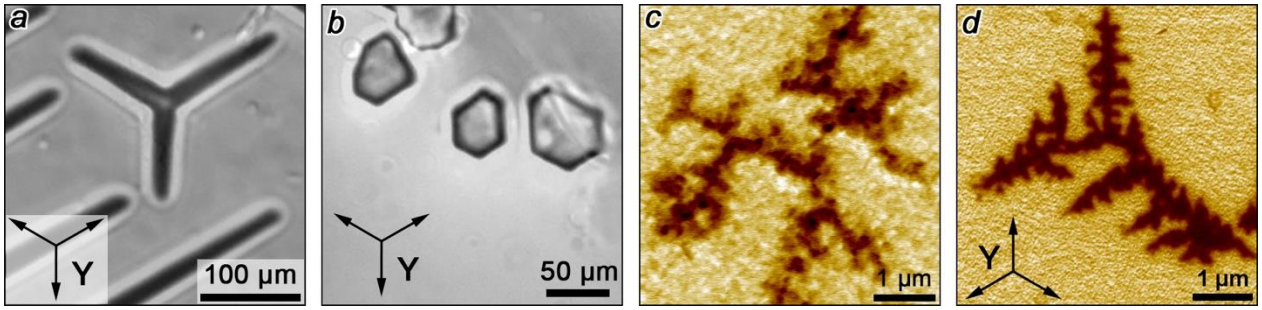

Figure 1. Domain shape evolution for various ΔE: (*a, c*) ~0 kV/mm, (*b*) 2 kV/mm, (*d*) 6 kV/mm. (*a-b*) ion irradiated CLN, optical microscopy; (*c-d*) vacuum annealed CLN, PFM at $-Z$ surface.

The equipment of Ural Center for Shared Use "Modern Nanotechnology" UrFU was used.

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The photovoltaic properties of organic heterostructures «semiconductor-ferroelectric»

V. V. Lazarev, L. M. Blinov, S. G. Yudin, S. P. Palto.

Shubnikov Institute of Crystallography of Federal Scientific Research Centre "Crystallography and Photonics" of Russian Academy of Sciences, Russia
lbf@ns.crys.ras.ru

Film heterostructures are widely used in modern instrumentation (solar panels, transistors, photonic crystals, etc.), and often ferroelectric (FE) layers are the most important elements of such devices, as they allow one to control the magnitude and direction of the internal ("built-in") electric field in the active element of the heterostructures. This electric field significantly affects the technical characteristics of the devices. In this work we study organic heterostructures of a thickness of ~100 nm marked as: «ITO-PcM-FE-Al» and «ITO-FE-PcM-Al», where ITO ($(In_xSn_{1-x})_2O_3$) is a transparent electrode on glass substrate, PcM is a layer of metal complex of phthalocyanine of copper (Cu) or of zinc (Zn), deposited by thermal vacuum evaporation technique, FE is a layer of ferroelectric copolymer polyvinylidene fluoride with trifluoroethylene P(VDF-TrFE), formed by Langmuir-Schaefer technology or by vacuum evaporation technique, and Al is a top aluminum electrode. The copolymer P(VDF-TrFE) is well established as one of the best organic ferroelectric materials, preserving the ferroelectric properties of ultra-thin layers of thickness less than 10 nm [1], although its spontaneous polarization is usually not higher than ~0.1 C/m^2. Organic semiconductors CuPc (or ZnPc), the absorption bands of which are in the spectral range of 500-800 nm, are widely used as electron donor in solar energy cells [2].

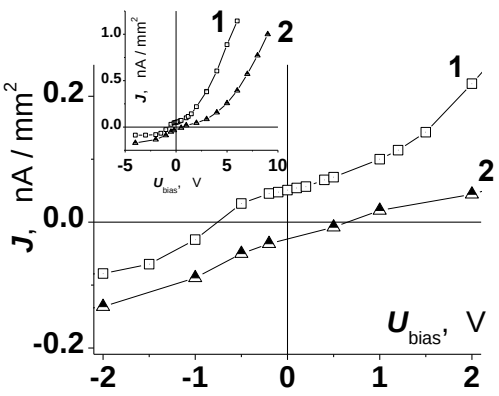

Fig. 1. The photocurrent density dependence on bias voltage applied to the Al-electrode for the two heterostructures: «ITO-FE-CuPc-Al» (curve 1) and «ITO-CuPc-FE-Al» (curve 2) measured at 630 nm.
Insert: the same in an enlarged scale.

In this work, spectra of photosensitivity of the heterostructures and their current-voltage characteristics (at λ = 630 нм) depending on the bias voltage applied (U_{bias}) are measured. The light from monochromator (~1 μW) is modulated by the chopper at a frequency of 300 Hz. From the Fig. 1 it can be seen that in the studied heterostructures the photovoltaic currents have different signs at the zero bias voltage. This indicates that the location of the ferroelectric layer in the heterostructure affects the direction of the "built-in" electric field.

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The SHG diagnostic of RF sputtered thin PZT films under variation of the substrate-target distance

Stanislav Senkevich[1,2], Igor Pronin [1,2], Andrey Elshin[3], Elena Mishina[3]

1-Ioffe Institute, Russia
2-The Herzen State Pedagogical University of Russia
3-Moscow Technological University (MIREA)
Corresponding author SenkevichSV@mail.ioffe.ru

The relationship between the signal intensity of the second optical harmonic and the microstructure of thin PZT films was investigated. For this purpose, a series of PZT films was produced by varying the distance from the target to the substrate (d) in the range 30-70 mm. The films were deposited on a cold (150°C) Pt/TiO_2/SiO_2/Si substrate by the RF magnetron sputtering of a ceramic target. To crystallize the perovskite phase, they were annealed in air at a temperature of 580°C. The thickness of the films was nearly 500 nm. The phase state of the films was determined using a scanning electron microscope Tescan Vega II LMU (SEM). To study the SHG signal, we used femtosecond laser (Ti: sapphire, Avesta-Project, Russia) with a wavelength of 800 nm, and a pulse duration of 100 fs, and a repetition rate of 100 MHz was used. The sample was irradiated using the confocal microscope Alpha 300 (WITec).

The microstructure of the films was a set of polycrystalline spherulite blocks with a radiant structure (Fig. 1). In the films deposited at d = 30 mm, the blocks consisted of a large number of radiant segments. With increasing distance, the density and shape of the segments changed significantly. In films deposited at d = 70 mm, the radiant structure was barely noticeable, and the blocks were characterized by greater structural homogeneity. The distribution of magnitude of the SHG signal by film area is presented at Fig. 2. Its magnitude strongly changed with the distance with a maximum corresponding to films deposited at d = 50 mm. The magnitude of the SHG signal at one edge of the range (d = 70 mm) decreased by more than an order compared to maximal magnitude. In the work, the relationship the between SHG signal and microstructure of the films is discussed.

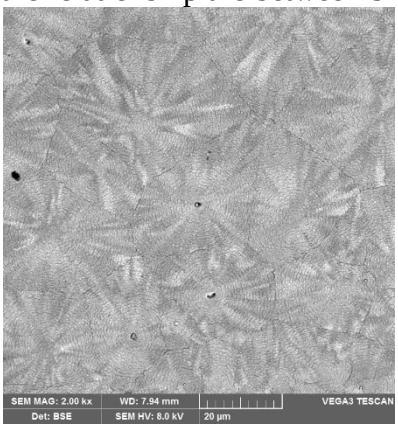

Fig. 1. SEM image of the spherulite microstructure of PZT film (d = 30 mm).

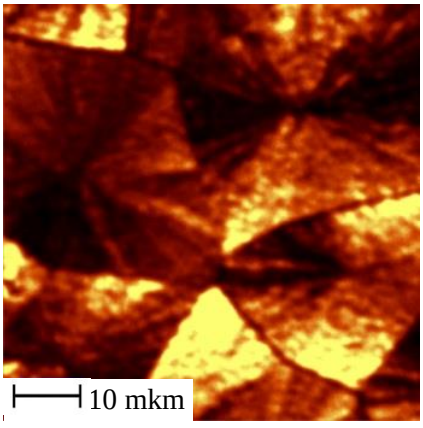

Fig. 2. An image of the SHG signal of the spherulite microstructure of PZT film (d = 30 mm).

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Phase formation, phase transitions, ferroelectric and relaxor properties of nonstoichiometric $[(Na_{0.5}Bi_{0.5})_{1-x}K_x]TiO_3$ ceramics

A.V. Mosunov[1*], E.D. Politova[1], N.V. Golubko[1], G.M. Kaleva[1], D.A. Belkova[2], D.A. Strebkov[2], 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.
[*]Corresponding Author: amosunov@nifhi.ru

Last decade, 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, 2]. Presence of polar nanoclusters leading to high mobility of boundaries "domain walls/polar clusters" comprise peculiarity and advantage of the NBT-based compositions.

In this work, phase formation, crystal structure parameters, microstructure, dielectric, relaxor and ferroelectric properties of nonstoichiometric ceramics $[(Na_{0.5}Bi_{0.5})_{1-x}K_x]TiO_3$ with x = 0 – 0.1 have been studied.

Ceramic samples were prepared by the two-step solid-state reaction method at temperatures T_1 = 1000 K (6 h), and T_2 = 1300 K (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 increased in the system in accordance with the ionic radii changes, while main size of grains decreased with x increasing.

Ferroelectric phase transitions were observed at ~ 600 K in the dielectric permittivity versus temperature curves. In the samples with x>0.05 additional anomalies in the $\varepsilon(T)$ dependences were revealed above the ferroelectric transition temperature, with energy of relaxation activation E_a~1.9eV.

At the room temperature, non monotonous changes of the dielectric parameters were observed in modified compositions studied, and influence of the A-sublattice stoichiometry changes in the $(Na_{0.5}Bi_{0.5})TiO_3$ compositions modified by K^+ cations on structure parameters and functional properties of ceramics was proved.

The results obtained confirmed prospects of new lead-free materials development by modification of NBT-based compositions with aliovalent cation substitutions.

Acknowledgment

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Polarisation switching of ferroelectric-ferroelastic gadolinium molibdate in magnetic field

E.D.Yakushkin

Shubnikov Institute of Crystallography, Federal Research Center Crystallography and Photonics, Russian Academy of Sciences, Moscow, Russia

yakushkin@crys.ras.ru

This work continues studies of magnetic phenomena in ferroelectric materials without magnetoelectric interaction (not multiferroics) [1]. To date any clear physical picture of mechanisms of such effects is still absent. At the same time, according to the existing experimental data, effects observed in a magnetic field are due to a change in the relaxation motion of domain walls and to the corresponding modification of the ferroelectric domains configuration. This is in turn caused by a change in the structure of defects of the lattice in the magnetic field, which are pinning centers of domain walls. In a certain sense, the situation is qualitatively similar to the effect of the magnetoplasticity in nonmagnetic crystals.

In this case it has been studied the action of the magnetic field on a GMO single-crystal sample with a single planar domain wall and on a sample with multiple domain walls. A drastically change in the character of the electric switching of polydomain gadolinium molybdate single-crystal in an external magnetic field has been detected. This change is attributed to a magnetically stimulated increase in the pinning of domain walls. Under certain conditions, the loop of switchable polarization is degenerated into an ellipse characteristic of a common linear insulator with leakage current.

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Yet another *P-E* hysteresis loops tester

V.A.Sandler, E.D.Yakushkin

Shubnikov Institute of Crystallography, Federal Research Center Crystallography and Photonics, Russian Academy of Sciences, Moscow, Russia

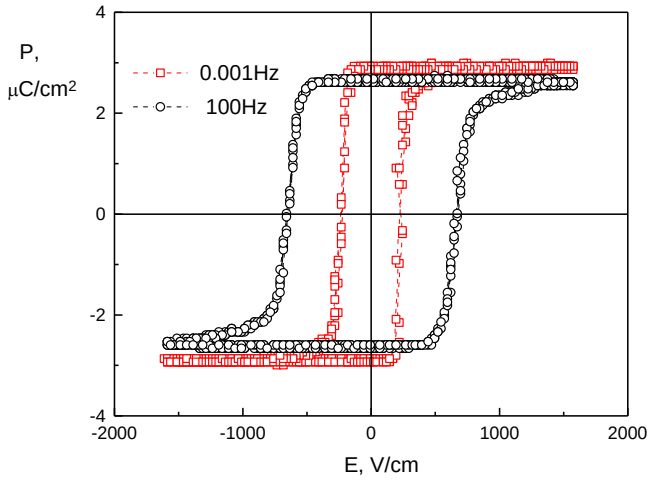
yakushkin@crys.ras.ru

The most often used technique for hysteresis loop measurement is based on a scheme of Sawyer and Tower [1]. A numerous subsequent modifications of this technique are known also [2-4]. Now are available some commercial variants of corresponding devices that uses the same universal scheme.

Nevertheless here is proposed yet another variant of such devices. The proposed device is simpler in construction than existing loop tracers and has a lower production cost. Along this our device has quite good measuring capabilities. That is wide range of measuring voltages and frequencies, the compensation capabilities for the losses of the samples and for the additional capacitance of the sample plus sample holder, etc.

Here by way of example are shown a typical hysteresis loops for a triglycine sulphate single crystal at two measuring frequencies and for the triangular form of a measuring signal obtained at room temperature. One can see characteristic changes of shape of the loops.

The proposed device is exposed.



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This work was supported by the Federal Agency of Scientific Organizations (Agreement No 007-ГЗ/Ч3363/26)

POSTER SESSION 2

Wide-band dielectric response of a magnetoelectric-relaxor solid solution $Pb(Fe_{1-x}Sc_x)_{2/3}W_{1/3}O_3$

Gennady Komandin[1], Oleg Porodinkov[1], Igor Spektor[1], Sergey Chuchupal[1], Alexander Bush[2], Anastasia Koroleva[2], Victor Torgashev[3]

1-A.M. Prokhorov General Physics institute of Russian Academy of Scienses, Russia
2-Moscow Technological University (MIREA), Russia
3- Southern Federal University, Russia.
Corresponding_author_gakomandin@mail.ru

The cation substitution in a B' position of complex heterovalent perovskites $AB'_{2/3}B''_{1/3}O_3$ can form new and enhance the existing electrodynamic properties. Among them magnetoelectric – relaxor solid solution $Pb(Fe_{1-x}Sc_x)_{2/3}W_{1/3}O_3$ (PFSW) are a new and insufficiently studied material [1]. Replacement of iron by scandium in the B' position of the perovskite structure makes it possible to achieve magnetic ordering without suppression of the relaxor-ferroelectric properties. It opens the prospects of creating magnetoelectric materials with high values of the dielectric permittivity – high-k materials. As all relaxor materials with diffuse phase transitions [2], PFSW has a complex spectrum of IR phonons. Interpretation and fitting of frequency-broadened bands of IR modes are complicated by the asymmetry of the absorption lines. Therefore, the use of the simple additive dispersion models to describe experimental spectra is limited by the strong anharmonisity of the response and by impact of low-frequency polarization on the parameters of the vibrational spectrum of these solid solutions. In our work, we considered the features of the anharmonic response and compared the results of the of dispersion modelling performed within the framework of classical oscillator model and semi-quantum four-parameter one. As a result, we determined the complex response function $\varepsilon^*(\nu)$ of the PFSW solid solutions in the frequency range of 13 decades. It made possible to estimate the effect of low-frequency polarization on the accuracy of determining the parameters of spectra.

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Infrared radiometry in experimental studies of pyroelectric properties of materials

G. Gavrilov, A. Kapralov, K. Muratikov, E. Smirnova, and G. Sotnikova

Ioffe Institute, Politekhnicheskaya 26, St. Petersburg, 194021, Russian Federation
Corresponding author: g.sotnikova@mail.ioffe.ru

Investigation of pyroelectric properties is a powerful tool of studying polarization processes and is necessary for the development of highly efficient pyroelectric materials. Recently, the thermal wave method has become widely used for this purpose. The practical implementation of this technique uses a modulated laser radiation providing the thermal waves penetrating into a sample [1].

We propose a new experimental technique for the precise determination of the pyroelectric coefficient “p” based on the analysis of both pyroelectric and thermal responses of the sample after the step-like laser thermal excitation. The peculiarities of the sample heating by laser radiation using different modulation laws are considered. It is shown that the correct interpretation of the experimental data is possible only when taking into account the knowledge of the true values of the heat transfer coefficient "H" that characterizes the heat exchange efficiency between the sample and ambient under the specific conditions of the experiment.

For a test sample with linear dimensions considerably exceeding its thickness, the direct measurements of the actual surface temperature allows us to obtain its thermal transient characteristic and, therefore, the true value of the coefficient "H" for arbitrary experimental conditions [2]. The direct temperature measurements allows also the monitoring of the rate of its changing (dT/dt) for a long time after the laser step-like thermal impact including the time interval corresponding to the steady-state process. This improves the accuracy of the experimental determination of the coefficient “p” [3] and allows one to separate different contributions to the measured pyroelectric signal.

The thermal impact was carried out by the semiconductor laser module with λ=0,635 μm and adjustable radiation power of 0.05- 0.3W modulated by an external signal pulse generator. To measure the sample surface temperature, IR- radiometric sensors based on A^3B^5 photodiodes sensitive in the spectral range of 4.1 ± 0.5 μm were used. They do not require cooling and provide sensitivity no worse than 0.1 ° C in the temperature range of 20-200 ° C at the fast response of about 1 ms. The diodes are completely insensitive to background illumination of laser radiation with $\lambda \leq 1$ μm [3].

The experimental results of the pyroelectric study of the ferroelectric single crystal (Z-cut) $LiTaO_3$, poled PZT ceramics as well as relaxor PMN based ceramics are presented. The preliminary results on the pyroelectric coefficient measurements for AlN single crystal and AlN films are also included. The analysis of both pyroelectric and thermal responses shows that a number of transient processes occur in the pyroelectric output signal. They are characterized by different time constants, including those faster than the thermal process associated with the primary pyroelectric effect. This fact can lead to the overestimation of the pyroelectric coefficient determined experimentally in nonstationary conditions.

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Dielectric/electrical properties of graphite, MWCNT and hybrid MWCNT/GNP composites

I. Kranauskaite[1], J. Macutkevic[1], A. Borisova[2], A. Martone[3], M. Zarrelli[3], A. Aniskevich[2], V. L. Kuznetsov[4], S. I. Moseenkov[4], V. Fierro[5], A. Celzard[5] J. Banys1[2]

1-Vilnius University, Physics Faculty, Radiophysics Department, Vilnius, Lithuania
2-Institute of Polymer Mechanics, University of Latvia, Riga, Latvia
3-Institute for Composite and Biomedical Materials, NRC of Italy, Portici, Italy
4-Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
5-IJL – UMR Université de Lorraine – CNRS 7198, ENSTIB, Épinal,
Ieva.kranauskaite@ff.vu.lt

Polymer composites with various carbon inclusions like multiwalled carbon nanotubes (MWCNT), graphite or graphene are interesting for fundamental reseach and are attractive for various applications [1]. The electrical percolation threshold of these composites could be very low and it is important to obtain as low percolation threshold as possible in order to reach optimal mechanical properties of composites and to use minimal concentration of expensive fillers. Adding several different fillers in the matrix the percolation threshold can decrease in comparison with single filler composites due to synergy effect between the different components [2].

In this contribution the dielectric/electrical properties of composites filled with different fillers were investigated: graphite filler (concentration 0-2 wt.%), MWCNT filler (0-4 wt.%), hybrid MWCNT/GNP filler (total concentration 0.3 wt.%). The measurements were performed in frequency range from 20 Hz to 3 GHz at room temperature and at low frequencies (20 Hz – 1 MHz) in temperature range from 30 K to 300 K. The percolation threshold for graphite composites is high except exfoliated graphite for which percolation threshold is similar to MWCNT composites. Combining two types of carbon fillers MWCNT and GNP the quantitative synergy effect on the material electrical conductivity was obtained.

In this presentation the results of dielectric/electrical investigations of polymer composites filled with different fillers will be presented, compared and discussed in wide frequency and temperature range

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Grain size effect on dielectric properties of submicron ranged $BaTiO_3$ ceramics

Vlad-Alexandru Lukacs, Ina Turcan, Mirela Airimioaei, Lavinia Curecheriu, Liliana Mitoseriu

Dielectrics, Ferroelectrics & Multiferroics Group, Faculty of Physics, "Alexandru Ioan Cuza" University, Iasi, Romania
Corresponding_author_lukacs_alx@yahoo.com

$BaTiO_3$ is one of the main multifunctional materials used for building passive and active components in microelectronics. Two main important tasks are related to the effect of ceramic grain size: (i) to preserve high functional characteristics at specific grain size levels, in particular when reducing grain size at nanoscale [1]; (ii) to understand the role of intrinsic/extrinsic contributions to the exceptional dielectric and piezoelectric properties around the critical size of 1μm, which is still an open problem [1-2]. The aim of the present work is to investigate in depth the functional properties of $BaTiO_3$ ceramics in the range of 1μm.

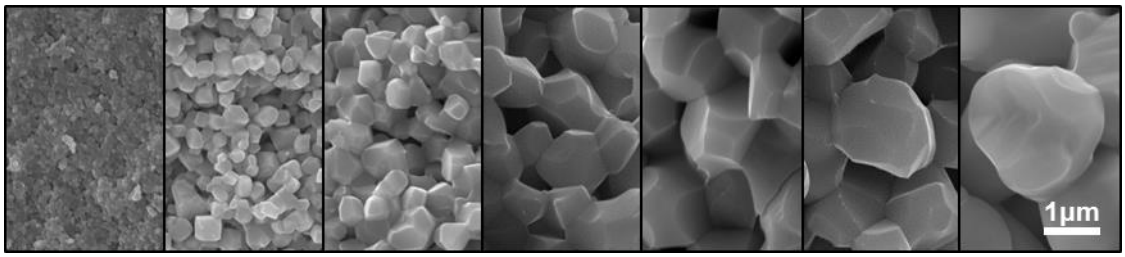

Fig. 1: Fracture micrographs of BaTiO3 dense ceramics with various grain sizes.

Dense ceramics with various micron and submicron grain sizes were synthesized by spark plasma sintering (SPS) starting with $BaTiO_3$ fine powders, followed by various steps of subsequent thermal growth treatment. Phase purity and morphology of final ceramic samples, along with the dielectric functional properties have been investigated and addressed. Orthorhombic and tetragonal phase superposition with variable amounts of the two phases was observed, as a function of grain size. Permittivity values, the temperature evolution feature regarding the ferroelectric-paraelectric transition and tunability behavior show the typical dependence on the ceramic grain size with a maximum in the range of 1μm. The role of intrinsic/extrinsic contributions on such behavior is discussed.

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Structure and Properties of $Ca_{10.5-x}Pb_x(VO_4)_7$ Single Crystals

Daria Petrova[1,2], Dina Deyneko[1], Sergey Stefanovich[1], Bogan Lazoriak[1]

1- Lomonosov Moscow State University, Russia
2- Gubkin Russian State University of Oil and Gas (National Research University), Russia
Corresponding_author:_petrova.msu@gmail.com

The whitlockite-like compounds manifest multifunctional properties and have been under research recently [1,2]. These compounds are considered as new advanced materials with ferroelectric and antiferroelectric, piezo-electric, nonlinear optical, ionic-conductive, luminescence, nonlinear optical and laser properties. We have obtained by the Czochralski method and studied new whitlockite-like $Ca_{10.5-x}Pb_x(VO_4)_7$, x = 1.8; 3.5; 4.9 single crystals with record properties. According to the X-ray diffraction analysis, the compound crystallizes in *R*3*c* space group. Structures of $Ca_{10.5-x}Pb_x(VO_4)_7$ were refined by the Rietveld method and Pb^{2+} cations was occupied over the *M*1 - *M*2 and *M*3 sites in the β-$Ca_3(PO_4)_2$-type lattice. The crystals are ionic conductors. Conductivity measurements were carried out in the interval 500-1000 K and values are from 10^{-6} to 10^{-2} Sm/cm. Ca^{2+}-ion mobility in the solid solutions is manifold higher than in $Ca_3(VO_4)_2$ and other previously studied β-$Ca_3(PO_4)_2$-type compounds. Lead substitution for calcium in is investigated as a factor controlling ferroelectricity, ionic-conductivity and non-linear optical activity. Non-linear optical activity in the second harmonic generation effect strongly increases with x, in keeping with investigated $Ca_{10.5-x}Pb_x(VO_4)_7$ system in form of powders and ceramics in [3].

The combination of low temperature conductivity with high nonlinear optical activity and ferroelectricity extends ability of ion-exchange technology of integrated optical devices for a new class of materials. Based on the obtained data control of important properties in whitlockite-like phases aimed at creating multifunctional materials at their basis is possible.

Acknowledgement

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Pure, lithium- or magnesium-doped ferroelectric single crystals of $Ca_9Y(VO_4)_7$: cation arrangements and phase transitions

Dina Deyneko[1], Daria Petrova[1,2], S.M. Aksenov [3], Sergey Stefanovich[1], Bogan Lazoriak[1]

1 - Lomonosov Moscow State University, Russia
2 - Gubkin Russian State University of Oil and Gas (National Research University), Russia
3 - IC RAS, Russia.
Corresponding_author_ deynekomsu@gmail.com

The non-centrosymmetric vanadates $Ca_9R(VO_4)_7$ (*R* = rare earth elements, Bi, Y) [1] are isostructural to *β*-$Ca_3(PO_4)_2$ [2], and belong to the whitlockite mineral family [3]. These compounds are currently considered promising for white light emission LEDs, phosphors and light converters, for example [4]. Single crystals of $Ca_9Y(VO_4)_7$ (**1**), $Ca_9Y(VO_4)_7$:Li^+ (**2**) and $Ca_9Y(VO_4)_7$:Mg^{2+} (**3**) were grown by the Czochralski method. Their chemical composition was analysed by ICP spectroscopy and their crystal structure was examined by single crystal X-ray analysis. The crystals are characterized by trigonal symmetry, space group *R*3*c*. Hexagonal unit-cell parameters are: *a* = 10.8552(1) Å, *c* = 38.0373(2) Å, *V* = 3881.65(1) Å^3 for **1**; *a* = 10.8570(1) Å, *c* = 38.0161(3) Å, *V* = 3880.77(4) Å^3 for **2**; *a* = 10.8465(1) Å, *c* = 38.0366(2) Å, *V* = 3875.36(3) Å^3 for **3**. All crystals are characterized by *β*-$Ca_3(PO_4)_2$-type structure with statistical distribution of Ca^{2+} and Y^{3+} over *M*1, *M*2 and *M*5 sites in different ratios and with completely empty *M*4-cationsite. The impurity of Mg^{2+} in structure **2** has been detected in octahedral *M*5 site. Ferroelectric phase transitions are evidenced by DSC and SHG. At about 1220 and 1300 K, they demonstrate phase transitions. Upon heating the symmetry of the crystal structure changes according to the scheme *R*3*c* → *R*-3*c* → *R*-3*m* and is restored during consequent cooling. The first of them is of ferroelectric and the second of non-ferroelectric nature. Even a small amount of impurities in $Ca_9Y(VO_4)_7$ structure is accompanied by a noticeable decrease in the temperature of the ferroelectric-paraelectric phase transition.

This research was supported by Foundation of the President of the Russian Federation (Grant MK-3502.2018.5) and RFBR (Project № 17-03-01297).

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Phase composition and electro-optical properties of channel proton-exchanged $LiNbO_3$ waveguides

S.M. Kostritskii[1], Yu.N. Korkishko[1], V.A. Fedorov[1], O.G. Sevostyanov[2], I.M. Chirkova[2]

1-RPC Optolink Ltd, Russia,
2- Kemerovo State University, Russia
Corresponding_author_skostritskii@optolink.ru

All the above indicates the need to develop a nondestructive method for determining the phase composition and estimating the electro-optic coefficients in channel proton-exchanged waveguides. In order to solve this problem, we use micro-Raman spectroscopy, since Raman spectra of different phases are quite different from each other [1] and the use of a confocal microscope in a micro-Raman spectrometer provides high spatial resolution (~1 μm) [2], enough for a detailed study of the cross section of channel waveguides and integrated optics systems based on them.

For calibration of the micro-Raman data, we used samples of planar waveguides whose phase composition and electro-optic properties were determined by the IR and UV spectroscopy methods [1]. This lets us establish clear correlations between the parameters of the micro-Raman spectra and the values of the electro-optic coefficients r_{13} and r_{33}, which we used to optimize the conditions for preparation of electro-optic phase modulators based on proton-exchanged channel waveguides in $LiNbO_3$ crystals. Micro-Raman spectroscopy allows for fast and easy analysis of the electro-optic properties of proton-exchanged waveguides, since there is no need for a number of complicated processing operations (polishing the ends, optical coupling and deposition of electrodes) with the integrated optics elements, which is required for optimization of the technology when using direct measurements of the electro-optic efficiency of waveguides.

All the previous studies showed a significant decrease in the electro-optic coefficients after proton exchange [2, 3]. After high-temperature annealing, the effective values of the electro-optic coefficients are partially restored [1, 3] and reach ~2/3 of the values for the original $LiNbO_3$ crystal. Therefore the micro-Raman method is used to study annealed proton-exchanged channel waveguides which contain α^*, α^{**}, κ_1, and κ_2 phases, depending on the processing conditions for their preparation. Thus, the results obtained allow us to optimize the process of preparation of electro-optic phase modulators based on proton-exchanged channel waveguides in $LiNbO_3$ crystals.

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Electron beam induced current method for investigation of conductivity mechanisms in the ferroelectric thin films

Alexandr Antonovich[1], Aleksei Petrushin[2] Yuriy Podgorniy[3]

1- Graduate student, Moscow Technological University (MIREA), Russia
2- Graduate student, Moscow Technological University (MIREA), Russia
3- Ph.D. (Eng.), Leading Research Scientist, Head of Department of REC «Technological center»
alexant@phys.msu.ru

A significant part of applications of ferroelectric films is based on their application as capacitor structures. Leakage currents can limit their wide application [1]. In turn, solutions designed to reduce leakage currents can be developed only if the conduction mechanisms in structures based on ferroelectric films are sufficiently studied and correctly interpreted. Thus, the study of the mechanisms of charge transport in thin ferroelectric films is of great practical importance for various devices of micro- and nanoelectronics based on ferroelectric capacitors [2]

The results of studies of contact phenomena at the PZT-Pt interface in nanostructures based on ferroelectric $PbZr_{0.52}Ti_{0.48}O_3$ films are presented. The electron beam induced current method (EBIC) [3] was used to investigate the effect of the interface on charge transport in the capacitor structures with thin PZT film on a platinum electrode. The EBIC profiles were obtained and the possibility of direct recording of the space-charge region (SCR) near the PZT-Pt interface is shown depending on the polarity of the applied voltage. The linear dependence of the SPR thickness was determined with a negative voltage on the structure. At the same time, the width of the space-charge region near the platinum electrode does not depend on the positive voltage on the structure.

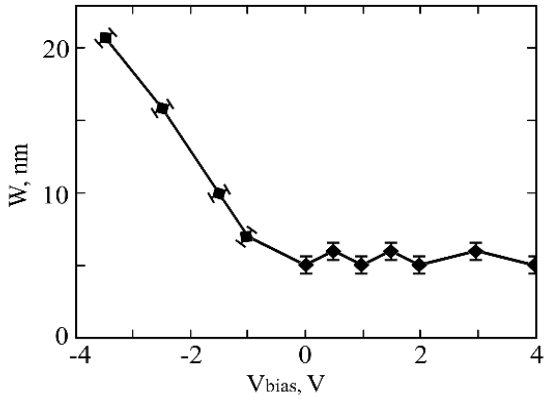

Figure 1.

So it has been established that the contact properties of platinum with thin PZT film are similar to those of a semiconductor diode with a p-n junction. The experimental results obtained by the electron beam induced current method confirm similar results obtained by studying the current-voltage characteristics of Pt-PZT structures with using the traditional methods [4].

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An evidence of electrochemical contribution to local electromechanical response in P(VDF-TrFe)/$LiNbO_3$

Maxim S. Ivanov[1], Maxim V. Silibin[2], Vladimir A. Khomchenko[1], Timur Nikitin[3], Arseny S. Kalinin[4], Dmitry V. Karpinsky[2], Igor K. Bdikin[2], Vyacheslav V. Polyakov[4], Rui Fausto[3] and Jose A. Paixão[1]

1-CFisUC, Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal
2-National Research University of Electronic Technology "MIET," Zelenograd, 124498 Moscow, Russia
3-CQC, Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
4-NTMDT Spectrum Instruments, Zelenograd, 124460 Moscow, Russia
maxim.ivanov@uc.pt
sil_m@mail.ru

The development of piezoelectric devices, sensors, transducers, and electromechanical actuators requires a preparation of new or/and an improvement of the existing materials that possess enhanced mechanical, electrophysical, and piezoelectric properties [1]. One possible way to reach this goal is to develop hybrid materials in which organic/inorganic nanofillers will be embedded in a polymer matrix [1–2]. For this purpose, a well-known poly(vinylidene fluoride-trifluoroethylene), P(VDF-TrFE), can be used as a matrix since it directly forms the ferroelectric β-phase without additional stretching as compared with the pure PVDF polymer and, thus, exhibits remarkable ferroelectric (pyroelectric and piezoelectric) capabilities, which, potentially, could induce a coupled effect between nanofillers and polymer matrix [2].

In this work, we demonstrate an alteration of mechanical, electrophysical, piezo- and ferroelectric properties of P(VDF-TrFE) polymer at the composition of 70/30 mol% in the presence of lithium niobate ($LiNbO_3$) nanofillers. The micro- and nanoscale measurements of the elastic modulus suggest a two-fold increase in the mechanical rigidity of P(VDF-TrFE) film after embedding the $LiNbO_3$ nanofillers. The enhancement of local piezo- and ferroelectric properties of the modified polymer is evidenced by the increase of the direct piezoelectric coefficient from 27.1 pm/V to 36.1 pm/V. This increase has been associated with the significant contribution of the Li-ion stimulus diffusion – the ionic phenomena due to the $LiNbO_3$ nanofillers [3], as unambiguously affirmed by electrochemical strain (ES) response, ES time spectroscopy, and Kelvin probe force microscopy methods.

The results obtained demonstrate crucial achievements towards the polymer nanofillers strategy, $LiNbO_3$ in particular, in attaining the desired functional behavior paving a way towards the development of adavanced sensors, transducers, actuators and piezoelectric devices.

This work was supported by the Russian Science Foundation (project number 16-19-10112).

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Dielectric Response and Elastic 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. 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.

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 broadening the ferroelectric phase transition.

Results of the dielectric permittivity, loss factor 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 (Figure 1.). Dependence of the maximums of dielectric permittivity and loss on temperature, frequency and concentration were examined. The observed curves of $\varepsilon_{max}(x)$ and $T_{max}(x)$ points to determine the thermodynamic type of solutions. The dielectric permittivity on the curve $\varepsilon(T)$ 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.

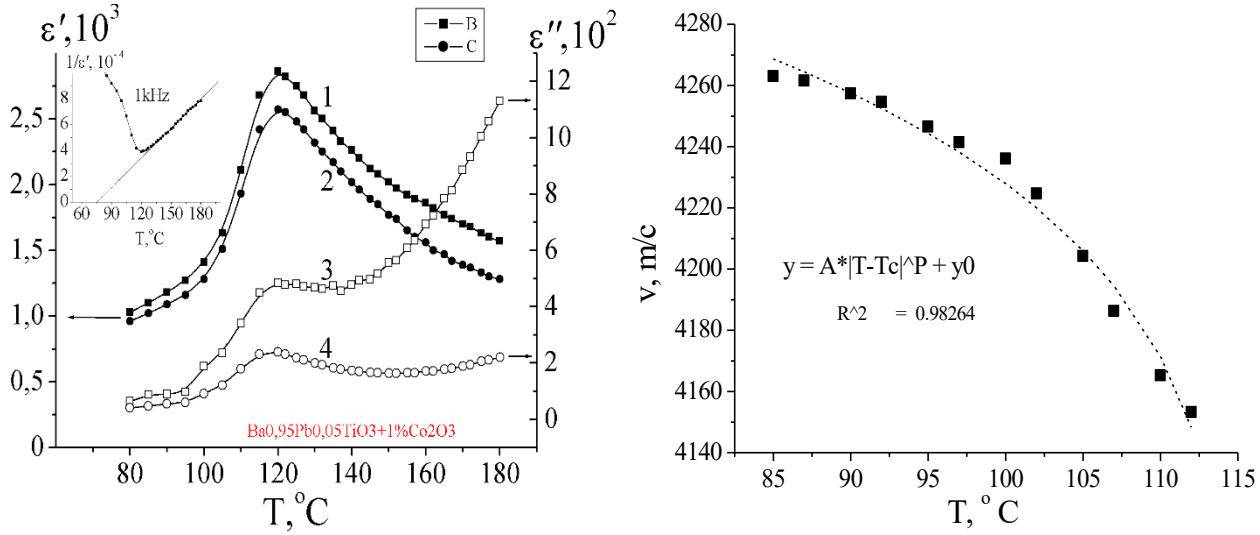

Figure 1. The temperature dependence of dielectric response (under weak E ≈ 1 V/cm field intensities) and acoustic wave velocity v(T) with approximation curve of the $Ba_{0.95}Pb_{0.05}TiO_3$+1wt%Co_2O_3 ceramics.

Investigation of planar waveguides in a lithium niobate crystal

Dmitry Irzhak[1], Artemy Irzhak[1], Dmitry Roshchupkin[1], Sergei Bozhko[2]

1- Institute of Microelectronics Technology and High-Purity Materials RAS, Russia
2- Institute of Solid State Physics RAS, Russia
irzhak@iptm.ru

Raman spectroscopy and X-ray diffractometry methods are widely used to study ferroelectric domain structures [1]. In this paper, using these methods, planar structures in a ferroelectric lithium niobate crystal are investigated and the results obtained are compared. We investigated the structure of the planar waveguides formed during diffusion of titanium in Y-cut $LiNbO_3$ crystal.

Figure 1(a) shows a map of the X-ray diffracted intensity along the crystal surface. It can be seen on the map that as a result of the diffusion of the metal, the crystal lattice has deformed both the layer directly processed and the crystal itself below this layer. The deformation of crystal lattice was calculated using a results of X-ray diffraction on the Y-cut of the lithium niobate crystal simulation.

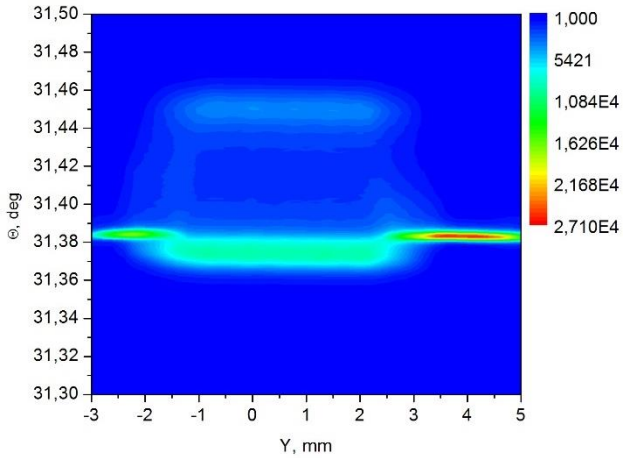

Figure 1. Map of the X-ray diffracted intensity along the crystal surface.

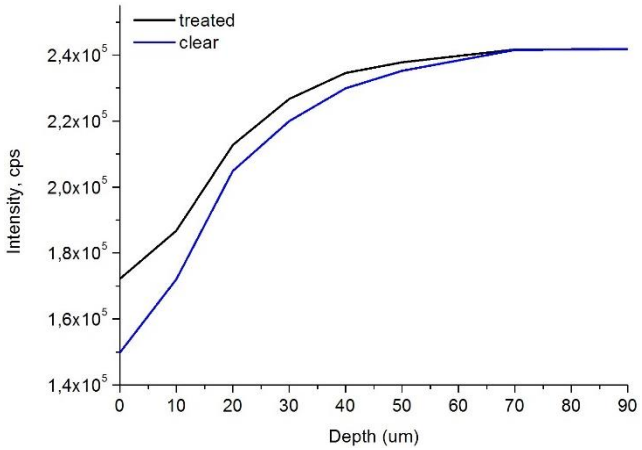

Figure 2. The change of the peaks intensity in the Raman spectrum, depending on the crystal depth.

The presence of both compression and stretching deformations was found in the subsurface layer and the deformation depth is ~ 70 μm.

Studies of the same sample using the Raman microscopy method also demonstrated the presence of a deformed layer. The change of the peaks intensity in the Raman spectrum, depending on the crystal depth was observed (Fig. 2).

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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]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
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. 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.

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.

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).

Ferroelectric films on silicon carbide substrates: properties and applications.

Andrey Tumarkin, Alexander Gagarin, Andrey Odinets, Michail Zlygostov, Evgeny Sapego

Saint-Petersburg Electrotechnical University, Russia
avtumarkin@yandex.ru

Now, there is a stable interest to ferroelectrics (FE) provided by a strong dependence of the material permittivity on applied electric field. This physical phenomenon makes it possible to realize microwave high-Q variconds, controlled filters, delay lines and phase shifters. It is known that a factor limiting the operating power of such devices is the superheating of ferroelectric elements. One of the methods of decreasing the superheating of the operation region of a device is assumed to be the use of substrates with a high thermal conductivity [1,2]. From this standpoint, the most promising substrate for powerful microwave devices is single-crystal silicon carbide (SiC). The realization of "a ferroelectric film on silicon carbide" heterostructure can lead to a radical increase in operating powers of microwave devices.

The present work was aimed at studying the structure and high-frequency dielectric properties of thin $BaSrTiO_3$, $BaZrTiO_3$ and $BaSnTiO_3$ layers in the paraelectric state, which were grown in situ by RF magnetron sputtering of a ceramic targets onto semi-insulating silicon carbide substrates and were intended for use in high-power nonlinear elements operating in the microwave range.

The phase composition of obtained FE films was studied by X-ray diffraction (XRD).The microstructure and surface morphology were studied by atomic force microscopy. The microwave characteristics of planar capacitors based on FE films were determined at a frequency of 1.5 GHz.

XRD data of all investigated film solid solutions grown on silicon carbide substrate showed a well-formed perovskite structure with pronounced (h00) growth texture. Investigation of the surface morphology of deposited FE layers showed that the average surface roughness height amounted to 20 nm. The dimensions of perovskite grains varied within 100–300 nm. Microwave measurements showed that a tunability of capacitors was in a range of 1.7 - 2 for an applied field of 60 V/μm and the dielectric losses at 1.5 GHz did not exceed 2%.

The results of presented investigations showed that BST films grown on semi-insulating silicon carbide under structurization approach possessed well-formed perovskite crystalline structure free of secondary phase inclusions, which positively influenced the electrical properties of films, in particular, their nonlinearity and level of dielectric microwave losses. A comparison of the obtained data to analogous values reported for thin FE layers on widely used alumina substrates showed that the proposed thin BST films on semi-insulating silicon carbide can be promising base materials for the creation of tunable high-power microwave elements.

This work was supported by the RFBR, projects 16-29-05147 ofi_m and 16-07-00617 and the Ministry of Education and Science of the Russian Federation (3.3990.2017/4.6).

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Principle of optimal impulse front compression in nonlinear transition line based on ferroelectric varactors

Sergey Ptashnik, Valentina Medvedeva, Andrey Altynnikov and Andrey Tumarkin
Saint-Petersburg Electrotechnical University "LETI", Russia
avtumarkin@yandex.ru

The effect of the shock front transformation into an oscillating region in nonlinear dispersion media has been known for a long time [1] and is currently used, in particular, for the generation of solitons [2,3]. This effect can be occurred in two cases. The first one is the situation where the signal entering the nonlinear medium initially has jumps, i.e. bounded in amplitude regions with a shock front [1,3]. The second one is where the shock front appears from the compression of the front of initially continuous pulse entering the medium [1,2]. However, in the context of pulse front compression, the appearance of such oscillations is a negative factor limiting the compression potential. In the frames of this work we suggest the solution of the problem.

The case of the oscillations is the superposition of two factors: the front steepness of the initial pulse and the steepness of the voltage-capacitance dependence (VCD) of the nonlinear varactor. The maximum compression of the pulse front can be obtained with so-called optimum compression principle. The matter of this principle is the mutual compensation of two above-mentioned factors. Namely, the sections of the smallest steepness of the VCD should correspond to the sections of the greatest steepness of the front of the initial pulse and vice versa.

More strictly this principle can be formulated with next equation:

$$\Delta t(U) = \sqrt{C(U)L} = \tau_0\text{-}t(U) + U/\alpha,$$

where – t(U) — reverse time function of pulse front U(t); Δt(U) — line delay depended on voltage U; τ_0 — small-signal line delay (U → 0); α — required steepness of resulting pulse front defined by cut-off frequency of the transition line (see Fig.1).

This work was supported by the RFBR, projects 16-29-05147 ofi_m, 16-07-00617 A and the Ministry of Education and Science of the Russian Federation (3.3990.2017/4.6).

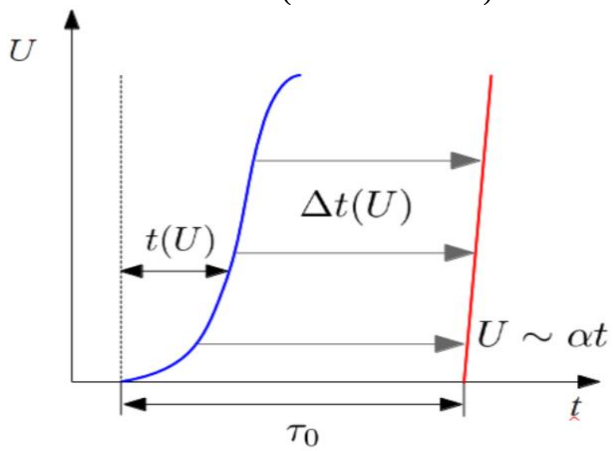

Figure 1 – Illustration of optimal compression principle

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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
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. 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.

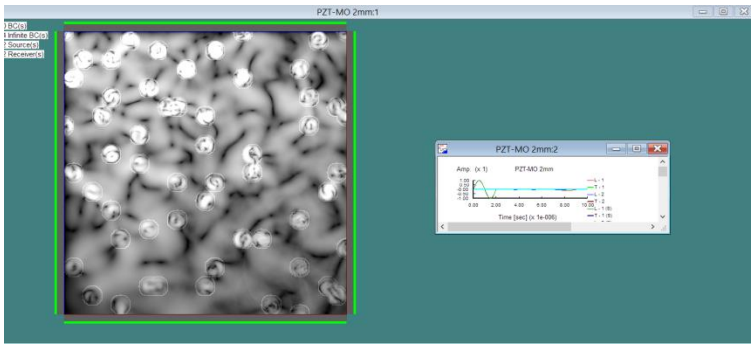

Figure 1. Wave 3000 Pro models of ceramics/polymer composites

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.

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).

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Experimental study of 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]

[1]Southern Federal University, 344090, 194 Stachky Ave., Rostov-on-Don, Russia
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]. 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.

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Synthesis and characterization of multifunctional BST thin films

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
dm.kiselev@gmail.com

Thin ferroelectric layers embedded into heterostructures are of interest both to fundamental research and to electronic applications. Barium titanate doped with strontium 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 etc. Properties of film structures strongly depend on their fabrication, electrode materials and substrate [1-3]. 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. 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 [4], dot-shaped Ni top electrodes 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).

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Dead layer thickness estimation at the ferroelectric film-metal interface

Yu. V. Podgorny, K. A. Vorotilov, and A. S. Sigov

Moscow Technological University (MIREA), Moscow, Russia
Corresponding_author_podgorny@mirea.ru

Conception of a passive dead layer at the metal-ferroelectric interface plays an important role in electrical properties characterization of metal-ferroelectric-metal structures, it considered as a reason for properties degradation with the ferroelectric film thickness decrease, including decreasing polarization, hysteresis slope, dielectric permittivity, etc. Origin of the dead layer may associate with physical or technological issues, however it is important limiting factor in FRAM scaling. In this work we consider different techniques for experimental estimation of dead layer value in different PZT capacitor structures.

A. K. Tagantsev *et al.* [1] proposed the method of dead layer thickness calculation from the slope of the hysteresis loops of the films with different film thickness. However, it doesn't take into account a leakage current and relaxation losses and can give an error that value increases with the test voltage amplitude. At the same time leakage current and relaxation losses leave the tips of the hysteresis loops unaffected. The experimental dependences of polarization (P_t) at the tips of the hysteresis loops were approximated by the sigmoidal MMF function.

Figure 1 shows the $P_t(E_m)$ and $P_t(E_{mf})$, dependences, where E_m and E_{mf} are the values of the applied field and the field into the ferroelectric volume.

The dead layer thickness (l) can be found by two ways. Figure 1 illustrates the first of them - the iterations method. The value of l increases until the slopes of the curves coincide (dotted curves). The second method consists in solving of the system of equations for a definite value of the polarization in the region of maximum steepness.

Dead layer calculation for structures with different film thickness and crystalline structures (dense and porous) results in good correlation between capacitance and hysteresis tips techniques.

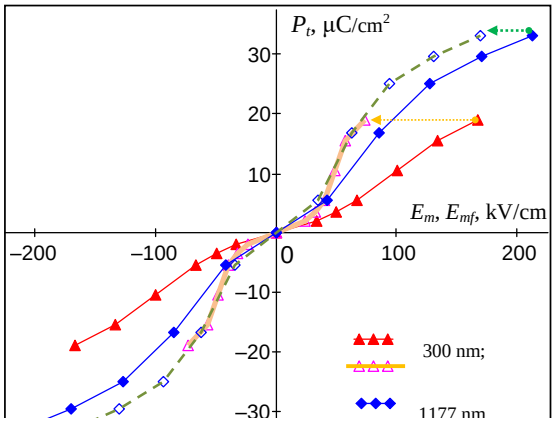

Figure 1. The dependencies of the polarization on the tips of the hysteresis loops of the structures with porous PZT films with the thickness of 300 and 1177 nm.

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Dendrite domain growth in lithium niobate crystals

Maria Chuvakova[1], Andrey Akhmatkhanov[1], Alexander Esin[1], Evgeniy Saveliev[1], Dmitriy Chezganov[1], Denis Alikin[1], Maksim Nebogatikov[1], Alexey Lobov[1], Vladimir Shur[1]

1- School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
M.A.Chuvakova@urfu.ru

The dendrite domain growth is a result of the domain wall shape instability which happened under nonequilibrium conditions with domination of the stochastic nucleation and retardation of the bulk screening [1-3]. These conditions can be realized in lithium niobate during polarization reversal at elevated temperature in the plate with artificial dielectric layer.

In this work dendrite domain growth was studied by in situ visualization at temperature 250°C in the polar-cut plates of congruent lithium niobate crystals covered by silicon dioxide film with transparent indium tin oxide electrodes. The main stages of domain structure evolution were revealed. The step-like velocity increase of the branch growth after splitting and increase of the branch diameter before tip splitting were observed. Analysis of the static domain structures demonstrated the field dependence of the envelop shape and filling ratio. The envelop shape changes from triangular to hexagonal and the filling ratio (ratio of domain and envelop areas) increase with field increase. The visualization of the domain structure in the bulk by second harmonic generation microscopy allowed measuring of the dendrite structure depth - about 10 μm. The qualitative change of domain shape was revealed at the depth about 150 μm.

The phase-field simulation was used to verify the analogy between self-organized growth of dendrite domains and dendrite crystals during the first order phase transition taken into account the crystal symmetry C3v [4]. The similarity of simulated and experimentally observed domain shapes was achieved. The phase diagram of growth domain morphology was constructed by computer simulation.

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).

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Domain kinetics during field cooling and polarization reversal in tetragonal PMN-PT single crystals

Andrei Ushakov[1], Alexander Esin[1], Dmitry Chezganov[1], Qingyuan Hu[2], Andrey Akhmatkhanov[1], Xiaoyong Wei[2], Vladimir Shur[1]

1-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
2-Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, China
andrey.ushakov@urfu.ru

Over the past few decades, the relaxor based ferroelectric *(1-x)*$Pb(Mg_{1/3}Nb_{2/3})O_3$-*x*$PbTiO_3$ (PMN-PT) crystals have attracted an attention of many researchers due to the outstanding electromechanical properties provided by the compositions corresponded to morphotropic phase boundary [1,2] with complex domain structure [3]. Application of the domain engineering for improvement of the crystal properties is impossible in these compositions, but tetragonal phase of PMN-PT ($x > 37$) is suitable for it. At the moment, the creation of single domain state as an important stage for creation of electro-optical devices is not fully developed. There is few data on domain structure evolution during field cooling in tetragonal phase PMN-PT single crystals.

In this work we have shown the outcome of the study of domain kinetics investigation during field cooling and polarization reversal in PMN-39PT single crystals. The evolution of the initial domain structure states were visualized during zero-field heating and in-field cooling by optical microscopy. The used procedure allowed us to achieve an almost single domain state. In situ optical visualization of the domain kinetics and switching current data has been recorded during polarization reversal. The optical contrast, corresponding to 180°-domains has been revealed and the time dependence of the switched area has been compared with the switching current data. The channeling-contrast backscattered electron mode by scanning electron microscopy has been used for visualization of slow domain structure evolution during polarization reversal with high spatial resolution [4]. The field dependencies of the main parameters characterizing domain kinetics have been revealed in temperature range.

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 RFBR (grant 17-52-80116-BRICS_a).

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Permittivity dispersion of the potassium sodium niobate ceramics

Grigory Shishkov, Olga Malyshkina, Ekaterina Barabanova

Tver State University, Russia
Pechenkin_kat@mail.ru

Potassium sodium niobates (KNN) have good dielectric and piezoelectric characteristics, as well as a high Curie temperature. Therefore, they are considered as possible candidates to replace lead-containing piezoelectric ceramics. Unfortunately, due to the peculiarities of the synthesis, it is difficult to obtain the repeatability of the ceramics properties.

To obtain the studied in this work $K_{0.5}Na_{0.5}NbO_3$ ceramics, potassium niobate and sodium niobate were synthesized at 650 °C for 4 hours. As raw materials Nb_2O_5, KCO_3 and $NaCO_3$ powders were used, they were grinded up in ethanol. The sintering of KNN was realized at a temperature of 1100 °C for 4 hours.

Dielectric properties were studied in the frequency range from 25 Hz to 1 MHz in the temperature region 30 to 500 °C. It is shown that the temperature dependence of the permittivity has two maxima (Fig. 1,a). The first (200 °C) corresponds to the phase transition from the orthorhombic to the tetragonal phase, the second (407 °C) – from the tetragonal to the cubic phase [1, 2]. At the same time, at the phase transitions temperatures, the dielectric loss has a minimum. Measurements of the permittivity in the heating-cooling process showed a small thermal hysteresis.

At low frequencies, an increase in the dielectric constant and dielectric losses was observed. In the first phase transition region (200 °C), an increase of the phase transition smearing and a shift of the maximum position to the region of higher temperatures are observed when the frequency was decreased (Fig. 1,b).

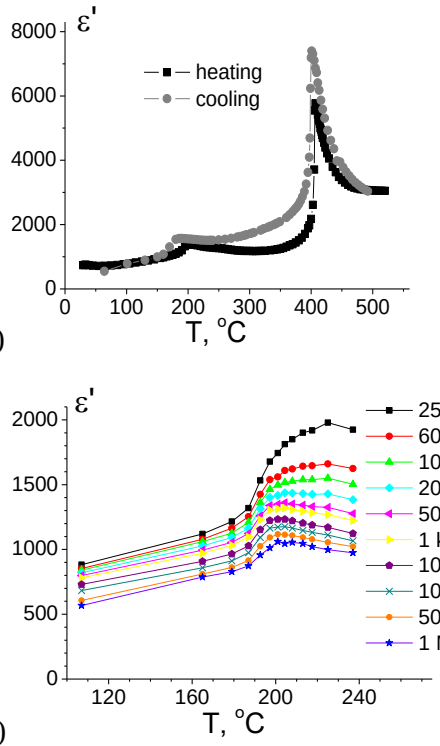

Figure 1. Temperature dependence of the permittivity for KNN at 1kHz (a), from 25 Hz to 1 MHz (b).

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Domain structures formation by electron and ion beam irradiation in relaxor SBN single crystals

Vera Shikhova[1], Vyacheslav Fedorovykh[1], Dmitriy Chezganov[1], Eugene Vlasov[1], Lubov Gimadeeva[1], Pavel Zelenovskiy[1], Eugene Greshnyakov[1], Andrei Kholkin[1,2], Lyudmila Ivleva[3], Vladimir Shur[1]

1-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
2-Department of Physics and CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal
3- Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia
vera@urfu.ru

We have studied the formation of the domain structures after irradiation of the single crystals of relaxor ferroelectric strontium barium niobate ($Sr_{0.61}Ba_{0.39}Nb_2O_6$, SBN61) by electron and ion beams. SBN61 single crystals were grown by modified Stepanov technique. The irradiation was carried out in the crystals with (1) multi-domain structure (created by Zero-Field Cooling (ZFC)) and (2) quasi-singledomain structure (created by Field Cooling (FC)).

The scanning electron microscope (Auriga CrossBeam workstation, Carl Zeiss NTS,) was used for e-beam and ion beam irradiation. The dot and stripe exposure regimes with different irradiation doses were used [1]. The created domain structures were visualized by piezoresponse force microscopy (PFM) (at the surface) and Raman confocal microscopy (in the bulk).

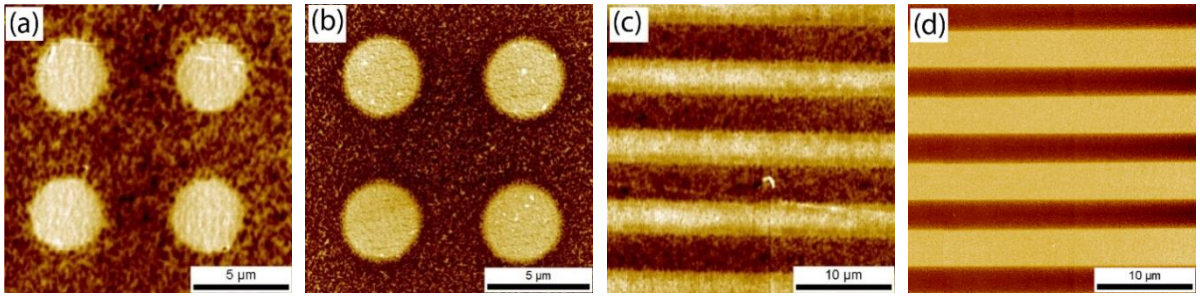

Fig. 1. PFM image of domain structure in SBN after ZFC after dot (a,b) and stripe (c,d) irradiation by e-beam (a,c) and ion beam (b,d). Doses: (a) 11 pC, (b) 5 pC, (c, d) 350 μC/cm^2.

The isolated circular domains were formed as a result of dot exposure (Fig. 1 a, b). The domains radius increased with saturation with irradiation dose increasing. The formation of regular chains of isolated domains (at doses below 100 μC/cm^2) and the stripe domains (at doses above 100 μC/cm^2) were observed in the stripe exposure (Fig. 1 c ,d). The domain walls roughness formed in FC crystals was significantly less than in ZFC crystals. The dependence of the depth of the created domains on the irradiation dose was obtained. The obtained results can be used for the domain engineering in ferroelectrics.

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

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Self-assembled domain structures created by local switching on non-polar cut of lithium niobate

Anton Turygin[1], Denis Alikin[1], Mikhail Kosobokov[1], Anton Ievlev[2], Sergei Kalinin[2], Vladimir Shur[1]

1-School of Natural Sciences and Mathematics, Ural Federal University, Ekaterinburg, Russia
2-The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, USA
anton.turygin@urfu.ru

Experimental study of the formation of quasi-regular arrays of needle-like domains on X and Y lithium niobate $LiNbO_3$ (LN) cuts was provided. Domain arrays were formed during scanning by biased SPM tip and grounded SPM tip in the vicinity of previously formed wedge-like domain. Domain structure was visualized by piezoresponse force microscopy and spatial distribution of the surface potential was measured by Kelvin force probe microscopy.

Effect of period multiplication of domain array (doubling and quadrupling) and chaotic behavior has been observed. Similar formation of quasi-periodic domain structures has been reported in polar [1] and non-polar [2] cut of LN, while formation of the domain chains with variation of spacing between the points of bias application. The key role of the charges injected during pulse application for formation of self-assembled domain structure without external electric field was demonstrated. Similar effect has been obtained earlier on the polar cut of LN [3]. Formation of self-assembled domain structure was attributed to electrostatic interaction of the charged domain walls.

The domain length in the arrays demonstrated: (I) uniformity, (II) doubling, (III) quadrupling, and (IV) chaotic behavior. The phase diagram of array types as a function of the electric field and domain spacing was simulated.

The demonstrated self-assembled domain growth and interaction of the charged domain walls can 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 Science Foundation (Grant 14-12-00826).

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Structural and magnetic phase transitions in the $Rb_x(NH_4)_{1-x}MnF_3$ mixed perovskites ($0.0 \leq x \leq 0.25$)

L.Smirnov[1], I.Natkaniec[2], M.Dlouha[3], S.Vratislav[3], J.Rubin[4]

[1]FSBI SSC RF Institute for Theoretical and Experimental Physics KI, Moscow, Russia
[2]Faculty of Physics, A. Mickiewicz University, 61-614 Poznanr, Poland
[3]CTU, Fac. of Nucl. Sci&Phys.Eng., Dept. of Solid State Engineering, Prague, Czech Republic
[4]Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Zaragoza, Spain.
Corresponding_author_LSS018@yandex.ru

Earlier it was shown that the NH_4MnF_3 undergoes two phase transitions: a transition from cubic ***(Pm-3m.*** Z = 1**)** to orthorhombic ***(Pnma.*** Z = 4) structure at Tc = I82 K and a magnetic transition at T_N = 75 K [1]. Phase transition at Tc is described as order-disorder for account of ammonium ion disorder and phase transition at T_N is described as para-antiferromagnetic. These results were obtained by neutron powder diffraction (NPD) method. The dynamics of phonon and librational modes of ammonium ions NH_4 in NH_4MnF_3 perovskite was studied by inelastic incoherent neutron scattering (IINS) for disordered cubic and ordered orthorhombic phases [2,3].

The report is devoted to the study of crystal structures of disordered cubic and ordered orthorhombic phases of mixed $Rb_x(NH_4)_{1-x}MnF_3$ crystals as function of rubidium concentration x and temperature by methods of the NPD and the IINS.

Using the NPD method, the values of the crystal lattice parameters in the *Pm-3m* and *Pnma* phases, the positions of the N, H, Mn and F atoms and the positions of the reflections determining the magnetic structure of $Rb_x(NH_4)_{1-x}MnF_3$ mixed crystals as a function of temperature and rubidium concentrations x in the range $0.0 < x < 0.25$, were determined.

The measured spectra of IINS from mixed crystals of $Rb_x(NH_4)_{1-x}MnF_3$ by the time-of-flight method make it possible to represent the obtained spectra in the I (r, t) and S (Q, E) curves for different temperatures and rubidium concentrations. The spectra of I (r, t) from the disordered phase of mixed crystals at T = 200 K are represented by the significant contribution of quasi-elastic incoherent neutron scattering (QENS) on the left wing of elastic coherent neutron scattering to the intensity of IINS represented by a wide peak. At a temperature T = 100 K, the mixed crystal is in the ordered phase, which is proved by the absence of the contribution of QENS, and the spectrum of I (r, t) is represented by a series of peaks arising in IINS from phonon and librational modes, which at T = 200 K as a result broadening of the widths and overlapping of the peaks form a wide maximum. The spectrum S (Q, E) of the ordered phase at T = 22 K represent scattering from spin modes in the range of transferred energy $6.5 < E < 8.0$ meV, from phonon modes in the range from $8.0 < E < 35.0$ meV, and from the librationl modes in the range $35.0 < E < 50.0$ meV. The selected modes are treated and presented in the tables and figures.

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Local piezoelectric properties and pyroelectric effect in lithium tantalate films

Alexander Solnyshki[1,2], Inna Kislova[1], Sergey Gudkov[1], Alexey Belov[2], Dmitry Kiselev[3], Roman Zhukov[3], Mikhail Malinkovich[3]

[1]Tver State University, Tver, Russia
[2]National Research University of Electronic Technology, Zelenograd, Moscow, Russia
[3]National University of Science and Technology "MISiS", Moscow, Russia
Corresponding author: a.solnyshkin@mail.ru

Ferroelectric materials integrated in thin film structures have become the basis for a significant improvement in the parameters of existing types of instruments, as well as the production of new microelectronic devices. Thin ferroelectric layers embedded into heterostructures are of interest both fundamental research and electronic applications. Lithium tantalate has stable pyroelectric and piezoelectric parameters over a wide temperature range, which can be useful, in particular, for some sensors and transducers. The aim of this work is to investigate the pyroelectric and local piezoelectric properties of nanostructured thin lithium tantalate films deposited on a silicon substrate suitable for the silicon integrated circuit technologies.

The samples of the thin film of $LiTaO_3$ were deposited by means of magnetron sputtering. The film thickness was 150 ± 1 nm. For studying the pyroelectric properties, copper circular electrodes with diameters 1 mm were deposited on free surface of the film by the magnetron sputtering. The dynamic method was used for a registration of pyroelectric response caused by periodically modulated heat flux. Semiconductor laser module CLM – 1845 IR – 980 (λ = 980 nm) was used as a radiation source. Laser power was equal to P = 220 mW. A lock-in amplifier was used to register signal occurring on electrodes.

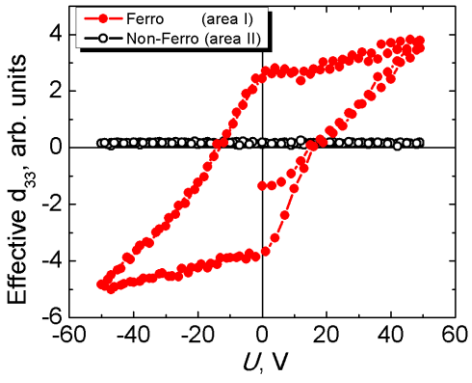

Fig. 1. PFM hysteresis loops in ferroelectric active and non-ferroelectric active regions.

According to the piezoelectric force microscopy (PFM) data, there were two types of regions in the $LiTaO_3$ films. The first type corresponded to regions with the switchable polarization directed from the free surface to the substrate. For the second type of regions, the local piezoelectric response was equal to zero. Remnant loops of the local piezoelectric response have been received on the film samples using switching spectroscopy PFM (SS-PFM). The hysteresis loops presented in Fig. 1 confirmed the presence of the polarization switched by external fields. The d_{33} piezoelectric coefficient was derived from PFM data. A value of the remanent d_{33} was found to be ~11 pm/V.

On the basis of experimental data, the pyroelectric coefficient of the ferroelectric film of lithium tantalate was calculated. The value of the pyroelectric coefficient was about $2 \cdot 10^{-5}$ $C \cdot m^{-2} \cdot K^{-1}$ which is approximately 10 times less than the one for a $LiTaO_3$ single crystal. Such a discrepancy may be associated with either a small content of the ferroelectric phase in the film sample or different orientations of the polarization vectors in the various regions of the $LiTaO_3$ film.

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Ferroelectric and Low Frequency Noise Characteristics of Phosphorous Chalcogenide Crystals

Ilona Zamaraitė[1], Andrius Džiaugys[1], Yulian Vysochanskii[2], Juras Banys[1]

1-Vilnius University, Faculty of Physics, Lithuania
2-Uzhgorod University, Ukraine
Corresponding_author_ilona.zamaraite@ff.vu.lt

Layered phosphorous chalcogenide crystals are an attractive analogue of graphene that combines ferroelectric properties with a semiconductive properties. Layered van der Waals structure makes it easy to form 2D atomic sheets with extraordinary properties. It is essential to understand physical processes that takes places during ferroic phase transition. There are several methods for evaluation of processes of interest. Low frequency noise spectroscopy is highly informative method for physical processes analysis at phase transition region [1].

In this work, a detailed noise study of lamellar phosphorous chalcogenide crystals has been carried out using the low frequency noise spectroscopy. The white noise spectra are observed at room temperature. Voltage noise spectra are characterized by 1/f noise above the phase transition temperature. The analysis of experimental data revealed that the source of the 1/f noise in the phosphorous chalcogenide crystal is the carrier number fluctuation due to the recombination between defect levels. The ferroelectric hysteresis loop was measured in order to show the crystal being of ferroelectric origin and to prove the presence of some defects.

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Change nonlinear-optical response of electro-optic crystal in conditions of contributions incoherent background illumination

A.V. Pustozerov, A. S. Perin, V. M. Shandarov

Tomsk State University of Control Systems and Radioelectronics, Russia
extomsk@gmail.com

In nonlinear optical media, may occur the effects of self-focusing and defocusing narrow light beams at different sign of a nonlinear optical medium. [1, 2]. These effects be significant interest, especially when the medium exhibits photorefractive properties and demonstrates very large nonlinear response at low light intensity. One of promising way to use that effect is based on photovoltaic properties of this material involves combinations of light fields with different wavelengths [3, 4]. In this work, we study the possibility of optical nonlinearity sign cross-over from self-defocusing to self-focusing in conditions of incoherent background within $LiNbO_3$:Fe sample. For incoherent background we use LED´s with central wavelengths of 455 nm, 470 nm, 525 nm. In experiment used sample of $LiNbO_3$:Fe (0,005 wt%) with dimensions of $5\times10\times10$ mm^3 along X, Y, and Z axes. “Signal” beam of He-Ne laser with linear polarization is incident onto the sample surface (YZ) to X axis in XZ surface of the crystal. Red beam polarization corresponds to the extraordinary wave of the crystal. For introduce the background light into the crystal, we use hollow metal tubes with mirror-like internal surface. Observation of light pictures was made by means of the analyzer of light beams.

As the result experimental study we observe compensation of the nonlinear part of the diffraction by photovoltaic mechanism in a lithium niobate crystal. This work reveals that short wavelength incoherent background illumination may be successfully used to change diffraction characteristics of narrow light beams in ferroelectric crystals like lithium niobate.

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Dielectric dispersion in thin $LiNbO_3$ films

Sergei Gudkov[1], Mikhail Kamenshchikov[1], Alexander Solnyshkin[1,2], Inna Kislova[1], Alexey Belov[2], Dmitry Kiselev[3], Roman Zhukov[3], Mikhail Malinkovich[3]

[1] Tver State University, Tver, Russia
[2] National Research University of Electronic Technology, Zelenograd, Moscow, Russia
[3]National University of Science and Technology "MISiS", Moscow, Russia
becauseimaphysicist@gmail.com

Ferroelectrics are promising materials for various applications of the modern electronics, in particular opto-, piezo-, acoustoelectronics. One of the most important ferroelectric materials is lithium niobate ($LiNbO_3$) [1]. This material has unique properties which are used in various applications [2]. Along with the unique optical properties, this material also has thermally stable piezoelectric modules and pyroelectric coefficient. Producing the high quality $LiNbO_3$ thin films on silicon substrates is particularly attractive. The study of the physical properties of $LiNbO_3$ films and their structure is due to a wide range of applications. As a rule, the properties of lithium niobate thin films may depend on many factors such as a fabrication method, substrate material and others. The purpose of this work was to study the dispersion of dielectric characteristics (capacitance, the dielectric loss tangent) and electrical conductivity of $LiNbO_3$ thin films prepared by various methods.

Thin lithium niobate films were fabricated in the National University of Science and Technology "MISiS". Deposition of a thin ferroelectric layer on silicon substrates was carried out by two methods: laser ablation method and RF magnetron sputtering. The substrates had (111) orientation and were previously cleaned. The film thickness is equal to 200±1 nm. Copper electrodes with a diameter of 2.4±0.2 mm were deposited on a free surface of the films by RF magnetron sputtering. Thus, the structure of $Cu/LiNbO_3/Si$ was produced.

The dielectric and conductivity studies were conducted by means of LCR meter E7-20. The amplitude of a measuring electric field was chose as 0.04 V. The measurements were carried out in the frequency range from 25 Hz to 1 MHz.

During the experiment, the frequency dependences of dielectric parameters of the film samples were obtained. It was found that a significant dispersion of the capacitance, the dielectric loss tangent and the ac electrical conductivity. With frequency increasing, the capacitance values decreased for both types of the $LiNbO_3$ film structures. However, the frequency ranges characterized by the sharpest decrease in capacitance are significantly different from each other. The differences in the frequency dependences were observed for the dielectric loss tangent. The dielectric characteristics behavior was discussed on the base of the barrier effects at the ferroelectric-semiconductor interface.

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The dynamics of light-induced absorption in $Bi_{12}SiO_{20}$ crystal for coherent illumination with circular polarization of the opposite signs

Elena Sim, Nikolai Burimov, Alexei Litvyakov, Marina Kisteneva, Stanislav Shandarov

Department of Electronic Devices, Tomsk State University of Control Systems and Radioelectronics, Tomsk 634050, Russia
lenoliya@rambler.ru

The changes in optical absorption in sillenite-type crystals are appeared due to photoinduced redistribution of the charge carriers over the defect centers with different photoionization cross-sections [1]. In this work, we present the studies of the dynamics of light-induced changes in absorption for laser irradiation with the wavelength of 532 nm possessing circular polarization (CP) with different signs in undoped $Bi_{12}SiO_{20}$ (BSO) crystal having the thickness of 2.64 mm along the [110] crystallographic direction. The typical experimental results for time evolution of normalized changes in the transmission of the sample under investigation are shown in Figure 1.

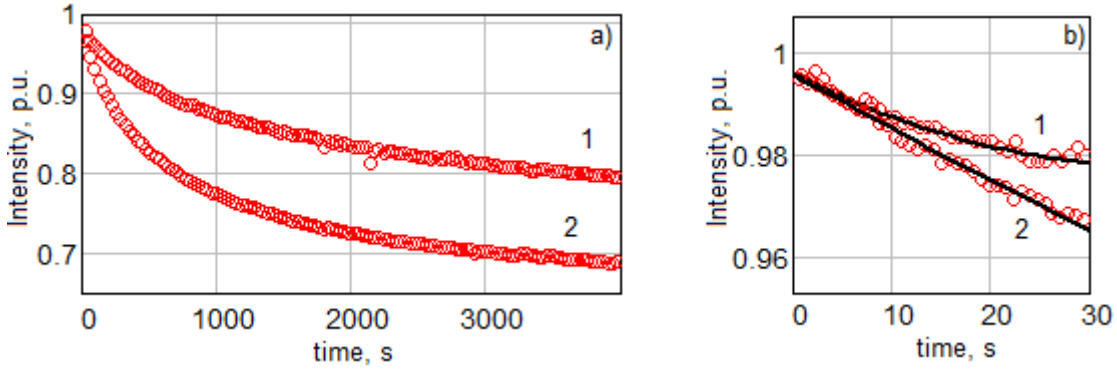

Figure 1. The time evolution of normalized changes in the transmission of BSO sample for laser beam (532 nm) with right (1) and left (2) circular polarizations and with intensities I_{10} = 13.2 W/cm^2 (1) and I_{20} = 34.4 W/cm^2 (2). The open circles are the experimental data and the solid lines are the fits on the base of Eq. (1).

To estimate the effect of sign of circular polarization on the rate of light-induced changes in inherent optical absorption we have approximated the initial stage of ones (see Figure 1, b) by second degree polynomial

$$I_m(t) = I_{m0}\left(1 - a_m t + b_m t^2\right), \qquad (1)$$

where numbers m = 1 and m = 2 are related to the light waves with right and left polarization, respectively. It was established that $a_2 \approx 2.6a_1$ as well as $I_{20} \approx 2.6I_{10}$. Thus, the reaction of defect centers in BSO does not depend on the sign of circular polarization of light waves with λ = 532 nm.

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The photoelectric properties in doped ferroelectric polymers

K.A.Verkhovskaya[1]*, V.V.Savel'ev[2], T.V.Krivenko[2]

[1] *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*

[2] *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 photoelectric properties and bulk photovoltaic effect were observed in ferroelectric polyvinylidene fluoride with trifluoroethylene(PVDF-TrFE) doped with carbon nanotubes,which are spectral sensitizers to laser beam 532 nm. The PVDF–TrFE films that are fabricated using centrifuging exhibit the spontaneous polarization Ps ~ 0.065 C/m^2 in the polar orthorhombic phase 2 mm [1]. The dipole moment is perpendicular to the polymer chain. In the ferroelectric phase, the polymer molecules are characterized by the TT conformations . We use PVDF–TrFE that contains single walled carbon nanotubes (SWCNTs, 0.52 wt %) . The thickness of the composite is 6μ.The photoelectric properties and bulk photovoltaic effect are measured using a DHOM-W532 laser with a radiation wavelength of 532 nm. We investigated photocurrent-voltage characteristic of unpoled sample of copolymer VDF-TrFE with dye under illumination. The value of photoconductivity $\sigma_{ph} = dJ/Vs = 1{,}3\times10^{-13}$ Ω^{-1} cm^{-1} (s is the area of illumination of the film, which is equal to 0.07 cm^2, d - the distance between the electrodes).

The polymeric ferroelectrics, like other media without a symmetry center, should reveal the bulk photovoltaic effect (BPE). If a homogeneous medium without a symmetry center is subjected to a uniform illumination in the region of an impurity or intrinsic absorption , it leads to the generation of a steady-state electric current J_{pv}[2]. Undoped copolymer films are nonphotosensitive and not reveal the BPE. The photosensitivity and photovoltaic effect are observed in polarized samples of copolymer with carbon nanotubes The current-voltage characteristics of the poled samples under laser excitation of intensity 2.8 W/cm^2 were investigated. When V=0 photovoltaic current $J_{pv} = 30\times10^{-9}$ A/cm^2. The switching of the ferroelectric copolymer sample changes the sign of the photovoltaic current. Photovoltaic current induces the photovoltage V_{pv}=200 V. The expression for the photovoltaic current can be written as $J_{pv} = \alpha G_{31} I$, where α -absorption coefficient, G_{31} - a component of the photovoltaic tensor for symmetry group C_{2v}, I - the light intensity. In the open-circuit conditions the photovoltaic current generates the photovoltage V_{pv}: $V_{pv} = J_{pv}\, d/(\sigma_d + \sigma_{ph})$, where σ_d and σ_{ph} are darkconductivity and photoconductivitiy. If $\sigma_{ph} > \sigma_d$, the electric field E_{pv} photoinduced due to the BPE is given by $E_{pv} = J_{pv}/\sigma_{ph}$. It is possible to estimate the efficiency of converting of light energy into electrical energy by the formula: $\eta = G_{31}E_{pv}$. For a sample P (VDF / TrFE) with carbon nanotubes for I = 2,8 W/cm^2 and λ = 532 nm, d = 6 μ, α = 16 cm^{-1}, $G_{31} = 6{,}7\times10^{-10}$ cm/V, $E_{pv} = 3{,}3\times10^5$ V/cm, $\eta = 2\times10^{-4}$ (0,02%) The efficiency of conversion of light energy into electricity is low and amounts to 0.02% for the composite P (VDF / TrFE) with carbon nanotubes .

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Author Index