

Engineering of defects in fast neutron irradiated synthetic diamonds

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Abstract. Chemical vapor deposited (CVD) diamonds have been irradiated with fast reactor neutrons at fluencies $F = 1 \cdot 10^{18}$ and $3 \cdot 10^{18} \text{ cm}^{-2}$ and then heated at temperatures up to 1600 °C. The processes of annealing in and annealing out of various complexes of intrinsic defects responsible for vibrational and electron-vibrational bands in the IR absorption spectra have been studied in detail. Some tens of local vibrational modes and zero-phonon lines with rather small width caused by numerous complexes of intrinsic defects were observed in the 400-11000 cm^{-1} range.

1. Introduction

The further prospects of diamond in science and technology are determined both by improving the technology for producing structurally perfect ultrapure diamond, and by developing methods for defect engineering, which allow obtaining materials with controlled properties. Traditional techniques, such as *in situ* doping in the synthesis process, are not always appropriate due to the ultra-dense crystal lattice of diamond. Ion implantation and irradiation by electrons and neutrons are effective methods for defect engineering and are widely used for emerging diamond applications for quantum optics and sensing [1-2]. To engineer the defects and to improve the radiation damage resistance of diamond sensors [3] we must first understand defect's formation, diffusion, annihilation, interaction with impurities and aggregation into larger complexes. Investigation of radiation defects in ion-implanted diamonds is a challenge as the damaged sample volume is very small and the damage is not homogeneous through the bulk of the diamond. One of the solutions is to simulate ion implantation damage with heavy neutron irradiation.

IR spectroscopy is a powerful technique to study radiative defects in neutron irradiated diamonds. The several intensive local vibrational modes were examined in IR spectra of neutron irradiated diamonds [4-15], most of them are hydrogen [8-11, 13-14] – and nitrogen [4, 6, 8-11, 15]–related. The effect of neutron irradiation on defect-induced one-phonon absorption band was also examined in a number of works [5, 8, 10, 12, 15]. The effect of annealing on the IR absorption spectra of radiation-



modified diamonds was also studied in [4-15]; however, the ranges of radiation damage, annealing temperatures, and the spectral interval under study were rather limited. It was found that in the diamonds, where nitrogen content is higher than concentration of radiation induced vacancies, nearly all vacancies are trapped by the nitrogen impurity [10], as a result of which information on the behavior of intrinsic defects in radiation-modified diamonds is incomplete and contradictory.

The aim of this work is to investigate in a wide spectral range the transformations of the IR absorption spectra of diamonds with a low nitrogen content irradiated with fast neutrons as a result of successive annealing at temperatures up to 1600C.

2. Samples and experimental

Transparent polycrystalline CVD diamond films of thickness $>500 \mu\text{m}$ and mean dimensions of crystallites $\sim 50\text{-}70 \mu\text{m}$ have been grown on Si substrates from CH_4/H_2 mixtures using a microwave plasma-enhanced CVD system ASTeX-PDS19 as described elsewhere [16]. The nitrogen concentration in the substitution position (determined from optical UV absorption spectra as reported in [17]) in the examined specimens was $\sim 10^{18} \text{cm}^{-3}$ and of bound hydrogen $\sim 2 \cdot 10^{19} \text{cm}^{-3}$. Mechanically polished CVD diamond plates were irradiated with neutrons in a wet channel of an IVV-2M nuclear reactor in the fast neutron flux of $\sim 10^{14} \text{cm}^{-2} \cdot \text{s}^{-1}$ [18] at fluencies $F = 1 \cdot 10^{18}$ and $3 \cdot 10^{18} \text{cm}^{-2}$ at temperature of 325 K. The neutron irradiated samples have been subjected to annealing (60 min at fixed temperature) in an oven with graphite walls in a vacuum of 10^{-5} Torr at different temperatures of 200 to 1600 °C. To remove the graphite which could be formed on external surfaces [19] after the heat treatment, the samples were etched in hot $\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$ solution at ≈ 180 °C. After each annealing step FT-IR spectra were recorded at room temperature with PerkinElmer Spectrum 100 FT-IR spectrometer in the spectral range of 400–7800 cm^{-1} and with Bruker 70v FT-IR spectrometer in a wider range of 370–25000 cm^{-1} .

3. Results and discussion

After the neutron irradiation the samples became completely opaque to the eye and remain relatively transparent only in the far infrared range. This is due to an absorption continuum with its gradual increase toward the UV spectrum, that is characteristic for radiation damaged diamonds and is caused by partial amorphization of diamond [20], and appearance of carbon with sp^2 -hybridization of bonds. The annealing reduces the degree of radiation damage and leads to an increase in transmission of diamond in the entire IR range (Fig. 1 and 2). Note that at all stages of annealing, we did not observe in the spectra sufficiently intense absorption bands characteristic for centers with nitrogen atoms in their structure, in particular, which are usually observed in IR spectra of neutron-irradiated natural diamonds type I [20]. This allows us to assert that the spectral features in the spectra in Figs. 1-3 have the intrinsic nature. The transformation of the absorption spectra upon annealing occurs nonmonotonically since simultaneously with the annealing of defects of the same type, more complex defects can be generated, which is characteristic of radiation-modified diamond.

One of the advantages of diamond is its high transparency in the range from ultraviolet to far infrared. The only rather intense (up to 13cm^{-1}) absorption bands in pure and defect-free diamond are two- and three-phonon absorption in the range up to 2650cm^{-1} and up to 4000cm^{-1} , respectively [21]. Irradiation with fast neutrons leads to a long-wavelength shift [12] of the intrinsic two-phonon absorption; however, the magnitude of this shift for the samples irradiated with $F = 1 \cdot 10^{18} \text{cm}^{-2}$ does not exceed 1.5cm^{-1} and for $3 \cdot 10^{18} \text{cm}^{-2}$ - 3cm^{-1} .

The IR spectra of polycrystalline CVD diamonds are characterized by the presence several bands in the region of $2800\text{-}3000 \text{cm}^{-1}$, due to stretching vibrations of CH_x groups at intercrystalline boundaries. The neutron irradiation modifies the intercrystalline boundaries in CVD diamonds, displacing hydrogen atoms into the bulk of diamond crystallites to distances of several micrometers at least [14] which leads to a change in the IR spectra (Fig. 1 and 2). The effects of fast neutrons irradiation and subsequent annealing of CVD diamonds on the IR spectra of CH_x -groups are described in detail in [14].

One-phonon absorption is not possible in intrinsic diamond due to the symmetry of the crystal lattice [22]. Neutron irradiation damage introduces defects which destroy the local symmetry and creates a

characteristic one-phonon spectrum in the range $400\text{--}1340\text{ cm}^{-1}$ [10, 12] with maxima at 1005 , 1115 and 1195 cm^{-1} (Fig. 1 and 2). The spectral shape of the one-phonon absorption band ($500\text{--}1350\text{ cm}^{-1}$) for diamond irradiated with a fluence $F = 3 \cdot 10^{18}\text{ cm}^{-2}$ changes insignificantly upon annealing to $800\text{ }^{\circ}\text{C}$, although the amplitude of the band decreases by a factor of three in relation to the spectra measured after irradiation (Fig. 1). After annealing at $800\text{ }^{\circ}\text{C}$, the intensity of the band with a maximum at 1110 cm^{-1} significantly decreases (Fig. 1). For the sample irradiated with fluence of $F = 1 \cdot 10^{18}\text{ cm}^{-2}$, similar transformations of the one-phonon absorption band shape occur at lower annealing temperatures ($650\text{--}700\text{ }^{\circ}\text{C}$) (Fig. 2). Such temperatures are characteristic for the activation of vacancy diffusion in diamond.

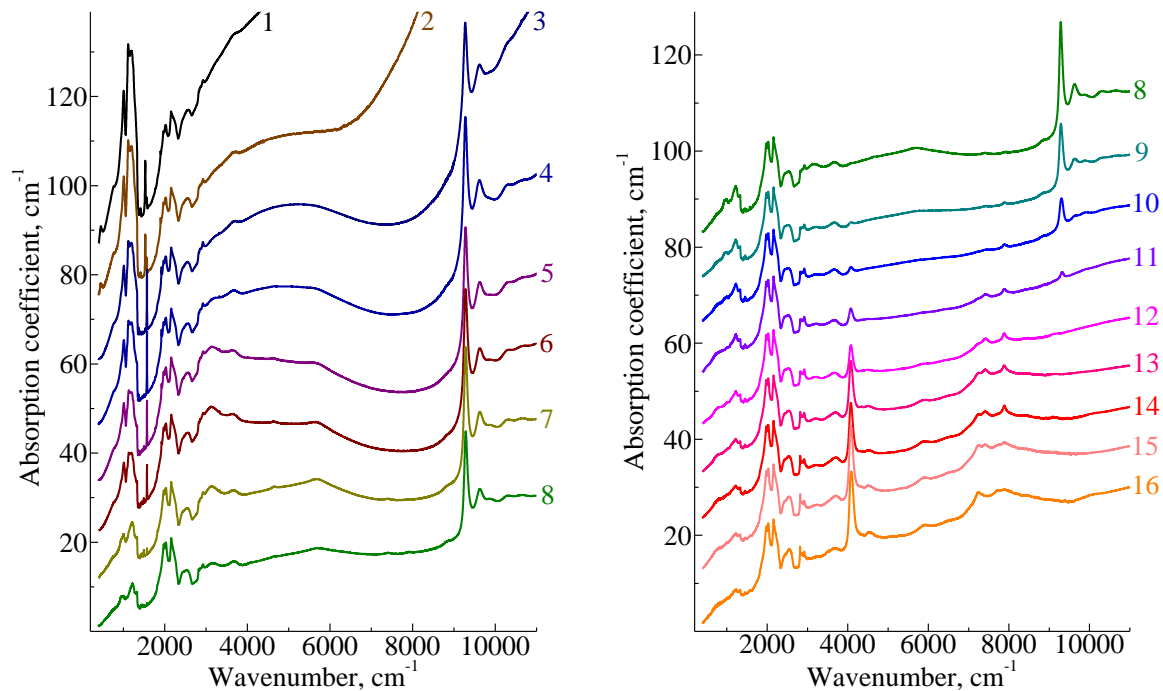


Figure 1. IR absorption spectra of CVD diamond film irradiated by fast neutrons with fluence $F = 3 \cdot 10^{18}\text{ cm}^{-2}$ and annealed for 1 hour at different temperatures: 200 (1), 300 (2), 400 (3), 550 (4), 630 (5), 700 (6), 850 (7), 940 (8), 1000 (9), 1045 (10), 1100 (11), 1175 (12), 1260 (13), 1310 (14), 1390 (15) and $1540\text{ }^{\circ}\text{C}$ (16). For clarity, the spectra are shifted relative to each other vertically.

To obtain information on radiation defects in diamond from IR spectroscopy data, the most informative are the so-called local vibrational modes (LVM) and zero-phonon lines (ZPL), which are present in the spectra as absorption bands with rather small width. The LVM are observed at the phonon frequency range above the diamond Raman frequency 1332 cm^{-1} as a result of the vibration of a lighter atom than carbon (for example, a hydrogen atom), the bonding being tighter than that of the lattice (for example, at an interstitial atom), or a combination of the two. Such high-frequency vibrational modes cannot propagate in the crystal and are localized in space and frequency. In neutron irradiated type-IIa diamond the strongest LVMs are at 1530 cm^{-1} and 1571 cm^{-1} [4] (Fig. 3c). As LVM 1531 cm^{-1} absorption peak anneals out after treatment at $350\text{--}400\text{ }^{\circ}\text{C}$, the 1571 cm^{-1} mode exhibits a correlated increase in intensity reaching maximum after annealing at $475\text{ }^{\circ}\text{C}$ and anneals out after treatment at $1000\text{ }^{\circ}\text{C}$. In type Ib diamond these LVMs are stable up to 450 and $650\text{ }^{\circ}\text{C}$, respectively [4]. The defects responsible for these LVMs contain only carbon atoms in their composition; however, the exact structure of these centers remains controversial. The local vibrational modes at 1571 cm^{-1} follow the annealing behavior expected for the isolated neutral $\langle 001 \rangle$ -split self-interstitial (I_{001}) defect [13]. For the 1530 cm^{-1} LVM, the $^{12}\text{C}:^{13}\text{C}$ isotopic splitting suggests that the defect responsible may have four equivalent carbon atoms and given the low thermal stability of this defect, it is tempting to speculate that this could be a T_d symmetry interstitial [10].

Several tens of other relatively narrow (FWHMs down to 5 cm^{-1}) less intensive LVM with different dependences on the annealing temperature are observed in the spectra of diamonds irradiated with fast neutrons (Fig. 3, a). The study of the nature of these IR bands is the subject of a separate work. A large amount of LVM is characteristic for the optical spectra of high dose neutron irradiated diamonds [11-13, 24] due to the formation of complexes of various intrinsic defects.

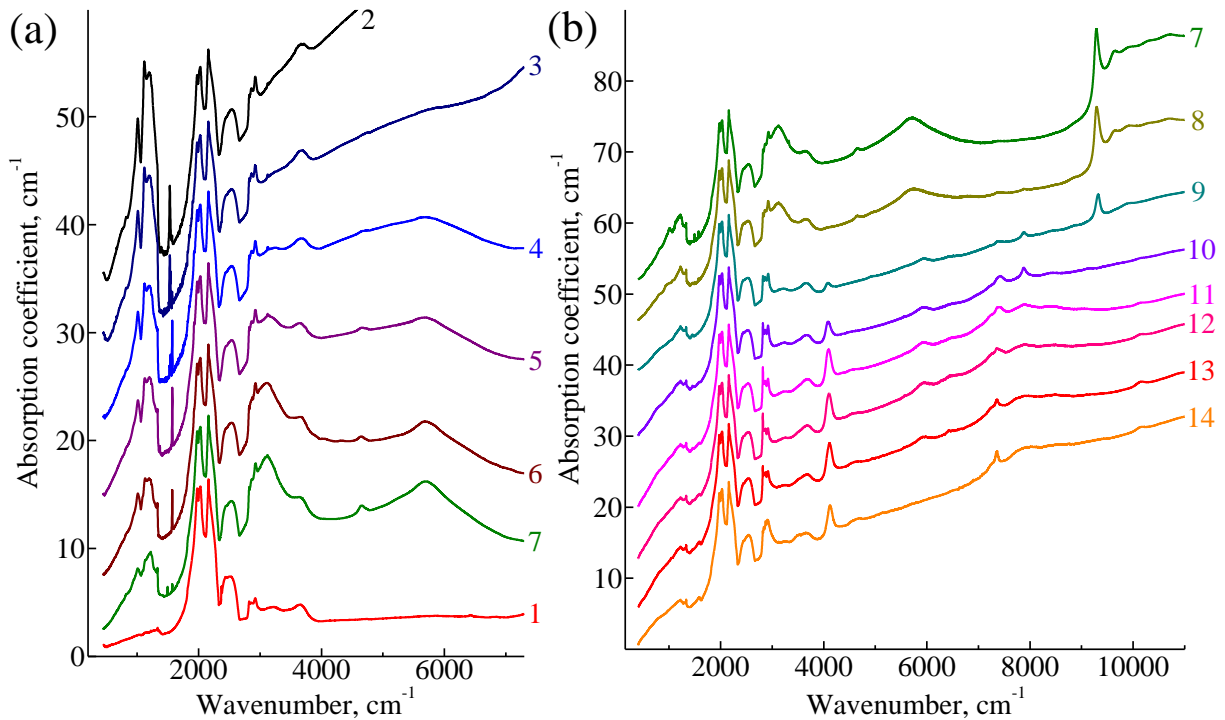


Figure 2. Infrared absorption spectra of the diamond film before (1), after irradiation with $F = 1 \cdot 10^{18}\text{ cm}^{-2}$ (2) and after 1 hour subsequent annealing runs at (a): 300 (3), 400 (4), 550 (5), 650 (6), 800 °C (7); (b): 990 (8), 1100 (9), 1250 (10), 1370 (11), 1480 (12), 1545 (13) and 1590 °C (14). The spectra are shifted relative to each other vertically.

Sharp absorption features called ZPLs - electronic transitions between the states of the defect within the band gap are observed in absorption and luminescence spectra of diamond predominantly in visible range [22]. The most studied ZPLs in the IR range are due to the acceptor impurity of boron [22], as well as the so-called amber centers [10, 22-25], which are usually observed in brown type Ia diamonds colored via plastic deformation.

Measurements in a wide spectral range ($400\text{--}11000\text{ cm}^{-1}$) made it possible to detect more than ten ZPL in the IR spectra of irradiated with fast neutrons CVD diamonds with a low nitrogen impurity content (Fig. 1-3). For example, the relatively wide band in the range $2000\text{--}8500\text{ cm}^{-1}$ with local maxima at 3110 , 4640 , and 5665 cm^{-1} (Fig. 3, b) anneals in starting at 300 °C , attains its maximum at $700\text{--}750\text{ °C}$, and anneals out between 1100 °C and 1200 °C . These ZPLs may be due to some kind of interstitial defects without an unambiguous identification as they are annealed at temperatures where the carbon interstitial is known to be mobile. Annealing at $950\text{--}1000\text{ °C}$ caused the appearance of the ZPL at 4100 cm^{-1} (Fig. 1 and 2). Band with the same spectral shape and position is known to refer to “amber centers” which are closely related complex vacancy based defects and usually observed in brown type diamonds colored via plastic deformation [10, 13, 24-25]. The less intensive ZPLs at 4500 and 5875 cm^{-1} increase synchronously with the 4100 cm^{-1} band, probably having the same nature. ZPLs at 7415 cm^{-1} and 7880 cm^{-1} are also observed, which have similar temperature dependences – they anneal in at 800 °C and reach a maximum at $\sim 1300\text{ °C}$ (Fig. 1 - 3). To date, there is no information in the literature on the observation of ZPL at 3100 , 4640 , 5665 , 5875 , 7415 and 7880 cm^{-1} in the spectra of diamonds.

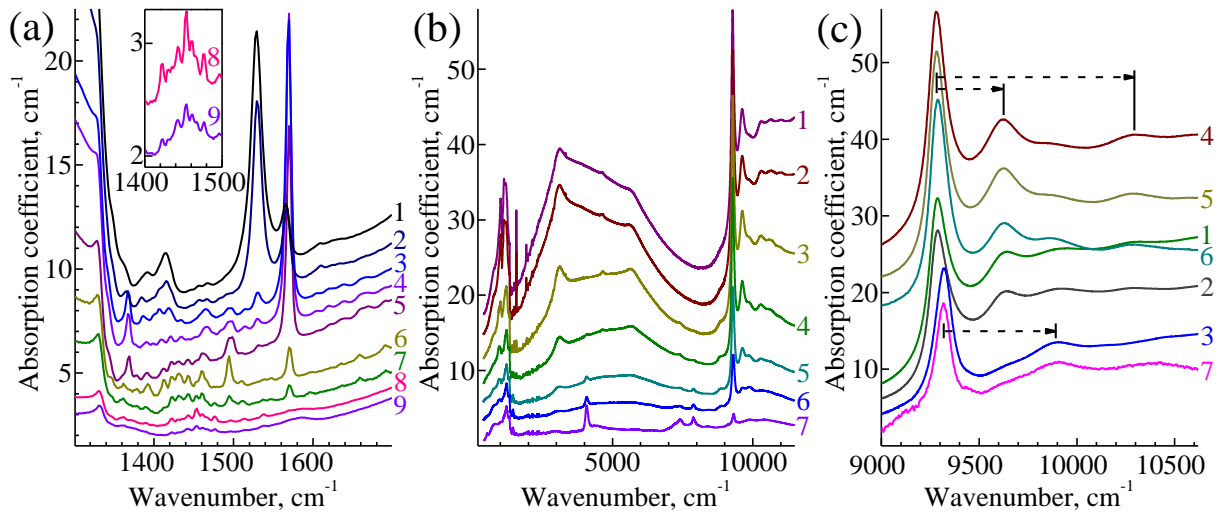


Figure 3. (a) Transformations of local vibration modes in the IR absorption spectra for fast neutron irradiated diamonds after successive 1 h. anneals at 200 (1), 300 (2), 400 (3), 475 (4), 630 (5), 850 (6), 940 (7), 1045 °C (8) (all for $F = 3 \cdot 10^{18} \text{ cm}^{-2}$) and 1175 °C (9) (for $F = 1 \cdot 10^{18} \text{ cm}^{-2}$). A vertical expansion of $5\times$ is used to highlight the cluster of LVM after annealing at 1045 and 1175 °C (see inset). (b) IR absorption spectra for neutron irradiated sample ($F = 3 \cdot 10^{18} \text{ cm}^{-2}$) after successive 1 hour anneals at 630 (1), 700 (2), 850 (3), 940 (4), 1000 (5), 1045 (6) and 1100 °C (7). The spectrum for pristine (unirradiated) diamond has been subtracted. (c) Superposition of 9280 and 9320 cm^{-1} ZPLs in IR spectra of CVD diamonds irradiated with fast neutrons with fluence $F = 1 \cdot 10^{18} \text{ cm}^{-2}$ – annealing at 800 (1), 880 (2), 1100 °C (3) and with fluence $F = 3 \cdot 10^{18} \text{ cm}^{-2}$ – annealing at 700 (4), 850 (5), 1000 (6) and 1175 °C (7). Spectra (1), (2) and (6) multiplied by a factor of two, (3) – by a factor of five and (7) – by a factor of ten. The arrows point to the features on the phonon sidebands of 9280 and 9320 cm^{-1} ZPLs. For clarity, all spectra at (a) – (c) are shifted relative to each other vertically.

In contrast to the few published studies on the effect of heat treatments on IR spectra of the neutron-irradiated diamonds, we chose a small step (minimum $\Delta T = 45\text{--}50 \text{ }^\circ\text{C}$) in the annealing temperature, which made it possible to trace in detail the transformations of the IR absorption spectra and, in some cases, to spectrally separate the overlapping bands. In particular, the shift to higher frequencies of the most intense band near 9300 cm^{-1} in the samples under study during annealing is caused not by mechanical stress, but by the superposition of two ZPLs - 9280 cm^{-1} , which dominates at low annealing temperatures, and a less intense and more thermally stable ZPL at 9320 cm^{-1} (Fig. 3c). Both of these bands were previously observed separately in the spectra of diamonds. ZPL at 9320 cm^{-1} (1077.9 nm) is present in the IR absorption spectra of type 1b and 2a diamonds irradiated with fast neutrons with $F = 1 \cdot 10^{18} \text{ cm}^{-2}$ [11]. ZPL at 1.149 eV (9280 cm^{-1} , 1077.9 nm) was observed in the cathodoluminescence (CL) spectra of type IIa and Ib natural diamonds after ion implantation [26]. Measurements of the IR absorption spectra with a small step in the annealing temperature made it possible to study the phonon sidebands of these ZPLs. The electron-phonon coupling at the 9320 cm^{-1} center is dominated by interaction with 575 cm^{-1} (71 meV) vibrations (see row under spectra 3 at Fig. 3, c), which coincides with the frequency of the TA (L) phonon in diamond. It was noticed that center intensity decreases with increase in nitrogen content, however CL center with 9280 cm^{-1} ZPL does not relate to nitrogen and anneals out at temperatures above 1000 °C [23]. The same dependence on the annealing temperature has 9280 cm^{-1} ZPL in the IR absorption spectra (Fig. 3, c). The 9280 cm^{-1} center predominantly interacts with vibrations of energy 41 and 125 meV (340 and 1005 cm^{-1}). A local mode at 37–41 meV is characteristic for diamond centers with a vacancy in their structure [13]. The feature in the phonon sideband at 1005 cm^{-1} (Fig. 3c) is related to LA(L) and/or TO(W) phonons in diamond. The both centers at $\sim 9300 \text{ cm}^{-1}$ are related possibly to a multivacancy complex or they are precursors of “amber centers” that appear in the IR spectra with a several characteristic absorption bands near 4100 cm^{-1} [24–25].

4. Conclusion

The results of IR spectroscopy of fast neutron irradiated CVD diamonds demonstrate once again the complexity of the defect structure of a heavily radiation-damaged diamond. Several tens of LVMs and ZPLs observed in the IR absorption spectra of SVD diamonds irradiated with fast neutrons ($F = 1 \cdot 10^{18}$ and $3 \cdot 10^{18} \text{ cm}^{-2}$) reflect the processes of migration, dissociation, and aggregation into larger complexes of intrinsic radiation defects in diamond. The ZPL at 3100, 4640, 5665, 5875, 7415 and 7880 cm^{-1} previously does not observe in the optical spectra of diamonds. An analysis of the temperature dependences of phonon sidebands of centers with ZPL at 9280 and 9320 cm^{-1} showed that these ZPLs interacts predominantly with vibrations of energy 41, 125 meV and 71 meV, correspondingly.

Acknowledgments

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