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Raman and Infrared Vibrational Spectra of $PbGa_2S_4$ Crystal

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Abstract: Raman scattering spectrain different geometries at temperatures 10 - 300 K and infrared vibrational spectra in polarizations E||c and E⊥c for range 50 - 4000 cm^{-1} at 300 K were investigated for $PbGa_2Se$ crystals. Contours of reflection spectra in polarizations E||c and E⊥c were calculated and parameters of phonons and dielectric constants were determined. Temperature dependences of Raman spectra were investigated and soft modes with different temperature dependences in intervals 80 - 150 and 150 - 370 K were discovered. A group of lines attributed to Davydovmultiplets was found out and their polarization dependences temperature changes were investigated. Effective ion charges were calculated and a polarizability of ionic charges of Pb, Ga and S in $PbGa_2S_4$ lattice was determined.

Keywords: Raman scattering; infrared reflection spectra; vibrational modes; Davydovmultiplets; effective ion charges;

INTRODUCTION

A lead thiogallate ($PbGa_2S_4$) compound belongs to a wide class of ternary chalcogenide materials of $A^{II}B_2^{III}C4^{VI}$ group, which uses in different devices of linear and nonlinear optics [1 - 6]. The $PbGa_2S_4$ compound crystallizes in rhombic lattice and is a layered semiconductor crystal with well pronounced anisotropy of optical properties. Crystal is easy cleaved along (100) plane. Excitonic states at room temperature with binding energies of 292 meV (Frenkelexcitons) were discovered [7, 8].

A new technology of grow for crystals of lead thiogallate was proposed by authors of Ref. [1 - 4]. The lead thiogallate crystals in consequence of a nonisovalent substitution of bivalent lead ions by trivalent rare-earth ions and a crystalline structure peculiarity can contain active ions in positions with different local surroundings. A change of such positions amount and its population by active impurity allows to operate on spectroscopic and generation properties of lasers in dependence of synthesis technology. It is possible to make a management of spectroscopic properties of optical centers and correspondingly parameters of laser emission in crystals activated by dysprosium ions at the expense of nanosize modifications of nearest surroundings of rare-earth ions.

Lead thiogallate is a semiconductor with three kind of atoms and has a strong anisotropy of optical properties and in visible and in infrared spectral regions [7 - 10].An investigation of dynamic properties of such crystals presents an interest for ascertainment an ionicity of each atom and anisotropy of chemical bond in crystal lattice. Long-wavelength vibrational spectra is used for calculations of force constants and effective ion charges of cations and anions in compound crystals. Raman scattering and IR vibrational spectra of $PbGa_2S_4$ crystals were investigated in Ref. [11, 12].

New information about dynamic of lead thiogallate lattice is presented in this work. Raman scattering in actual geometries at 10, 77 and 300 K was investigated. Reflection spectra in E||c and E⊥c (E||a) polarizations were measured for 50 - 4000 cm^{-1} range. Contours of reflection spectra were calculated by help of dispersion equations and main phonon parameters were determined. A temperature influence on vibrational modes of Raman scattering were discussed for temperature interval from 10 to 300 K. An effective Szigeti and effective Pb, Ga and S ion charges for both polarization were calculated.

EXPERIMENTAL METHODS

Investigated monocrystals were grown by Bridgman method at temperature gradient 20 - 30 K/cm and pulling speed 0.25mm/hour [2, 3]. Crystals have $2\times2\times5$ cm^3 size and easy cleave along direction [100] withsmooth facets formation with excellent mirror-like surfaces. Raman scattering spectra were measured at temperatures 10 - 300 K on a double spectrometer DFS - 32 with resolution 5 Å/mm in a cryostat LTS-22 C330 Workhorse. A bandwidth of spectrometer slit at scattering spectra measurements does not exceed a value 0.1 Å. Spectra were excited by lines of Spectra-Physics Ar^+ laser. IR reflection spectra were measured on Specord M 80 spectrometer (7000 - 200 cm^{-1}) and vacuum spectrometer KSDI-82 (300 - 50 cm^{-1}).All spectrometers were computerized.

EXPERIMENTAL RESULTS

A lead thiogallate is crystallized in the lattice of rhombic system with space group D_{2h}^{24}, lattice parameters a = 20.706, b = 20.380 and c = 12.156 and z = 32 [14]. An amount of phonons of different symmetries is equal to 192 for symmetry D_{2h}^{24} at z = 32.In center of Brillouin zone vibrational modes can be presented as $\Gamma=24A_g + 24A_u + 24B_{1g} + 24\ B_{2g} + 24B_{3g} + 23\ B_{1u} + 23\ B_{2и} + 24B_{3u} + (B_{1и} + B_{2u}+B_{3u})$. According selection rules the modes with A_g, B_{1g}, B_{2g} and B_{3g}symmetry are Raman-active and $B_{1и}$, B_{2u} and B_{3u} are active in IR absorption and reflection [11, 12]. Phonons of A_u symmetry are not active neither in IF nor in Raman scattering. Phonons of B_{1u} symmetry and phonons of $B_{2u}+B_{3u}$ are active in E||c and E⊥c polarizations, respectively. A first order tensor of light Raman scattering for crystals with D_{2h} symmetry has a next view:

$$\begin{matrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{matrix} \sim A_g \qquad \begin{matrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{matrix} \sim B_1 \quad \begin{matrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{matrix} \sim B_{2g} \qquad \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{matrix} \sim B_{3g} \tag{1}$$

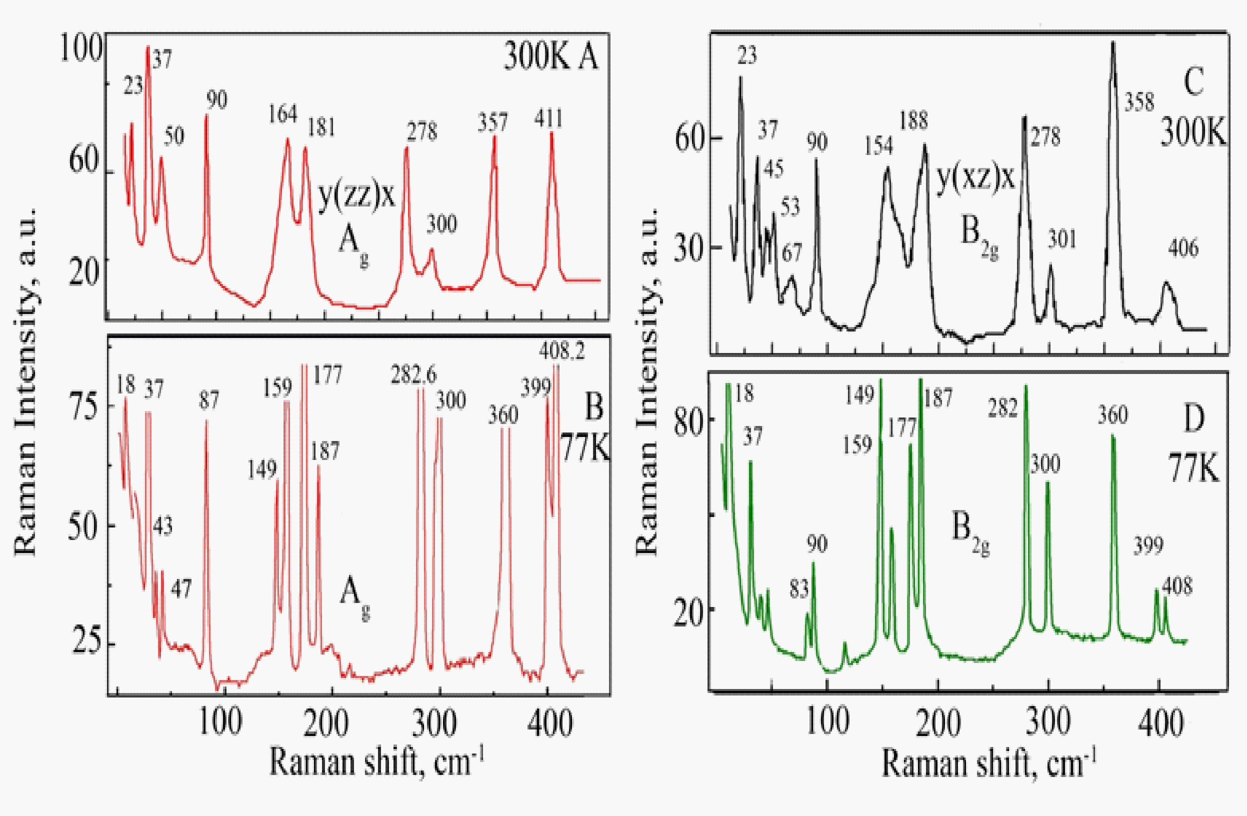

Fig1. *Raman scattering spectra of $PbGa_2S_4$ crystals measured at 300 K (A, C) and 77 K (B, D).*

Figure 1 shows Raman scattering spectra in y(zz)x and y(xz)x geometries measured at 77 K and 300 K. Phonons with symmetries A_g and B_{2g} are discovered at temperature 300 K in y(zz)x and y(xz)x geometries, respectively. Frequencies of observed vibrational modes are represented on the figure. The high-frequency mode A_g (411 cm^{-1}) at temperature reducing from 300 K to 77 R splits on two components 399 and 408.2 cm^{-1}. The high-frequency mode B1g split also at temperature decreasing in y(xz)x geometry but its intensity is considerably small.

Temperature decreasing down to 77 K leads to insignificant change of Raman spectra and vibrational modes in frequency interval 411 - 270 cm^{-1} shift on a value of the order of few inverse centimeters for both investigated geometries. Intensive lines 164 and 181 cm^{-1} due to A_g mode and lines 154 and 188 cm^{-1}due to B_{2g} mode are marked out at temperature 300 K. On four modes for each symmetry (A_g and B_{2g} 149, 159, 177 and 187 cm^{-1}) are recognized at 77 K.Raman lines 149 and 187 cm^{-1} in y(xz)x geometry caused by B_{2g} modes are more intensive than lines 159 and 177 cm^{-1}. Spectra changes insignificantly in low-frequency mode region (18 - 100 cm-1) with temperature decreasing (see Fig. 1).

Figure 2 shows Raman scattering spectra in y(xy)x geometry measured at temperatures 300K, 77 K and 10 K. Twelve vibrational modes of B_{1g} symmetry are observed at room temperature. A temperature reduction from 77 to 10 K leads to Raman scattering lines narrowing and new lines arising. Four lines are observed at 300 K and six lines at 10 K at high-frequencies interval 250 - 425 cm^{-1}. The vibrational modes 278 cm^{-1} and 369 cm^{-1} shift most strongly no 9 cm^{-1} and 12 cm^{-1}, respectively with temperature decreasing from 300 to 10 K. Two lines 162 and 179 cm^{-1} are discovered at room temperature in frequencies interval 150 - 240 cm^{-1}. Four lines 151, 161, 180 and 188 cm^{-1} are observed at 77 K, these lines are presented and at temperature 10 K (see Fig. 2, B and C).

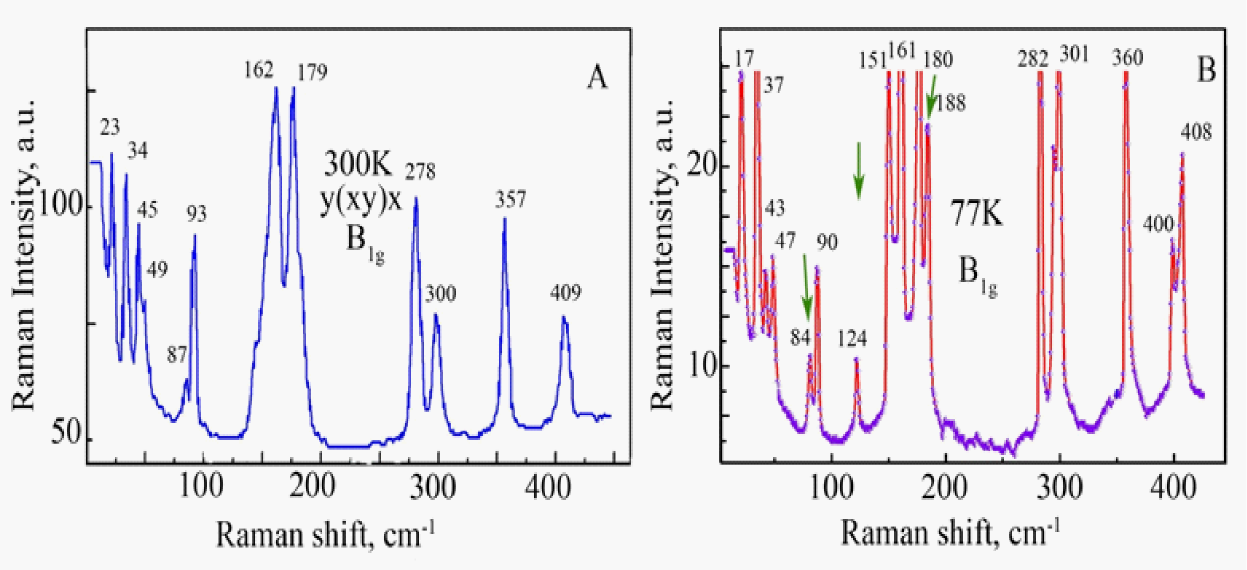

Fig2. *Raman scattering spectra of $PbGa_2S_4$ crystals measured in y(xy)x geometry at temperatures 300 K (A), 77 K (B).*

A temperature change from 77 to 10 K has the greatest influence on 188 cm^{-1} vibrational mode it shifts on 12 cm^{-1}. The over three lines practically do not shift. Six vibrational modes are observed in frequencies interval 10 - 100 cm^{-1} (Fig.2 and Fig. 3, A). Low frequency vibration mode B_{1g} (23 cm^{-1} at 300 K and 16 cm^{-1} at 10 K) shifts the most distant at temperature decreasing. Vibration mode $B_{1g}(4)$ is discovered at 87 cm^{-1} at 300 K. It shifts to 84 and 63.3 cm^{-1}frequencies at temperature decreasing to 77 and 10 K, respectively. The line 124 cm-1 is observed at 77 K and it isn't discovered at temperatures 10 and 300 K. It should be noted that frequencies of vibrational modes at high-frequency increase with temperature decreasing but in low-frequency the situation is opposite. Figure 3 shows a temperature dependence of frequency square for two vibrational modes $B_{1g}(1)$ and $B_{1g}(4)$.

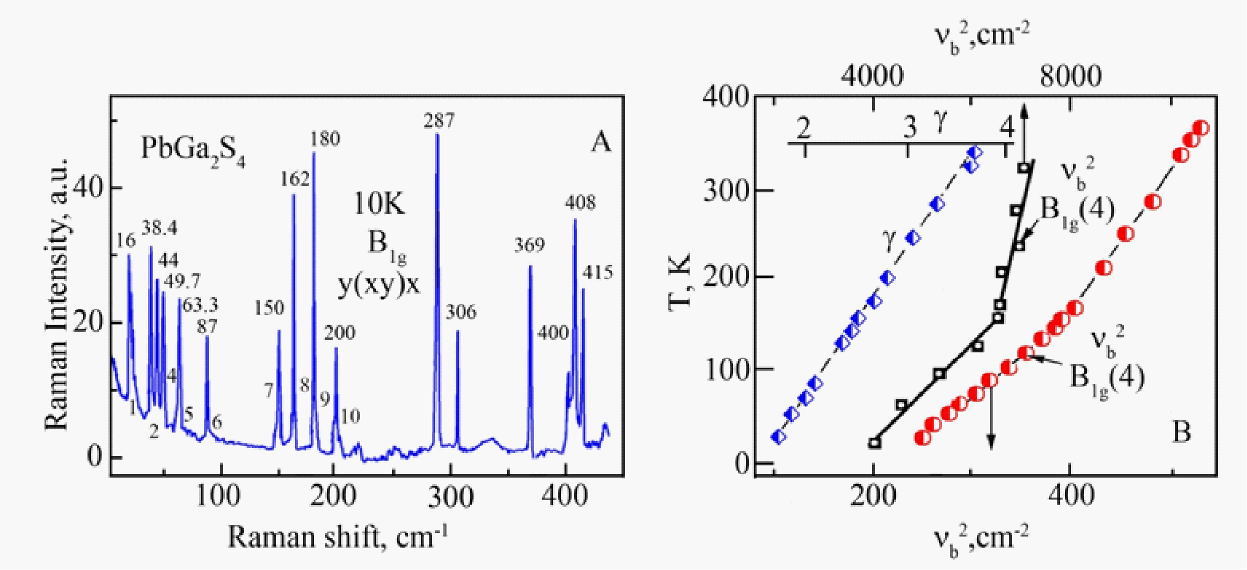

Fig3. A - Raman scattering spectra of PbGa2S4 crystals measured in y(xy)x geometry at temperature 10 K . B - *The temperature dependence of two vibrational modes 23 cm^{-1} (300 K) and 86 cm^{-1} frequency square (300 K) of B_{1g} symmetry.*

Thus all examined Raman scattering lines at temperature reduction shift to higher energies on a value of few cm^{-1} or practically do not shift. Simultaneously with this general regularity an opposite dependence takes place for some lines. Four lines (49, 45, 34 and 23 cm^{-1}) appear at low-frequencies. Lines 49, 45 and 34 cm^{-1} do not practically shift with temperature decreasing. The most low-frequency band 23 cm-1 (mode B_{1g}) has the biggest temperature shift coefficient and moves to long-wavelength side in contrast to high-frequency lines. A temperature decreasing from 370 to 10 K leads to this band frequency reduction on 7 cm^{-1}. This change is monotonic and has two parts with different shift coefficients (Fig. 3, B). The similar dependence is revealed for vibrational mode B_{1g}(87 cm^{-1} at 300 K).

Such change of vibrational mode in $PbGa_2S_4$ crystals indicates about structural instability of this crystal. We suppose that $PbGa_2S_4$ crystal suffers a phase transition at low temperatures. One can speculate that lines 23 and 87 $cm^{-1}$are soft modes. Figure 3 shows temperature dependences of frequency square (υ^2) and line 23 cm^{-1}half-width (γ). Two linear segments with different shift coefficients in temperature intervals 10 - 150 K and 150 - 300 K is revealed for frequency square. The temperature dependence of frequency square for both lines is described by relationship , where $\gamma = 1.1 \pm 0.1$ for interval 10 - 150 K and $\gamma = 0.7 \pm 0.1$ in interval 150 - 300 K. At the same time a line 278 cm-1 shifts strongly to high-frequency part with temperature decreasing (Fig. 2). The dependence of soft mod half-width on temperature for this crystals takes place linearly and is explained by usual broadening of scattering line at temperature rising. The damping of soft mode (17 and 87 cm^{-1}) isn't found out in investigated temperature interval.

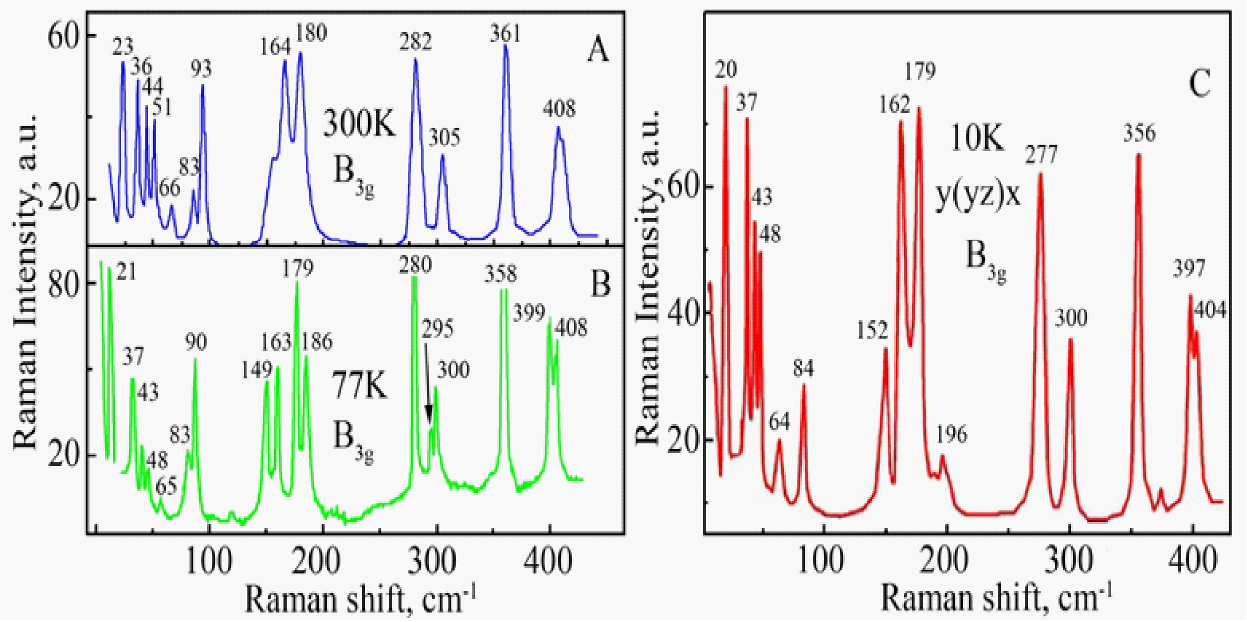

Fig4. *Raman scattering spectra of $PbGa_2S_4$ crystals in y(yz)x geometry measured at temperatures 300 K (A), 77 K (B) and 10 K (C).*

Figure 4 shows vibrational modes of B_{3g} symmetry spectra discovered in Raman scattering in y(yz)x geometry at 300, 77 and 10 K. Twelve modes are observed at room temperature. Raman lines become narrower at temperature decreasing down to 77 and 10 K. Four bands present in spectra at 300 K in interval 250 - 415 cm^{-1}, and six vibrational modes are observed at temperature 10 K. Frequencies of these modes change insignificantly with temperature decreasing form 300 K to 10 K. Two lines 164 and 180 cm^{-1} are revealed at room temperature in frequency interval 150 - 240 cm^{-1}. Four bands (149, 163, 179 and 186 cm^{-1}) observed both at 77 K and at 10 K (Fig. 2, B and C). A temperature change from 77 K down to 10 K influences mostly on vibrational mode 186 cm^{-1}, it shifts on 10 cm^{-1} to high-frequency sideways. Another three lines don't shift practically. Seven vibrational modes are revealed in interval 10 - 100 cm^{-1}, Fig. 2. A temperature decreasing almost doesn't influence on low-frequency vibrational mode B_{3g} in contrast to B_{1g} mode (23 cm^{-1} at 300 K and 16 cm^{-1} at 10 K). Frequency of vibrational mode B_{3g} (83 cm^{-1}) doesn't change at changing of temperature. A scattering band at 90 cm^{-}1 are discovered at 300 K and 77 K in short-wavelength side form B_{3g} (83 cm^{-1}) mode. This vibrational mode at temperature 10 K is not distinguished.

Eight vibrational modes with B_{1u}, B_{2u} and B_{3u} symmetries are observed in reflection spectra measured for E⊥c(E||b) and E||c polarizations in $PbGa_2S_4$ crystals (see Fig. 5). A splitting of every polar vibration with symmetries B_{1u}, B_{2u} and B_{3u} on longitudinal (LO) and transversal (TO) modes takes place under influence of macroscopic electric filed caused by optical oscillations. Optical function have been calculated from reflection spectra of $PbGa_2S_4$ crystals by Kramers-Kronig relations for a LO- and TO- modes parameters determination.

One can see from spectra presented in Fig. 5 and 6 that high-frequency modes 7 and 8 in E⊥c(E||b) polarization and lines 6 and 8 in E||c polarization have the largest oscillator strength. It can be seen that frequencies of IR active phonons have a good agreement with Raman active modes at comparison of IR spectra with Raman one.

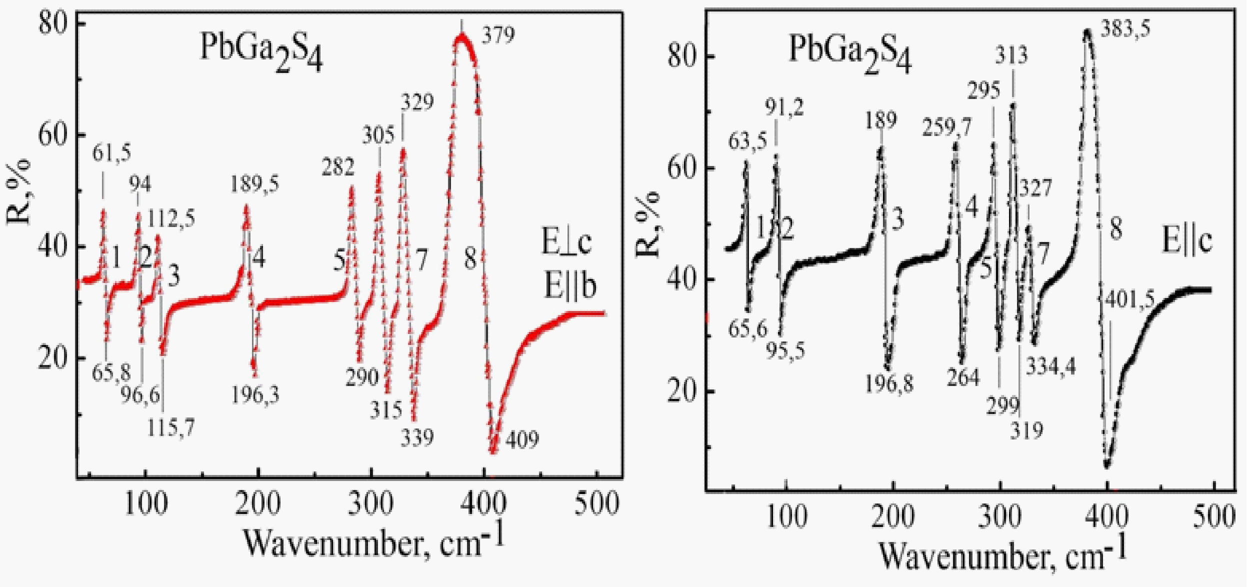

Fig5. *IR reflection spectra measured in $PbGa_2S_4$ crystals.*

Since $PbGa_2S_4$ crystals have a rhombic symmetry and layered structure and in its unit cell consists of 4 layers so a layer-to-layer interaction exists between layers. At the same time the strong modes, which determine the main chain frequency, become apparent as **Davydovmultiplets**. The coupling (strong interaction) of two layers leads to the series of 2 or 4 vibrational modes. Wherein the Raman-Raman, IR-IR and Raman-IR active modes are possible and can appear. Attention is drawn tothe fact that all vibrational modes in discussed spectra appear as doublets which allowed in every geometry. Similar situation is observed in molecular crystals and in crystals on the base ofIn and S [2].The symmetrized shifts of atoms for all normal modes are possible in $PbGa_2S_4$ (D_{2h}^{24}) crystals, while the pairs of modes A_g and B_{1g}, B_{1g} and B_{3g}, B_{3u} and B_{2u} are coupled relative to the symmetry elements.These pairs can make doublets similar to Davydov one in the molecular crystals and transfer into each other the translationallynonequivalentpackets. In lead thiogallate due to the symmetry rules the both personally polarized components of almost all Davydovmultiplets are active either in Raman scattering or in IR. Exactly such tendency is observed in experimentally measured spectra. The lines in frequencies intervals 390 - 425, 270 - 306 and 151 - 200 cm^{-1} are Raman active. These modes are caused by oscillations of molecules Ga-S and S-S. The presence of Davydov pairs is possible and in the more low-frequency range but them identification is not so demonstrable due to a presence of a multitude of lines especially in vicinity of 50 cm^{-1}. The Davydovmultiplets and its frequency distribution are scrutinized in Ref. [12].

Analysing reflection and Raman spectra of lead theogallate one can assume that Davydovmultiplets of IR active modes have been observed in this crystal. This circumstance (Davydov interaction) leads to a splitting of IR active modes on few components (numbers 5 and 6 in E||c polarization and 6 and 7 in E⊥cpolarization). Weak bands 322(2) and 328(3) cm^{-1} are due to perhaps the presence of vibrational modes B_{2u} by measured geometry B_{3u} or vice versa. Thus one can assume that bands 282(5) - 305(6) cm^{-1} in E⊥c polarization and 295(5) - 313(6) cm^{-1} in E||c polarization are the Davydovmultiplets active in IR spectra. In the last case the splitting magnitude of IR Davydov components are rather more (16 - 22 cm^{-1}) than Raman components splitting (4 - 10 cm^{-1}). This condition is alsoindicative of the factthat both different polarized components of Davydov doublets are active either in IR or in Raman scattering in the case of lead thiogallate. The doublet character of Raman scattering Davydov lines of different vibrational modes and its changing with temperature are presented in Ref. [11,12].

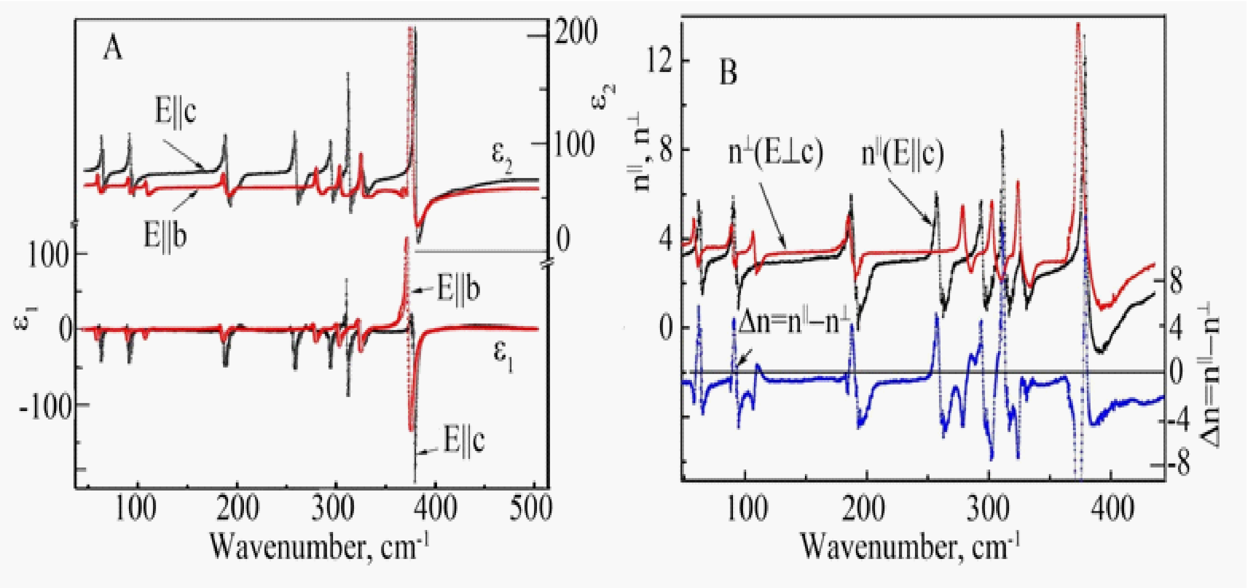

Fig. 6. Real ε_1 and imaginary ε_2 parts of dielectric constant (A) and refractive indices for E||c and E⊥c polarizations and its difference Δn (B) of $PbGa_2S_4$ crystals.

Every allowed in IF spectra band can have 3 Davydov components B_{1u}, B_{2u} and B_{3u}in $PbGa_2S_4$ crystals with D_{2h}^{15} space group in which positional symmetry of atoms is C_j. Since all three orientations of vibrational modes are reciprocally perpendicular at IR radiation on monocrystall plane that only 2 Davydov components will be observed in spectrum. The magnitude of Davydov splitting does not exceed 6 - 8% of a value of basic frequency. The Raman scattering spectra of $PbGa_2S_4$ crystals become practically nonpolarized at temperature decreasing while a doublet character of vibration modes is preserved. It seems that the positional symmetry of atoms changes and corresponds to C_{2h} symmetry at temperature lowering. The scattering tensors for C_{2h} symmetry allow the observing of vibrational modes B_{2g} and B_{3g} in B_g geometry, that is observed in experiment evidently. It was determined by numerous investigations that an electron cloud of ion cores under the light waves is polarized [15 -18].

The electron cloud by the ion cores in a crystal lattice specifies the character of chemical bond. The density of electron cloud along direction of interaction between ions determines a lot of crystals properties. The anisotropy of physical properties is observed in the crystals with an lattice anisotropy. The electron cloud orientation near ions influences definitely on the mechanical properties, resulting in the existence oflayered(strongly anisotropic) andnonlayeredcrystals. The density of electron cloud inside layer in higher than between layers in anisotropic (layered) crystals. Inside the layer the density is differ along directions of crystal lattice. The density of electron cloud along the main directions of crystal lattice is determined by an orientation relative to the lattice axis of ion's dimoles, which formed this compound.

The density of electron cloud near ion core of atoms is determined by ion charge of this ion. An investigations of vibrational spectra allows to calculate and in the range of define assumptions evaluate the effective ion charges even in ternary anisotropic materials [15 - 18].Electron ion charges in anisotropic materials are differ for different directions of crystal axes. The effective ion charges were calculated at a light wave orientation E⊥c and E||c for abovementioned crystals.Received effective charges contain some error due to used calculation method. But this error the same for both polarization.

Therefore a parameter of ion charges anisotropy ($\Delta Z = Z_{eff}^{\parallel} - Z_{eff}^{\perp}$, where $Z_{eff}^{\parallel}$ and $Z_{eff}^{\perp}$ are effective ion charges of respective atom in E||c and E⊥c polarizations) was introduced for further discussions. Parameter ΔZ can have and positive and negative values, characterizing the electron cloud of ion core and it's deviation from spherical shape. The cloud is stretched along c axis at positive ΔZ.

Effective charges of semiconductor crystals are determined by relations between υ_{LO}, υ_{TO} and dielectric properties:

$$4\pi^2 c^2 \sum_{j=1}^{N} \left(\nu_{LO_j}^2 - \nu_{TO_j}^2\right) = \frac{4\pi e^2 N}{V}\left[\frac{(z_a e^*)^2 n_a}{m_a} + \frac{(z_b e^*)^2 n_b}{m_b} + \frac{(z_c e^*)^2 n_c}{m_c}\right] \tag{2}$$

$$n_a z_a e + n_b z_b e - n_c z_c e = 0 \tag{3}$$

Relation (3) is aelectroneytrality condition, where c is a light velocity; e is an electron charge; V is a volume of unit cell; N is a atom amount in unit cell; n_a, n_b, n_c are stoichiometric coefficients; m_a, m_b, m_c are atomic masses of semiconductor crystal elements. The effective ion charges in crystal can be estimated by using these two equations at additional assumptions. An equation was used in Ref. [5]:

$$\varepsilon_\infty - 1 = 2/x + x^2 \tag{4}$$

where $x = e_z^* / z_{eff}\, e$ is an additional condition. It is true for many binary and ternary semiconductor compounds. The effective charges from condition (2) and (3) at given values $z_a e^*$ as variable part calculated $z_b e^*$ and $z_c e^*$ were determined at Ref. [11, 12]. The result of these calculations is three straight lines which intersection gives sought magnitudes. The magnitude $e_s^*/z_{eff}e$ is also lied in a dependence ε_∞-1 (received for many materials [15 - 19]) for investigated crystal of lead thiogallate. Simultaneously the magnitudes divided on z_0 have been used for an evaluation of the effective ion charge, and they are equal in crystals $HgIn_2S_4$ and $CdIn_2S_4$to 2, 3 and 2 for atoms Hg or Cd, In and S, respectively [19]. It is clear from data of Ref. [7] that effective charges $e_s^*/z_{eff}e$ and e_s^*/ze are bigger from E||c polarization than in the case of E⊥c polarization. The behavior of relative effective charge z/z_{eff} is analogous for both polarizations. Born effective charge has an inverse relation since the oscillator parameters differ in E||c and E⊥c polarizations. This means that, relations (2) - (4) give different effective charges of anions and cations in both polarizations. S anions and Pb and Ga ions in E||c polarization have a higher iconicity than in E⊥c polarization, i.e. at light wave field orientated parallel to c axis all ions are polarized by electric field weaker than at E⊥c and thus they give a smaller contribution into the matter permittivity. It should be simultaneously noted that the sulfur ionicity is smaller from all three kinds of charges (Pb, Ga and S) and the gallium ionicity is the biggest one in both polarizations. All this shows a strong anisotropy of chemical bond in this material.

CONCLUSIONS

The temperature reduction in interval 300 - 10 K influences in different mod on the vibrational modes of Raman scattering in $PbGa_2S_4$ crystals. At high-frequencies the frequency of vibrational modes grows with temperature decreasing and it goes down at low-frequencies. The frequencies squares (ν^2) of vibrational modes B_{1g} and B_{1g} possess the different shift coefficients for temperature intervals 10 - 150 K and 150 - 130 K. $PbGa_2S_4$crystal has a phase transition at temperature ≈ 150 K. Vibrational modes B_{1g} and B_{1g} are the soft modes.

High-frequency (ε_∞) and static (ε_0) dielectric constants in polarization E||c (B_{1u} modes) and E⊥c (B_{2u} modes) differ insignificantly each other in $PbGa_2S_4$ crystals. Dielectric constants ε_1 and ε_2 have the largest change in the region of high-frequency vibrational mode B_{1u}. The calculations of effective ion charges show that S anions and Pb and Ga ions in E||c polarization have bigger ionicity than in E⊥c polarization. Ions are polarized by a light wave weaker in E||c polarization than at E⊥c and give a less contribution into permittivity of crystal. The strong anisotropy of chemical bond in $PbGa_2S_4$ crystals is caused by high ionicity of gallium and low ionicity of sulfur.

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