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## VIBRATIONAL SPECTRUM OF LEAD THIOGALLATE CRYSTALS

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Raman scattering (RS) of light in a  $\text{PbGa}_2\text{S}_4$  crystal has been studied. The method of factor-group analysis was applied to calculate, for the first time, the phonon spectrum of this crystal. The number of modes, which are active in Raman spectra, their symmetry, and selection rules have been determined. The identification of modes, which are observable in the Raman spectra, with the vibrations of atoms that make up the crystal has been carried out.

Crystals of lead thiogallate  $\text{PbGa}_2\text{S}_4$  are related to a wide class of ternary chalcogenide compounds  $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ , where  $\text{A}^{\text{II}}$  is Mn or Pb;  $\text{B}^{\text{III}}$  is Ga or In; and  $\text{C}^{\text{VI}}$  is S, Se, or Te. Some compounds of this group – in particular,  $\text{CdGa}_2\text{S}_4$ ,  $\text{CdGa}_2\text{Se}_4$ , and  $\text{HgGa}_2\text{S}_4$  – have been studied rather well [1, 2]. At the same time, the physical properties of the  $\text{PbGa}_2\text{S}_4$  compound have practically not been investigated, except a few works [3, 4]. From the viewpoint of the generality of their chemical formula and taking into account the fact that crystals of the concerned group of compounds are effectively used in various devices of nonlinear optics and in optical filters, one should expect that  $\text{PbGa}_2\text{S}_4$  crystals may be of interest for the applications. In this work, we used the method of Raman light scattering to study the phonon spectrum of those crystals. Besides the independent identification of the compound structure, this method allows a valuable information to be obtained concerning the character of the interaction between atoms that make up the crystal, as well as the nature of the chemical bond between them.

Researches were carried out at a temperature of 300 K and using polarized light. Single crystals of  $\text{PbGa}_2\text{S}_4$  were fabricated by the Bridgman method. The rate of crystallization front motion was 0.1 – 0.3 mm/h;

the temperature gradient in the crystallization zone was 2 – 4 K/mm. Crystals were annealed at a temperature of 473 K for 3 days; then they were cooled down to room temperature at a rate of 30 K/h. In such a way, there were obtained homogeneous single-crystalline specimens of  $\text{PbGa}_2\text{S}_4$  with a good optical quality (the transmission coefficient was about 90% in the visible range of spectrum), 25–55 mm in length and 15–22 mm in diameter.

For the single crystals of the compounds concerned, the phonon spectra have not been calculated. Therefore, first, we used the method of factor-group analysis [5, 6] to calculate the vibrational spectra of crystals under investigation. The basic initial data for carrying out the calculations within the method specified are the symmetry parameters of the crystal lattice of the compound under investigation. The X-ray diffraction studies carried out by us for  $\text{PbGa}_2\text{S}_4$  powders (a DRON-4-07 diffractometer, filtered  $\text{CuK}\alpha$  irradiation, the scattering angle range  $2\theta = 10 \div 120^\circ$ ,  $R_{\text{Bragg}} = 8.6\%$ ) testify that the crystalline structure of  $\text{PbGa}_2\text{S}_4$  belongs to the  $Fddd$  structural type. This conclusion is in agreement with the data of works [7, 8], where it was found that the  $\text{PbGa}_2\text{S}_4$  compound crystallizes into a rhombic structure (the  $Fddd$  spatial group is  $D_{2h}^{24}$ ) and contains 32 formula units in an elementary cell. The atoms occupy the following positions in the crystal lattice:

8Pb<sup>1</sup> at position (a): (1/8, 1/8, 1/8),

8Pb<sup>2</sup> at position (b): (1/8, 1/8, 5/8),

16Pb<sup>3</sup> at position (e): (0.8724(5), 1/8, 1/8),

32Ga<sup>1</sup> at position (h): (0.0003(1), 0.8042(1), 0.1638(1)),

32Ga<sup>2</sup> at position (h): (0.0009(1), 0.2383(1), 0.3743(1)),

32S<sup>1</sup> at position (*h*): (0.1649(2), 0.2474(4), 0.0052(4)),  
 32S<sup>2</sup> at position (*h*): (0.1643(2), 0.5023(2), 0.2474(4)),  
 32S<sup>3</sup> at position (*h*): (0.9975(2), 0.3438(2), 0.0008(3)),  
 32S<sup>4</sup> at position (*h*): (0.0008(2), 0.4184(2), 0.2663(3)).

The lattice constants are  $a = 20.72 \text{ \AA}$ ,  $b = 20.30 \text{ \AA}$ , and  $c = 12.12 \text{ \AA}$ . Since the corresponding Bravais lattice is face-centered, the primitive cell contains 56 atoms. The spatial group  $D_{2h}^{24}$  is characterized by the following set of possible atomic positions:  $2D_2(2)$ ,  $2C_i(4)$ ,  $3C_2(4)$ , and  $C_1(8)$ . The results of the aforementioned X-ray diffraction analysis testify that the Pb atoms occupy the positions, the symmetry of which is described by the point group  $D_2$ , the Ga atoms do the positions with the symmetry  $C_2$  and  $C_1$ , and the S atoms do the positions with the symmetry  $C_1$ . Taking this information into account, the factor-group analysis of the vibrational spectrum of the PbGa<sub>2</sub>S<sub>4</sub> crystal gave results, which are presented in Table 1.

From this table, one can see that lattice vibrations in the crystals concerned are distributed over the irreducible representations of the factor-group  $D_{2h}$  of the crystal at the center of its Brillouin zone as follows:

$$\Gamma = 19A_g(xx, yy, zz) + 22B_{1g}(xy) + 22B_{2g}(xz) + 21B_{3g}(yz) + 19A_u + 21B_{1u} + 21B_{2u} + 20B_{3u}.$$

The acoustic modes have the symmetry  $\Gamma_{\text{acoust}} = B_{1u} + B_{2u} + B_{3u}$ , therefore,

$$\Gamma_{\text{opt}}(k = 0) = 19A_g(\text{RS}) + 22B_{1g}(\text{RS}) + 22B_{2g}(\text{RS}) + 21B_{3g}(\text{RS}).$$

The given crystals possess the center of symmetry; therefore, the exclusion principle is relevant, and there are only 84 active vibrational modes in the Raman spectra: nineteen modes of symmetry  $A_{1g}$ , twenty two modes of symmetry  $B_{1g}$ , twenty two modes of symmetry  $B_{2g}$ , and twenty one modes of symmetry  $B_{3g}$ .

Experimental researches of the Raman spectra were carried out on a DFS-24 Raman-spectrometer at the temperature  $T = 300 \text{ K}$ . A photoelectric multiplier FEU-79 served as a radiation detector. The sequence of the instant intensity values of the light flux, averaged with the use of the given time constant, was registered by an electric circuit and a PDA-1 recorder. Then, the data obtained were treated with the help of computer facilities.

Raman spectra were excited with an LGN-215 helium-neon laser ( $\lambda = 0.6328 \text{ \mu m}$  and  $W = 50 \text{ mW}$ )

operating in a single-mode regime. The 90°-geometry of scattering was used, which provided the most complete registration of the scattered light. Such an experimental geometry allowed the parasitic Tindall and Rayleigh scattering to be avoided as much as possible. The polarization of scattered radiation was controlled by a Thompson polarization prism. The spectral resolution ability and the noise level were  $1 \text{ cm}^{-1}$  and 5 – 6% of the signal amplitude, respectively. The relative measurement error for intensities at the curve peaks was no worse than 1%. For measurements, single crystals oriented with respect to planes (100), (010), and (001) were used.

Figure 1 exhibits the obtained Raman spectra of the PbGa<sub>2</sub>S<sub>4</sub> crystal, and Table 2 reports the frequencies of the registered RS lines, their symmetries, and the halfwidth  $\Delta\lambda_{1/2}$ . We also determined the depolarization degree of the RS lines, which, although being forbidden by the selection rules, were observed in the scattering geometries. In Table 3, the selection rules for the chosen scattering geometries are listed. The halfwidth of a RS line was determined as the peak width at the half of its amplitude, and the depolarization degree as the ratio between the intensity of the line in the Raman spectrum, where its occurrence is forbidden by the selection rules, to its intensity in the spectrum, where it has to reveal itself according to the selection rules. The depolarization degree  $\rho$  of the RS lines was 0.12 and 0.16 for  $A_g$ -symmetry modes with frequencies of 277 and 354  $\text{cm}^{-1}$ , respectively; 0.44 for  $B_{1g}$ -symmetry modes ( $\nu = 356 \text{ cm}^{-1}$ ); and 0.18 and 0.21 for  $B_{3g}$ -symmetry modes with the frequencies 21 and 150  $\text{cm}^{-1}$ , respectively.

While interpreting the results obtained, it should be noted that the numbers of lines in Raman spectra calculated theoretically (84) and measured experimentally (56) turned out different. It evidences for a complicated, nonelementary character of some lines. It is worth noting a low intensity of some RS lines at  $T = 300 \text{ K}$ , which prohibited them from being reliably identified. Nowadays, the lack of the results of

**Table 1. Factor-group analysis of lattice vibrations in a PbGa<sub>2</sub>S<sub>4</sub> crystal**

Factor-group $D_{2h}$	Number of vibrations	Symmetry	Activity
$A_g$	19	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	RS
$B_{1g}$	22	$\alpha_{xy}$	RS
$B_{2g}$	22	$\alpha_{xz}$	RS
$B_{3g}$	21	$\alpha_{yz}$	RS
$A_u$	19		
$B_{1u}$	21	$\mu_z$	IR
$B_{2u}$	21	$\mu_y$	IR
$B_{3u}$	20	$\mu_x$	IR

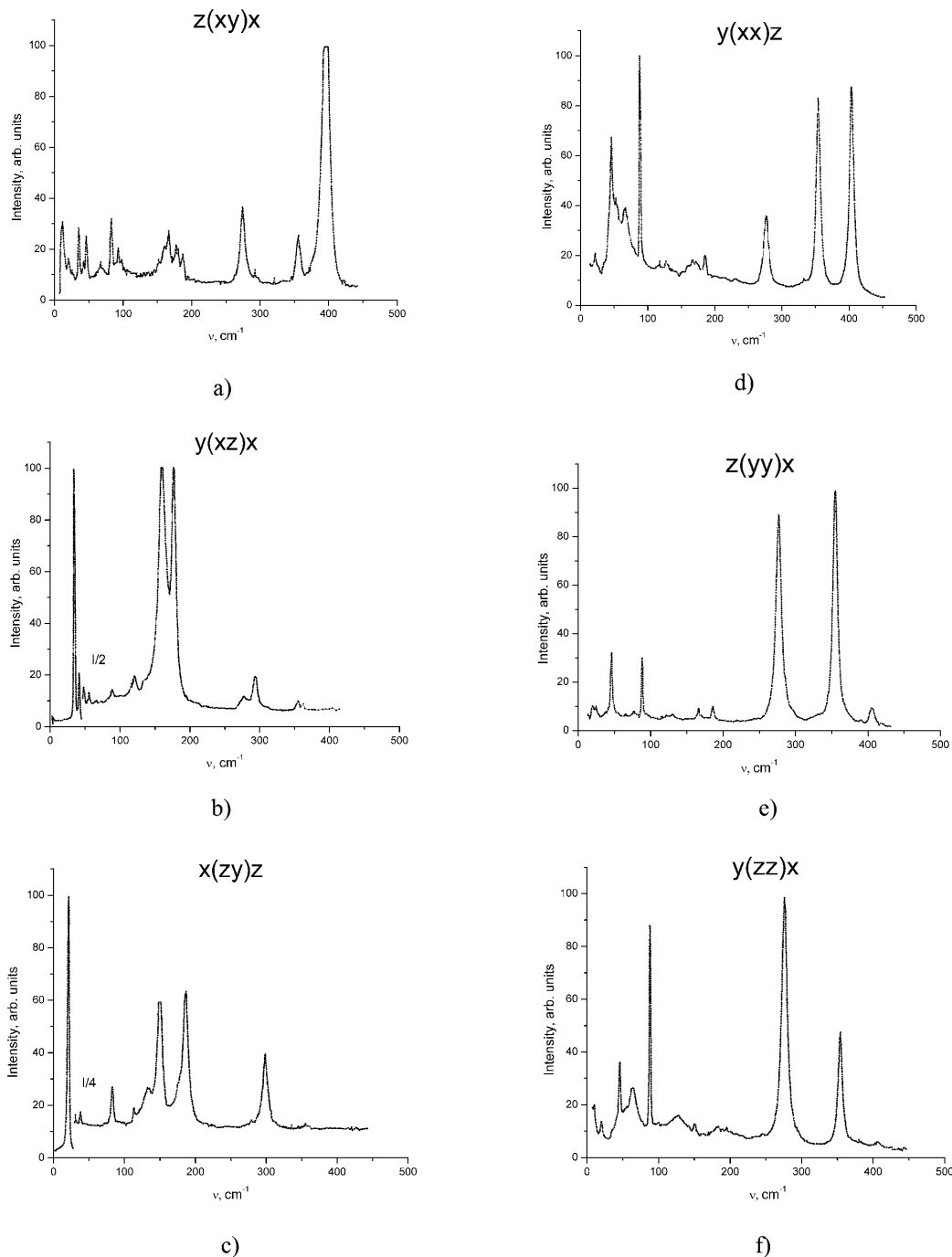


Fig. 1. Raman spectra of a  $PbGa_2S_4$  crystal in various scattering geometries:  $z(xy)x$  (a),  $y(xz)x$  (b),  $x(zy)z$  (c),  $y(xx)z$  (d),  $z(yy)x$  (e), and  $y(zz)x$  (f)

experimental researches concerning the IR-spectra of  $PbGa_2S_4$  crystals makes the analysis of the data obtained more complicated. The analysis of the Raman spectra of the  $PbGa_2S_4$  crystal is expedient to be fulfilled

proceeding from the structural ordering of atoms that compose the crystal lattice of this compound. Owing to a plenty of atoms in the elementary cell of those crystals (224 atoms), the structure analysis should be made in

projections onto planes  $ab$ ,  $bc$ , and  $ac$ , where  $a$ ,  $b$ , and  $c$  are the parameters of the elementary cell in the  $x$ -,  $y$ -, and  $z$ -directions in the rectangular coordinate system.

In Fig. 2, the projection of the crystal structure onto plane  $ab$  is shown. Two groups of tetrahedra,  $\text{GaS}_4$  and  $\text{SGa}_2\text{Pb}_2$ , can be distinguished, with the Ga and S atoms being common for those two tetrahedra. The coupling between the tetrahedra in direction  $b$  is fulfilled through common S atoms located at the vertices of a  $\text{GaS}_4$  tetrahedron. From Fig. 2,*a*, one can see that the tetrahedra  $\text{GaS}_4$  and  $\text{SGa}_2\text{Pb}_2$  form densely packed layers in the  $a$ -direction. The bond between the adjacent layers occurs through the Pb atoms, which are common for two  $\text{SGa}_2\text{Pb}_2$  tetrahedra, also located in the adjacent layers. Since the Pb–S bond has a clearly pronounced ionic character, it is obvious that the coupling between the layers composed of  $\text{GaS}_4$  tetrahedra is much weaker than the coupling in the layer consisting of those tetrahedra. This fact can explain the layered structure of the crystals concerned in direction  $a$ .

In Fig. 2,*b*, the projection of the crystal structure onto plane  $bc$  is shown. The figure demonstrates that, in this projection, one can distinguish layers formed by Pb atoms and oriented normally to the  $c$ -direction. The distance between Pb atoms calculated by us amounts to 10.19 Å along the  $b$ -direction. The space between Pb atoms includes two  $\text{GaS}_4$  tetrahedra bound through the common sulfur atom. According to our calculations, the distance between two nearest Ga atoms from two neighbor groups amounts to 7.36 Å. Two adjacent layers are shifted with respect to each other by a distance of 5.095 Å along the  $b$ -direction.

In Fig. 2, the projection of the crystal onto plane  $ac$  is depicted. One can easily distinguish the layers formed by sulfur atoms along the  $c$ -direction, which alternate with layers composed of lead and gallium atoms. Along the  $a$ -direction, we have dense layers consisting of  $\text{GaS}_4$  tetrahedra and separated by the layers of lead atoms. The sulfur atoms, which are located in positions  $S_1$  and  $S_2$ , form the tetrahedra  $\text{S}^1\text{Pb}_2\text{Ga}_2$  and  $\text{S}^2\text{Pb}_2\text{Ga}_2$ . The lead atoms – in both tetrahedra – are located between two dense  $\text{GaS}_4$  layers. The sulfur atoms in positions  $S_3$  and  $S_4$  form the tetrahedra  $\text{S}^3\text{Pb}_2\text{Ga}_2$  and  $\text{S}^4\text{Pb}_2\text{Ga}_2$ , where the lead atoms of each tetrahedron are located in the adjacent layers made up of lead atoms and separated by a dense  $\text{GaS}_4$  layer.

The fulfilled structure analysis made it possible to identify RS lines of the  $\text{PbGa}_2\text{S}_4$  crystal as follows. Since the Pb–S bond has a clearly expressed ionic character and its length is equal to 3.03 Å, it is clear that the coupling between the layers of  $\text{GaS}_4$  tetrahedra is much weaker than the coupling in the layer composed of those tetrahedra, where the Ga–S bond length amounts to 2.32 Å.

The Ga–S bond, similarly to what takes place in  $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^{\text{V}}$  and  $\text{A}^{\text{I}}\text{B}^{\text{III}}\text{C}_2^{\text{VI}}$  compounds, is predominantly covalent. Whence, it follows that the variation of polarizability in this bond manifests itself more strongly than it occurs in the Pb–S bond, which is ionic. Therefore, we may assume that RS bands with high intensities are caused by vibrations of atoms that form the Ga–S bond. Accordingly, vibrations with low intensities can be attributed to the Pb–S bond.

**Table 2. Mode frequencies, intensities, halfwidths, and symmetries**

$A_g$			$B_{1g}$			$B_{2g}$			$B_{3g}$		
frequency, $\text{cm}^{-1}$	intensity, rel. units	halfwidth, $\text{cm}^{-1}$	frequency, $\text{cm}^{-1}$	intensity, rel. units	halfwidth, $\text{cm}^{-1}$	frequency, $\text{cm}^{-1}$	intensity, rel. units	halfwidth, $\text{cm}^{-1}$	frequency, $\text{cm}^{-1}$	intensity, rel. units	halfwidth, $\text{cm}^{-1}$
46	67	5	25	12	1	34	92	3	21	97	2
53	43	12	35	28	2	41	21	2	31	16	3
67	39	19	42	15	3	47	15	2	38	17	2
78	8	8	46	25	3	55	13	1	83	27	4
88	98	2	67	15	7	89	14	6	114	19	2
118	18	1	83	32	5	121	20	7	132	27	14
127	18	3	93	20	4	160	98	14	150	63	9
149	12	4	98	16	2	176	98	8	175	28	3
166	18	3	152	16	7	293	19	7	187	63	11
172	17	10	161	21	8	362	9	2	280	14	2
185	20	5	167	27	6				298	39	11
277	97	9	178	22	5				336	13	2
332	11	3	187	18	5				345	12	2
354	77	7	274	36	9						
404	87	7	292	12	3						
			321	9	2						
			356	25	10						
			398	98	15						

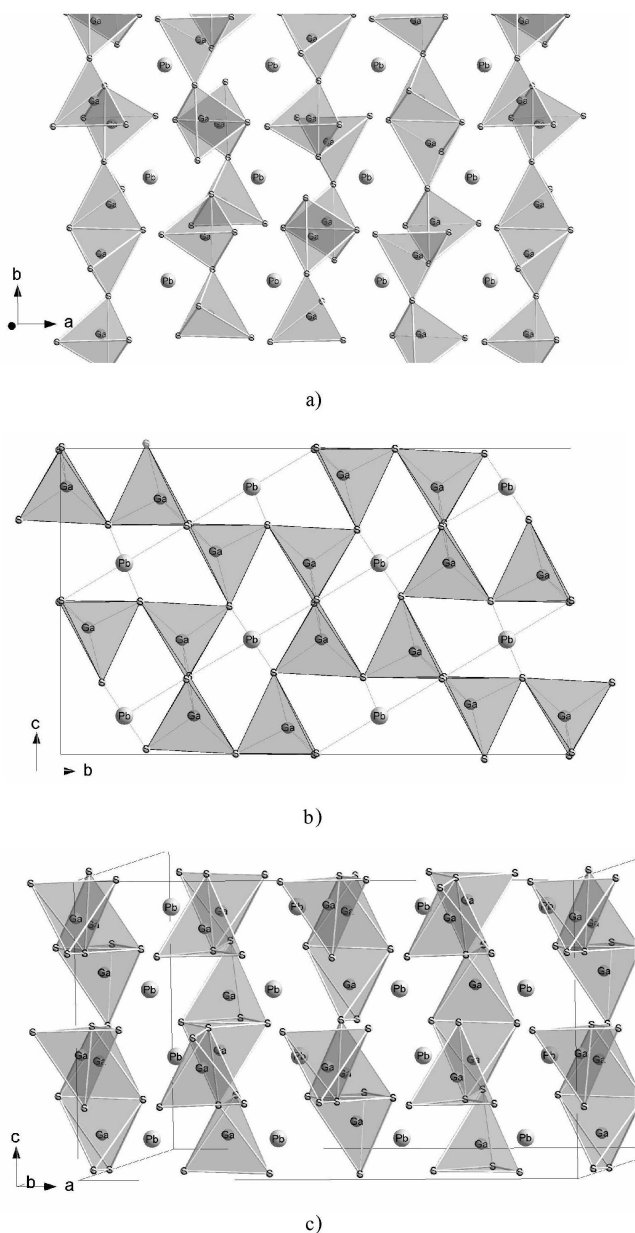


Fig. 2. Structure of a PbGa<sub>2</sub>S<sub>4</sub> crystal projected onto planes (001) (a), (100) (b), and (010) (c)

Vibrational modes of the PbGa<sub>2</sub>S<sub>4</sub> crystal can be conditionally classified into internal and external ones. On the basis of considerations dealing with the structure

**Table 3. Selection rules for chosen scattering geometries of RS spectra**

$A_g$	$B_{1g}$	$B_{2g}$	$B_{3g}$
$y(xx)z$	$z(xy)x$	$y(xz)x$	$x(zy)z$
$z(yy)x$		$y(zx)z$	$y(zy)x$
$y(zz)x$		$z(xz)y$	

of the PbGa<sub>2</sub>S<sub>4</sub> crystal, the gallium and sulfur atoms form an almost regular tetrahedron GaS<sub>4</sub>. Vibrations of gallium and sulfur atoms in the Ga–S bond can obviously be classified as internal. Then, vibrations of lead and sulfur atoms, which form the Pb–S bond, can be attributed to external ones.

The registered RS spectra demonstrate that the range of vibrations of Pb atoms in the Pb–S bond extends over the frequency interval 20 – 55 cm<sup>-1</sup>. The calculations support the following types of vibrations for Pb atoms: a non-degenerate one of the  $A_g$ -symmetry; four vibrations for each of the symmetries  $B_{1g}$  and  $B_{2g}$ , and three vibrations of the  $B_{3g}$ -symmetry. The analysis of the intensity of the RS lines with the frequency  $\nu = 21$  cm<sup>-1</sup> in various scattering geometries allowed us to classify them as the modes of the  $B_{3g}$ -symmetry.

The modes of the symmetries  $A_g$  and  $B_{1g}$ , that manifest themselves as RS lines at a frequency of 46 cm<sup>-1</sup> in scattering geometries concerned satisfy the selection rules. Therefore, the following identification of the registered modes (Fig. 1), associated with the vibrations of lead atoms, can be done:  $A_g$  – 46 cm<sup>-1</sup>;  $B_{1g}$  – 25, 35, 42, and 46 cm<sup>-1</sup>;  $B_{2g}$  – 34, 41, 47, and 55 cm<sup>-1</sup>;  $B_{3g}$  – 21, 31, and 38 cm<sup>-1</sup>.

The registered spectra demonstrate the absence of RS lines in the range from 200 to 250 cm<sup>-1</sup>. We may assume that this frequency interval separates the ranges of vibrational spectra of gallium and sulfur atoms. Therefore, the RS lines, which correspond to the vibrations of gallium atoms, will probably be localized in the range 50 – 200 cm<sup>-1</sup>, while the modes corresponding to the vibrations of sulfur atoms in the range 250 – 500 cm<sup>-1</sup>.

It should be noted that low-temperature measurements of RS spectra will allow the absent lines to be reliably detected and the total identification of the vibrational spectrum of the PbGa<sub>2</sub>S<sub>4</sub> crystal to be made.

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## КОЛИВАЛЬНИЙ СПЕКТР КРИСТАЛІВ ТІОГАЛАТУ СВИНЦЮ

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## Резюме

Досліджується комбінаційне розсіяння світла (КРС) у кристалі  $\text{PbGa}_2\text{S}_4$ . Методом фактор-групового аналізу вперше виконано розрахунок фононного спектра даного кристала. Визначена кількість мод, що активні у спектрах КР, їх симетрію і правила добору. Проведено ототожнення спостережених у спектрах КР мод з коливаннями атомів, що складають кристал.

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