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STRUCTURE
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Crystal Structure and Specific Features of Formation of Vibrational Spectra of Pb_2GeS_4

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Abstract—The structure of Pb_2GeS_4 single crystals is confirmed and the polarized Raman spectra of these crystals are recorded. The vibrational spectra was considered in terms of analysis of intramolecular vibrations of $[\text{GeS}_4]$ tetrahedral formations, the main structural elements of this compound. © 2003 MAIK “Nauka/Interperiodica”.

According to the equilibrium PbS-GeS_2 phase diagram, two ternary compounds, PbGeS_3 and Pb_2GeS_4 , are formed in this system [1]. The Pb_2GeS_4 compound melts the open maximum at 894 K with, which indicates its stability and the possibility of growing these crystals from melt. The Pb_2GeS_4 compound was synthesized either by melting lead sulfide and germanium disulfide in an equimolar ratio or by directly melting the elementary components in quartz ampules pumped out to 0.013 Pa under vibrational mixing. The maximum heating temperature was 1100 K. The melts were cooled in a switched-off furnace. The alloys were homogenized by 200-h-annealing at 830 K.

Pb_2GeS_4 single crystals were grown by the directional crystallization method from a Bridgman–Stockbarger melt in a vertical electric furnace. The velocity of the crystallization front (0.12–0.18 mm/h) and the temperature gradient in the crystallization zone (3–5 K/mm) were optimal for the growth of high-quality Pb_2GeS_4 crystals. Under these conditions, we obtained homogeneous single-crystal boules 16–20 mm in diameter and 60–70 mm in length.

The crystals grown were identified by X-ray phase analysis. Indexing of the X-ray diffraction pattern obtained on a DRON-05 diffractometer ($\text{CuK}\alpha$ radiation) and subsequent calculation and the least-squares refinement of the unit-cell parameters were performed on a computer. The unit-cell parameters of the monoclinic (sp. gr. $P2_1/c$) unit cell of Pb_2GeS_4 ($a = 8.01(3)$ Å, $b = 8.86(4)$ Å, $c = 10.91(3)$ Å, $\beta = 114.4(4)^\circ$; $Z = 4$) proved to be close to the those reported in [2]. The main structural fragments are isolated coordination tetrahedra of germanium atoms $[\text{GeS}_4]$ (four germanium atoms per unit cell) located in infinite channels along the X axis. These channels are formed by ψ -octahedra of lead atoms $[\text{PbS}_5E]$, which share the edges (E is a lone electron pair of lead). Figure 1a shows isolated tetrahedra of the structure projected onto the XZ plane.

Figures 1b and 1c show the projection of the structure onto the $bcsin\beta$ plane. The $[\text{GeS}_4]$ “junctions” are shown in Fig. 1b; the $[\text{PbS}_5]$ junctions, in Fig. 1c. Two such germanium tetrahedra are located in the voids formed by eight $[\text{PbS}_5]$ junctions. The interatomic Ge–S distances range within 2.18–2.22 Å (which is consistent with the sum of the corresponding covalent radii ($1.22 + 1.04 = 2.26$ Å)), while the Pb–S distances, range within 2.28–3.25 Å (which is close to the sum of the ionic radii of S^{2-} and Pb^{2+} ($1.82 + 1.26 = 3.08$ Å)).

Raman spectra were measured in polarized light on a DFS-24 spectrometer at room temperature. The spectra were excited by the radiation of an He–Ne laser (wavelength $\lambda = 6328$ Å). The polarized Raman spectra of the Pb_2GeS_4 crystal are shown in Fig. 2 for all the components of the scattering tensor.

The frequencies of the Raman-active modes are summarized in the table. The factor-group analysis of the normal vibrations of the Pb_2GeS_4 lattice was performed by the positional symmetry method [3]. The primitive unit cell contains 84 branches, while the long-wave phonons are distributed over the irreversible representations as follows:

$$\Gamma = 21A_g + 21B_g + 21A_u + 21B_u.$$

Consider the formation of the Pb_2GeS_4 vibrational spectrum proceeding from analysis of the transformation of intramolecular vibrations under deformation of isolated $[\text{GeS}_4]$ tetrahedra (main structural element) in a crystal field. The intramolecular vibrations of the regular tetrahedral $[\text{GeS}_4]$ molecules not distorted by the crystal field are decomposed into irreducible representations of the factor-group T_d as follows:

$$\Gamma = A_1 + E + 2F_2.$$

The A_1 representation corresponds to the totally symmetric valence vibration ν_1 . Since the direction of the displacement of a sulfur atom with respect to the central

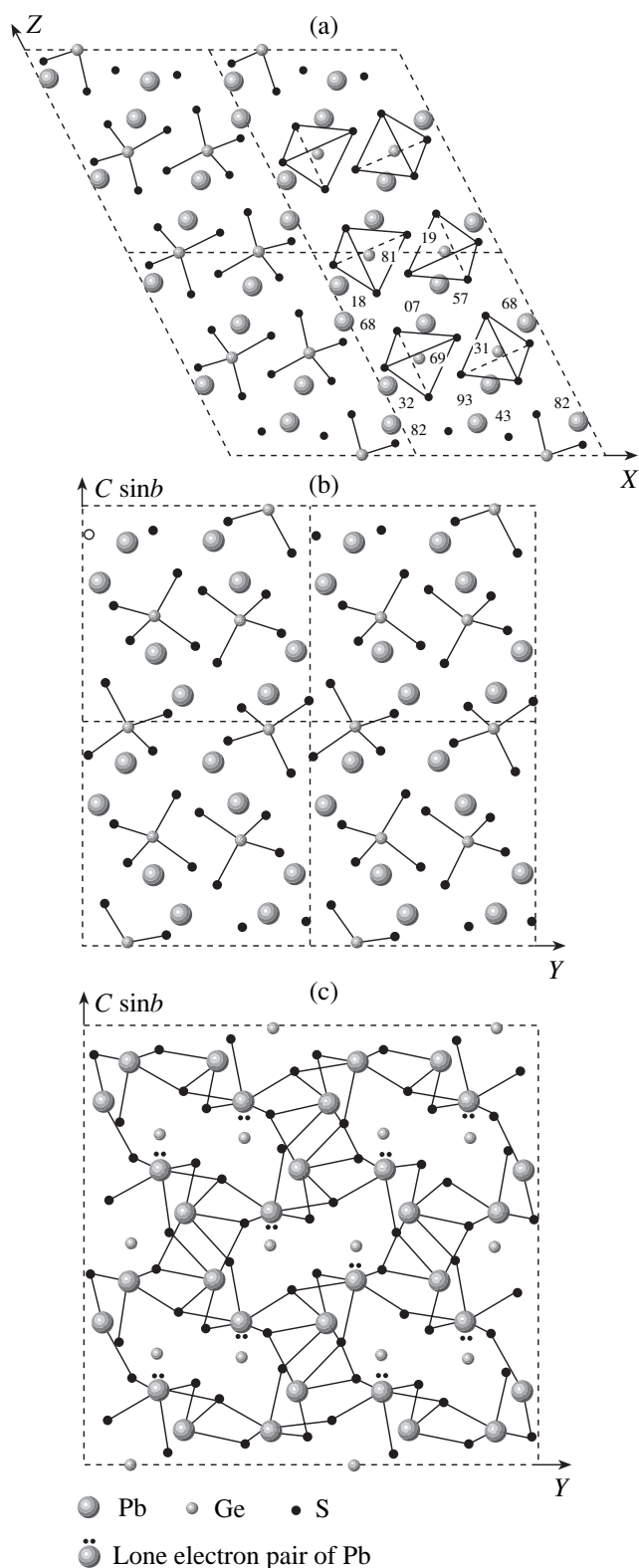


Fig. 1. Projections of the Pb_2GeS_4 structure onto the (a) XZ and (b, c) $bcsin\beta$ planes. Four unit cells are shown with (a, b) coordination $[\text{GeS}_4]$ tetrahedra. Infinite channels containing the $[\text{GeS}_4]$ tetrahedra are formed by (c) ψ -octahedra $[\text{PbS}_5E]$ sharing their edges.

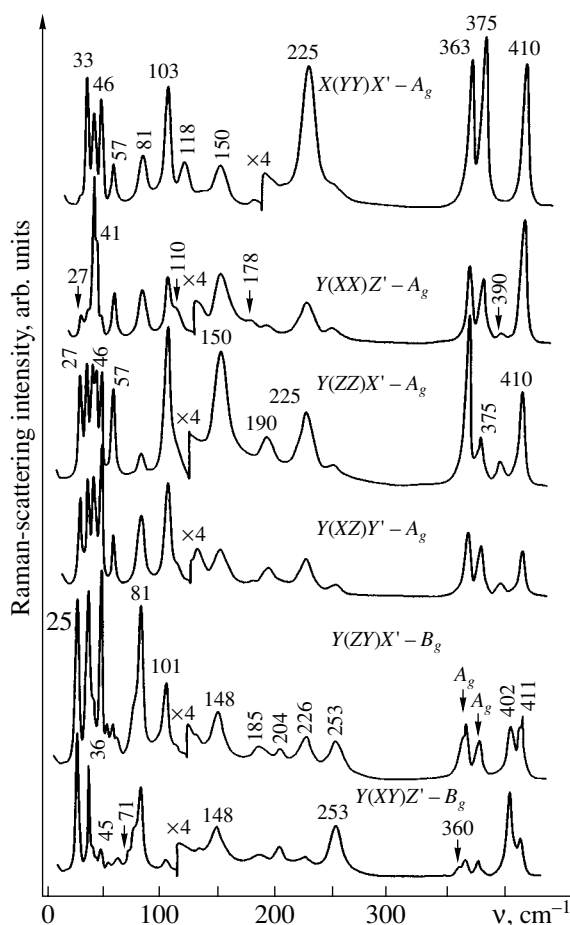


Fig. 2. Polarized Raman spectra of Pb_2GeS_4 .

germanium atom at rest coincides with the direction of the Ge–S valence bonds, and, therefore, the ν_1 vibration is of a purely valent nature. Of two triply degenerate vibrations with the symmetry F_2 , one, ν_3 , is responsible for the variations in the Ge–S bond lengths and the other, ν_4 , for the variation in the S–Ge–S angles. The doubly degenerate E -representation describes deformation vibrations of tetrahedra with the frequency ν_2 . For a free $[\text{GeS}_4]$ molecule, $\nu_1 = 386$, $\nu_2 = 170$, $\nu_3 = 417$, and $\nu_4 = 205 \text{ cm}^{-1}$ [4].

Deformation of $[\text{GeS}_4]^{4-}$ anions in a static crystalline field results in the removal of the degeneracy of the ν_2 , ν_3 , and ν_4 vibrations, whereas their frequencies are split into two ($\nu_2 \rightarrow \nu_2^1 + \nu_2^2$) and three ($\nu_3 \rightarrow \nu_3^1 + \nu_3^2 + \nu_3^3$; $\nu_4 \rightarrow \nu_4^1 + \nu_4^2 + \nu_4^3$) components. Since the Pb_2GeS_4 unit cell contains four translationally non-equivalent $[\text{GeS}_4]^{4-}$ anions, each of the modes considered above also forms a Davydov quartet with the components polarized in the A_g , B_g , A_u , and B_u geometries. An individual Davydov quartet is also formed by the valence vibration of a tetrahedron ν_1 . Thus, four

Frequencies (cm^{-1}) of vibrational modes in a Pb_2GeS_4 crystal

Frequency		A_g				B_g		IR
vibration type		XX	YY	ZZ	XZ	YZ	YX	
Internal	ν_3^1	410	410	410	410	411		410
	ν_3^2	390		390	390	402	402	389
	ν_3^3	363	363	363	363	360	360	359
	ν_1	375	375	375	375	374	374	
	ν_4^1	248	248	248	248	253	253	240
	ν_4^3	225	25	225	225	226	226	215
	ν_4^2	190	190	190	190	204	204	
	ν_2^1	178	178		178	185	185	184
	ν_2^2	150	150	1150	150	148	148	
External	Translational–librational						133	
		130	130		130	113		
			118			101	101	120
		110		110	110	81	81	
		103	103	103	103	76	76	103
		81	81	81	81		71	70
	Translational, Pb^{2+}	57	55	57	57	61	61	
		46	46	46	46	58	58	57
		41		41	41	52	52	52
		39	39	39	39	45	45	
		33	33	33	33	6	36	
		27		27	27	25	25	

valence modes should be observed in the high-frequency range of the Raman spectrum, which is consistent with the experiment (see Fig. 2). Usually, the intensity of the ν_1 mode in the Raman spectra of the tetrahedral molecules is much higher than the intensity of the ν_3 modes. In the IR spectra, the intensity of this mode is low because of the almost spherical symmetry of the anion [4]. In the Pb_2GeS_4 crystal, considerable splitting of the vibration is associated with strong deformation of a $[\text{GeS}_4]^{4-}$ anion by the crystal field, whereas the intensities of the ν_1 and ν_3 modes are comparable, which hinders their identification.

It is assumed that the deformation vibrations in the $[\text{GeSe}_4]$ complex are in the frequency range 148–253 cm^{-1} , while the translational-librational vibrations are in the range 81–118 cm^{-1} . The range of the Raman

spectrum of Pb_2GeS_4 characterized by the lowest frequency, 25–61 cm^{-1} , is formed by the translational vibrations of Pb^{2+} cations with respect to the anion sublattice.

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