

CONDENSED-MATTER SPECTROSCOPY

Edge Absorption Spectra of Crystalline and Glassy PbGeS₃

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Abstract—Edge absorption spectra of crystalline and glassy lead thiogermanate (PbGeS₃) have been measured in the temperature range from 77 to 470 K. It is shown that the dependence of the absorption coefficient on the photon energy for the glassy and crystalline states in the polarization $\mathbf{E} \parallel \mathbf{c}$ is described by the Urbach rule. For the crystal in the polarization $\mathbf{E} \parallel \mathbf{b}$, at $T < 300$ K, an almost parallel shift of the intrinsic absorption edge to lower energies occurs with an increase in temperature, whereas at $T \geq 300$ K, the Urbach absorption edge is observed. The parameter σ_0 , related to the electron–phonon coupling constant, and the energy $\hbar\omega_{\text{ph}}$ of the effective phonons involved in the formation of the absorption edge of crystalline PbGeS₃ are determined from the temperature dependence of the parameter of the absorption edge slope. The contributions of the dynamic and static disorders to the diffusion of the absorption edge of crystalline PbGeS₃, as well as the topological disorder of glassy PbGeS₃, have been estimated.

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INTRODUCTION

For a deeper understanding of the electronic processes occurring in chalcogenide glassy semiconductors (CGSs), the study of the same properties of ordered (crystalline) and disordered (glassy) phases of the same chemical composition is of great importance. To date, such information exists mainly for binary glass formers, such as As₂S₃, As₂Se₃, GeS₂, and GeSe₂. Taking into account that lead thiogermanate (PbGeS₃) can be obtained in both the crystalline and glassy states [1], a possibility opens to extend the range of objects with a more complex structure in order to detect new regularities manifesting themselves in the crystal–glass transition. Previously, we showed by the methods of vibrational spectroscopy [2] that the short-range order in the glassy phase of PbGeS₃ remains the same as in the crystalline state. Detailed analysis of the phonon spectra of crystalline lead thiogermanate was performed by PbGeS₃ [3, 4]. Concerning the study of the electronic properties, the data in the literature are mainly related to the ordered phase. In particular, the first results of the investigation of the intrinsic absorption edge of crystalline PbGeS₃ were reported in [5]. Analysis of the conductivity and stationary characteristics of photoconductivity was performed in [6, 7].

In this paper, we report the results of studying the anisotropy of the intrinsic absorption edge of crystalline PbGeS₃ and the effect of topological disorder during the crystal–glass transition on the intrinsic absorption edge.

EXPERIMENTAL

A polycrystalline charge of PbGeS₃ was obtained by joint alloying of the compound-forming elements taken in the stoichiometric ratio. Alloying was performed in quartz ampoules evacuated to a residual pressure of 10^{−3} Pa. The sulfur used for synthesis was additionally subjected to preliminary purification by vacuum distillation. Single crystals were grown by directed crystallization from melt (the vertical Bridgman method). The temperature gradient in the crystallization zone was 20–30 K/cm and the pulling rate was 0.2–0.3 mm/h. Crystals were grown in the form of a cylinder with a diameter of 18–20 mm and a length of up to 60 mm.

The structure and unit-cell parameters of single crystals were determined by X-ray diffraction. PbGeS₃ is crystallized in a monoclinic lattice (space group *P*2₁/*c*, lattice parameters $a = 7.224$ Å, $b = 10.442$ Å, $c = 6.825$ Å, $\beta = 105.7^\circ$, and $Z = 4$). These data are in agreement with those obtained in [8]. The main structural lattice elements are GeS₄ tetrahedra, sharing vertices and forming infinite chains along the *Z* axis. These chains are linked by chains of PbS₃E ψ -octahedra (*E* is an unshared electron pair) sharing edges with each other. These chains in the structure are directed parallel to chains of GeS₄ tetrahedra [1, 2].

Taking into account the fact that these crystals are easily cleaved over the cleavage plane with formation of mirror surfaces, samples of necessary thickness with natural mirror surfaces were prepared immediately before measurements.

To obtain glasses, melts with a total mass of 8–10 g were cooled at a rate of ~17 K/s. Microstructural and

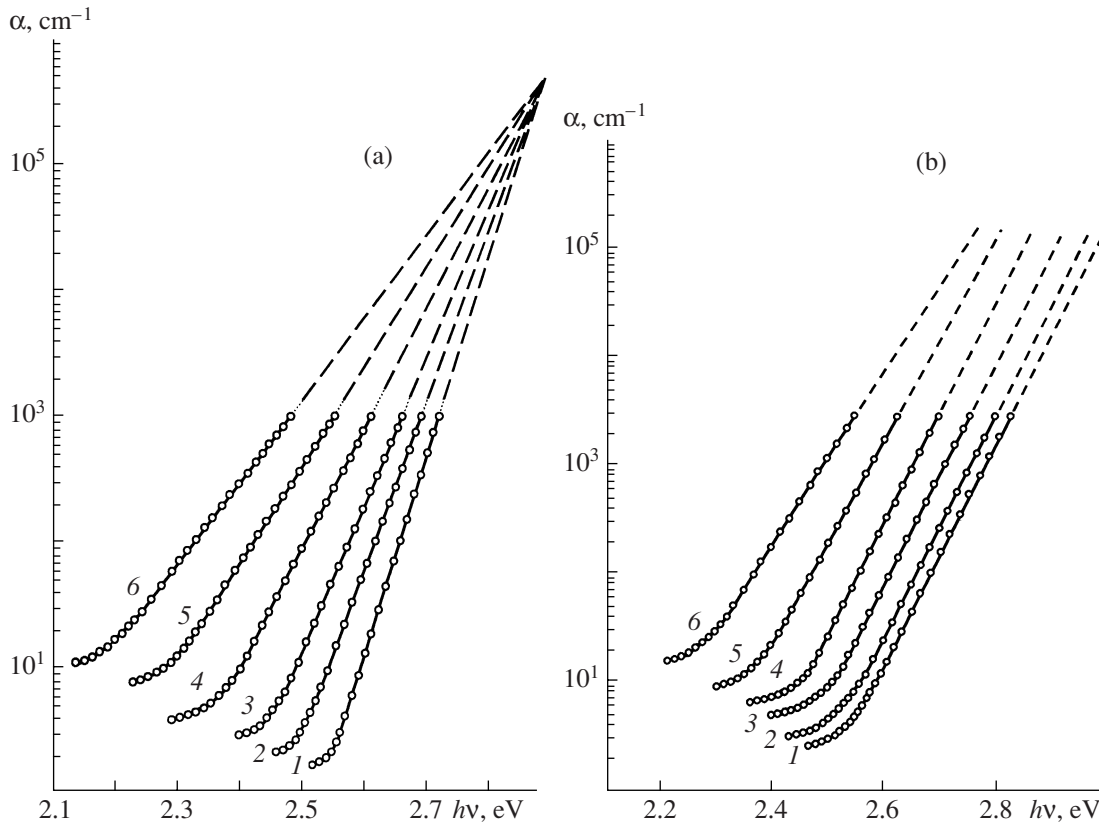


Fig. 1. (a) Spectral dependences of the absorption coefficient of crystalline PbGeS₃ in the polarization $\mathbf{E} \parallel \mathbf{c}$ at $T = (1)$ 77, (2) 150, (3) 220, (4) 300, (5) 368, and (6) 469 K. (b) Spectral dependences of the absorption coefficient of crystalline PbGeS₃ in the polarization $\mathbf{E} \parallel \mathbf{b}$ at $T = (1)$ 77, (2) 150, (3) 220, (4) 300, (5) 368, and (6) 469 K.

X-ray diffraction analysis showed that all glasses were homogeneous and did not contain any crystalline inclusions. For optical measurements, plane-parallel plates of different thicknesses were cut from the bulk glass and then ground and mechanically polished.

The absorption coefficient α was determined from the measured values of the transmittance T and surface reflectance R using the well-known formula [9]

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2 + \sqrt{(1-R)^4 + 4T^2 R^2}}{2T} \right], \quad (1)$$

where d is the sample thickness. The relative error $\Delta\alpha/\alpha$ in determining the absorption coefficient did not exceed 10% at $0.3 \leq \alpha d \leq 3$.

RESULTS AND DISCUSSION

The spectral dependences of the absorption coefficient of crystalline PbGeS₃, which were measured at two different polarizations, $\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{b}$, are shown in Figs. 1a and 1b, respectively. In the experimental spectra $\alpha = f(h\nu)$, one can select two characteristic portions, whose formation corresponds to different mechanisms of light interaction with crystalline PbGeS₃. On the first (long-wavelength) portion, the absorption

related to the presence of large-scale violations of the periodic lattice potential only slightly depends on the photon energy. This long-wavelength portion is generally associated with the presence of static lattice defects of different nature (unintentional residual impurities, pores, dislocations, cracks, etc.) [10, 11].

In the second portion, in the range of absorption coefficients from 10 to 10³ cm⁻¹, the behavior of the intrinsic absorption edge is described by the exponential dependence on the photon energy $\hbar\omega$ (the Urbach rule) [12, 13] in the form

$$\begin{aligned} \alpha(\hbar\omega, T) &= \alpha_0 \exp[\sigma(\hbar\omega - E_0)/kT] \\ &= \alpha_0 \exp[(\hbar\omega - E_0)/w], \end{aligned} \quad (2)$$

where the parameters α_0 and E_0 are the coordinates of the convergence point of the Urbach fan, σ/kT characterizes the slope of the absorption edge at this temperature, and $w = kT/\sigma$ is the absorption edge width. The parameters entering expression (2) are rather sensitive to different kinds of lattice defects; this circumstance is important in study of the crystal–glass transition.

For both polarizations, the absorption edge of the crystalline lead thiogermanate shifts to longer wavelengths with an increase in temperature from 77 to 470 K (Figs. 1a, 1b). This shift is a manifestation of the

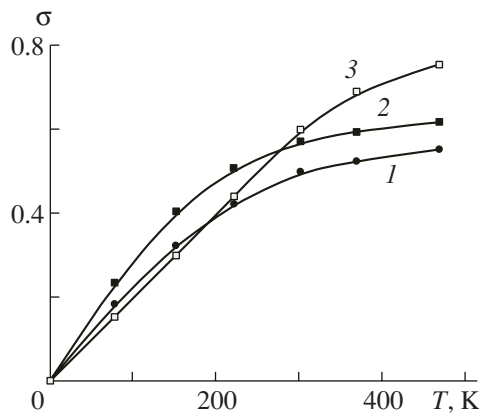


Fig. 2. Temperature dependences of the parameter σ for crystalline ((2) $\mathbf{E} \parallel \mathbf{c}$, (3) $\mathbf{E} \parallel \mathbf{b}$) and glassy (1) PbGeS_3 .

decrease in the band gap with increasing sample temperature. The parameter σ in expression (2) is temperature-dependent (Fig. 2); this dependence is described by the expression [14]

$$\sigma = \sigma_0 \frac{2kT}{\hbar\omega_{\text{ph}}} \tanh \frac{\hbar\omega_{\text{ph}}}{2kT}, \quad (3)$$

where σ_0 is a parameter that is related to the exciton–phonon coupling constant g as follows: $\sigma_0 = (2/3)g^{-1}$; $\hbar\omega_{\text{ph}}$ is the energy of the effective phonon that most strongly interacts with the electron (exciton). For most crystals, $\hbar\omega_{\text{ph}}$ is close to the energy of the highest energy LO -phonon [14].

Figure 1 indicates that only for the polarization $\mathbf{E} \parallel \mathbf{c}$ do the high-energy parts of the edge absorption spectra of crystalline PbGeS_3 in the studied temperature range from 77 to 470 K form a characteristic temperature fan, whereas for the polarization $\mathbf{E} \parallel \mathbf{b}$ at $T < 300$ K the intrinsic absorption edge undergoes an almost parallel shift to lower energies with an increase in temperature, and only at $T \geq 300$ K does the edge slope becomes temperature-dependent. Analogous behavior of the

Urbach edge was observed in layered GeS crystals in the study of the anisotropy of the intrinsic absorption edge in the cleavage plane of the polarization $\mathbf{E} \parallel \mathbf{b}$ [15]. The values of α_0 , E_0 , σ_0 , and $\hbar\omega_{\text{ph}}$ (see table) were obtained from the analysis of the absorption spectrum of the crystal in the polarizations $\mathbf{E} \parallel \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{b}$ (at $T \geq 300$ K) and the temperature dependences of the parameter σ . The obtained values $\sigma_0 < 1$ indicate strong electron–photon coupling in crystalline PbGeS_3 .

Although a strict and sufficiently general derivation of the Urbach rule is absent to date, there is no doubt that the formation of the Urbach tail in crystalline and glassy semiconductors is, in a particular way, related to the general structural disorder in the system. In the case of crystals, this is dynamic (thermal) disorder, whose source is the electron–phonon coupling due to lattice vibrations and static (structural) disorder, whose source is small-scale violations of the periodic lattice potential due to the presence of point charged defects in the crystal [16, 17]. With a decrease in temperature, phonons are frozen out; however, the absorption coefficient tails do not disappear. Their existence is attributed to the crystal inhomogeneity frozen in time. In glassy semiconductors, the topological disorder caused by the disorder of bond lengths and angles is additionally imposed. The absence of long-range order in glassy semiconductors leads to additional (in comparison with crystals) static spatial fluctuations of the potential.

Let us consider in more detail the effect of each source of disorder on the formation of the intrinsic absorption edge. In the crystals that were not intentionally doped, the edge diffusion is related to the thermally induced lattice distortions, which are characterized by the mean-square dynamic atomic displacements $\langle u^2 \rangle_{\text{dyn}}$ from the equilibrium position and the presence of a potential profile in the crystal caused by static displacements $\langle u^2 \rangle_{\text{st}}$ of lattice atoms near charged point defects [17]. The major intrinsic point defects in germanium and lead chalcogenides are vacancies in the cation and anion sublattices, which form donor and acceptor states [1].

As a measure of the absorption edge diffusion and, correspondingly, the degree of disorder, one can use the quantity w [16] (Fig. 3), determined from the slope of the straight lines in Figs. 1 and 4. In this case, the energy width of the Urbach absorption edge of solids is determined by the dynamic (thermal) and static (structural) disorders [17, 18]:

$$w(T, X) = K(\langle u^2 \rangle_{\text{dyn}} + \langle u^2 \rangle_{\text{st}}), \quad (4)$$

where X is a geometric parameter of the material, which is used to characterize the static disorder and $\langle u^2 \rangle_{\text{dyn}}$ and $\langle u^2 \rangle_{\text{st}}$ are the mean-square displacements of lattice atoms from the equilibrium position, which are caused, respectively, by dynamic (thermal phonons) and static (structural) disorder. The coefficient K has the meaning of the constant of the second-order deformation poten-

Parameters of the Urbach absorption edge for crystalline and glassy PbGeS_3

State	Crystal ($\mathbf{E} \parallel \mathbf{b}$)	Crystal ($\mathbf{E} \parallel \mathbf{c}$)	Glass
α_0 , cm^{-1}	–	4.8×10^5	3.9×10^5
E_0 , eV	–	2.89	2.54
$\hbar\omega_{\text{ph}}$, meV	62.6	37.3	44.9
σ_0	0.90	0.66	0.61
θ_E , K	726	433	521
w_0 , meV	34.3	28.1	37.2
w_1 , meV	72.7	57.3	72.9
w (469 K), meV	53.9	65.2	72.1

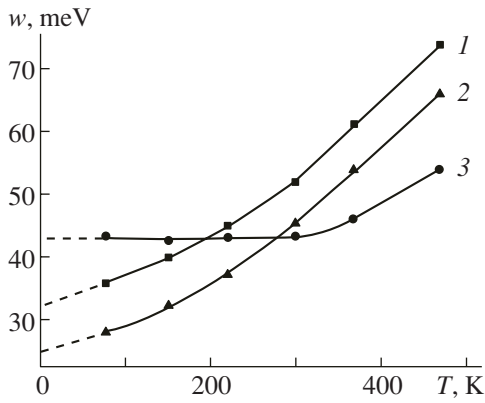


Fig. 3. Temperature dependences of the parameter w for crystalline ((2) $\mathbf{E} \parallel \mathbf{c}$, (3) $\mathbf{E} \parallel \mathbf{b}$) and glassy (1) PbGeS₃.

tial [18]. Since atomic displacements with respect to the equilibrium position lead to a change in the electric potential, formula (4) can be written as

$$w = k_0(W_{\text{dyn}}^2 + W_{\text{st}}^2) = w_{\text{dyn}} + w_{\text{st}}, \quad (5)$$

where k_0 is a constant; W_{dyn}^2 and W_{st}^2 are the mean-square deviations from the electric potential of the ideal ordered structure, which are caused, respectively, by dynamic (thermal) and static (structural) disorder; and the contributions of the dynamic (w_{dyn}) and static (w_{st}) disorder to w are assumed to be independent, equivalent, and additive.

To separate the contributions of different types of disorder to w , we used the technique proposed in [19]. In this case, we used the known relation describing well the temperature dependence of w [18, 20]

$$w = w_0 + w_1 \left[\frac{1}{\exp(\theta_E/T) - 1} \right]. \quad (6)$$

Here, w_0 and w_1 are constants and θ_E is the Einstein temperature, which corresponds to the averaged frequency of phonon excitations of a system of noninteracting oscillators. The values of the parameters w_0 and w_1 , obtained in the description of the experimental temperature dependences of w by relation (6), are listed in the table. Comparing (5) and (6), we find the values $w_{\text{dyn}} = 37.1$ meV (56.9% of w) and $w_{\text{st}} = 28.1$ meV (43.1%) at $T = 469$ K for the polarization $\mathbf{E} \parallel \mathbf{c}$ and $w_{\text{dyn}} = 19.6$ meV (36.4%) and $w_{\text{st}} = 34.3$ meV (63.6%) at $T = 469$ K for the polarization $\mathbf{E} \parallel \mathbf{b}$.

Investigation of the absorption spectra of glassy lead tegermanate showed that near the optical absorption edge the dependence of the absorption coefficient on the photon energy and temperature is also described by relation (2) (Fig. 4); the values of the parameters α_0 , E_0 , and σ_0 are given in the table. In addition, we found a red shift of the fundamental absorption edge in the glassy phase with respect to its position in the crystalline state;

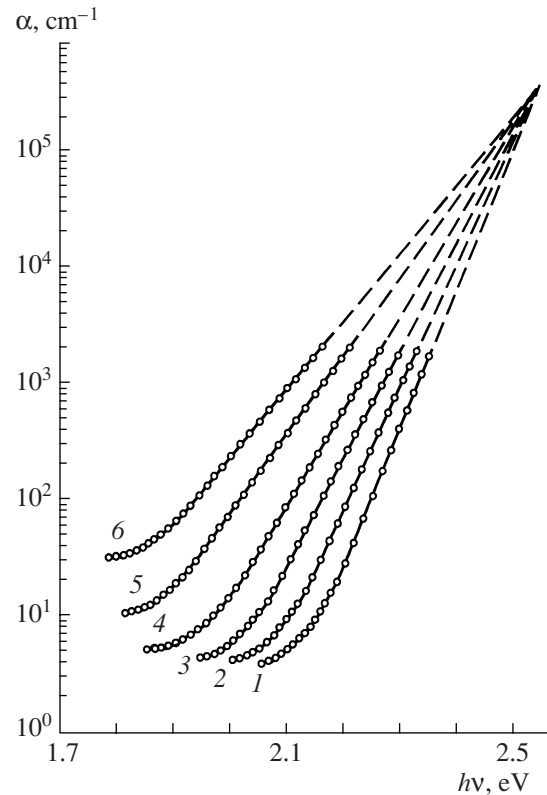


Fig. 4. Spectral dependences of the absorption coefficient of glassy PbGeS₃ at $T = (1)$ 77, (2) 150, (3) 220, (4) 300, (5) 368, and (6) 469.

this shift reflects the decrease in the band gap at the crystal–glass transition. Disappearance of the long-range order at the crystal–glass transition, along with the decrease in the band gap, also leads to the disappearance of anisotropy of the edge absorption spectra, which is due to the diffusion of the band edges and occurrence of tails of localized states near the edges of allowed bands as a result of the topological structure disorder.

In contrast to most CGSs, which exhibit an almost parallel shift of the curve $\alpha = f(\hbar\omega)$ with a change in temperature, glassy PbGeS₃ is characterized by an absorption edge of the Urbach type. Comparison of Figs. 1a and 4 shows that at the transition from the crystalline to the glassy phase the absorption edge diffuses and its energy width w increases. Since w characterizes the length of the exponential tails of the density of states near the allowed band, the increase in w at the crystal–glass transition indicates an increase in the disorder in the glassy phase due to the presence of topological disorder. Indeed, direct diffraction methods for studying the glass structure show a spread of angles and bond lengths. This fact indicates that glass formation is accompanied by a strong increase in the fluctuation of the potential profile caused by the disorder in angles and bond lengths; i.e., additional topological disorder is

present in glasses. The origin of this disorder is related to random grids, and its effect on the electronic spectrum manifest itself in fluctuations of the diagonal and off-diagonal eigenenergy matrix elements. The presence of the component related to the disorder of bond lengths and angles in the total disorder leads to broadening of the profile spectral characteristics and appearance of features characteristic of glassy semiconductors.

Analogous calculations for glassy PbGeS_3 using relations (5) and (6) gave the following values: $w_{\text{st}} = 34.9$ meV (48.4% of w) and $w_{\text{st}} + w_{\text{top}} = 37.2$ meV (51.6%) at $T = 469$ K. The absorption edge diffusion related to the presence of topological disorder can be estimated from the difference $w_{\text{top}} = w - w_{\text{dyn}} - w_{\text{st}}$, where w_{st} is the static component for crystalline PbGeS_3 (polarization $\mathbf{E} \parallel \mathbf{c}$). The thus obtained contribution of the topological disorder is 9.1 meV or 12.6% of w .

CONCLUSIONS

The edge absorption spectra of crystalline and glassy PbGeS_3 have been investigated in the temperature range from 77 to 470 K. Anisotropy of the temperature behavior of the intrinsic absorption edge in crystalline PbGeS_3 has been found. Specifically, for the polarization $\mathbf{E} \parallel \mathbf{c}$, the Urbach form is observed in the entire temperature range under study. At the same time, for the polarization $\mathbf{E} \parallel \mathbf{b}$, at $T < 300$ K, there is an almost parallel shift of the absorption edge to lower energies with an increase in temperature, whereas at $T \geq 300$ K, the Urbach dependence is observed for the absorption edge. The distinctive feature of the absorption spectrum of PbGeS_3 glasses in comparison with binary glasses GeS_2 , GeSe_2 , As_2S_3 , and As_2Se_3 is the presence of a temperature-dependent exponential portion in the absorption edge, which obeys the Urbach rule. The contributions of the structural, dynamic, and topological disorder to the diffusion of the absorption edge of lead thiogermanate in the crystalline and glassy states have been estimated.

The temperature invariability and large values of the absorption edge width w at $T < 300$ K for the polarization $\mathbf{E} \parallel \mathbf{b}$ in comparison with those for the polarization $\mathbf{E} \parallel \mathbf{c}$ are apparently related to the anisotropy of the lattice disorder caused by the chain quasi-one-dimensional structure of PbGeS_3 . The parameters of the

Urbach absorption edge and electron–phonon coupling are determined.

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