Journal of Applied Spectroscopy, Vol. 84, No. 4, September, 2017 (Russian Original Vol. 84, No. 4, July-August, 2017)

RAYLEIGH AND MANDELSTAM–BRILLOUIN LIGHT SCATTERING IN CHALCOGENIDE GLASSES OF THE (Sb₂S₃)_x(GeS₂)_{100-x} SYSTEM

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UDC 535.36:666.13.01

Rayleigh and Mandelstam–Brillouin light scattering has been investigated in chalcogenide glasses of the Ge–Sb–S system along the $(Sb_2S_3)_x(GeS_2)_{100-x}$ set (x = 0-50 mol %). Propagation velocity of the longitudinal hypersound wave, the high-frequency longitudinal elastic modulus, the extinction coefficient at the wavelength $\lambda = 0.6328$ microns, and the Landau–Placzek ratio are determined. The Landau–Placzek ratio for the glassy alloys of the Ge–Sb–S system depends strongly on the average coordination number and becomes maximal at Z = 2.67.

Keywords: chalcogenide glasses, Rayleigh and Mandelstam–Brillouin light scattering, Landau–Placzek ratio, propagation velocity of the longitudinal hypersound wave, extinction coefficient, coordination number.

Introduction. Rayleigh and Mandelstam–Brillouin scattering of light (RS and MBS, or RMBS), increasingly applied in research and for control of materials used in optical instrumentation and quantum electronics, is the basis of one of the practical and accurate metrological methods of nondestructive testing for the determination of elastic and photoelastic constants of crystals and glasses [1–5]. In [2], the ratio I_R/I_{MB} , where I_R and I_{MB} are the intensities of the Rayleigh and Mandelstam–Brillouin scattering components, respectively, was considered an optical "purity" criterion used to estimate the number and size of both dynamic (fluctuations of density, concentration, etc.) and static (foreign impurities and inclusions) optical inhomogeneities, which reduce the optical strength of materials. Elastic and photoelastic constants, and losses due to Rayleigh scattering were measured by the MBS method [2, 4]. Recently, attention has been focused on investigating the microinhomogeneous structure of chalcogenide vitreous semiconductors (CVSs) used in modern optoelectronics of the mid-and far-IR range by this method [2, 3, 5]. Glassy alloys of the Ge–Sb–S system, widely used in photoacoustic materials science as active elements in deflectors and laser radiation modulators, can be classified as CVSs [6–8]. Therefore, measurements of the photoelastic characteristics of such glasses, especially the level of optical losses in them, by RS and MBS spectroscopy is undoubtedly of interest due to sensitivity of these techniques to structural features of the sample.

In this paper, the results of measuring RMBS spectra of chalcogenide glasses of the $(Sb_2S_3)_x(GeS_2)_{100-x}$ system with a systematically changing composition are presented along with the results of their analysis and determination of the Landau–Placzek (LP) ratio, and also calculations of the longitudinal hypersound velocities, high-frequency elastic modulus, adiabatic photoelastic constants, and scattering losses at $\lambda = 0.6328 \mu m$ (extinction coefficient) as a function of the average coordination number Z of the alloys with a changing composition.

Experimental Methodology. Phase equilibria and the features of the glass-formation process in the Ge–Sb–S system were investigated in [9, 10]. The technique of two-temperature glass synthesis was used, in which ampoules with weighed out amounts of the elementary components prepared in appropriate proportions are first heated to 820–850 K at a rate of 3–4 K/min, and then are cured at these temperatures for 12–15 h. Then the temperature of the ampoules is increased by 20–30 K above the melting point at a rate of 1–3 K/min, and the melt is cured for 15–20 h. The initial components used were elementary Ge with a resistivity of \geq 50 Ω ·cm, Sb, and S of no less than 99.999999% purity.

Investigations of RMBS spectra were carried out by the method and on the apparatus described in [2, 4]. The measurement method and approach to calculating the elastic and photoelastic parameters, described in detail in [2], are based on the fact that the frequency shifts of the components of the MBS spectrum are proportional to the product of

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the corresponding sound velocity v and the refractive index n, and the component intensities depend on the photoelastic constants p_{ij} , v, n and density ρ . In the experiments using the photon counting method, MBS spectra were measured with a 90-degree scattering geometry. The dispersing element was a Fabry–Perot three-pass pressure-scanning interferometer with an interference pattern sharpness of 35 and a dispersion range of 2.51 cm⁻¹. Scattering was excited by a single-mode He–Ne laser ($\lambda = 0.6328 \,\mu\text{m}$, ~50 mW power) with beam polarization perpendicular to the scattering plane. Light of both polarizations was analyzed. Samples were prepared as parallelepipeds with subsequent polishing. Determinate error in measuring R_{LP} was ± 4 –10%. The error in determining the propagation velocity of the hypersound wave was no more than 2%. The refractive index of the investigated glasses at the wavelength of the He–Ne laser was measured by the prism method using a G-1.5-LOMO goniometer. The samples had the form of triangular prisms with refractive angles of ~11–13°, polished to 14th grade of purity, ensuring measurement uncertainty of no more than ± 0.004 . The density of the alloys was measured by hydrostatic weighing in toluene with an uncertainty of ± 0.01 .

Results and Discussion. Upon excitation of monochromatic light scattering with a frequency v in an isotropic medium, an unbiased Rayleigh component appears in the spectrum along with symmetrically located (with respect to v) doublets with a shift of Δv , which are due to light scattering by adiabatic density fluctuations propagating through the medium at a hypersound wave velocity [1]:

$$\Delta v/v = 2n(v/c)\sin\theta/2, \qquad (1)$$

where v is the frequency of the incident light; n is the refractive index at the wavelength of the incident light; θ is the scattering angle; v is the propagation velocity of the longitudinal hypersound wave; c is the speed of light in a vacuum.

One of the contributors to the intensity of the unshifted component in the scattering spectrum is the refractive index $\langle \delta n^2 \rangle$ related to inhomogeneities that are slowly relaxing or "frozen" upon cooling of the glass-forming melt and correspond to a certain "fictitious" temperature $T_f \sim T_g$, where T_g is the glass transition temperature. These include isobaric density fluctuations $\langle \delta \rho^2 \rangle$ and fluctuations in the concentration $\langle \delta c^2 \rangle$ [3, 11]. As a result, the intensity of RS for substances in the vitreous state can be higher than in the liquid or crystalline state. The parameter characterizing the development of "frozen" fluctuations in the glass is the LP ratio $R_{\rm LP} = I_{\rm P}/2I_{\rm MB}$, determined from the RS and MBS spectra, where $I_{\rm R}$ and $I_{\rm MB}$ are the intensities of the central (Rayleigh) and Mandelstam–Brillouin components of the spectrum (Fig. 1). The results of the study of RS and MBS in oxygen-containing and, especially, in CVS systems indicate anomalously high $R_{\rm LP}$ values and scattering losses [3–5, 11–14].

Theoretical difficulties in explaining such R_{LP} values have been overcome by taking into account the relaxation properties of the glass-forming melts and introducing the notions of "freezing" the fluctuations that determine RS as the melt passes through the glass transition interval [11–13]. For this, a theory of "freezing" isobaric density fluctuations was proposed for a transition from a liquid state to a glassy one. This made it possible to obtain the LP ratio as a parameter characterizing the microinhomogeneous structure of a multicomponent glass in the form of a sum of contributions from isobaric density fluctuations (R_p) and concentration fluctuations (R_c) [2, 5, 11, 14]:

$$R_{\rm LP} = I_{\rm R}/2I_{\rm MB} = R\rho + R_c \,, \tag{2}$$

$$R_{\rho} = (T_{f}/T)(\beta_{Tf,0} \ \rho v_{T,\infty}^{2} - 1), \qquad (3)$$

where *T* is the measurement temperature (room temperature); $T_f \sim T_g$ is the "fictitious" (structural) temperature (at which the rate of structural rearrangements is less than the cooling rate of the glass-forming melt); $\beta_{Tf,0}$ is the static (equilibrium) isothermal compressibility at T_f ; $v_{T,\infty}$ is the velocity of propagation of the elastic perturbation at room temperature and extrapolation to the region of infinitely large frequencies; in the case of a glass, v_{∞} can be determined from Δv from the equation (1); C = N/N' is the concentration of the second component; *N* and *N'* represent the number of moles of solute and solvent; μ is the chemical potential; *V* is the volume.

The contributions of the density R_{p} and concentration R_{c} fluctuations to the R_{LP} are isolated using equation (2). First, the values of R_{p} are calculated using equation (3) and the experimental glass transition temperatures, density, and acoustic measurements [8, 15]. Taking into account the R_{LP} value found from the RMBS spectra, the value of R_{c} is calculated as $R_{c} = R_{LP} - R_{p}$. Having determined the frequency shifts Δv_{L} and Δv_{T} of the longitudinal and transverse components of the MBS spectrum, one can find from (1) the velocities of the longitudinal and transverse hypersound waves in the glass. The distances between the components and the intensities of doublets in the RMBS spectra contain complete information on the photoelastic constants of the glasses, and the LP ratio makes it possible to estimate the extinction coefficient for the Rayleigh component α_{R} , cm⁻¹ [2, 11]:



Fig. 1. RS and MBS spectra of glassy alloys of the Ge–Sb–S system in the $(Sb_2S_3)_x(GeS_2)_{100-x}$ set: x = 50 (1), 30 (2), 20 (3), 10 (4), 2 (5).

$$\alpha_R = (R_{\rm LP} + 1)8\pi^3 \kappa T/3\lambda^4 (n^4 p_{12})^2 c_{11}^{-1}, \qquad (5)$$

or for scattering losses in glasses, dB/km:

$$\alpha_R' = 0.434 \cdot 10^6 \alpha_R, \tag{6}$$

where $c_{11} = M_{\infty} = \rho v_L$ is the high-frequency longitudinal elastic modulus; p_{12} is the photoelastic constant.

By measuring the intensity ratio $R = I_{MB}/I_{MB}^0$ of the investigated sample and the reference sample with the known constant $(p_{12})_{0}$, it is possible to determine $(p_{12})_{ad}$ by the formula [2]:

$$(p_{12})_{\rm ad} = (p_{12})_0 [R(\rho/\rho_0)]^{1/2} (n_0/n)^4 [(n+1)/(n_0+1)]^2 (\nu_L/\nu_{L0}) .$$
⁽⁷⁾

Fused silica was chosen as the reference sample, for which all the necessary parameters are known: $\rho = 2.20 \text{ g/cm}^3$, n(6328 Å) = 1.457, $p_{12} = 0.270$ [2]. The MBS spectra of fused silica are shown in [2–4], and of the investigated glasses — in Fig. 1. The intensity of the longitudinal components I_{MB} in the glasses is proportional to the extinction coefficient α_{MB} , determined for one component of MBS [2, 3]:

$$\alpha_{\rm MB} = (8\pi^3/3)(\kappa T/\lambda^4)[(p_{12})^2/(\rho v_L^2)]n^8, \qquad (8)$$

where ρ is the density, *n* is the refractive index.

Table 1 shows the results of calculating the velocity of hypersound and other parameters of the RMBS spectra of the investigated glasses, as well as the indices of refraction of the glasses and the frequencies f = v of the longitudinal hypersound phonons at which light scattered. It can be seen that for all the compositions of glasses below the frequency of ~2·10¹⁰ Hz there is no dispersion of the sound velocity (at $T \sim 20^{\circ}$ C), as one would expect [1, 2]. This means that the differences between the hypersound velocities obtained from the RMBS spectra using relation (1) and from acoustic measurements at a frequency of 20 MHz (see Table 1) do not exceed the measurement error (~2%). The change in the composition of the glasses determines the redistribution of chemical bonds with different force constants, and a gradual transition from glasses with tetrahedral structural units (GeS₂) to pyramidal structural units (Sb₂S₃) having less rigidity takes place [6–8]. Due to the greater number of metal–chalcogen (M–Ch) bonds in the tetrahedron GeS_{4/2} compared to the trigonal pyramid SbS_{3/2}, the stabilizing effect of Ge on the rigidity of the structural framework of a binary glass manifests at lower contents of metal. Monotonic decrease in hypersound velocity $V_L(x)$ (Fig. 2, curve 1) due to the change in composition (increase in the content of Sb₂S₃) is due to the fact that the difference in the force coupling constants (force constants of the Ge–S and Sb–S bonds) is several times greater than the force constants of homopolar bonds [6, 7, 10]. This leads to the fact that, even at low concentrations of metal in the composition of alloys, the rigidity of the structural-chemical framework of the investigated alloys and the hypersound velocity in them undergo substantial changes.



Fig. 2. Dependence of the propagation velocity of longitudinal hypersound wave V_L (1) and the ratio R_c/R_ρ (2) on the composition of glassy alloys $(Sb_2S_3)_x(GeS_2)_{100-x}$.

TABLE 1. The Average Coordination Number *Z*, Hypersound Frequency v, Refractive Index *n*, Propagation Velocities of the Low-Frequency V_L^U and Hypersound V_L^G , Landau–Placzek Ratio R_{LP} Values, the Adiabatic Photoelastic Constant $(p_{12})_{ad}$, the Longitudinal High-Frequency Elastic Modulus M_{∞} and the Extinction Coefficient α_R , for Glassy Alloys of the System $(Sb_2S_3)_x(GeS_2)_{100-x}$

Composition	Z	v, GHz	$n_{\lambda} = 0.6328 \ \mu m$	V_L^G , m/s	V_L^U , m/s	R _{LP}	(<i>p</i> ₁₂) _{ad}	$\psi, \mathbf{K} \cdot \mathbf{P} \mathbf{a}^{-1}$	M_{∞} , 10 ⁻¹⁰ J/m ³	$\alpha_R \cdot 10^3$, cm ⁻¹
GeS ₂	2.67	13.2	2.111	2798	2778	878	0.30	773.2	2.22	9.8
x = 2	2.65	13.2	2.113	2795	_	803	0.29	727.5	2.25	9.3
4	2.65	13.2	2.160	2716	2698	563	0.28	693.7	2.27	8.2
10	2.63	13.4	2.230	2696	_	317	0.27	632.7	2.31	5.3
30	2.58	15.0	2.500	2685	2660	164	0.27	437.2	2.37	3.0
50	2.53	19.5	2.801	2598	2620	117	0.28	383.4	2.49	1.8

The role of concentration fluctuations in RS can be estimated using the relation $R_c/R\rho$ (or $R_c/R_{\rm LP}$), shown as a function of the content of Sb₂S₃ in alloys in Fig. 2, curve 2. It can be seen that the ratio R_c/R_ρ as a function of alloys composition decreases monotonically with increasing Sb₂S₃ concentration, and when $x \le 20$ mol. % of Sb₂S₃ and the composition approaches GeS₂ the curve is steeper. Such behavior of this parameter is apparently determined by a decrease in the isobaric fluctuations in the density of alloys "frozen" in the glass transition range, since the concentration behavior of $\beta_T(x)$ and $T_g(x)$ is symbatic, while a slight decrease in $\beta_T(x)$ is compensated by a more strongly pronounced dependence of T_g on x [8, 9, 15]. A comparison of the concentration behavior of the ratio R_c/R_ρ (Fig. 2) and the extinction coefficients α_R (Table 1) indicates the predominant contribution of concentration fluctuations to the total optical losses in the alloys under study. The calculated scattering losses for the investigated alloys are several orders of magnitude higher than for glasses in the optical catalog, laser glasses and specially purified materials for fiber optics [2]. It should be taken into account here that concentration fluctuations in the melt (which after its cooling determine the microinhomogeneous structure of the glass), "frozen" at $T = T_g$, can be amplified by microscopic internal stresses or interaction with microimpurities, that is, the existence of inhomogeneities of technological origin also affects the LP ratio and, consequently, the contribution of R_c . We note that the concentration fluctuations increase with increasing crystallization ability of the glasses [9]. All this confirms the concept of the determining role of the "frozen" concentration fluctuations in RS of multicomponent glasses [3–5, 11–14].

To describe the connectedness of the structural-chemical framework of noncrystalline materials (according to the topological Phillips–Thorpe model), the average number of covalent bonds per atom *Z* (the average coordination number) [16, 17] is calculated according to the formula $Z_{ave} = (4x + 3y + 2z)/100$, where *x*, *y*, and *z* are atomic (molecular) fractions

of Ge, Sb, and S; 4, 3, and 2 are their coordination numbers in the covalently bound structural glass matrix, respectively. The transition from a chain-layered structure to a three-dimensionally linked glass framework with strong directional covalent bonds is realized at the point $Z_{ave} = Z_c$ (2.67) and is called topological [16]. For the glasses of the Ge–Sb–S system, elastic moduli (shear modulus *G*, Young's modulus *E*, bulk modullus *B*) change sharply at this value of Z_c due to topological changes in their structure [17, 18]. The parameter $\psi = 10^9 Tq \chi \sim \langle \Delta \rho / \rho \rangle^2$ exhibits a similar concentration behavior, where $\langle \Delta \rho / \rho \rangle^2$ is the mean square of the difference in the electron density, χ is the adiabatic compressibility (Table 1), which is a measure of the development of isobaric density fluctuations [7] in RS of the investigated alloys. Therefore, it can be assumed that such a concentration behavior of the elastic moduli, extinction coefficient, and R_{LP} is related to the realization of a topological phase transition in the system (Sb₂S₃)_x(GeS₂)_{100-x} at $Z_{ave} \approx 2.67$ corresponding to the stoichiometric compound GeS₂.

Analysis of the vibrational spectra by IR and Raman spectroscopy shows that when a small amount of Sb is introduced, a strong deformation of the tetrahedra [GeS₄] and shortening of the length of the tetrahedral chains occur, which are the main structural motif of the GeS₂ glass, which results in a slight smearing of the main vibrational mode of GeS₂ in the 340-360 cm⁻¹ spectral range [18, 19]. Consequently, in the composition range of x < 20 mol. % Sb₂S₃, the statistical distribution and the mutual influence of the structural units (SU) (GeS_{4/2} and SbS_{3/2}) that are dissimilar in composition and symmetry leads to an increased dispersion of their associates. Breakage of chemical bonds due to spatial incompatibility and the energy factor (difference in the energy of chemical bonds) is possible [20, 21]. The changes in the structure-sensitive parameters determined from RMBS spectra, such as RLP, propagation velocity of longitudinal hypersound waves VL and scattering losses α_R (Table 1), with changing composition in the region where the structure of alloys is determined by the rigid tetrahedral groupings of $\text{GeS}_{4/2}$ (Z = 2.66) are more significant than for glasses with a chain-layer structure (x > 20 mol. % Sb₂S₃). In this region, these parameters are characterized by a practically sublinear dependence on the composition (Fig. 2), since the distribution of the SU $GeS_{4/2}$ and $SbS_{3/2}$ is predominantly statistically uniform in the case of nonadditive manifestation of spatially separated tetrahedra [GeS₄] and associated [SbS₃] structural groupings and is partially topologically disordered. Indeed, the results of the study (the radial distribution function of the electron density and X-ray scattering intensity) as a function of the composition x show that the structure of the investigated alloys in the range $0 \le x \le 50$ cannot be regarded as an ideal solution of the basic SU $\text{GeS}_{4/2}$ and $\text{SbS}_{3/2}$ [18, 20]. Nonmonotonic character of the change in the temperatures of the glass transition T_g , crystallization T_c , and melting T_m of glasses in this concentration interval [8, 20, 21] confirm this assumption. For concentrations x < 20, the introduction into GeS₂ clusters of SbS₃ in the form of strongly deformed inclusions causes a sharp increase in the first diffraction peak (first sharp diffraction peak, FSDP). With a further increase in the content of antimony, the formation of chain-layered Sb_2S_3 clusters leads to the branching of GeS₂ clusters, the intercluster distances decrease and the magnitude of the FSDP decreases. The concentration curves of the integrated FSDP intensity and the correlation length D as a function of the average coordination number for the Ge–Sb–S system assume extreme values at $Z_{\rm ave} = Z_{\rm c} \, [16-18].$

Conclusions. The results of experimental measurements of Rayleigh and Mandelstam–Brillouin scattering in chalcogenide glassy alloys of the Sb₂S₃–GeS₂ set indicate that there is no dispersion of the hypersound velocity at room temperature up to frequencies of ~ 20 GHz. The most significant changes in the structure-sensitive parameters determined from these spectra (R_{LP} , extinction coefficient, hypersound velocity and ψ) are observed in the regions of a low content of antimony sulfide in the alloys. The weak dependence of the high-frequency longitudinal modulus and the photoelastic constant on the average coordination number with a change in composition reflects a gradual transition from the tetrahedral structure of the continuous random structural-chemical grid of glasses to the chain-layered glass. The Landau–Plachek ratio in the alloys of the Ge–Sb–S system depends on the average coordination number (Ge concentration) and increases significantly as Z = 2.67. This behavior, apparently, is related to the possibility of realizing a topological transition in glassy alloys of this system.

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