

STRUCTURE, DIELECTRIC AND PHOTOELASTIC PROPERTIES OF GLASSES IN THE SYSTEM Ge-Sb-S *

P. P. Shtets, V. I. Fedelesh, V. M. Kabatsij, V. I. Malesh, I. I. Shpak, A. A. Gorvat

Uzhgorod National University, Pidhirna St. 46, Uzhgorod, 88000, Ukraine

Radial atomic distribution curves, transmission spectra, optical absorption edge, dielectric and photoelastic properties of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses are studied. The short - range atomic order is shown to be related to the optical, dielectric and photoelastic parameters of the glasses.

(Received June 25, 2001; accepted November 29, 2001)

Keywords: Chalcogenide glass, Short-range order, Elastic moduli, Urbach rule

The possibility to apply the glasses from the system Ge-Sb-S in optical device construction due to their high photosensitivity, transparency in the visible, near- and medium - infrared (IR) range is the reason for the interest to their studies.

In the present paper the results of radial atomic distribution curves (RADC), IR transmission spectra, optical absorption edge, dielectric and properties of quasibinary $\text{GeS}_2\text{-Sb}_2\text{S}_3$ glasses are reported.

The interest to the studies of the glasses of this particular section of the Ge-Sb-S system is determined first of all by the difference of the short-range order and properties for the pure binary compounds. The structure of glassy GeS_2 is studied rather extensively. The glass matrix is build mostly by GeS_4 tetrahedra linked together by two - fold coordinated sulphur atoms. The first coordination sphere radius R_1 , determined from RADC, for GeS_2 glass is 2.26 \AA [1] what is the evidence for the nearest neighborhood of Ge and S atoms. The structural groups are arranged in clusters with intercluster distances $\sim 7.6 \text{ \AA}$.

The short-range order parameters for glassy Sb_2S_3 were determined from the RADC maxima (Fig. 1b), calculated from the experimental curve of scattered X-ray intensity $I(s)$ Fig. 1a). The presence of the main maximum is determined by strong chemical interactions of the atoms. Its splitting into two maxima (2.10 and 2.50 \AA^{-1}) is related to the existence of two types of atomic distributions. At low s values ($\sim 1.20 \text{ \AA}^{-1}$) the $I(s)$ function exhibits a diffraction maximum caused by the presence of large scattering complexes [2]. For GeS_2 glass this maximum is located at $s \approx 1.02 \text{ \AA}^{-1}$ [3].

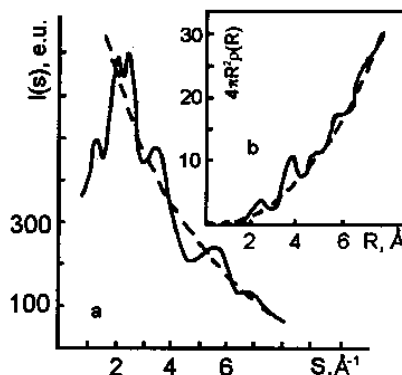


Fig. 1. Scattered X-ray intensity curve (a) and radial atomic distribution curve (b) for glassy Sb_2S_3 .

* accepted for the First International Workshop on Amorphous and Nanostructured Chalcogenides, Bucharest, June 25 - 28, 2001

Sb_2S_3 glass RADC is characterized by three distinct maxima at $R_1 = 2.50 \text{ \AA}$, $R_2 = 3.86 \text{ \AA}$, $R_3 = 4.64 \text{ \AA}$. The R_1 value, close to the sum of Sb and S atoms covalent radii, is the evidence for the nearest neighborhood. This enables us to assume the Sb_2S_3 glass matrix to be constructed mainly of SbS_3 trigonal pyramids, linked together by two-fold coordinated sulphur atoms. However, the calculated values of coordination numbers for Sb_2S_3 glass ($z_{\text{S}}(\text{Sb}) = 4.0$; $z_{\text{Sb}}(\text{S}) = 2.4$) are higher than for the crystal (3 and 2) what is probably related to the presence of a great number of structural groups with homopolar bonds (S-S and Sb-Sb) in its structure. The obtained results show a good correlation with the vibrational spectroscopy data. The IR spectrum of the Sb_2S_3 glass consists of an intense broad absorption band with a maximum at $\sim 290 \text{ cm}^{-1}$ and a weak absorption band in the range of $\sim 190 \text{ cm}^{-1}$ (Fig. 2, curve 7). The intense absorption band results from the vibrations of covalently bonded atomic pairs in SbS_3 trigonal pyramids while the weak band at 190 cm^{-1} is due to the presence of structural groups with homopolar S-S and Sb-Sb bands. This assumption is also confirmed by the results of Raman scattering studies of Sb-S glass system [4].

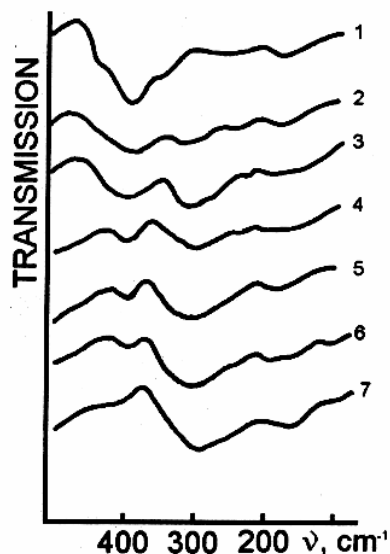


Fig. 2. IR transmission spectra of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses: $x = (1), 0.9 (2), 0.8 (3), 0.5 (4), 0.3 (5), 0.1 (6), 0 (7)$.

The structure of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ ($0 < x < 1$) glasses somewhat differs from the structure of GeS_2 and Sb_2S_3 glasses. Far-infrared transmission spectra for this glass system are shown in Fig. 2. The main changes in the spectra with the increase of Sb_2S_3 content occur in the high - frequency range. Here for glassy GeS_2 three overlapping bands in the frequency range from 320 to 450 cm^{-1} are observed (Fig. 2, curve 1). Already at the first admixtures of Sb_2S_3 to GeS_2 the bands in the range of 450 cm^{-1} are revealed. With the increase of Sb_2S_3 content these bands grow in intensity and gradually shifts to lower frequencies. For glassy Sb_2S_3 the band maximum is located at 290 cm^{-1} . Meanwhile the band at 375 cm^{-1} vibrations of atomic pairs in tetrahedral structural groups GeS_4 shifts to higher frequencies. The predominantly two-mode character of vibrational spectra transformation was also observed at Raman studies of GeS_2 - Sb_2S_3 glass system [5]. It should be noted that in the IR spectra of some of the $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses with a considerable content of germanium disulphide the weak bands in the range of $\sim 240 \text{ cm}^{-1}$ are observed (Fig. 2, curves 2 - 4). They can be related to the presence of a small amount of $\text{S}_3\text{Ge-GeS}_3$ structural groups in the glass matrix.

Thus, the analysis of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glass system vibrational spectra enables one to assume the formation of a single glass network built by GeS_4 and SbS_3 structural groups which are linked together by sulphur atoms.

The investigation of the absorption coefficient spectra for GeS_2 - Sb_2S_3 glasses has shown that in the fundamental absorption range they are well described by the Urbach rule $\alpha = \alpha_0 \exp \Gamma (h\nu - h\nu_0)$. The Γ parameter varies with the glass composition from 13 eV^{-1} for GeS_2 to 18 eV^{-1} for Sb_2S_3 , this being the evidence of the difference in the short-range order for these compounds. The optical gap

value E_g , determined from the spectral plot of α , varies depending on the composition of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses from 1.65 eV for Sb_2S_3 to 3.06 eV for GeS_2 . The values of E_g for the $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses series are listed in Table 1. As shown in [6], the compositional dependence of E_g for glasses of this system is non-linear. This is related to the fact that already small admixtures of Sb_2S_3 (GeS_2) result in strong distortion of GeS_4 tetrahedra (SbS_3 pyramids) and shortening of tetrahedral (trigonal) chains being the main structural pattern of GeS_2 (Sb_2S_3) glass. Strong fluctuations of the bond lengths and angles resulting from this distortion, lead to additional broadening of the density-of-states tails at the allowed band edges and, as a result, to the deviation of the $E_g(x)$ dependence from linearity.

Table 1.

Parameters	x, mol.%				
	1.00	0.96	0.80	0.70	0.50
E_g , eV	3.06	3.00	2.78	2.62	2.37
$\varepsilon(10^5 \text{ Hz})$	5.3	6.8	8.0	8.6	11.7
$\rho \cdot 10^{-3}$, kg/m^3	2.84	2.90	3.14	3.30	3.60
V_l , m/s	2778±10	2698±10	2670±10	2660±10	2622±10
V_t , m/s	1784±20	1641±20	1589±20	1484±20	1438±20
μ	0.149	0.206	0.226	0.283	0.285
$G \cdot 10^{-9}$, Pa	9.04	7.81	7.93	7.07	7.44
$E \cdot 10^{-9}$, Pa	20.7	18.8	19.4	18.1	19.1
$\varkappa \cdot 10^{11}$, Pa^{-1}	10.2	9.38	8.47	7.19	6.75
$K \cdot 10^{-9}$, Pa	9.8	10.6	11.8	13.9	14.8
$M_2 \cdot 10^{15}$, s^3/kg	110	134	314	325	340
$\gamma(100 \text{ MHz})$, dB/cm	1.20	1.33	1.33	1.40	1.41

The strong deformations of the structural groups, forming the glass matrix, at the admixture of the other component result not only in the changes in optical properties, but also to the variation of other parameters. The measurements have shown that the density ρ of the $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses varies from $2.84 \times 10^3 \text{ kg/m}^3$ to $4.14 \times 10^3 \text{ kg/m}^3$, and the dielectric permeability ε - from 5.3 to 28.4. Especially considerable variation of the glass parameters occurs in the range of compositions, close to the binary compounds Sb_2S_3 and GeS_2 . In the compositional interval $0.05 < x < 0.10$ a knee at the $\rho(x)$ plot is observed, as well as a maximum at the compositional dependence of ε . In the vicinity of GeS_2 glass the changes in ρ and ε with composition are smaller (Table 1).

The variation of structure and composition is also revealed in the photoelastic properties of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses. The values of longitudinal (v_l) and transverse (v_t) ultrasonic wave propagation rates, measured by coherent optical radiation diffraction on ultrasonic waves in the sample [7], are listed in Table 1 as well as the acoustooptical figure of merit M_2 , measured by Dixon-Cohen method.

The photoelastic parameters of the glasses, calculated from the expressions [6]

$$K = \frac{\rho(3v_l^2 - 4v_t^2)}{3}; \quad E = \rho v_t^2 \frac{(3v_l^2 - 4v_t^2)}{(v_l^2 - v_t^2)}; \quad (1)$$

$$G = \rho v_t^2; \quad \mu = \frac{(v_l^2 - 2v_t^2)}{2(v_l^2 - v_t^2)}; \quad \varkappa = \frac{1}{K}. \quad (2)$$

are also given. Here K , E , G , are bulk, Young's and shear moduli, μ - Poisson coefficient, \varkappa - adiabatic compressibility.

It is seen from Table 1 that glassy germanium disulphide possesses the highest values of Young's and shear moduli. This is, perhaps, related to the highest linking degree of GeS_2 glass among the chalcogenide glassy semiconductors. Under the ultrasonic wave the structural groups in the glass are distorted mostly along the pressure direction. This is also confirmed by the compositional dependences of the Poisson coefficient. Introduction of Sb_2S_3 into GeS_2 and increase of its content in the glass composition results in the decrease of E and G moduli, providing the evidence for the decrease of linking in the $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glass network.

The acoustooptical figure of merit M_2 increases with Sb_2S_3 content in the glass and at $x = 0.50$ reaches the values, characteristic for the best chalcogenide glass compositions, applied as acoustic lines in acoustooptical devices [9]. The damping, γ , of ultrasonic waves of the investigated glasses is relatively low (Table 1).

Thus, based on the performed studies, one may conclude that due to the transparency in the visible spectral range, high acoustooptical figure of merit, small damping of ultrasonic waves and significant mechanical strength, Ge-Sb-S glasses can be used as active elements in acoustooptical devices.

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