PECULIARITIES OF THE ABSORPTION EDGE AND PHOTOCONDUCTIVITY SPECTRA OF $(GeS_2)_x(Bi_2S_3)_{1-x}$ GLASSES

D. I. Bletskan, V. N. Kabatsiy[*], V. V. Frolova

Uzhhorod National University, Uzhhorod, Ukraine
[*]Mukachevo technological Institute, Mukachevo, Ukraine

The results of spectral investigations of the absorption edge α and photoconductivity (PC) of $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses ($0.4 \leq x \leq 1$) within the temperature intervals of 77-400 K have been reported. For the GeS_2 binary glass the absorption edge is described by the Urbach rule. For ternary glasses, the long-wave tail of dependence $\alpha = f(h\nu)$ shows two exponential regions changing with the temperature and having different slopes. For all the compositions of ternary $(GeS_2)_x(Bi_2S_3)_{1-x}$ glassy alloys, the PC spectra within the wavelengths region of 0.4-1 μm exhibit "hysteresis" when the scanning direction is changed from UV to IR. The observed spectral dependences of absorption and PC have been qualitatively explained by the complex band model of the binary GeS_2 due to the formation of several types of structural units when the composition is moved toward the ternary glass system based on the atoms of different valency.

1. Introduction

The problem of an effective doping of chalcogenide glassy semiconductors (CGS) has attracted the investigators' attention for a long time. The greatest results have been achieved while introducing bismuth into glassy germanium chalcogenides. In particular, while modifying $Ge_xS(Se)_{1-x}$ glasses with bismuth a sharp variation in the electrical conductivity, optical pseudogap and, as we believe, to be the most important, especially, – the inversion of conductivity type from p to n- type at Bi concentrations observed [1-4] at 8-10 at.%. Such a variation of physical properties of glassy germanium chalcogenides opens new possibilities for their various applications. As an example, thin amorphous $(GeS_3)_{1-x} Bi_x$ layers may be used as optical recording medium for holograms storage with an unusual pattern [5].

In the present article the results of absorption edge investigations and photoconductivity spectra of $GeS_2)_x(Bi_2S_3)_{1-x}$ ($0.4 \leq x \leq 1$) glasses within a wide range of temperatures $T = 77$–400 K have been presented.

2. Experimental method

$(GeS_2)_x(Bi_2S_3)_{1-x}$ glasses ($0.4 \leq x \leq 1$) were synthesized in evacuated thin-wall quartz from elemental substances (total amount being 5-10 g). The ampoules were heated stepwise at 600–700 K with the time delay during 10 hours. The mechanical rotation was used for homogenization. The maximal synthesis temperature exceeded the melting temperature of GeS_2 by 100 K (T_m for GeS_2 is ~ 1123 K). The quenching of the melt was performed by dipping the ampoule into the ice water starting from the maximal synthesis temperature.

The glassy state was identified by a typical bright blistered fracture, the absence of lines on the debyegrams, and the presence of the softening effect on thermograms on differential thermal analysis curves (DTA). The homogeneity of the obtained glasses did not depend on the duration of synthesis within the limits from 20 to 48 hours, but the cooling rate and cooling conditions were of great importance. For example, at slow cooling of the melt in large-diameter ampoules a considerable region of heterogeneity is formed in the center of the sample. The same glasses quenched in thin-wall ampoules with the inner diameter of 6–8 mm did not contain visible inclusions of liquating or crystalline phase. The optical transmission and photoconductivity spectra were measured at the samples in the form of plane-parallel plates. These were cut from the ingot and then mechanically polished using suspensions of powders and pastes of different type based on water or mineral oil. To measure the photoconductivity the dag electrodes or thermally evaporated gold ones were used. The photoconductivity spectra were recorded under the conditions of the DC electric field applied to the sample and modulated illumination. Mechanical chopper was used for the modulation. The load resistance was chosen with the account of the condition $R_{\text{н}} \ll R_0$ (where R_0 being the resistance of the sample under study). The desired signal after intensification and phase-modulation detection was registered by the potentiometer (model KSP-4). As a spectral device the double monochromator (type DMR-4) was used. The absorption coefficient α within the absorption edge region the glasses under study was defined by the technique of various thicknesses, thus, the necessity to measure the reflection was excluded.

3. Results and discussion

3.1. Absorption edge

Based on the frequency dependence of the absorption coefficient the investigation of the absorption edge of glassy semiconductors is directed at obtaining the picture of optical transitions defined by the peculiarity of electronic states density distribution in disordered systems. In multi-component glassy semiconductor alloys due to an accidental character of the displacement of atoms both compositional (chemical) or topological disorder may be realized. This results in the change of the band states density and increase in the density of localized states in the band-gap. This manifests itself in the edges spreading of energy bands and rearrangement of the spectrum. That is why we have investigated the peculiarities of the intrinsic absorption edge of $(GeS_2)_x(Bi_2S_3)_{1-x}$ glasses within the interval of temperatures 77–400 K as a function of composition. The glasses under study are characterized by the transmission values of 50–75 %, which coincide with the expected ones based on the values of the refraction index. The latter was defined from the study of reflection losses. The obtained spectral dependences of the absorption coefficient $\alpha(h\nu)$ for different compositions are given in Fig.1. As far as the molar portion of bismuth trisulfide in $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses increases, the absorption edge shifts to the long-wave region which reflects the optical gap decreasing. This is because the crystalline Bi_2S_3 has the band-gap ($E_g = 1.3$ eV) much less than the glassy germanium disulfide ($E_g = 3.1$ eV). As the band-gap energy we selected the photon energy, corresponding for the absorption coefficient value of 10^3 cm^{-1}. The concentration dependence of band-gap of ternary glasses is given in fig.2. As it is seen from this fig., considerable inflexion E_g is in small concentration range of Bi_2S_3 (0.1–10 mol. %). With increasing of Bi_2S_3 concentration the optical gap changes almost linearly.

α, cm^{-1}
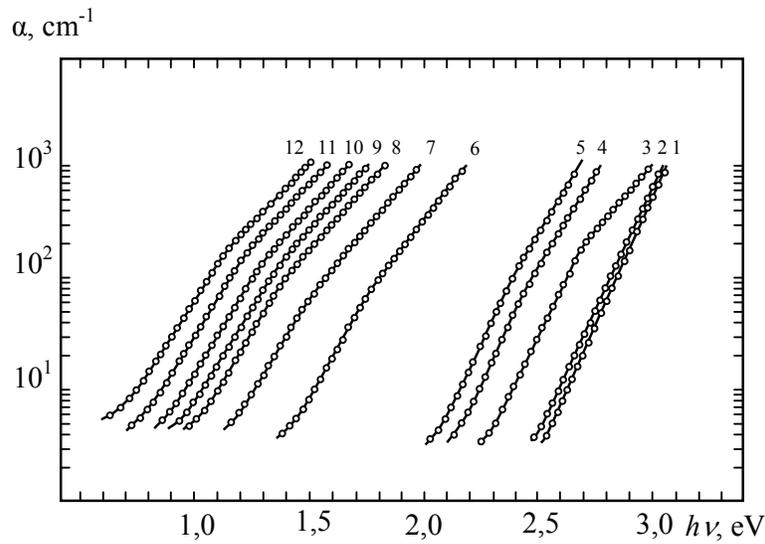

Fig. 1. Absorption edge of $(GeS_2)_x(Bi_2S_3)_{x-1}$ glassy alloys.
x: 1 – 1.0; 2 – 0.9999; 3 – 0.999; 4 – 0.995; 5 – 0.99; 6 – 0.95;
7 – 0,9; 8 – 0,8; 9 – 0,7; 10 – 0,6; 11 – 0,5; 12 – 0,4. T = 293 K

From Fig.1 it is seen also that only for the GeS_2 binary glass the absorption edge is described by the exponential dependence:

$$\alpha(h\nu) = \alpha_0 \exp\left(\frac{h\nu - E_0}{\overline{W}}\right), \tag{1}$$

where α_0, E_0 are the constants depending of the material, $h\nu$ is the energy of incident light, $\overline{W}$ is the characteristic energy of the structural disorder.
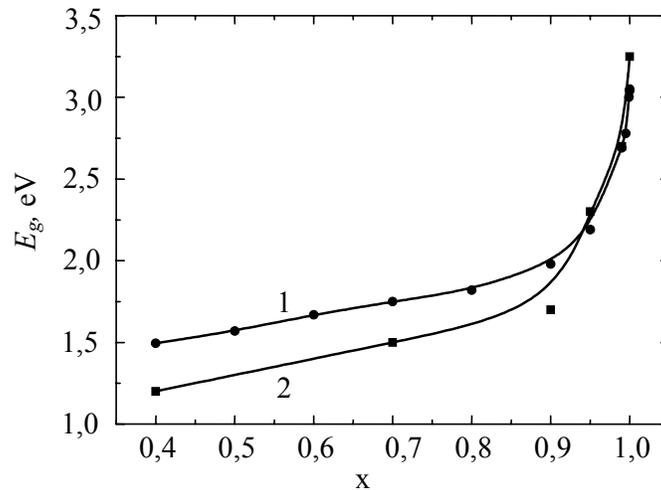

Fig. 2. Concentration dependence of band-gap in $(GeS_2)_x(Bi_2S_3)_{x-1}$ glasses:
1- present data, 2 – [9].

With increasing Bi_2S_3 content in the glassy $(GeS_2)_x(Bi_2S_3)_{1-x}$ in the region of energies less than E_g, the absorption curves become to decline from the simple dependence (1) and two

exponential parts appear in the spectrum. In the same time, the steepness of a low-energy part is about twice as large as that of a high-energy one. This deviation is more clearly revealed at low temperatures (Fig.3) and points to a very complicated kind of the states density function in the low-energy region lower than the absorption edge of ternary glasses. One of the possible mechanisms defining optical properties of $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses is the Rayleigh scattering on microinclusions of bismuth trisulfide in the matrix of the ternary glass also mentioned earlier in Raman spectra [6,7]. However, as it is known, the Rayleigh scattering is proportional to $1/\lambda^4$. This is the reason that, in contrast to the dependences shown in Fig.1, the Rayleigh scattering should have exceeded α with wavelength decreasing. Moreover, a monotonic character of the Rayleigh scattering can't explain the presence of the change in the slope in spectral dependence of absorption.

The exponential shape of the absorption edge in the high-energy region (Figs.1,3), together with significant (in comparison with data for GeS_2–As_2S_3 glasses [8]), concentrational shift of E_g and dispersion curves $n(\lambda)$ which correlates with it shows that the distribution of localized states $\rho(E)$ in the gap of ternary glasses essentially changed. The presence of two exponential regions in the $\alpha = f(\hbar\omega)$ spectrum points to a very complicated shape of the density states in the region lower than the absorption edge of ternary glasses.
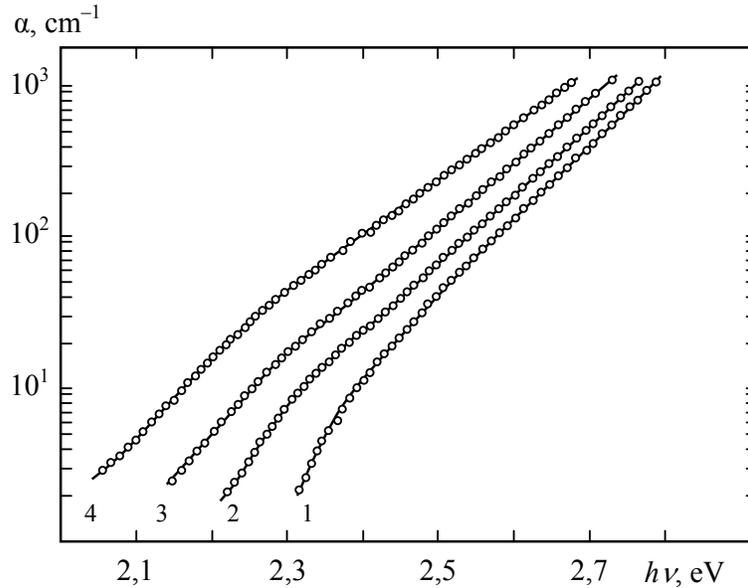

Fig. 3. The absorption edge of $(GeS_2)_{0,99}(Bi_2S_3)_{0,01}$ glassy at different temperatures:
1 – 77; 2 – 150; 3 – 220; 4 – 300 K.

For GeS_2, the disorder in the angles and lengths of bonds typical for the glassy state results in the appearance of the density of electronic states tails in the vicinity of C–V bands (Fig.4, *a*). Moreover, these states are localized. We explain the changes in the shape of the absorption edge of $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses for $0.9 \leq x < 1.0$ with the further spreading of band edges due to the potential fluctuations (Fig.4, *b*) appearing in strongly doped semiconductors caused by the charge located on the impurity centers. The latter are spatially chaotically distributed. The change of the optical gap and appearance of additional absorption at energy of photons less than E_g in such a model occurs due to the tunneling of charge carriers via barriers formed by the potential fluctuations. At $x < 0.9$, more probable are the cardinal changes in the properties of the material, formation of the alloy with varying interatomic distances, bond angles and increasing the degree of compositional disordering. One can suppose that for these x values during melt cooling there exists the tendency of small regions forming within which the concentration of Bi_2S_3 differs to some extent from average-statistical despite the absence of

possible local crystallization effect on DTA. These regions in the glassy matrix can efficiently contribute to formation of new regions of localized electronic states B_c and B_v responsible for a low-energy region of the absorption edge (see Figs.4, *b* and 4, *d*).
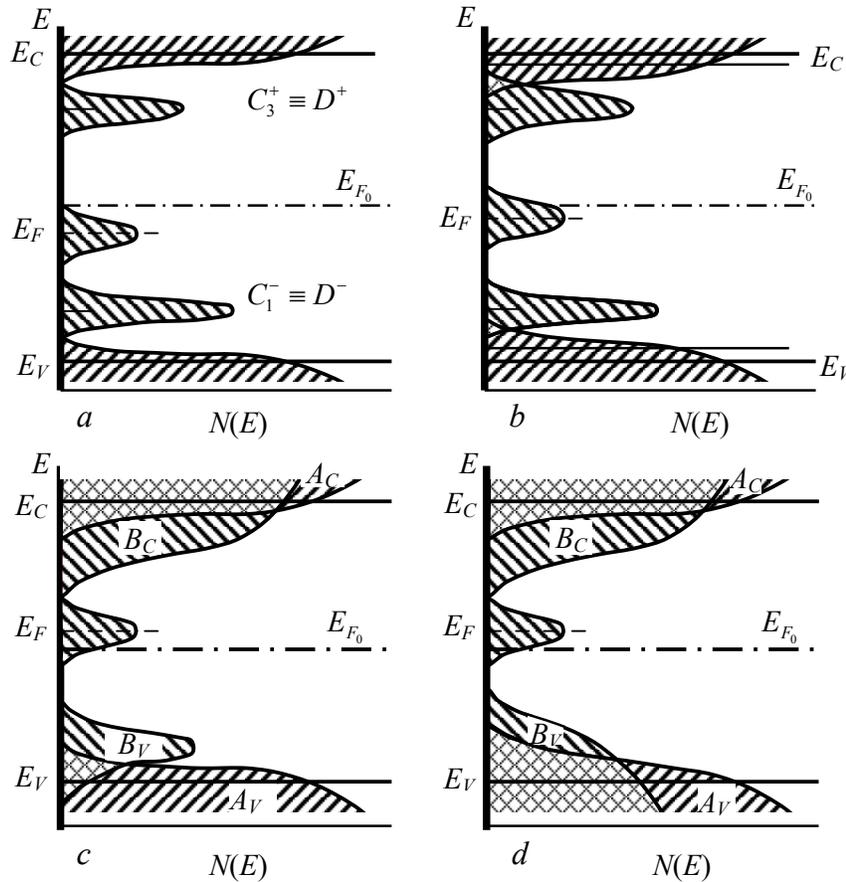

Fig. 4. Proposed band models for GeS$_2$ (a) and (GeS$_2$)$_x$(Bi$_2$S$_3$)$_{x-1}$ ternary glass for x > 0.9 (b) and x < 0.9 (c,d).

3.2. DC conductivity and photoconductivity.

Among CGS a glassy germanium disulfide (GeS$_2$) is the most high-resistant and poorly photosensitive. The room-temperature dark conductivity is $\sigma_T = (1–6)\times10^{-16}$ ohm^{-1}cm^{-1} for the samples from different batches of the glass. Introducing Bi$_2$S$_3$ into a glassy germanium disulfide leads to increasing the electrical conductivity and the sensitization of ternary glasses. The ratio of the electrical conductivity changing, $K = \sigma_i/\sigma_d$, (where σ_i is the electrical conductivity under illumination) increases with the molar fraction of Bi$_2$S$_3$ in (GeS$_2$)$_x$(Bi$_2$S$_3$)$_{1-x}$ ternary glasses and reaches the maximum for the composition $x = 0.5÷0.6$. The presence of the photosensitivity in ternary glasses allowed us to measure the photoconductivity. Comparison of the PC with the absorption edge spectra allowed us to answer the question about the nature of observed bands in PC spectra.

The photoconductivity spectra of (GeS$_2$)$_x$(Bi$_2$S$_3$)$_{1-x}$ glasses measured in modulated and steady-state conditions, as well as at different wavelength scanning directions of the exciting radiation are given in Fig.5 and 6. Clearly seen that irrespective to the excitation conditions and compositions of ternary glasses two bands occur in photoconductivity spectra but their location and intensity depend on the composition of glasses. Both low and high-energy maxima with increasing the molar portion of Bi$_2$S$_3$ shift into a low-energy region of the spectra from

$hv_{max1} = 1.30$ eV and $hv_{max2} = 1.84$ eV for $x = 0.9$ to $hv_{max1} = 1.15$ eV and $hv_{max2} = 1.60$ eV for $x = 0.4$, respectively (Fig.5). To identify the bands observed in the PC spectra of ternary glasses, the comparison of the latter with the edge absorption spectra of the corresponding composition (Fig.1, 3) is necessary. From such a comparison it follows that the low-energy maximum in the PC spectrum for all the compositions is within the values of $\alpha < 10^2$ cm^{-1}, i.e. lower than the point of inflexion in the spectral dependence of α. The high-energy maximum corresponds to the values of $\alpha > 10^2$ cm^{-2} from the region of exponential dependence $\alpha = f(hv)$. Taking this fact into account the presence of two maxima in the PC spectra of $(GeS_2)_x (Bi_2S_3)_{1-x}$ ternary glasses may be explained in terms of states density model shown (Fig.4). In fact, as it is seen from Fig.4, transitions from different valence subbands into different subbands of the conductivity band change the condition of carriers generation.

It is important to note the unusual behaviour of the PC spectra for $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses at constant (non-modulated) regime of irradiation which depends on the hv scanning direction.

When measuring PC, the scanning was from the side of UV wavelength, low-energy maximum is the dominating feature of the PC spectrum, while a high-energy one is observed as a shoulder in the wing of the main band. In contrast, in the case of reverse scanning a high-energy maximum dominated the spectrum and low-energy one is observed only as a shoulder. Such hysteresis is observed for all composition studied in the range 0.4–1 μm.

Finally, let us discuss the general peculiarities of the distribution of electronic states density in $(GeS_2)_x(Bi_2S_3)_{1-x}$ glasses which can explain the observed peculiarities of the spectra. One can consider the exponential edges in the absorption of binary GeS_2 connected with exponential tails of states distribution and related to the effect of disordering of the glass structure (Fig.4, a). It is evident that in the ternary glass the appearing of B_v and B_c subbands (Fig.4, c ,d) is connected with the presence of [BiS$_3$] pyramids and with an additional disordering. They should have exponential tails (not necessarily with the identical value of parameter E_1 in the exponent for the case of GeS_2).
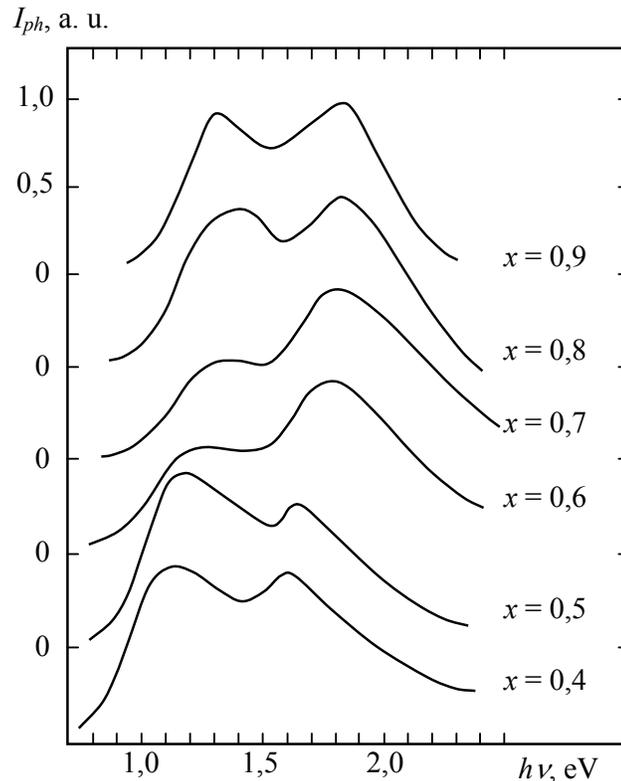

Fig. 5. PC spectra of $(GeS_2)_x(Bi_2S_3)_{x-1}$ glasses measured at modulated illumination for composition shown (T=293K).
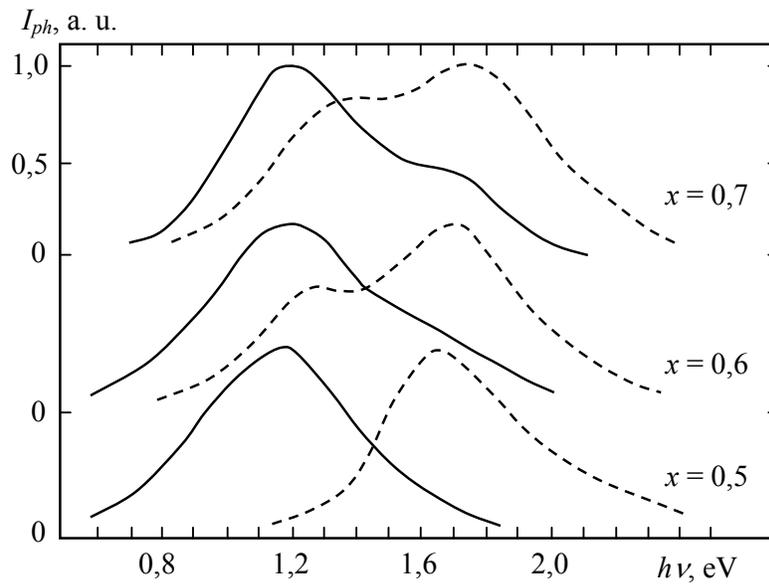
Fig. 6. Steady-state PC spectra of $(GeS_2)_x(Bi_2S_3)_{1-x}$ glasses measured at different scanning directions of illumination wavelength (solid curves UV→IR, dotted curves IR→UV). T = 293 K.

As mentioned above, one can suppose that $(GeS_2)_{1-x}(Bi_2S_3)$ glass forming during cooling there exists the tendency to form and, probably, to grow small region. Within which the concentration of Bi_2S_3 not differs a little from the average. This fact may be considered either as the appearance of additional structural disorder or, on the contrary, as some ordering with the phase separation and, possibly, crystallization in a very limited volume. However, as we believe phase separation with or in the absence of crystallization is unlikely. In such a case location and the shape of the absorption edge would be defined by electronic transitions in a more narrow-band crystalline counterparts Bi_2S_3 and practically becomes independent on the composition x. On the other hand, compared with the average-statistical one the excess of Bi content in some microvolume due to a different valence of Bi and Ge and, correspondingly, their different coordination respectively by sulfur atoms should necessarily influence the structural reorganization of the glass in this region (including, probably, the lengths of bonds and angles and the component Ge-S.) As a result it may occur that the energy structure of the glass in the local region given differs in the minimal of the pseudogap value from neighbouring regions (Similarly to the difference of Figs.4, *c* and 4, *d*). The situation is similar to that one, which was considered by the authors of article [10]. In this model of glasses microregions with the different short-range order, adopted from different crystalline modifications of the same material alternate chaotically. In our case the physical reason of appearing of such microregions with different short-range order ("disordering of a special kind" in the terminology of article [10]) is a chemical and structural diversity of two glass-forming components.

It is very important that the similar situation should be expected in all cases when the glass is formed from several binary compounds (not necessarily – glass formers) sufficiently differing by the short-range order.

3. Conclusions

A spectral investigation of the absorption edge α and photoconductivity (PC) of $(GeS_2)_x(Bi_2S_3)_{1-x}$ ternary glasses ($0.4 \leq x \leq 1$) within the temperature intervals of 77-400 K has been carried out. The absorption edge for the GeS_2 binary glass is described by the Urbach rule. For ternary glasses, the long-wave tail of dependence $\alpha = f(h\nu)$ exhibits two exponential regions

changing with the temperature and having a different slope. For all the compositions of ternary $(GeS_2)_x(Bi_2S_3)_{1-x}$ glassy alloys, the PC spectra within the wavelength region of 0.4-1 μm show the "hysteresis" when the scanning direction changes from UV to IR. The observed spectral dependences of absorption and PC have been qualitatively explained by the complex band model of the binary GeS_2 due to the formation of several types of structural units when the composition is moved toward the ternary glass system based on the atoms of different valency.

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