Optical and Photoelectric Properties of Non–Crystalline Antimony Chalcogenides

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Abstract

The structure, fundamental absorption edge, d. c. and a. c. conductivity and photoconductivity for Sb-S glasses have been studied. The optical band gap values have been found to be in the range of 1.52-1.76eV. Structure of monophase Sb_xS_{1-x} glasses $(0.35 \leq x \leq 0.45)$ is predominantly determined by SbS_3 structural units, linked with two-fold coordinated sulfur atoms. Under the direct current the delocalized state conductivity prevails in the investigated materials. The $\sigma_{dc}(T)$ and $\sigma_{dc}(\omega)$ dependences have been interpreted within the framework of the model of the charged defect centres (D^-, D^0, D^+ and accounted for the combined jumping charge transfer by bipolarons and polarons between these centres. Photosensitivity of Sb_xS_{1-x} glasses lies in 500 - 1200 nm spectral range. The highest photosensitivity is inherent in the glassy Sb_2S_3. The nature of the peaks in the photoconductivity spectra for the glasses has been ascertained.

Keywords: absorption edge, short-range order, conductivity, photoconductivity.

Chalcogenide vitreous semiconductors have found applications as mediums for image recording due to their high photoconductivity and relatively low charge carrier mobility. However, the majority of the chalcogenide glasses, used for these purpose are the arsenic glassy chalcogenides. From this standpoint the glassy materials based on chalcogenides of antimony appear to have considerable promise.

In the binary Sb-S system the only well-known compound in the non-crystalline state (glassy and amorphous) is Sb_2S_3 [1–3]. The crystalline Sb_2S_3 possesses high photoconductivity, that has brought about its wide use for the deposition of the photoconductive layers on the targets of the camera tubes [4]. The considerable sensitivity to the light beam is typical also for thermally evaporated Sb_2S_3 layers, the highest photoconductivity being characteristic of the crystallized films of this composition. Optical, electric and photoelectric properties are principally determined by the study of the energy band structure of the materials, which, in its turn, depends on the atomic arrangement. That is why a transition to disordered structures inherent to the glassy materials is accompanied by a significant change in their properties. In this context the study of the non-crystalline materials with different compositions within Sb-S system is of an interest, because the variation in the composition, as a rule, results in the broadening of the variation range for the basic glass or amorphous film parameters, and thus, the expanding of their application areas.

In this paper the results of the investigation of Raman spectra, fundamental absorption edge, d.c. (σ_T) and a.c. $\sigma_{dc}(\omega)$ conductivity and photoconductivity (σ_{ph}) for the glasses of Sb-S system have been given.

The Raman spectra for the Sb_xS_{1-x} glasses were measured in the reflection geometry with the help of DFS-24 spectrometer and Kr^+-laser (λ= 676.4 nm, power – l00 mW) with a resolution better than 4 cm^{-1} (Fig.l). In Raman spectrum for glassy Sb_xS_{1-x} (Fig.l, curve 2) the intensive broad band with a peak at 290 cm^{-1}, the band at 200 cm^{-1} and the shoulder in the range of 155 cm^{-1} have been observed. The Raman spectrum for this material obtained under the specta recording technique within "rectangular geometry" has been studied earlier [5]. The bands with peaks at 293 and 480 cm^{-1}, have been revealed and the bands at 155 and 200 cm^{-1} have not been observed. This seems to be related to the fact that they fall into the range of the intensive Rayleigh scattering for this measurement configuration and are not observed in Raman spectrum. The band at 293 cm^{-1} results from the changes in polarization under the valence vibration of the antimony and sulphur atomic pairs in triangular SbS pyramids, and the weak band at 480 cm^{-1} is attributed to the vibrations of Sg molecules. The presence of the ring-shaped S_8 molecules in the matrix of Sb_xS_{1-x} glasses (x = 0.36; 0.40; 0.43) is responsible for the band at 200 cm^{-1}, because the deformational vibrations for these molecules
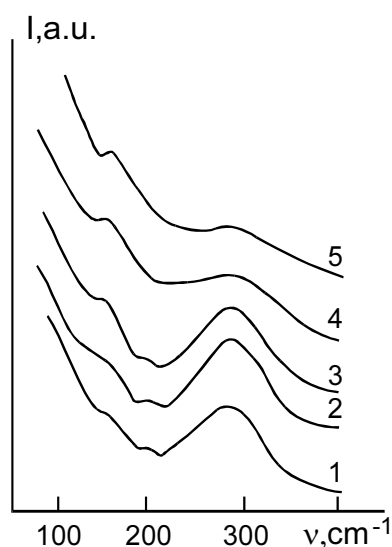
can be found just at 200 cm^{-1} [6]. The intensity of this band drastically drops with the decrease in sulphur content in the composition of the glasses under investigation (Fig.l, curves 1-3), and for $Sb_{0.50}S_{0.50}$ glass this band is missing in general. These data allow to deduce, that the matrix of the glassy Sb_2S_3 and glasses of the neighbouring compositions is basically built from triangular SbS_3 pyramids linked by two-fold coordinated sulfur atoms. This deduction is also supported by the results of the X-ray diffraction studies [7].

The presence of the homopolar bonds (Sb-Sb) is responsible also for the band at 155 cm^{-1}. These bonds most likely are realized in $SbSb_{3/3}$ structural units. This assumption is supported by the increase in the intensity of the band at 155 cm^{-1} (Fig. 1, curves 4, 5) with antimony content increasing composition of the glasses under investigation. At the same time with the increase in x the intensity of the band at 290 cm^{-1} goes down that indicates the decrease of the number of SbS_3 structural units in the glass matrix.

The absorption coefficient spectrum for Sb_xS_{1-x} glasses (0.35≤x≤0.50) near the fundamental absorption edge follows the Urbach's rule:

$$\alpha = \alpha_0 \exp\Gamma\left(h\nu - h\nu_0\right) \qquad (1)$$

It has been found experimentally, that Γ parameter, describing the slope of the linear part of the $\ln\alpha=f(h\nu)$ dependence for glassy Sb_2S_3 is about 18 eV^{-1} and varied slightly for other Sb_xS_{1-x} glasses. For the optical band gap (mobility gap). E_g, the photon energy value at which the α coefficient reaches 10^3 cm^{-1} has been taken. The derived E_g values for Sb_xS_{1-x} glasses have been found in the range of 1.52 – 1.65 eV (Table 1). The increasing of the antimony content in glass compositions leads to a decreasing of the E_g.

As a result of the study it has been found, that conductivity σ_T exponentially increase with increasing of temperature that correspond to the

Fig.1. Raman spectra for Sb_xS_{1-x} glasses. x = 0.36 (1); 0.40 (2); 0.43 (3); 0.50 (4); 0.55 (5).

Table 1. Physical, electric and photoelectric parameters for Sb_xS_{1-x} glasses.

Composition, x	E_g, eV	σ_T, S×m^{-1}	E_a, eV	σ_ω (at 10^5 Hz), S×m^{-1}	s	σ_{ph}/σ_T	E_{max}, eV
0.35	1.58	3.0×10^{-11}	0.79	3.0×10^{-7}	0.80	8.0×10^2	1.70
0.38	1.60	5.0×10^{-11}	0.83	4.0×10^{-7}	0.90	9.0×10^2	1.57
0.40	1.65	1.0×10^{-10}	0.82	8.2×10^{-8}	0.78	3.0×10^3	1.38
0.43	1.58	2.0×10^{-11}	0.81	4.0×10^{-8}	0.83	2.0×10^3	1.26
0.45	1.56	2.0×10^{-10}	0.81	2.0×10^{-8}	0.94	9.0×10^2	1.24
0.50	1.52	3.0×10^{-10}	0.80	5.0×10^{-8}	0.85	1.0×10^2	1.22

semiconductor behaviour of the conductivity in the given materials. In the temperature range of 250–500 K for all of the investigated samples the dependence $lg\sigma_T = f(l/T)$ is linear, i.e. the conductivity depends only on the activation energy and is described by the relation [8]:

$$\sigma_T = \sigma_0 \exp[-E_a/kT], \qquad (2)$$

where E_a is the conductivity activation energy at T = 0 K.

The direct current conductivity mechanism can be judged from the value obtained by the extrapolation of the line $lg \sigma_T = f(l/T)$ to T=∞. For the given glasses σ_0 constant is found to be in the range of $1.0 \times 10^4 \sim 5.0 \times 10^5$ S×m, that corresponds to the case, when the conductivity is initiated by the carriers, excited to the delocalized states close to the mobility edge of the valence band. As is evident from the Table 1, the doubled energy $2E_a$ for Sb_xS_{1-x} glasses is approximately equal to the optical band gap E_g, that is typical also for other isostructural glasses (As_xS_{1-x} and As_xSe_{1-x}).

The study of the alternative current conductivity for Sb–S glasses have shown, that in the frequency range of $10^4 \sim 10^8$ Hz σ_ω increases with frequency (Fig. 2) following the relation:

$$\sigma_\omega = A \times \omega^s \qquad (3)$$

The values of the index of a power s at T = 293 K are given in the Table 1. For all of studied glasses the character of the $\sigma_\omega \sim f(\omega)$ dependence almost does not change with composition. The s values are found in the range

of 0.78 ~ 0.94, indicated the jumping mechanism of the alternative current conductivity [8, 9]. With increasing of the temperature s index decrease (Fig. 2).

Fig. 3 shows σ_ω temperature dependences for $Sb_{0.40}S_{0.60}$ glass, typical of the whole Sb–S system. It is seen, that temperature dependences of σ_T (Fig.3, curve 1) and σ_ω (Fig.3, curve 2-4) are different. The conductivity σ_ω at comparatively low T and high ω shows weak temperature dependence. The conversion to an exponential dependence σ_ω, on T is observed in the range of low frequencies.

The slight change of σ_ω and s values point to the fact that σ_ω in the range of moderate temperatures result mainly from the charge carriers jumping over the localized states near the Fermi level [9].

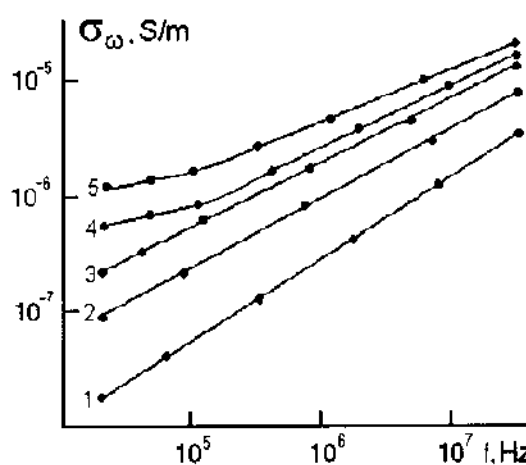**Fig. 2.** Frequency dependence of σ_ω for $Sb_{0.40}S_{0.60}$ glass. Temperature, K: 1 - 300; 2 - 350; 3 - 400; 4 - 430; 5 - 450.
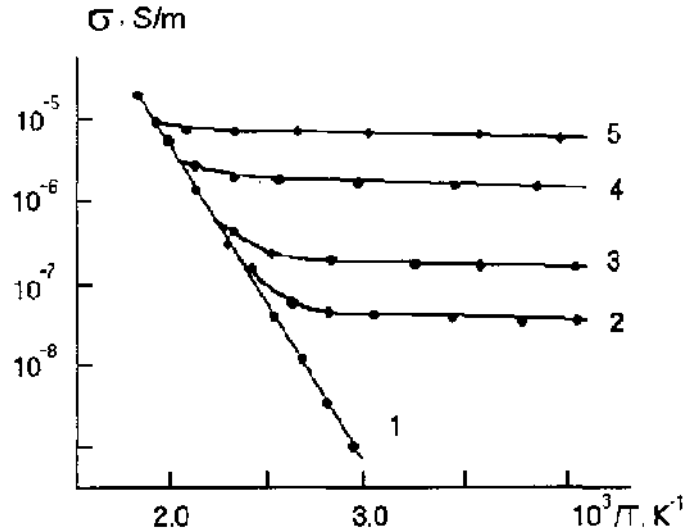
Fig.3. Temperature dependencies of σ_T (1) and σ_ω (2-5) for $Sb_{0.40}S_{0.60}$ glass at frequencies: 2 - 10^5 Hz; 3 - 10^6 Hz; 4 - 10^7 Hz; 5 - 4×10^7 Hz.

In general [8, 9], the Fermi level localization is associated with the presence of D^+ and D^- charged defect centres (D^+ and D^- are the dangling bonds without any or with two free electrons). In the low temperature range σ_ω is followed by the jumps of bipolarons over the barriers between these centres ($D^+ + 2e \leftrightarrow D^-$) [10]. Two electrons (bipolaron), that are found on D^- centre, transit to D^+ centre by the jumping over the potential barrier, which in the framework of the Elliott's model is given by the expression [10]:

$$W = W_M - [8e^2/\varepsilon R_\omega^2], \qquad (4)$$

where, W_M is the activation energy when the state separation is infinitely large, that can be equal to the band gap E_g in chalcogenide glasses; R_ω is the distance between two states; ε is permittivity.

In this model the conductivity for N/2 centres appears as [10]:

$$\sigma_\omega = \frac{\pi^2 N^2 \varepsilon}{24} \left(\frac{8e^2}{\varepsilon W_M} \right)^6 \frac{\omega^6}{\tau_0^\beta}, \qquad (5)$$

where τ_0 is typical relaxation time, that can be found from the expression:

$$\tau = \tau_0 \exp (W/kT), \qquad (6)$$

where W is the height of the potential barrier, the carriers have to jump over. It should be noted, that for the majority of chalcogenide glasses τ_0 values are found in the range of $10^{-13} \sim 10^{-12}$ s [10].

The parameters s and W_M are related by the equation:

$$\beta = 1 - s = 6kT/W_M. \qquad (7)$$

Following this relationship the index of a power s in the Eq. (3) goes down with an increasing of the temperature, that was observed experimentally (Fig. 2).

In the range of the elevated temperatures ($T \sim T_g$) the stronger temperature dependence of σ_ω is observed (Fig.3). It can be explained, by assuming that the neutral D^0 centers take part in the conductivity process [11].

The increasing of D^0 center concentration with the increasing of the temperature leads to the considerable contribution to the σ_ω of the electron jumps between D^0 and D^+ centers and the holes between D^0 and D^+ centers, which exceed bipolar jump contribution. Thus, the conductivity σ_ω in the wide temperature interval is determined by three processes: jumps of bipolarons between D^- and D^+ centers, jumps of "simple" polarons between D^0 and D^+ centers and between those of D^0 and D^+ ones. The last two processes give an exponential rising of σ_ω.

The study of photoelectric properties of

Sb_xS_{1-x} glasses showed that photosensitivity of the materials lies in a wide spectral range (500–1200 nm). In the photoconductivity spectrum of each singlesphase glass ($0.35 \leq x \leq 0.45$) one wide band (Fig.4) is observed, the peak position of which depends on the chemical composition of the glass.

The high photosensitivity is typical for the glassy Sb_2S_3. The ratio of the change in σ_{ph}/σ_T at T=293 K (where σ_{ph} is photoconductivity at illumination of about 10^4 Lx) is near 3×10^3. At T=293 K the peak of the photoconductivity spectrum for glassy Sb_2S_3 takes place at the photon energy value of $E_{max}= h\nu_{max} = 1.38$ eV (Fig.4, curve 2).
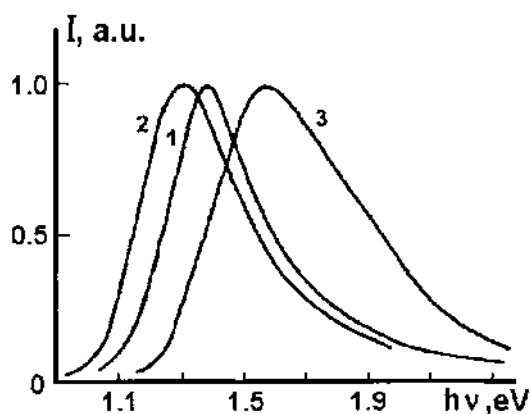

Fig. 4. Photoconductivity spectra of the Sb_xS_{1-x} glasses: x= 0.35(1); 0.40 (2); 0.43 (3).

With a rising of the temperature the peak in the photoconductivity spectrum for $Sb_{0.40}S_{0.60}$ glass shifts to the longer wavelengths with a temperature coefficient of $\partial E_{max}/\partial T = = 6\times10^4$ eV/K similar to the changes of the E_g [12]. The variation of the component ratio in the glass composition results in a decrease of σ_{ph}/σ_T (Table 1).

With the increasing of the antimony content in the composition of Sb_xS_{1-x} glasses the peak of the photoconductivity spectrum shifts to the longer wavelengths, as well as the sulfur content leads to the shifting of this peak to the shorter wavelength range. This behaviour is characteristic of the singlephase glasses only. Note that the singlephase glass region exists only for the compositions with x < 0.50. For non-singlephase glasses two peaks in the photoconductivity spectrum are present [12].

The studies of the photoconductivity spectra and absorption edge at T = 293 K on the same composition samples of different thickness have shown, that an energy peak position in the photoconductivity spectrum for Sb_2S_3 glass belongs to the range of the exponential part of the fundamental absorption edge matching the α range of 50 ~ 80 cm^{-1}. These results attest that the peak of the photoconductivity spectra of glassy Sb_2S_3 is intrinsic and results from the electron transitions from the occupied localized states near the mobility edge of the valence band into the extended states in the conductivity band.

References

1. Cervinka L., Hmby A. J. Non-Cryst. Solids, (1982) **48** 231-264.
2. Melekh B.T., Maslova Z.V., Ablova M.S. et al. Phys. and Chem. of Glasses, (1976) **2** 189-190. (in Russian).
3. Kulibaba V.D., Polishchuk V.A. Electronic Engineering. Materials issue, (1986) **2** 70-72. (in Russian).
4. Herberg A.E. Camera Tubes with the Photoconductive Effect. Leningrad, Energia, (1973) 256 p.(in Russian).
5. Turianitsa I.D., Vodopianov L.K., Rubish V. M., et al. J. Appl. Spectrosc., (1986) **44** 798-802.(in Russian).
6. Rosola I.I., Puha P.P., Chepur D.V. In: Multinary semiconductors (preparation, properties, application), Uzhgorod, (1981) 83-92.(in Russian).
7. Rubish V. M., Shtets P.P., Stefanovich B.A. et al. In.: Structure, Physical and Chemical Properties and Application of Non-crystalline Semiconductors (Proc. of the Conf. "Non-crystalline semiconductors–89"), Uzhgorod, (1989) 79-81.(in Russian).
8. Rubish V. M., Turianitsa I.D., Shtets P.P. Ukr. J. of Phys., (1984) **29** 1532-1535.(in Russian).

9. Mott N., Davis E. Electron Processes in Non-crystalline Materials. M.: Mir, 1988, vol. 2, 658 p.(in Russian)

10. Shtez P.P., Bletskan D.I., Turianitsa I.D., Bodnar M.P., Rubish V. M. News of Acad. Sc. USSR. Nonorg. Mat. (1989) **25** 933-937. (in Russian).

11. Elliott S.R. Phil. Mag. (1977) **36** 1291-1304.

12. Shimakawa K., Nitta S., Mori M. Phil. Mag. (1982) **46** 123-135.