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Electric and dielectric properties of glasses of Cu-Sb-S-I system

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Abstract. D.c. and a.c. conductivity ($\sigma(0)$ and $\sigma(\omega)$) and dielectric parameters (ϵ and $\text{tg}\delta$) of Cu-Sb-S-I system glasses are investigated in $1.0 \cdot 10^4$ – $6.0 \cdot 10^7$ Hz frequency range and 170–400 K temperature interval. In the glasses of SbSI–CuSbS₂ system the d.c. conductivity along delocalized states prevails. A.c. conductivity is explained by a combined hopping mechanism of charge transfer by bipolarons and “simple” polarons. A high concentration of charge carriers and availability of dipole structural units Cu⁺S[–]SbS_{2/2} in the glass matrix define dielectric properties of glasses.

Keywords: chalcogenide glasses, conductivity, activation energy, dielectric properties

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1. Introduction

A considerable copper amount may be introduced into the composition of chalcogenide glasses [1–3]. As a result both the structure of glasses and their properties are changed. The electronic properties of copper-containing glasses are especially sensitive to the variation in the composition. But up to date the electronic properties of copper-containing glasses based on arsenic chalcogenides were mainly investigated. Therefore, the study of other glasses based on antimony chalcogenides and, in particular, glasses of Cu-Sb-S-I system is of great interest. Besides, a pure scientific interest to study these substances has a practical importance as the photomodulation absorption in IR spectral region [4] and switching effect [5] are revealed in the glasses of the given system, and depending on copper content one can get one- and two-threshold switching mechanism.

In the present work the results of the study of d.c. and a.c. conductivity ($\sigma(0)$ and $\sigma(\omega)$) and dielectric properties (ϵ and $\text{tg}\delta$) of the (SbSI)_{1-x}(CuSbS₂)_x glasses have been presented.

2. Experimental

The glasses of Cu-Sb-S-I system were synthesized by vacuum fusion of the mixture of initial pure components in accordance with the procedure given in [6]. The samples for measurements were prepared in the form of parallel-sided plates onto the largest areas of which aquadag electrodes were deposited. Voltage-current characteristics of structures C|sample|C had a symmetric form and for them Ohm's law is valid for fields $\sim 5 \cdot 10^4$ V/m. Temperature and frequency dependences $\sigma(\omega)$, ϵ and $\text{tg}\delta$ were studied by the resonance method [7] within the range of frequencies $1.0 \cdot 10^4$ to $6.0 \cdot 10^7$ Hz and temperature interval of 170–400 K. The investigations were performed in vacuum. Relative measurement errors were: ϵ – 3%, $\sigma(\omega)$ and $\text{tg}\delta$ – 10%.

3. Results and discussion

The studies have shown that in the indicated temperature interval $\ln\sigma(0)$ is a linear function of $1/T$, that is d.c. conductivity is described by the expression with one activation energy $E_{\sigma(0)}$ [3]:

$$\sigma(0) = C \exp(-E_{\sigma}(0)/kT).$$

The activation energy values of conductivity of $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses at $T = 0$ are given in Table 1.

By the value C obtained by extrapolating the straight line $\lg\sigma(0) = f(1/T)$ to $T = \infty$, one can conclude about the mechanism of d.c. conductivity. If the conductivity is determined by carriers activated into delocalized states, C value may have the meanings within $10^3-10^6 \text{ Ohm}^{-1}\cdot\text{m}^{-1}$ [3, 8, 9]. If the value C is 2 to 3 orders of magnitude less, the conductivity is effected by charge carrier hopping along localized states. For the studied $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses C has the values that lie within the limits of $2\cdot 10^3-5\cdot 10^4 \text{ Ohm}^{-1}\cdot\text{m}^{-1}$ (Table 1). That is why one may draw a

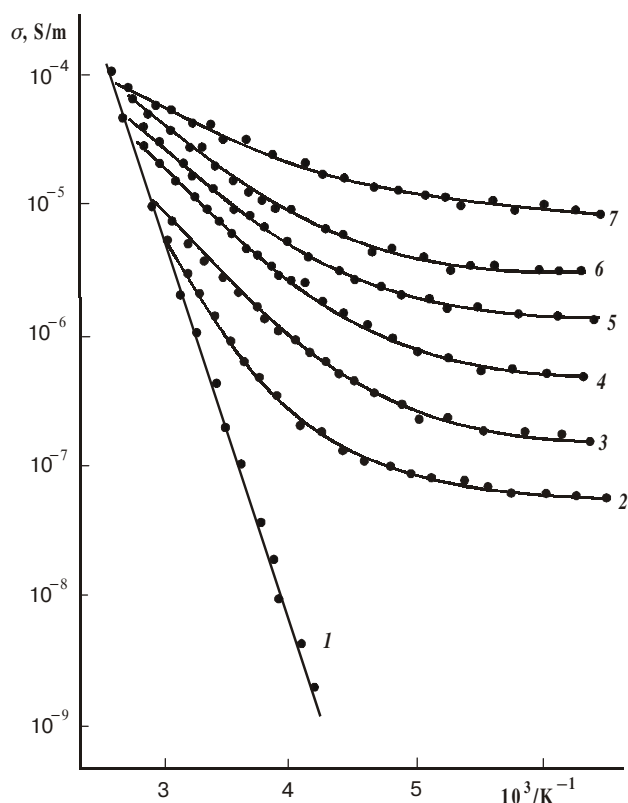


Fig. 1. Temperature dependences of $\sigma(0)$ (1) and $\sigma(\omega)$ (2–7) of $(\text{SbSI})_{0.50}(\text{CuSbS}_2)_{0.50}$ glass. Frequency, Hz: 2 – 10^4 ; 3 – $6\cdot 10^4$; 4 – 10^5 ; 5 – $4\cdot 10^5$; 6 – 10^7 ; 7 – $3\cdot 10^7$.

conclusion that in the glasses of the given system the d.c. conductivity along delocalized states near the mobility edge of the valence band prevails.

With increasing copper content in glasses from 0 to 16.7 at.%, $\sigma(0)$ increases by more than three orders of magnitude with simultaneous growth of the activation energy $E_{\sigma}(0)$ (Table 1). Concentrational dependences of $\sigma(0)$ and $E_{\sigma}(0)$ can be explained by the model of charged defects. In accordance with the given model, chalcogenide glass comprises charged defects that form acceptor D^- and donor D^+ levels in the middle of the mobility gap and define the position of the Fermi level [3]. If the glass comprises the elements with the number of orbital electrons equal to 4 or more, the concentration of D^- and D^+ -centres is practically constant and variations in the composition do not cause considerable changes in the conductivity. However, if the glass comprises negatively charged ions of impurities, the Fermi level shifts and this is the reason for a high conductivity in many cases.

It is well known [2, 10] that copper facilitates the formation of 4-fold coordination and becomes negatively charged due to accepting electrons from D^- centres. Respectively, the decrease in the concentration of D^- cen-

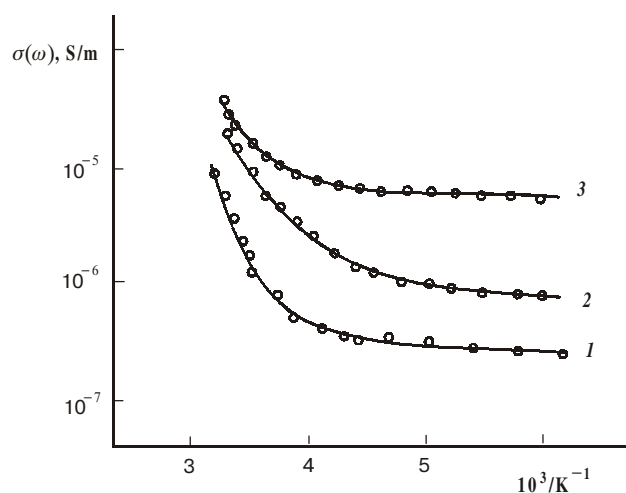


Fig. 2. Temperature dependences of $\sigma(\omega)$ of $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses at the frequency of 10^5 Hz on x , mol.%. 1 – 0.25; 2 – 0.33; 3 – 0.67.

Table 1. Electrical and dielectrical parameters of $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses.

Composition x , mol.%	$\sigma(0), \text{S}\cdot\text{m}^{-1}$	$E_{\sigma}(0), \text{eV}$	$C, \text{S}\cdot\text{m}^{-1}$	$\sigma(\omega), \text{S}\cdot\text{m}^{-1}$	s	ϵ
0	$4.0\cdot 10^{-10}$	0.73	$5.0\cdot 10^4$	$1.5\cdot 10^{-7}$	0.89	23.5
0.25	$5.0\cdot 10^{-8}$	0.59	$1.0\cdot 10^4$	$5.1\cdot 10^{-6}$	0.74	22.4
0.33	$1.0\cdot 10^{-7}$	0.57	$7.0\cdot 10^3$	$5.3\cdot 10^{-6}$	0.74	22.7
0.40	$3.0\cdot 10^{-7}$	0.55	$6.0\cdot 10^3$	$7.2\cdot 10^{-6}$	0.73	24.1
0.50	$7.0\cdot 10^{-7}$	0.53	$4.0\cdot 10^3$	$1.3\cdot 10^{-5}$	0.72	25.9
0.60	$9.5\cdot 10^{-7}$	0.50	$3.0\cdot 10^3$	$1.8\cdot 10^{-5}$	0.72	25.8
0.67	$2.0\cdot 10^{-6}$	0.47	$2.0\cdot 10^3$	$2.0\cdot 10^{-5}$	0.70	25.7

Note: values $\sigma(\omega)$ and ϵ are given at 100 kHz frequency

tres results in the shift of the Fermi level towards the valence band and increases in conductivity. Within the framework of the given model, in accordance with calculations of [10], the activation energy has to decrease ~ three times. And this accounts for the increase in $\sigma(0)$ at $T = 293$ K by approximately 10^5 times. Such an increase in $\sigma(0)$ (10^4 times) was revealed when introducing 5 at.% of Cu into As_2Se_3 [2]. Our studies have shown considerably smaller changes in $\sigma(0)$ and $E_{\sigma}(0)$ while changing the copper content in glasses of SbSI-CuSbS_2 system.

We suppose that a part of copper atoms have a coordination number 4 and others remain electro-positive and take part in the formation of the glass matrix of structural groups that contain copper. The study of concentrational dependences of infrared polarization and paramagnetic component of magnetic susceptibility [11] has allowed us to establish that such structural groups are $\text{Cu}^+\text{S-SbS}_{2/2}$ units. With the increase of copper content their concentration in these glasses also increases.

The value of $\sigma(\omega)$ also increases with the increase in copper concentration and temperature (Figs 1 and 2), and with the rise in frequency it increases proportionally to ω^s (Fig. 3). At $T = 293$ K the value of s depending on the composition varies within the limits of 0.89–0.70 (Table 1). With the growth of T , the value of s decreases (Fig. 3). A little change in $\sigma(\omega)$ (Figs 1 and 2) and value of s indicate the fact that in the region of low temperatures ($T < 250$ K) $\sigma(\omega)$ is mainly defined by charge carrier hopping over localized states near the Fermi level [3].

As stated above, localization of the Fermi level is connected with the presence of D^- and D^+ centres in the glasses (D^+ and D^- are the dangling bonds that possess no one or two free electrons). In the low temperature range $\sigma(\omega)$ goes by the jumps of bipolarons over the barriers between these centres ($\text{D}^+ + 2e \leftrightarrow \text{D}^-$) [12]. Two electrons

(bipolaron) that are found on D^- -centre transit to D^+ -centre jumping over the potential barrier separating these pairs.

Assuming a random character of the centre distribution, the expression for $\sigma(\omega)$ within the framework of the Elliott model for $N/2$ pairs of centres has the form [12]

$$\sigma(\omega) = \frac{\pi^2 N^2 \epsilon}{24} \left(8e^2 / \epsilon W_M \right)^6 \frac{\omega^s}{\tau_0^\beta}$$

Here W_M is the maximal height of a potential barrier that separates distant lands (in the first approximation one may assume $W_M = 2E_{\sigma}(0)$); τ_0 is the characteristic relaxation time that has the value of 10^{-13} – 10^{-12} s [12, 13] for the majority of chalcogenide glasses.

The parameters s and W_M are related by the equation:

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

From here it follows that s decreases with increasing the temperature.

As it is seen from Fig. 1 and 2, at $T > 250$ K for $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses a strong dependence of $\sigma(\omega)$ on T is observed, which does not arise from the model of over-barrier jumps of bipolarons [12]. Such a dependence of $\sigma(\omega)$ on T can be explained by supposing that neutral centres D^0 take part in the process of conductivity [13]. Such centres are formed as a result of a reverse reaction $2\text{D}^0 \leftrightarrow \text{D}^+ + \text{D}^-$. The increase of D^0 -centres concentration with the temperature results in a considerable contribution of jumps of polarons – electrons between centres D^0 and D^+ (process II) and holes between centres D^0 and D^- (process III), which exceed the contribution of jumps of bipolarons (process I) into $\sigma(\omega)$. In a general case, the a.c. conductivity may be written in the form of the sum

$$\sigma(\omega) = \sigma_I(\omega) + \sigma_{II}(\omega) + \sigma_{III}(\omega),$$

where $\sigma_I(\omega)$ is the contribution of bipolarons into the conductivity, $\sigma_{II}(\omega)$ i $\sigma_{III}(\omega)$ are contributions of simple polarons. The latter two members of this equation condition a strong temperature dependence of $\sigma(\omega)$ due to the decrease in the heights of barriers with the temperature and the increase in the quantity of the number of thermally activated pairs.

It should be noted that the united hopping mechanism of charge transfer by bipolarons and “simple” polarons between charged centres (D^- , D^0 , D^+) well explains the behaviour of $\sigma(\omega)$ for the studied compositions and for other chalcogenide glasses, too [8, 14].

The investigations of dielectric parameters have shown that the glasses of SbSI-CuSbS_2 system possess sufficiently high values of ϵ and $\text{tg}\delta$ (Table 1) (at the frequency 10^5 Hz and $T = 293$ K depending on the composition ϵ varying over the range 22.4–25.9 and $\text{tg}\delta$ – over the range of 10^{-2} – 10^{-1} , the increase of CuSbS_2 in the composition of glasses results in the rise of $\text{tg}\delta$). Over the range of temperatures

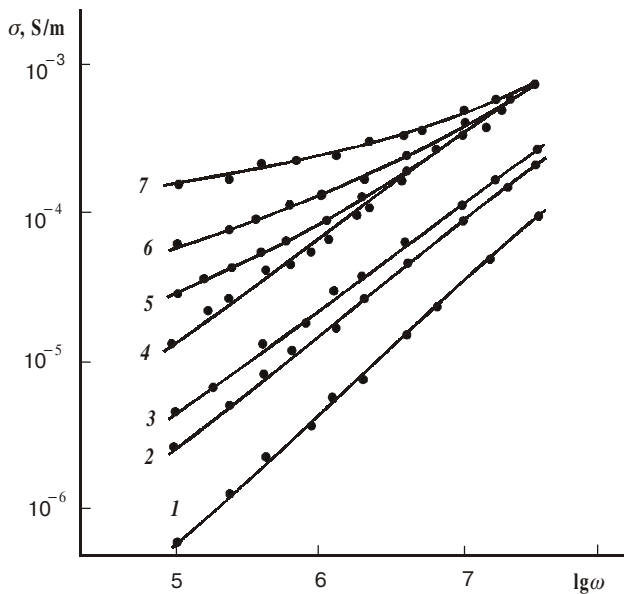


Fig. 3. Frequency dependences of $\sigma(\omega)$ of $(\text{SbSI})_{0.50}(\text{CuSbS}_2)_{0.50}$ glass. Temperature, K: 1 – 154; 2 – 250; 3 – 263; 4 – 293; 5 – 314; 6 – 333; 7 – 350.

$T < 250$ K, temperature and frequency variations in ϵ and $\text{tg}\delta$ are small, and at higher temperatures an essential dependences of these parameters on temperature and frequency are observed (Figs 4–6). It means that at relatively low temperatures ϵ is mainly determined by electronic and infrared polarizations [11]. However, even at low temperatures, the contribution of the charge carrier jumps into polarization is considerable. The charged defect D^- and D^+ centers, concentration of which in Cu–Sb–S–I glasses makes up to 10^{25} – 10^{26} m^{-3} , are the places of a random distribution of the electric charge in glass. The applied external field stimulates “the unipolarity” of junctions between the given centres. As a consequence, an electric moment of the glass volume unit is induced by this field. A small dispersion of ϵ over the region of low

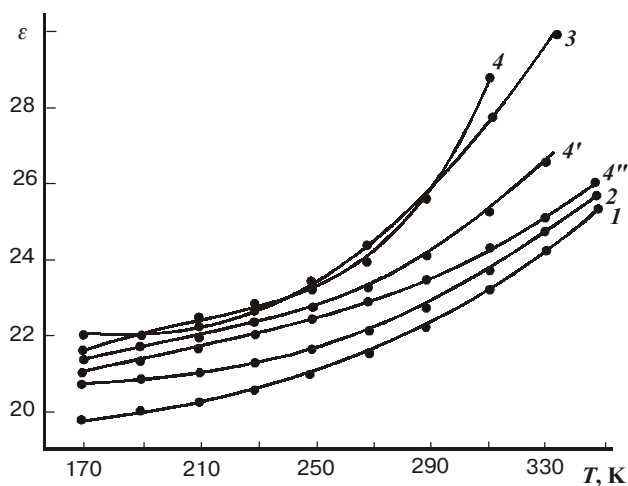


Fig. 4. Temperature dependences of ϵ in $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses at frequencies 10^5 (1–4), 10^6 (4') and 10^7 Hz (4'') for x values: 1 – 0.25; 2 – 0.33; 3 – 0.67; 4, 4', 4'' – 0.50 mol.%.

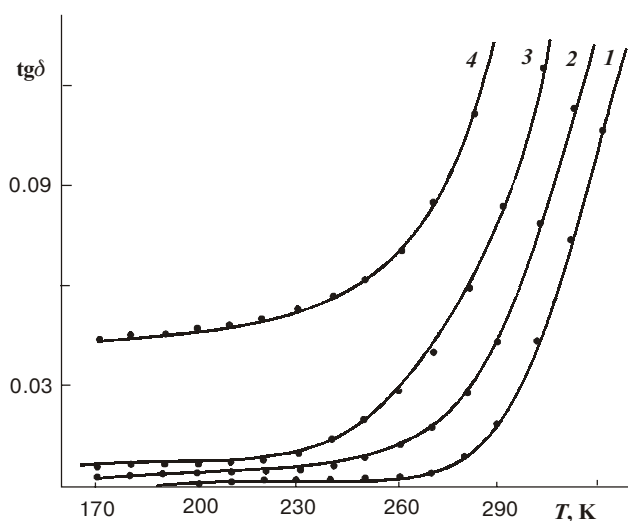


Fig. 5. Temperature dependences of $\text{tg}\delta$ for $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$ glasses at the frequency 10^5 Hz on x values: 1 – 0.25; 2 – 0.33; 3 – 0.50; 4 – 0.67 mol.%.

SQO, 6(1), 2003

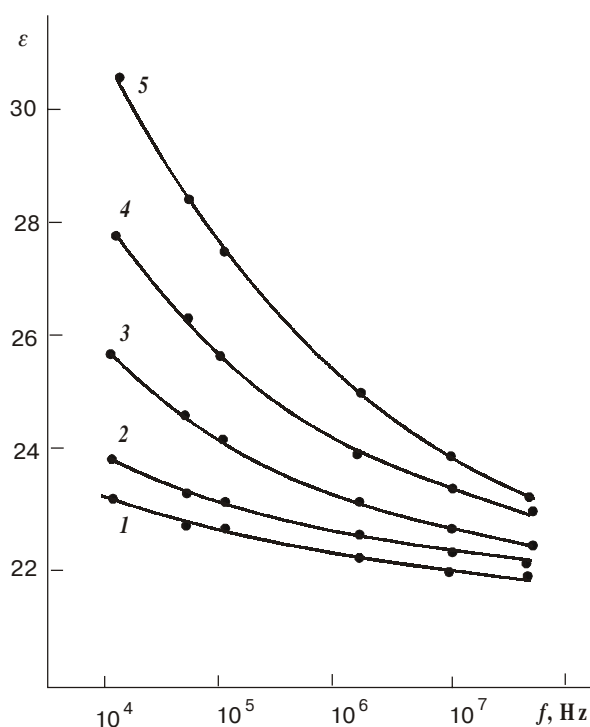


Fig. 6. Frequency dependences of ϵ for $(\text{SbSI})_{0.50}(\text{CuSbS}_2)_{0.50}$ glass at temperatures: 1 – 230; 2 – 250; 3 – 270; 4 – 293; 5 – 310 K.

temperatures (Fig. 6) is probably connected with the fact that the frequency of the applied field diverges from a reverse time of maxwellian relaxation t_M (the values of t_M make up 10^{-5} – 10^{-4} for $(\text{SbSI})_{1-x}(\text{CuSbS}_2)_x$).

At higher temperatures ($T > 250$ K), the role of D^0 centres becomes more important. The jumps of charge carriers between the centres become easier due to decreasing the height of potential barrier ($W_M' < W_M$). It stimulated the increase in the polarization and, in its turn, the increase in the dielectric constant.

However, it is rather difficult to explain the character of temperature-frequency dependences of dielectric parameters within the region of elevated temperatures by the variation only in the concentration of charge carriers. The measurements have shown that ϵ and $\text{tg}\delta$ decrease with the increasing of the frequency (Fig. 4 and 6). In this case, $\text{tg}\delta$ decreases in accord to the relationship close to the exponential one, but the power is not equal to unity. If the dielectric losses were determined only by conductivity losses, the power would be equal to unity [15, 16]. This enables one to assume a considerable contribution of relaxation losses into the dielectric ones as connected with the presence of dipole structural units in Cu–Sb–S–I glasses. As mentioned above, such units are $\text{Cu}^+\text{SbS}_2/2$ ones. At low temperatures the dipoles remain “frozen” and at higher temperatures they are able to rotate, which results in a considerable ϵ increase. The orientation of dipoles is not simply elastic. It is connected with overcoming considerable interactions of neighbouring units. The part of the electric field energy is spent on this. Therefore, due to the dipole polarization, Cu–Sb–S–I glasses

don't have the increased ε only, but the increased $\text{tg}\delta$ and dielectric losses, too.

4. Conclusions

In glasses of Cu–Sb–S–I system, the d.c. conductivity along delocalized states near the mobility edge of valence band prevails. The increase in the content of copper in the composition of glasses is accompanied by a considerable increase in the d.c. conductivity and decrease in the activation energy.

The a.c. conductivity varies with the frequency in accordance with the relationship $\sigma(\omega) \sim \omega^s$. This testifies to a hopping character of $\sigma(\omega)$. At $T < 250$ K the a.c. conductivity is effected by overbarrier jumps of bipolarons between charged centres D^- and D^+ . At $T > 250$ K the concentration of D^0 centres increases, which results in a considerable contribution of jumps of "simple" polarons between centres D^0 and D^+ as well as D^0 and D^- to $\sigma(\omega)$.

Over the range of temperatures $T < 250$ K, temperature and frequency variations of ε and $\text{tg}\delta$ are small. The dielectric constant ε is mainly determined by electronic and ionic polarization. At $T > 250$ K ε and $\text{tg}\delta$ as functions of temperature and frequency for glasses of Cu–Sb–S–I system have been revealed. Dielectric properties within this temperature range are conditioned by the increase in the charge carrier concentration and polarization connected with a partial orientation of dipole structural units $\text{Cu}^+\text{S}^-\text{SbS}_{2/2}$ in the glass.

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