

Structural and electrical investigation of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ superionic glasses*

Research Article

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Abstract: Structural studies of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ chalcogenide superionic glasses in the compositional range $x = 0.3 - 0.9$ were performed by scanning electron microscopy. Temperature and compositional dependences of transmission coefficient, electrical conductivity, and activation energy were investigated.

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1. Introduction

As_2S_3 glassy semiconductor has attracted wide interest from researchers due to the interesting photo-stimulated structural changes revealed by its optical properties [1–3] and has found practical applications as an efficient material in optical recording, holography and integrated optics. A large number of studies on the structure and physical properties of proustite Ag_3AsS_3 have been carried out because of the possibility of broad practical applications. It

was shown that defects in the silver substructure play a major role in the proustite conduction mechanism. Furthermore, silver transfer is equally probable within silver chains, spirals and between chains and spirals [4]. Silver containing chalcogenide glasses are also well known for use in optical and electrical recording. Ag_2S – As_2S_3 chalcogenide glasses are characterized by high conductivity [5] making them promising materials for solid-state ionics. The present work is devoted to structural and electrical investigation of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ superionic glasses.

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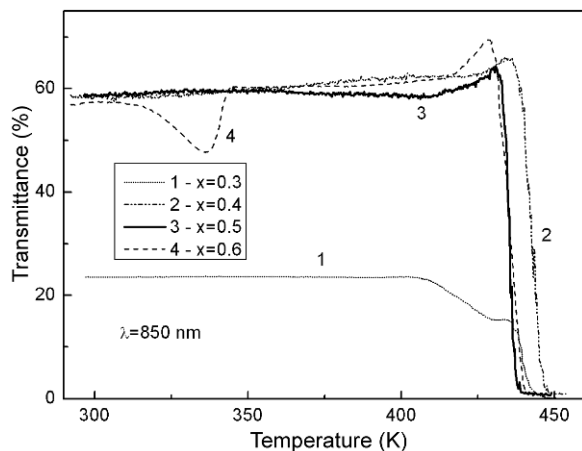


Figure 1. Temperature dependences of transmittance for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses measured in the heating mode.

2. Experimental details

$(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glassy alloys were prepared by vacuum melting (0.01 Pa) of the corresponding mixture components of As_2S_3 and Ag_3AsS_3 which were synthesized beforehand from the high purity elemental substances. The homogenization temperature of the melts ranged from 820–840 K over a period of 24 h with occasional stirring-mixed periodically. Cooling of the melts was carried out in cold water at 273 K. Samples were polished in the form of plates with thickness below 0.5 mm. Structural studies were performed using scanning electron microscopy (SEM) technique (Hitachi S-4300). Optical transmission spectra were studied in the temperature range 293–500 K using an MDR-3 grating monochromator. Measurements of complex electrical conductivity were carried out in the frequency range from 10 – 3 GHz and in the temperature range 300 – 400 K using a coaxial impedance spectrometer setup [5].

3. Results and discussion

Temperature measurements of the transmittance at a fixed wavelength of 850 nm chosen from the glass transparency range, show that transparency of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses with $x = 0.3, 0.4$, and 0.5 with a slight variation in the temperature range from 293–400 K accompanied by a sharp decrease down to zero at $T > 440 - 450$ K (Fig. 1). Inspection of the temperature-transmittance profile of the glass at $x = 0.6$, we observe an anomaly in behaviour which occurs as a minimum in the temperature dependence of transmittance at $T = 336$ K. The trans-

mittance anomaly at $T = 336$ K in $(\text{Ag}_3\text{AsS}_3)_{0.6}(\text{As}_2\text{S}_3)_{0.4}$ glass is probably related to temperature-induced structural changes which correlate with deviation of the temperature dependence of electrical conductivity from the Arrhenius behaviour. A noticeably lower transmittance value for $(\text{Ag}_3\text{AsS}_3)_{0.3}(\text{As}_2\text{S}_3)_{0.7}$ glass is explained by the highest structural disordering pattern among all the glasses under investigation. With subsequent cooling of the glasses, the transparency does not recover and glasses remain opaque at this wavelength.

Structural studies were performed for the glasses that were heated above 450 K and subsequently cooled down to 293 K. the SEM studies enabled imaging of the formation of nanostructures on the glass surface (Fig. 2) which is evidently responsible for a sharp decrease of transparency. Such formation of a nanocrystalline phase on the $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glass surface upon heating has been never reported before.

The SEM images presented in Fig. 3 have shown that the characteristic feature of all the glasses is the presence of a surface layer, the morphology of which depends on x . It is therefore obvious that the character of the temperature dependence of transmittance of the glasses is also different (Fig. 1). Compositional studies have shown that the electrical conductivity of the as-prepared $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ superionic glasses with increasing Ag_3AsS_3 content exhibits a non-monotonous behaviour with a maximum at $x = 0.5$ (Fig. 4). It should be noted that the activation energy (Fig. 4) decreases nonlinearly with x and the most noticeable change of the activation energy (decrease by more than 24%) is observed at the transition from $(\text{Ag}_3\text{AsS}_3)_{0.4}(\text{As}_2\text{S}_3)_{0.6}$ to $(\text{Ag}_3\text{AsS}_3)_{0.5}(\text{As}_2\text{S}_3)_{0.5}$. The correlation between the electrical conductivity and the activation energy for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses can be well traced from their compositional dependences (Fig. 4). A decrease of the potential barriers for Ag ions determined by their activation energy, contributes to the increase of their mobility resulting in the electrical conductivity increase.

Temperature studies have shown that electrical conductivity increases with temperature for all the superionic glasses under investigation. At temperatures $T < 350$ K, the temperature dependence of electrical conductivity is described by the Arrhenius equation. The linear character of the temperature dependence of electrical conductivity plotted in the Arrhenius coordinates reveals the thermal activation nature of electrical conductivity. Besides, we performed electrical studies of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses heated to 450 K and subsequently cooled down to $T = 300$ K. As follows from the experimental data, after heating above 450 K, The electrical conductivity of

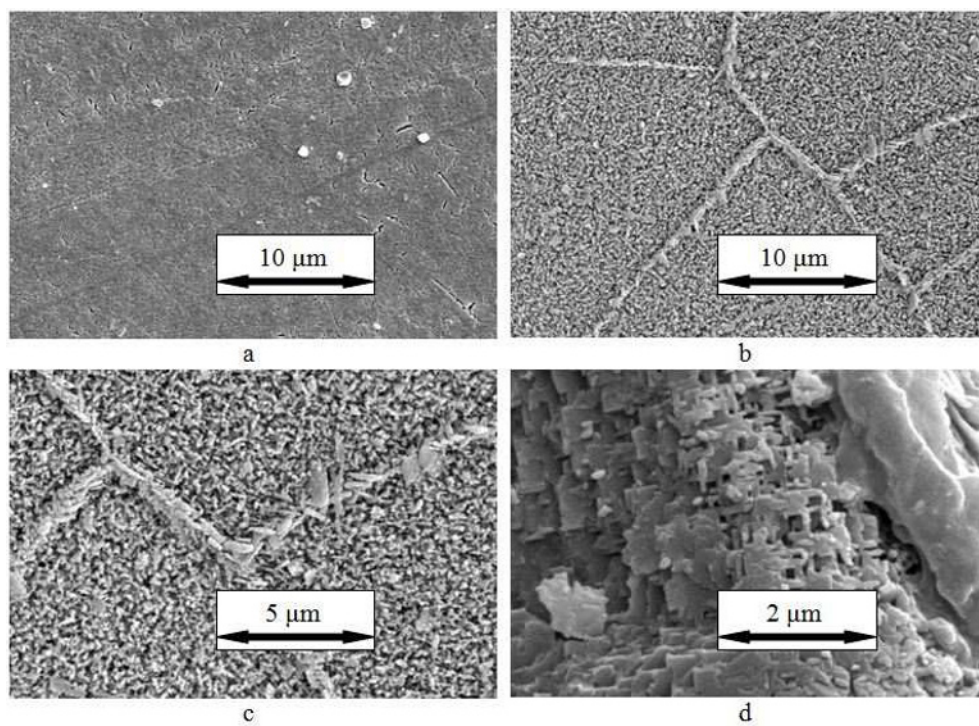


Figure 2. SEM images for as-quenched (a) and annealed (b-d) $(\text{Ag}_3\text{AsS}_3)_{0.3}(\text{As}_2\text{S}_3)_{0.7}$ glasses: (c) and (d) correspond to enlarged images of (b).

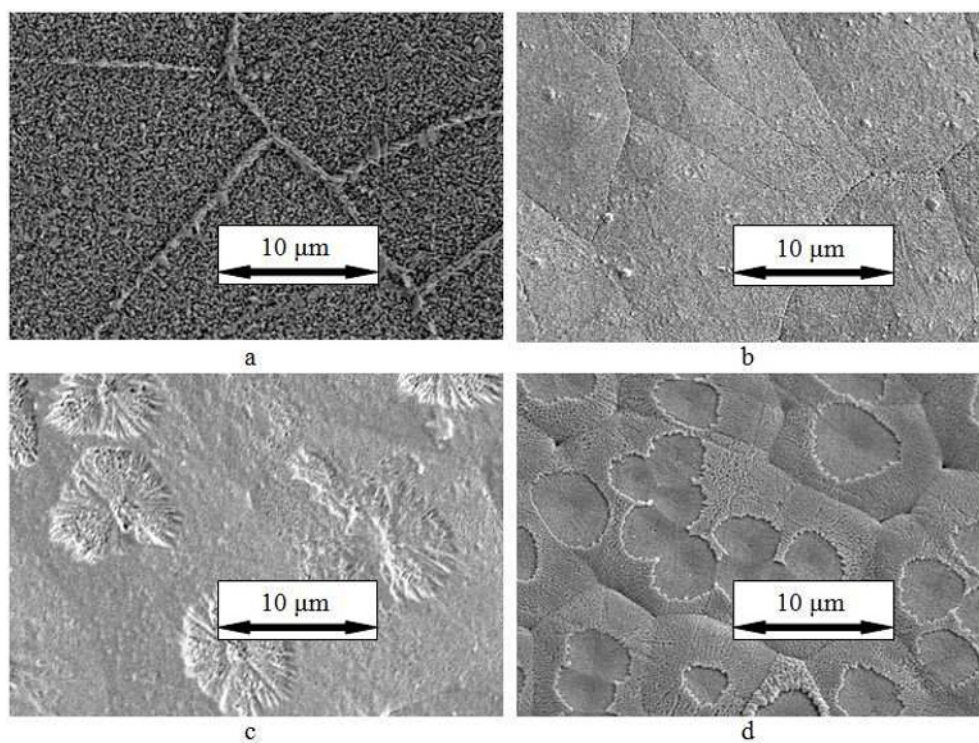


Figure 3. SEM images for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses with $x = 0.3$ (a), 0.4 (b), 0.5 (c), and 0.6 (d).

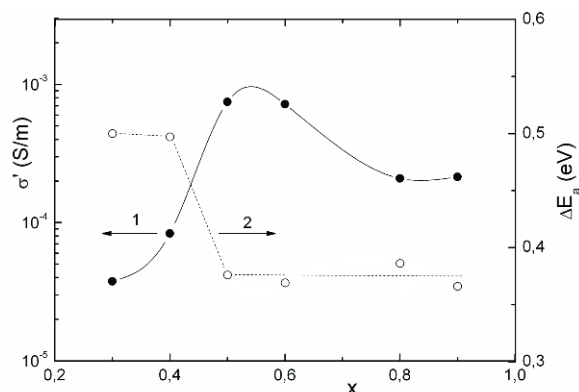


Figure 4. Compositional dependences of electrical conductivity (1) at 103 Hz and 300 K, and activation energy (2) for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses.

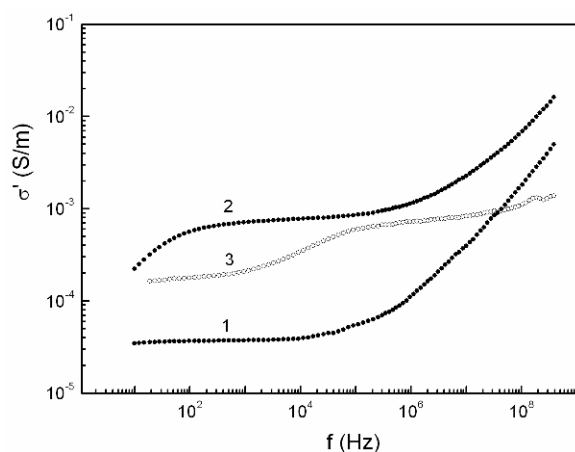


Figure 5. Frequency dependences of electrical conductivity at 300 K for $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses with $x = 0.3$ (1), 0.6 (2), and 0.9 (3).

the glasses increases. This fact can be related to the nanocrystalline surface layer appearing in this temperature range. For instance, for $(\text{Ag}_3\text{AsS}_3)_{0.3}(\text{As}_2\text{S}_3)_{0.7}$ and $(\text{Ag}_3\text{AsS}_3)_{0.6}(\text{As}_2\text{S}_3)_{0.4}$ glass, the conductivity increases by 34% and 25% respectively. From the studies of the elec-

trical conductivity at different frequencies, the electrical conductivity dispersion is revealed. The electrical conductivity increases with frequency (Fig. 5), and the dispersion decreases with temperature.

4. Conclusion

Compositional studies of $(\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ superionic glasses with $x = 0.3 - 0.9$ were carried out. Temperature measurements of transmittance at fixed wavelength (850 nm) show a sharp decrease of transparency down to zero at $T > 440 - 450$ K. Cooling of the glass does not lead to recovery in transparency. SEM studies of $\text{Ag}_3\text{AsS}_3)_x(\text{As}_2\text{S}_3)_{1-x}$ glasses heated above 450 K and cooled down to 293 K show the formation of nanostructures on the glass surface. The appearance of the surface layer with the nanostructures is responsible for the sharp decrease in optical transparency and an increase in electrical conductivity. The compositional dependence of the electrical conductivity exhibits a maximum at $x = 0.5$. The most noticeable change in the activation energy (a decrease by a quarter) is observed between $x = 0.4$ and 0.5.

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