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Optical absorption edge in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ superionic glasses

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Abstract. The spectrometric studies of optical absorption edge in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ superionic glasses were carried out within the temperature range 77 to 400 K. The influence of temperature and composition on the optical absorption edge, parameters of the Urbach absorption edge, parameters of electron-phonon interaction as well as ordering-disordering processes in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ superionic glasses are studied.

Keywords: superionic glass, absorption edge, Urbach rule, electron-phonon interaction.

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1. Introduction

Chalcogenide glasses are of a great interest at a development of new solid electrolytes because of the high values of their electrical conductivity in comparison with oxide glasses [1]. One has to note that these highly conductive glasses are transparent in the IR region, which is very useful for the creation of functional elements for optical devices. The unique combination of various properties in chalcogenide glasses and a possibility to change functional parameters during modifications, i.e. a change of chemical composition and production technology, influence of external factors, lead to a wide range of their applications in holography and microlithography, systems of information writing and reading, optoelectronics, infrared and nonlinear optics, sensorics, electronic technology, etc. [2-5].

Therefore, ternary As-S-Ag glasses are of a considerable interest. The As-S-Ag glasses were extensively studied, first of all, due to the potential possibility of their application as a solid electrolyte [6, 7]. The nature of electrical conductivity – ionic or electronic – depends mainly on a silver content in the given ternary glasses, which, in its turn, influences the other physical properties. The $As_2S_3 - Ag_3AsS_3$ glasses are practically unstudied yet.

Hence, as alluded to above, the main goals of the paper are as follows: (i) temperature investigation of the optical absorption edge, (ii) studying the temperature behavior peculiarities of optical parameters and (iii) studying the temperature, structural, compositional disordering processes in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ superionic glasses.

2. Experimental

The $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ vitreous alloys were obtained by a vacuum (0.01 Pa) melting of the corresponding mixture of As_2S_3 and Ag_3AsS_3 components, which were synthesized beforehand from highly pure elemental substances. The melt homogenization temperature was 820-840 K with the homogenization time 24 hours. The melt was mixed periodically and thereafter quenched in the ice water (273 K).

Spectrometric studies of the optical absorption edge were carried out within the temperature range 77 to 400 K using LOMO KSVU-23 grating monochromator [8]. For low temperature studies, the cryostat of UTREX type was used, stability and accuracy of temperature measurements were maintained at ±0.5 K. The relative error in determination of the absorption coefficient $\Delta\alpha/\alpha$ did not exceed 10% at $0.3 \le \alpha d \le 3$ [8].

3. Results and discussion

The optical absorption edge of $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ superionic glasses with $x = 0.3\ldots0.6$ was carried out within the temperature range T = 77…400 K. It was revealed that the absorption edge for $(Ag_3AsS_3)_{0.3}(As_2S_3)_{0.7}$ glass was strongly smeared and had an exponential shape. With temperature increase, it shifts towards longer wavelengths without the change of a slope of exponential parts of the absorption edge (Fig. 1a). With Ag_3AsS_3 content increase, the absorption edge gets the Urbach shape. The latter is well seen within the temperature ranges T = 250…400 K for $(Ag_3AsS_3)_{0.4}(As_2S_3)_{0.6}$ glass (Fig. 1b), T = 150…400 K for $(Ag_3AsS_3)_{0.5}(As_2S_3)_{0.5}$ glass (Fig. 1c) and T = 77…400 K for $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ glass (Fig. 1d). In the case of Urbach behavior of the absorption edge, its spectral and temperature dependences are described by the well known relation [9]:

$$\alpha(h\nu, T) = \alpha_0 \cdot \exp\left[\frac{\sigma(h\nu - E_0)}{kT}\right], \qquad (1)$$

where $\sigma = kT / E_U$ is the steepness parameter of the absorption edge, E_U is Urbach energy or the energy width of the exponential absorption edge, α_0 and E_0 are coordinates of the convergence point inherent to the Urbach bundle. For comparison, values of parameters α_0 and E_0 for As_2S_3 and $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses with x = 0.4, 0.5, 0.6 were shown in Table. Hence, with x increase the respective growth of both convergence point coordinates E_0 and α_0 is found to be present.

Parameters of the electron-phonon interaction (EPI) σ_0 and $\hbar\omega_p$ were estimated from the temperature dependences of the absorption edge slope parameter σ (see insets in Fig. 1) by the Mahr equation [10]:

$$\sigma(T) = \sigma_0 \left(\frac{2kT}{\hbar\omega_p}\right) \cdot th\left(\frac{\hbar\omega_p}{2kT}\right), \qquad (2)$$

where $\hbar\omega_p$ is the effective average phonon energy in a

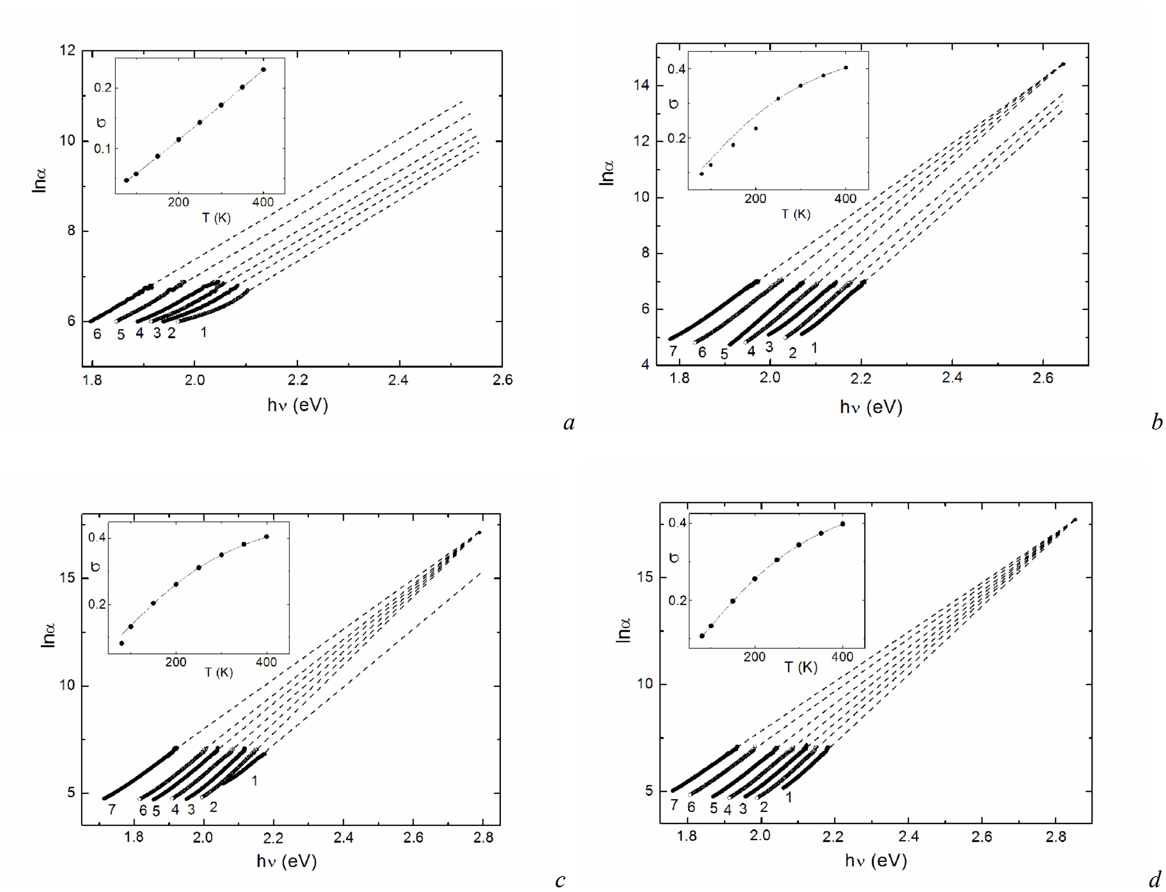

Fig. 1. Spectral dependences of the Urbach absorption edge for $(Ag_3AsS_3)_{0.3}(As_2S_3)_{0.7}$ (*a*), $(Ag_3AsS_3)_{0.4}(As_2S_3)_{0.6}$ (*b*), $(Ag_3AsS_3)_{0.5}(As_2S_3)_{0.5}$ (*c*), and $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ (*d*) glasses at different temperatures: (*a*) 77 K (*1*), 200 (*2*), 250 (*3*), 300 (*4*), 350 (*5*), 400 (*6*); (*b*)-(*d*) 77 K (*1*), 150 (*2*), 200 (*3*), 250 (*4*), 300 (*5*), 350 (*6*), 400 (*7*). Insets show temperature dependences of the absorption edge slope parameter σ.

single-oscillator model, which describes the EPI; σ_0 – parameter, related to the EPI constant g by the relation $\sigma_0 = 2/3g$. The parameters $\hbar\omega_p$ and σ_0 for As_2S_3 and $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses with $x = 0.4, 0.5, 0.6$ are shown in Table.

Fig. 2 illustrates the temperature dependences of the optical pseudogap E_g^* and Urbach energy E_U that are well described for $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses at $x = 0.4, 0.5, 0.6$ within the framework of the Einstein model by equations [11, 12]:

$$E_g^*(T) = E_g^*(0) - S_g^* k\theta_E \left[\frac{1}{\exp(\theta_E/T - 1)}\right], \quad (3)$$

$$E_U = (E_U)_0 + (E_U)_1 \left[\frac{1}{\exp(\theta_E/T - 1)}\right], \quad (4)$$

where $E_g^*(0)$ and S_g^* are the optical pseudogap at $T = 0$ K and a dimensionless constant, respectively; $(E_U)_0$ and $(E_U)_1$ are constants; θ_E is the Einstein temperature corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators. Parameters $E_g^*(0)$, S_g^*, $(E_U)_0$, $(E_U)_1$ and θ_E for $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses with $x =$ 0.4, 0.5, 0.6, obtained from dependences $E_g^*(T)$ and $E_U(T)$, are summarized in Table.

With addition of Ag_3AsS_3 to the glassy matrix As_2S_3 the absorption edge shifts towards longer wavelengths, moreover, the optical pseudogap E_g^* of $(Ag_3AsS_3)_{0.3}(As_2S_3)_{0.7}$ glass decreases by 12% in comparison with As_2S_3 (Fig. 3). At the same time, transition of x from 0.3 to 0.6 makes no change in the E_g^* value (within 1%). Hereby, the Urbach energy E_U increases almost by 3 times in the glass with $x = 0.3$ in contrast to the As_2S_3, and drops down afterwards almost by 2 times and then stays almost unchanged (within 2%) in the range $x = 0.4…0.6$.

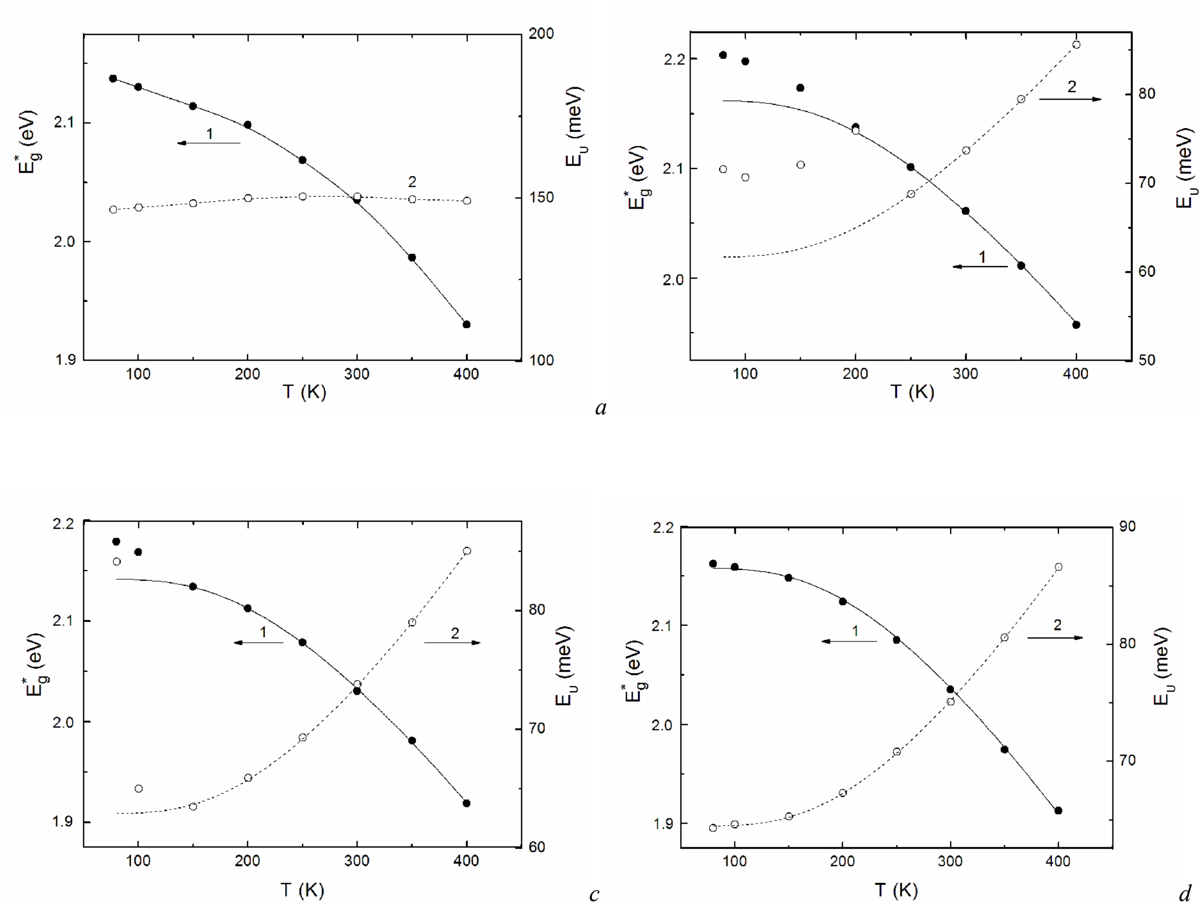

Fig. 2. Temperature dependences of the optical pseudogap E_g^* (*1*) and Urbach energy E_U (*2*) for $(Ag_3AsS_3)_{0.3}(As_2S_3)_{0.7}$ (*a*), $(Ag_3AsS_3)_{0.4}(As_2S_3)_{0.6}$ (*b*), $(Ag_3AsS_3)_{0.5}(As_2S_3)_{0.5}$ (*c*), and $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ (*d*) glasses.

Table. Parameters of the Urbach absorption edge and EPI for As_2S_3 ($x = 0$) and $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses ($x = 0.3…0.6$).

Glass	As_2S_3	$x = 0.3$	$x = 0.4$	$x = 0.5$	$x = 0.6$
α_0 (cm^{-1})	2.97×10^5	–	2.61×10^6	2.78×10^7	4.86×10^7
E_0 (eV)	2.605	–	2.644	2.790	2.853
E_g^* (eV)	2.323	2.035	2.061	2.030	2.035
E_U (meV)	51.0	150.5	73.7	73.8	75.1
σ_0	0.625	–	0.507	0.521	0.514
$\hbar\omega_p$ (meV)	43.9	–	62.6	65.6	66.3
θ_E (K)	510	–	726	761	769
$(E_U)_0$ (meV)	35.1	–	61.7	62.9	64.5
$(E_U)_1$ (meV)	70.7	–	123.3	126.1	129.1
$E_g^*(0)$ (eV)	2.395	–	2.163	2.142	2.158
S_g^*	7.6	–	16.9	19.3	21.9

Compositional studies reveal the reduction of the parameter σ_0 almost by 20% with x in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses. Furthermore, as x increases from 0.4 to 0.6, the value σ_0 slightly changes (within 1%) (Fig. 4). Like to As_2S_3 glass, $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses of the given ternary system have the parameter $\sigma_0 < 1$, which is an evidence of a strong EPI. Thus, with addition of Ag_3AsS_3 to As_2S_3, strengthening the EPI (i.e. decrease of the σ_0 value) is apparent, whereas the effective phonon energy substantially expands by 43% as compared with As_2S_3 and also increases with x (Fig. 4).

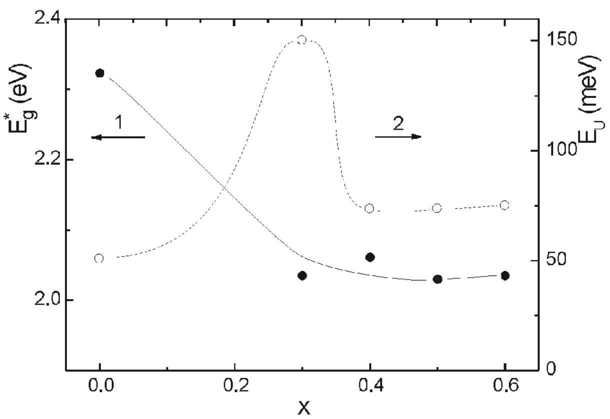

Fig. 3. Compositional dependences of the optical pseudogap E_g^* (*1*) and Urbach energy E_U (*2*) for $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses.

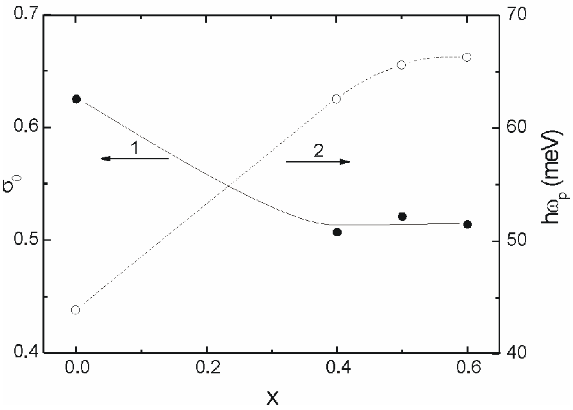

Fig. 4. Compositional dependences of the parameter σ_0 (*1*) and effective phonon energy $\hbar\omega_p$ (*2*) for $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses.

We note that besides the temperature and structural types of disordering (caused by thermal vibrations of atoms and structural elements on the one hand, and by defects and impurities of a structure and absence of a long-range order in atomic arrangement on the other hand), $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses have additionally manifested compositional one caused by addition of Ag_3AsS_3 into As_2S_3. According to [13], the effects of an influence of different types of disordering on the Urbach energy in solid solution are described by the relation

$$E_U = (E_U)_X + (E_U)_T + (E_U)_C = (E_U)_{X,C} + (E_U)_T , \quad (5)$$

where $(E_U)_X$ and $(E_U)_C$ are contributions of structural and compositional disordering to the Urbach energy E_U, respectively; $(E_U)_T$ is a contribution of temperature disordering to E_U. Comparison of two equations (4) and (5) evidences that $(E_U)_{X,C} \equiv (E_U)_0$ and $(E_U)_T \equiv (E_U)_1 / (\exp(\theta_E/T) - 1)$. Thus, the contributions of temperature independent $(E_U)_{X,C}$ (structural and compositional) and temperature dependent $(E_U)_T$ disordering were differentiated. Their compositional dependences are shown in Fig. 5. It is seen that $(E_U)_{X,C}$ contribution is prevailing and for As_2S_3 turns out to be 69% of the E_U value. With addition of Ag_3AsS_3 the $(E_U)_{X,C}$ contribution grows up to 84% for $x = 0.3$, and then increases for a bit with x growth (the contribution $(E_U)_{X,C}$ to E_U for $x = 0.6$ is equal to 86%).

Consequently, smearing the absorption edge at $T = 300$ K with an Ag_3AsS_3 content increase in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses occurs mostly due to temperature independent types of disordering, or, in other words, is determined by contributions of structural and compositional disordering (Fig. 5).

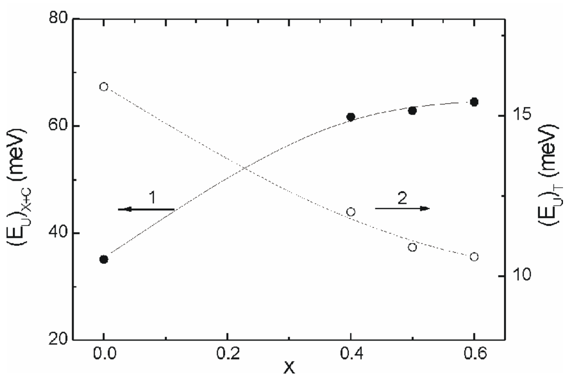

Fig. 5. Compositional dependences of contributions of temperature independent $(E_U)_{X,C}$ (*1*) and temperature dependent $(E_U)_T$ (*2*) types of disordering for $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses.

4. Conclusions

It has been shown in this paper that the absorption edge for $(Ag_3AsS_3)_{0.3}(As_2S_3)_{0.7}$ glass is strongly smeared and has an exponential shape. With temperature increase the exponential part of the absorption edge shifts towards longer wavelengths, while their slope remains unchanged. With x increasing the absorption edge becomes of the Urbach shape and keeps it in the following temperature ranges: T = 250…400 K for $(Ag_3AsS_3)_{0.4}(As_2S_3)_{0.6}$ glass, at T = 150…400 K for $(Ag_3AsS_3)_{0.5}(As_2S_3)_{0.5}$ glass, and at T = 77…400 K for $(Ag_3AsS_3)_{0.6}(As_2S_3)_{0.4}$ glass.

Parameters of electron-phonon interaction are obtained from temperature dependences of the absorption edge slope parameter σ. It was found that with addition of Ag_3AsS_3 to As_2S_3 EPI becomes stronger, i.e. the value σ decreases, whereas the effective phonon energy increases by 43% as compared with pure As_2S_3.

Temperature dependences of such parameters inherent to the Urbach absorption edge as the optical pseudogap E_g^* and Urbach energy E_U are well described within the framework of the Einstein model. With Ag_3AsS_3 content increase, one can observe a nonlinear decrease of E_g^*. Moreover, the Urbach energy E_U grows by almost three times in the glass with x = 0.3 in comparison with As_2S_3, and then decreases by almost two times and subsequently remains almost unchanged (within 2%) in the compositional range x = 0.4…0.6.

The contributions of the temperature independent (i.e. structural and compositional) and temperature dependent disordering to the Urbach energy were estimated. It turns out that, with Ag_3AsS_3 content increase in $(Ag_3AsS_3)_x(As_2S_3)_{1-x}$ glasses, smearing the absorption edge takes place mostly due to the temperature independent types of disordering.

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