

TEMPERATURE STUDIES OF OPTICAL ABSORPTION EDGE IN $(Ag_2S)_x(As_2S_3)_{1-x}$ ($x < 0.2$) SUPERIONIC GLASSES

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ABSTRACT

Synthesis of $(Ag_2S)_x(As_2S_3)_{1-x}$ superionic glasses for $x < 0.2$ are carried out. The spectrometric studies of optical absorption edge in $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses are performed in the temperature range 77-390 K. Optical absorption edge of $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses with addition of Ag_2S is strongly smeared and has an exponential shape. The influence of temperature and composition on the absorption edge behavior, parameters of optical absorption edge and electron-phonon interaction as well as ordering-disordering processes in $(Ag_2S)_x(As_2S_3)_{1-x}$ superionic glasses are studied.

EXPERIMENTAL RESULTS

Absorption edge studies of $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass have revealed two temperature ranges: a range of "parallel" red shift of the exponential absorption edge within the temperature interval $77 K \leq T < 300 K$ and a range of the Urbach behaviour of the absorption edge at $T \geq 300 K$, in which the dependence of absorption coefficient on the photon energy and temperature is given by the Urbach rule (Fig.1). The Urbach behaviour of the absorption edge is well described by the relation:

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

where $s = kT / E_U$ is the steepness parameter of the absorption edge, E_U is the Urbach energy (energy width of exponential absorption edge), α_0 and E_0 are coordinates of the convergence point of Urbach bundle. For comparison, values of parameters α_0 and E_0 for As_2S_3 and $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glasses were listed in Table 1. It is shown that with Ag_2S content increase an enhancement of the convergence point coordinates α_0 and E_0 is observed.

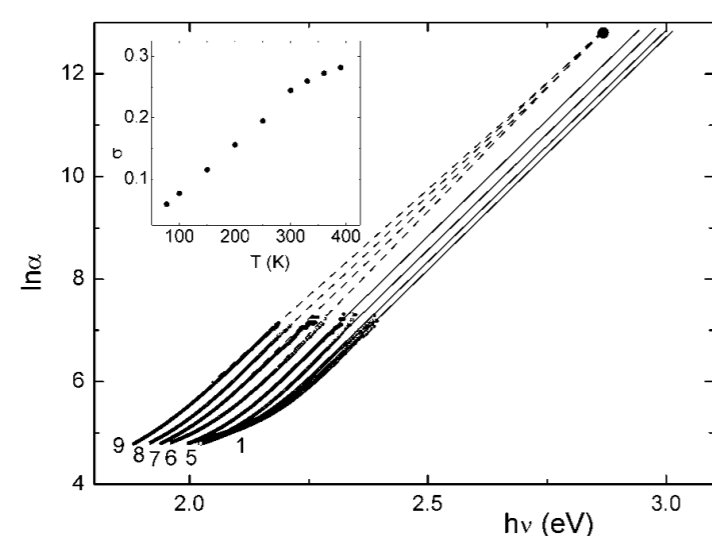


Fig. 1. Spectral dependences of the Urbach absorption edge for $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass at various temperatures: (1) 77, (2) 100, (3) 150, (4) 200, (5) 250, (6) 300, (7) 330, (8) 360 and (9) 390 K. The insert shows the temperature dependence of steepness parameter.

Parameters of the electron-phonon interaction (EPI) s_0 and $\hbar\omega_p$ were derived from the temperature dependences of the absorption edge slope parameter s (see insert in Fig. 1) by the equation [12, 13]:

$$\sigma(T) = s_0 \cdot \left(\frac{2kT}{\hbar\omega_p} \right) \cdot \tanh\left(\frac{\hbar\omega_p}{2kT} \right)$$

where: $\hbar\omega_p$ is the effective phonon energy in a single-oscillator model, describing the electron-phonon interaction (EPI), and s_0 is a parameter related to the EPI constant g as $s_0 = (2/3)g^{-1}$ (parameters $\hbar\omega_p$ and s_0 are given in Table 1). The parameters $\hbar\omega_p$ and s_0 for As_2S_3 and $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass are listed in Table 1. It is shown that for the $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass the parameter $s_0 < 1$, which is an evidence of a strong EPI. Thus, with addition of Ag_2S to As_2S_3 a strengthening of the EPI (i.e. decrease of the s_0 value) is revealed, whereas the effective phonon energy grows by 57% as compared with As_2S_3 (Table 1).

Table 1. Parameters of the Urbach absorption edge and parameters of EPI for $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses

Compound	As_2S_3	$(Ag_2S)_{0.05}(As_2S_3)_{0.95}$	$(Ag_2S)_{0.1}(As_2S_3)_{0.9}$	$(Ag_2S)_{0.15}(As_2S_3)_{0.85}$
α_0 (cm^{-1})	2.97×10^5	3.61×10^5		
E_0 (eV)	2.605	2.868		
E_g^* (300 K) (eV)	2.323	2.252	1.932	1.6640
E_U (300K) (meV)	51.0	105.8	437.7	452.4
σ_0	0.63	0.374		
$\hbar\omega_p$ (meV)	43.9	68.7		
θ_E (K)	510	797		
$(E_U)_0$ (meV)	35.1	91.7		
$(E_U)_1$ (meV)	70.7	183.8		
$E_g^*(0)$ (eV)	2.395	2.342		
S_g^*	7.6	17.5		

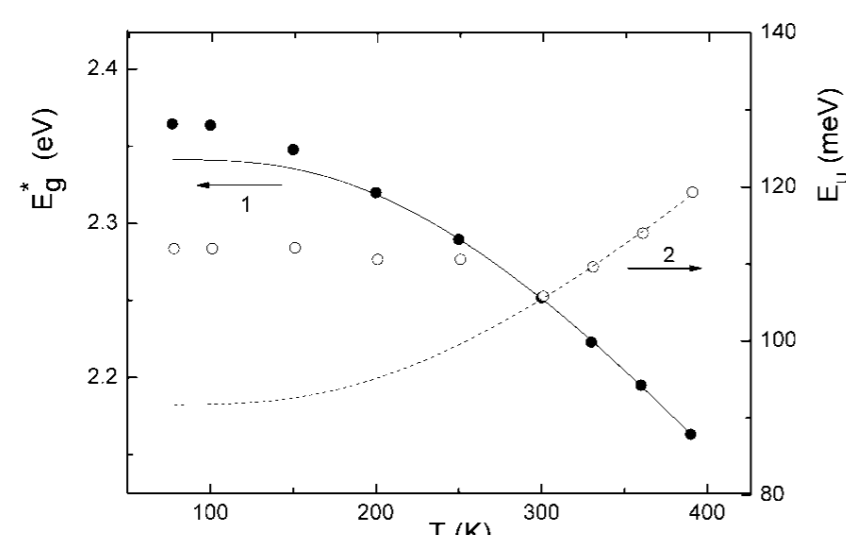


Fig. 2. Temperature dependences of optical pseudogap E_g^* (1) and Urbach energy E_U (2) of $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass: circles – experiment, curves – calculations.

Figure 2 illustrates the temperature dependences of the optical pseudogap E_g^* (spectral position of absorption edge at fixed value of absorption coefficient $\alpha = 10^3 cm^{-1}$) and Urbach energy E_U , which are well described in the temperature range of the Urbach behaviour by the equations [14, 15, 16]:

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

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

where $E_g^*(0)$ and S_g^* are the energy pseudogap at 0 K and a dimensionless constant, respectively; q_E is Einstein temperature, corresponding to the average frequency of phonon excitations of a system of non-coupled oscillators, $(E_U)_0$ and $(E_U)_1$ are constants. The obtained $E_g^*(0)$, S_g^* , q_E , $(E_U)_0$, and $(E_U)_1$ parameters for $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass are given in Table 1.

Temperature studies of the optical absorption edge in $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glasses showed that in the temperature interval $77 K \leq T \leq 390 K$ a red shift of the exponential absorption edge is observed with the temperature increase. The Urbach energy for $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ glass in the temperature interval $77 K \leq T < 300 K$ decreases, while at $T \geq 300 K$ remains unchanged; the Urbach energy for $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glass in the temperature interval under investigation is a constant value (Fig.3). The non-Urbach behaviour of the optical absorption edge in $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glasses can be explained using the formalism of separation of the contributions from static and dynamical structural disordering types. It is shown that in the temperature interval under investigation only the short-range order in the atomic arrangement $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glasses is present. With the temperature increase, the medium-range order is gradually established, resulting in a decrease of dynamic structural disordering contribution $(E_U)_{X,dyn}$. The decrease of $(E_U)_{X,dyn}$ along with the increasing contribution of the temperature-related disordering $(E_U)_T$ at the constant contribution of static structural disordering contribution $(E_U)_{X,stat}$ results in a temperature independence of the Urbach energy in the $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glasses.

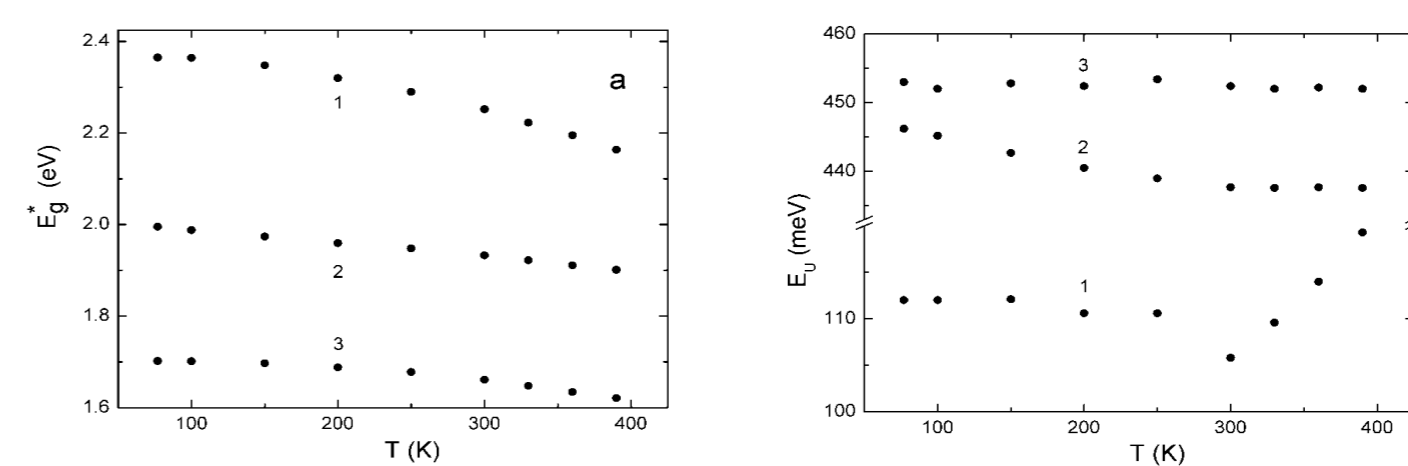


Fig. 3. Temperature dependences of optical pseudogap (a) and Urbach energy (b) for $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ (1), $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ (2) and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ (3) glasses.

Compositional studies of $(Ag_2S)_x(As_2S_3)_{1-x}$ superionic glasses showed that with increasing of Ag_2S content the optical absorption edge is shifted to the low-energy range and strongly smears (Fig.4). The nonlinear decrease of E_g^* as well as the sharp increase of Urbach energy (almost into 4 times) is observed at the transition from $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ to $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ (Fig.5).

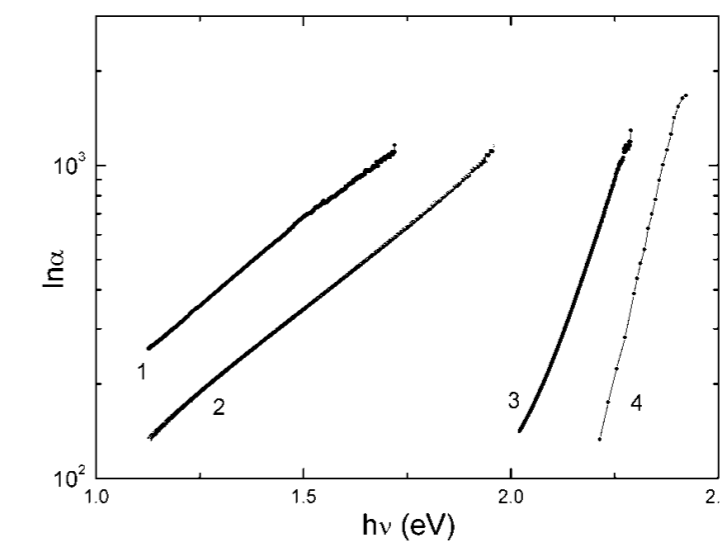


Fig. 4. Spectral dependences of the absorption edge for As_2S_3 (1), $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ (2), $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ (3) and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ (4) glasses at temperature $T = 300 K$.

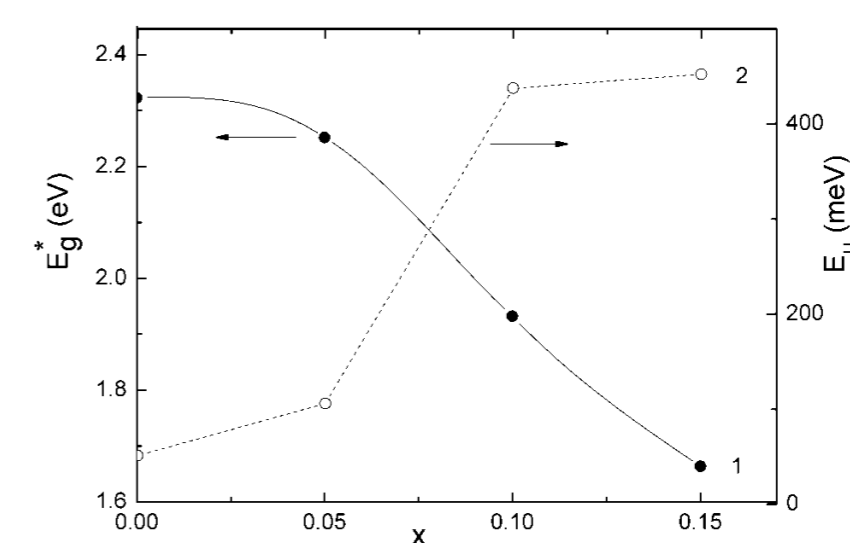


Fig. 5. Compositional dependences of optical pseudogap (1) and Urbach energy (2) for $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses.

It should be noted that besides the temperature and structural disordering in $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses the compositional disordering, caused by the addition of Ag_2S to As_2S_3 , is realized. The structural disordering in glasses under investigations is caused by (i) the thermal vibrations of atoms and structural elements, and (ii) by the defects and impurities of a structure and absence of a long-range order in an atomic arrangement. According to [17], the effects of different types of disordering influence on the Urbach energy in solid solution are described by the relation

$$E_U = (E_U)_T + (E_U)_X + (E_U)_C = (E_U)_T + (E_U)_{X+C}$$

where $(E_U)_T$, $(E_U)_X$ and $(E_U)_C$ are the contributions of temperature, structural and compositional disordering to (E_U) , respectively. It is seen from Eqs. (5) and (6) that $(E_U)_{X,C} \equiv (E_U)_0$ and $(E_U)_T \equiv (E_U)_1 / (\exp(\theta_E/T) - 1)$. For the estimation of the contribution of the different types of disordering into Urbach energy E_U we used the procedure described in Ref. [18, 19, 20]. Thus, the contributions of temperature in dependent $(E_U)_{X,C}$ (structural and compositional) and temperature dependent $(E_U)_T$ disordering were calculated. It is shown that with addition of Ag_2S the contribution of the sum of structural and compositional disordering into the Urbach energy grows up from 69% to 87% for $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass.

CONCLUSIONS

It has been shown that with addition of Ag_2S the absorption edge of $(Ag_2S)_x(As_2S_3)_{1-x}$ glasses is strongly smeared and has an exponential shape. For $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass two regions of absorption edge temperature behaviour were revealed: a range of "parallel" red shift of the exponential absorption edge within the temperature interval $77 K \leq T < 300 K$ and a range of the Urbach behaviour of the absorption edge at $T \geq 300 K$; for $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$ and $(Ag_2S)_{0.15}(As_2S_3)_{0.85}$ glasses in the temperature interval $77 K \leq T \leq 390 K$ a red shift of the exponential absorption edge is observed with the temperature increase. It was found out that with addition of Ag_2S to As_2S_3 the EPI becomes stronger, whereas the effective phonon energy in $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass increases by 57% comparing with pure As_2S_3 . With Ag_2S content increase one can observe a nonlinear decrease of E_g^* . Moreover, the Urbach energy E_U grows by almost four times at the transition from $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ to $(Ag_2S)_{0.1}(As_2S_3)_{0.9}$. The contributions of the temperature independent (i.e. structural and compositional) and temperature dependent disordering to the Urbach energy were estimated for $(Ag_2S)_{0.05}(As_2S_3)_{0.95}$ glass.