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OPTICAL ABSORPTION EDGE AND STRUCTURAL DISORDER IN ELECTRON-IRRADIATED As_2S_3 CHALCOGENIDE GLASSES

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Temperature behaviour of optical absorption edge in non-irradiated and electron-irradiated As_2S_3 chalcogenide glasses is studied. The parallel shift of the absorption edge, revealed in the temperature range $77 \le T \le 250$ K, is explained by the temperature variation of dynamical structural disordering due to the absence of the intermediate-range order of atoms. The effect of the irradiation dose on the temperature dependences of the Urbach edge parameters is analyzed.

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1. Introduction

Though optical properties of chalcogenide glasses As_2X_3 (X = S, Se) have been the object of studies for several decades since these materials are characterized by high transparency in near and medium infrared range and used as active or passive elements in optical devices [1], the investigation of their behaviour under external factors, especially irradiation, still remains an important task of today. It is emphasized [2–8] that noticeable changes in the properties of As_2X_3 (X = S, Se) glasses due to gamma- and electron irradiation with the energy $E<2.0$ MeV are revealed at the doses $\Phi \ge 10^5$ Gy. The increase of microhardness, red shift of the absorption edge, decrease of its steepness, darkening in the near infrared range are observed [2,3]. These radiation-stimulated changes of the properties of the glasses are determined by the processes of destruction-polymerization transformations, radiation-induced oxidation and radiation defect formation. The first process is related to the transformation of the main structural fragments of the matrix and the appearance of new quasistable structures due to the formation of interlayer bonds; the second one consists in the interaction of the intrinsic fragments of the glass and atmospheric oxygen; the third one is the variation of concentration of diamagnetic charged centres (over- and undercoordinated atoms), their transformation and formation of new types of diamagnetic defects.

Here we report the studies of the effect of electron irradiation and the resulting structural disordering on the absorption edge parameters of As_2S_3 chalcogenide glasses.

2. Experimental

The irradiation of the sample was carried out at room temperature with electrons of the average energy 1.2 MeV; the radiation source was SrY-16 with the activity of 12.2 Curie and the flux density of 10^{11} electrons/($cm^2 \cdot s$). The spectral dependences of the optical absorption edge were

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studied in the temperature interval 77–380 K using a LOMO MDR-3 lattice monochromator. The absorption coefficient α as a function of transmittance T and reflection of the surface R were calculated using the well known formula [9]:

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T}\right]^2 + R^2}\right\} \tag{1}$$

where d denotes the plane-parallel sample thickness. The relative error in the absorbance measurements $\Delta\alpha/\alpha$ did not exceed 10% at $0.3 \le \alpha d \le 3$ [10]. For the low-temperature measurements an UTREX cryostat was applied, the temperature being stabilized within 0.1 K.

3. Results and discussion

The temperature studies of the absorption edge have shown that in non-irradiated [11] and irradiated As_2S_3 glasses its shape is exponential. The temperature behaviour of the absorption edge has revealed two characteristic temperature intervals: (i) the range of parallel red shift within $77 \le T \le 250$ K; (ii) the range of Urbach behaviour at $T > 250$ K where the spectral and temperature behaviour of the absorption coefficient is described by a known relation [12]

$$\alpha(h\nu, T) = \alpha_o \cdot \exp\left[\frac{h\nu - E_0}{w(T)}\right], \tag{2}$$

where w is the energy width of the exponential absorption edge, α_0 and E_0 are the convergency point coordinates of the Urbach bundle.

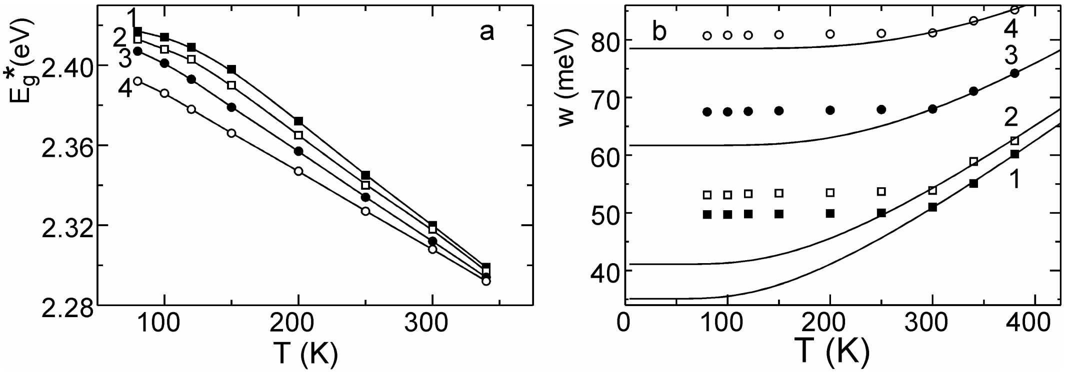

Fig. 1. Temperature dependences of optical pseudogap E_g^* (a) and absorption edge energy width w (b) for non-irradiated (1) and irradiated with 1×10^6 Gy (2), 8×10^6 Gy (3) and 4×10^7 Gy (4) As_2S_3 glasses.

Within the temperature interval $250 < T \le 380$ K the temperature behaviour of such absorption edge parameters as optical pseudogap E_g^* (E_g^* value corresponds to the energy position of the exponential absorption edge at the coefficient value $\alpha = 10^3$ cm^{-1} [7]) and the width w of the absorption edge energy (Fig. 1) is well described in the framework of Einstein model [13,14]

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

$$w = w_0 + w_1\left[\frac{1}{\exp(\theta_E/T)-1}\right], \tag{4}$$

where $E_g^*(0)$ is the energy gap at 0 K, θ_E is the Einstein temperature corresponding to the mean frequency of phonon excitations, S_g^*, w_0 and w_1 are constant values. The parameter values of θ_E, w_0 and w_1, obtained while describing the experimental temperature dependences of w (Fig. 1) by Eq. (4), are listed in Table 1.

Table 1. Urbach absorption edge parameters for non-irradiated and irradiated As_2S_3 glasses.

Sample	non-irradiated	1×10^6 Gy	8×10^6 Gy	4×10^7 Gy
E_g^* (eV) 300 K	2.320	2.318	2.312	2.308
w (meV) 300 K	51.0	53.9	68.0	81.2
$E_g^*(0)$ (eV)	2.395	2.381	2.356	2.339
S_g^*	7.60	7.69	10.82	15.67
θ_E (K)	510	590	907	1209
w_0 (meV)	35.1	41.0	61.7	78.5
w_1 (meV)	70.7	81.1	123.3	157.4

The temperature dependences of the absorption edge energy width w are known to reflect the effect of different types of disordering upon the long-wavelength edge of intrinsic optical absorption [15]:

$$w = k_0(W_T^2 + W_X^2) = w_T + w_X\,, \tag{5}$$

where k_0 is a constant; W_T^2 is the mean-square deviation from the electric potential of the ideally ordered structure, induced by temperature disordering; W_X^2 is the mean-square deviation characterizing structural disordering; w_X and w_T represent the contributions of structural disordering and temperature-related disordering into the absorption edge energy width w. However, in order to explain the parallel shift of the absorption edge in the temperature range $77\leq T\leq 250$ K in non-irradiated As_2S_3 one should consider structural disordering as the total of two constituents – static structural disordering $(w_X)_{stat}$ and dynamical structural disordering $(w_X)_{dyn}$. A similar procedure is effectively applied for such partially disordered systems as superionic conductors which are intermediate between crystalline and glassy solids [16]. In such case Eq. (5) for the absorption edge energy width w will be given by

$$w = w_T + (w_X)_{stat} + (w_X)_{dyn}\,. \tag{6}$$

It should be noted that the contribution of the temperature-related disordering w_T results from the thermal vibrations of atoms, the contribution of the temperature-independent static structural disordering $(w_X)_{stat}$ is due to the absence of the long-range and the presence of only short-range order of atoms, and the contribution of the temperature-dependent dynamical structural disordering $(w_X)_{dyn}$ is caused by the absence of the intermediate-range order. Thus, at low temperatures in the glasses under investigation only short-range order exists, and for increasing temperatures the intermediate-range order is gradually established, resulting in the decrease of $(w_X)_{dyn}$. The decrease of the dynamical structural disordering $(w_X)_{dyn}$ contribution along with the increasing contribution of the temperature-related disordering w_T at the constant contribution of $(w_X)_{stat}$ results in the absorption edge energy width w being temperature-independent (See Eq. (6)) and the parallel shift of the absorption edge. At T>250 K $(w_X)_{dyn}$=0, and the increase of the energy width w of the optical absorption edge is determined by the increase of the temperature-related disordering w_T contribution.

The irradiation studies have shown (Table 1) that electron irradiation results in a slight decrease of the optical pseudogap E_g^* (by 0.012 eV at T=300 K at the maximal irradiation dose $\Phi = 4\times10^7$ Gy) and a substantial increase of the absorption edge energy width w (by ≈30 meV i. e. by ≈ 60 % at T=300 K at the maximum irradiation dose). Using Eqs. (4)-(6) one can estimate the contributions of various types of disordering into absorption edge energy width w in glasses under investigation. The relative contribution of the static structural disordering into the absorption edge smearing increases from 58% at T=380 K in the non-irradiated glass to 92% at the highest irradiation dose.

4. Conclusions

Absorption edge of non-irradiated and electron-irradiated As_2S_3 chalcogenide glasses was studied in the temperature range 77–380 K. The temperature studies have revealed the ranges for the absorption edge parallel red shift at $77\leq T\leq250$ K and Urbach behaviour at T>250 K. The temperature-independent value of the absorption edge energy width w in the temperature interval $77\leq T\leq250$ K is explained by the temperature variation of static structural disordering due to the lack of intermediate-range order of atoms. With the increase of the electron irradiation dose to $\Phi=4\times10^7$ Gy the optical pseudogap E_g^* decreases and the absorption edge energy width w increases. The irradiation-induced additional smearing of the absorption edge is explained by the increased contribution of the static structural disordering into the w value due to radiation defects formation.

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