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OPTICAL CONSTANTS OF ELECTRON-IRRADIATED As_2S_3 CHALCOGENIDE GLASSES

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The effect of electron-irradiation on the optical and refractometric properties of As_2S_3 chalcogenide glasses is studied. Irradiation-induced optical pseudogap shrinkage as well as increase absorption edge energy width, refraction index and molar refraction are revealed. Additional absorption edge smearing is shown to result from the increase of contribution of static structural disordering into the absorption edge energy width, and the refractive index increase is caused by the increase of molar refraction (electron polarizability) due to the radiation-induced changes.

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1. Introduction

Investigation of optical constants of As_2X_3 (X = S, Se) chalcogenide glasses under external factors, especially irradiation, is of essential interest due to their applications in dosimetry [1–4]. It is emphasized [1–4] that noticeable changes in the properties of As_2X_3 (X = S, Se) glasses due to gamma- and electron irradiation with the energy below 2.0 MeV are revealed at the doses above 10^5 Gy. Increase of microhardness, red shift of the absorption edge, decrease of its steepness, darkening in the near infrared range were observed.

The present paper follows the earlier papers [5, 6] in the all-round studies of radiation-stimulated structural and chemical changes, changes of optical and refractometric parameters in chalcogenide glasses under high-energy electrons. Earlier we have studied the electron irradiation effect on the processes of structural and temperature-related disordering in the range of the fundamental absorption edge in glassy As_2S_3. For optical materials, besides the optical pseudogap, such refractometric parameters as refractive index n and its dispersion $n(\lambda)$ are very important [7, 8].

Thus, here we report on the studies of the effect of electron irradiation on the optical constants of As_2S_3 chalcogenide glasses, namely the optical pseudogap and the refractive index. Besides, in order to determine the molar refraction M the measurements of density ρ against the high-energy electron fluence were required.

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 studied at 300 K using a LOMO MDR-3 lattice monochromator. The absorption coefficient α as a

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function of transmittance T and reflection of the surface R was 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 refractive index investigation at room temperature we used the method of normal incidence on the prism constructed from the As_2S_3 glass [11]. The dimensions of the refracting faces were 5×10 mm^2; the angle between them was measured with a LOMO GS-1.5 goniometr with a precision of 10″, and the sample density was determined by hydrostatic weighting in toluene (±0.05%). The maximum absolute error in measuring n was not larger than $\pm2\times10^{-4}$.

3. Results and discussion

The temperature studies of the absorption edge have shown that in non-irradiated and irradiated As_2S_3 glasses its shape is exponential [5, 6]. The temperature behaviour of the absorption edge has revealed two characteristic temperature intervals: (i) the range of parallel red shift within $77\le T\le250$ K; (ii) the range of Urbach behaviour at $T>250$ K.

The studies of the irradiated samples have shown (Fig. 1) that electron irradiation results in a slight decrease of the optical pseudogap E_g^* (by 0.012 eV at the maximal irradiation dose $\Phi=1.8\times10^{17}$ cm^{-2}) and a substantial increase of the absorption edge energy width w (by ≈30 meV i. e. by ≈ 60 % at the maximal irradiation dose). It should be noted that E_g^* value corresponds to the energy position of the exponential absorption edge at the coefficient value $\alpha=10^3$ cm^{-1} [9]. Using the procedure, described in [6], one can estimate the contributions of various types of disordering into the absorption edge energy width w in the electron-irradiated glasses under investigation. It has been shown [6] that the absorption edge energy width w is given by

$$w = w_T + (w_X)_{stat} + (w_X)_{dyn}\,. \tag{2}$$

where 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. The performed analysis has shown that 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.

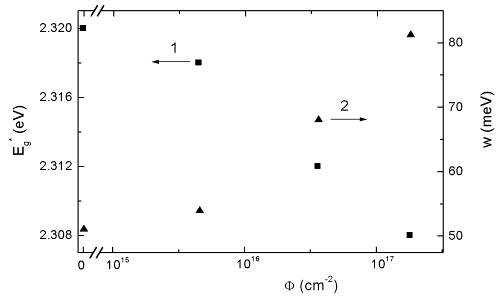

Fig. 1. Dose dependences of optical pseudogap E_g^* (1) and absorption edge energy width w (2) at T = 300 K for As_2S_3 glasses.

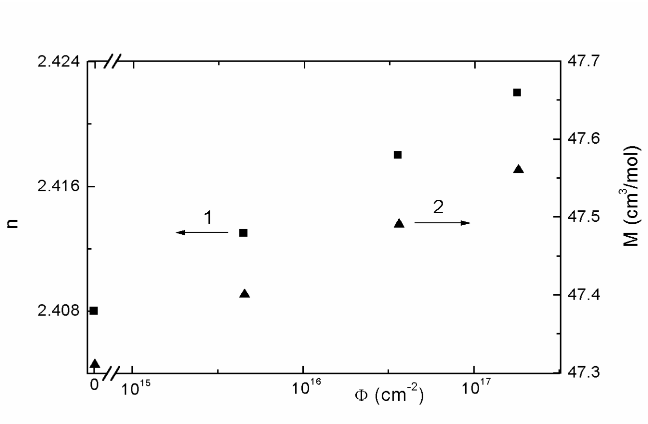

Fig. 2. Dose dependences of refractive index n (1) and molar refraction M (2) at T=295 K and λ=5 μm for As_2S_3 glasses.

We proceed with the electron irradiation effect on the refractometric parameters of As_2S_3 glasses. The refractometric parameters (n, ρ) and specific refraction r are known to be related as

$$F(n) = r \cdot \rho, \quad (3)$$

where $F(n)$ is the function of the refractive index expressed by Lorentz-Lorenz, Gladstone-Dale, Drude formulae [12, 13]. From Eq. (3), the expression for the dose rate of the refractive index can be given by

$$\partial n/\partial \Phi = [\partial F(n)/\partial n]^{-1}(r\cdot \partial\rho/\partial\Phi + \rho\cdot \partial r/\partial\Phi) . \quad (4)$$

For glasses the Lorentz-Lorenz model is theoretically more substantiated where the correction for the local field is taken into account [14]. Since under electron irradiation in the fluence range $\Phi=10^5$–$10^7 cm^{-2}$ the density was the same within the experimental error, the expression in Eq. (4) is simplified:

$$\partial n/\partial \Phi = [(n^2 + 2)(n^2 - 1) / 6n\rho] (\rho\cdot \partial r/\partial\Phi) . \quad (5)$$

Thus, the dose rate of the refractive index of the glass will be determined by the variation of its electronic polarizability under irradiation. Fig. 2 shows the dose dependences of the refractive index n and molar refraction M at the wavelength λ= 5 μm. It is seen that the increase of the high-energy electron fluence results in the increase of both the refractive index and the molar refraction. The latter is determined as $M=r\cdot\mu$, μ being the molar mass, and is the sum of covalent refractions of As and S, i. e. $M=2M_{As}+3M_S$. According to [13], only refractions of small cations can be considered constant, while polarizabilities of larger cations and all anions considerably vary and, taking into account the small contribution of the As refraction in the M value of the As_2S_3 glass (not exceeding 10%), it can be assumed that the effect of $n(\Phi)$ variation is mostly determined by the effect of electron irradiation on the sulphur refraction. Such variation of polarizability can be related both to topological reorientation of the pre-irradiation defects in the form of so-called variable-valence pairs, including switching of rigid covalent bonds, and to the electron-induced formation of new defects [15].

4. Conclusions

Optical absorption edge and refractive index dispersion of high-energy electron-irradiated As_2S_3 chalcogenide glass have been studied. The electron fluence increase is shown to result in the absorption edge shift towards longer wavelengths and smearing due to the effect of structural disordering induced by radiation defect formation. The increase of the refractive index with the high-energy electron fluence is related to the increase of the molar refraction (electronic polarizability) due to the changes in As_2S_3 glass caused by irradiation.

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