SOLID MATTER

ELECTRON-INDUCED CHANGES OF OPTICO-REFRACTOMETRIC PARAMETERS OF GLASSY ALLOYS OF THE Sb_2S_3–GeS_2 SYSTEM

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The effect of electron irradiation on the change of optico-refractometric parameters of chalcogenide glassy alloys of the Ge–Sb–S system in the Sb_2S_3–GeS_2 section is studied. The composition dependences of the electron-induced effects in the investigated system are analyzed. The obtained results are interpreted in the framework of the model of "switching" of homogeneous and heterogeneous chemical bonds of the matrix of chalcogenide glassy semiconductors.

1. Introduction

Chalcogenide glassy semiconductors (CGS) represent promising materials for optical instrument engineering of the mid- and far-infrared bands. They are characterized by a high transparency and chemical and radiation resistances and also provide the possibility to synthesize materials with a wide range of physical-chemical and optical parameters by means of changing the type and the quantitative relation between the cation and anion components in alloys.

The study of radiation-induced changes (RIC) of physical-chemical and optical parameters of CGSs is called for by the search for optimal active media for applications in optoelectronics in devices for the transmission and the storage of information, sensitive elements of industrial solid-body dosimetric systems, etc. Investigations of the physical essence of the processes running on the micro- and macrolevels under radiation loadings enable one to purposefully search for radiation-resistant materials and to modify their properties. These researches are also important for the development of controlled technological processes of synthesis of CGSs with preassigned functional parameters and for the consistent understanding of the nature of radiation- and photoinduced structural transformations in them.

Thus, the purpose of this work was to study the composition behavior of electron-induced changes of optical-refractometric parameters of glassy alloys of the Ge–Sb–S system in the section $(GeS_2)_{100-x}$ $(Sb_2S_3)_x$, $x = 0$–50 moles.%.

2. Experimental Part

The glass formation in the Ge–Sb–S system was investigated in a number of works [1–3]. The glasses were synthesized by means of the direct alloying of elementary components in the corresponding proportions. The initial components were elementary Ge with a specific resistance not lower than 50 Ohm·cm and Sb and S with a purity not worse than B6. We used the technique of two-temperature synthesis, where the ampoules with weights were first heated to 820–850 K with a rate of 3–4 K/min and after that were kept at these temperatures for 12–15 h. Then the ampoules were heated with a rate of 1–3 K/min to temperatures exceeding the melting temperature of the weights by 20–30 K, and the alloy was kept at these temperatures for 15–20 h. The synthesized glassy ingots were annealed during several hours at a temperature by 20—30 degrees lower than the temperature of glass formation in order to remove residual stresses that inevitably arise during the hardening of the alloy. The absence of crystalline inclusions and crystallization regions is confirmed by the typical conchoidal fracture obtained for ingots of all compositions and the results of the X-ray phase (DRON 4-3, CuK_α-radiation) and microstructure (MMU microscope) analyses.
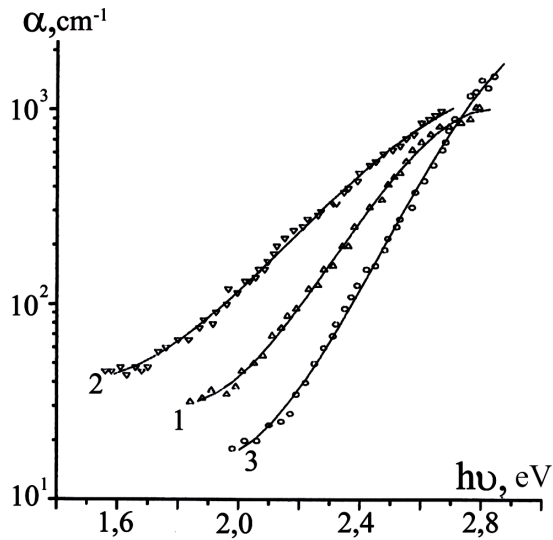
Fig. 1. Absorption edge α of glassy $(GeS_2)_{0.5}$–$(Sb_2S_3)_{0.5}$ before irradiation (*1*), after irradiation (*2*), and after annealing (*3*)

Optical investigations of the absorption spectra were carried out with the help of an MDR-3 diffraction monochromator. The spectral dependences of the absorption coefficient $\alpha(h\nu)$ were obtained from the experimental studies of transmission and reflectance using the technique and the set-up described in [4]. The samples under study had various thicknesses ($d = 40 \div 150~\mu m$), the error of determination of the absorption coefficient $\Delta\alpha/\alpha < 10\%$ at $1 \leq \alpha d \leq 3$. The refractive index was measured using the prism method. The size of the refracting prism faces was equal to 10×12 mm, while the angle between them amounted to $11 \div 13°$. The error of determination of the refractive index for the whole investigated region equaled 2×10^{-4}.

The chalcogenide glasses of the Ge–Sb–S system were irradiated using an M-10 microtron with an energy of accelerated electrons of 5 MeV and an electron flux density of 10^{11} electrons·cm^{-2}·s^{-1}, which allowed us to reach the particle flux onto the irradiated area in the range $10^{17} \div 10^{18}$ electrons·cm^{-2}. The energy homogeneity of the electron beam amounted to 0.05%, whereas the heterogeneity of the irradiation field did not exceed 8–10%. Samples of various compositions were fixed at a special holder and were simultaneously irradiated by a uniform electron beam.

The mean coordination number Z was calculated according to the relation

$$Z = (4x + 3y + 2z)/100, \tag{1}$$

where x, y, and z stand for the atomic (molecular) fractions of Ge, S, and Sb, respectively; 4, 3, and 2 denote their coordination numbers in the covalently bonded skeleton. The quantitative description of the RICs was performed using the relative change of the quantity $\Delta T(\lambda)$ or $\Delta\alpha(h\nu)$, that is the difference between the optical transmission (absorption) coefficients of the probe radiation at a fixed wavelength before and after the irradiation.

3. Experimental Results and Their Discussion

The performed experimental researches of the fundamental absorption edge of pure and irradiated glasses of the Ge–Sb–S system have demonstrated that the spectral dependence of the absorption coefficient is exponential. That is why we analyzed the obtained results using the relation [1, 5, 6]

$$\alpha(h\nu) = \alpha_0 \frac{h\nu - E_g^*}{E_0(T, X)}, \tag{2}$$

where E_g^* is the optical pseudogap corresponding to the energy position of the absorption edge at the fixed absorption level $\alpha_0 = 10^3$ cm^{-1}, $E_0(X, T)$ is the energy width of the exponential tail determined by the composition (X) and temperature (T) disorders.

Considering that $E_0(T, X)$ includes contributions of different types of disorder and separating them, we can write

$$E_0(T, X) = E_0(T) + E_0(X), \tag{3}$$

where $E_0(T)$ is the temperature disorder caused by the strong phonon anharmonicity, and $E_0(X)$ is the static structural disorder that can be presented as follows:

$$E_0(X) = E_0(X_0) + E_0(X'). \tag{4}$$

Here, $E_0(X_0)$ corresponds to the structural disorder of the "ideal" glass and $E_0(X')$ stands for the induced structural disorder due to radiation, technological and other loadings. In our case, $E(X')$ denotes the additional structural disorder induced by the electron irradiation of the samples. The temperature-independent term in formula (2) is present only in the expression for the absorption edge of amorphous and heavily doped materials [1, 6].

Figure 1 shows the fundamental absorption edges of the nonirradiated, annealed, and irradiated at 300 K (after the annealing) samples of $(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$ glass. Due to the action of electron irradiation, one observes

a long-wavelength shift of the edge and an increase of its energy width (Fig. 1, curve *2*). In the annealed samples, the radiation-induced shift of the absorption edge grows (Fig. 1, curve *3*). This is related to the fact that the absorption edge of the annealed samples is shifted to the short-wavelength region due to the absence of internal stresses and a more uniform distribution of the components as compared to the nonannealed samples. The temperature dependence of the slope of the fundamental absorption edge in the temperature range 80–300 K is inessential. The parameters of the edges for Sb_2S_3 and $(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$ glasses are listed in Table 1.

The presented experimental data and the analysis of the literature data [7–18] allow one to consider that the changes of physical properties of CGS glasses induced under the action of high-energy electron fluxes depend on the parameters of the radiation loading (dose, dose power, temperature in the source channel) and the thermal prehistory of the samples. The metastable state of glass after irradiation is characterized by a change of the ratio between heterogeneous and homogeneous bonds with respect to the initial state, as well as by the accumulation of the radiation energy. The preceding studies of RICs in chalcogenide glasses and film condensates on their basis [8, 9, 11, 16] have demonstrated that the electron irradiation of a medium energy $E \geq 1$ MeV induces a long-wavelength shift of their fundamental absorption edge and a variation of its parameters. A similar effect of the electron-induced darkening is also observed for glassy alloys of the Ge–Sb–S system in the GeS_2–Sb_2S_3 section. In this case, the total effect of RICs considerably depends on the chemical composition of alloys (Table 2), by correlating with the concentration behavior of the optical pseudogap of these alloys [1, 7, 19].

Figure 2 demonstrates that the maximum $\Delta\alpha/\alpha_0$ gradually decreases with time during several months after the electron irradiation, while its spectral position shifts to the short-wavelength region. Thus, the effect of electron-induced darkening is unstable and includes
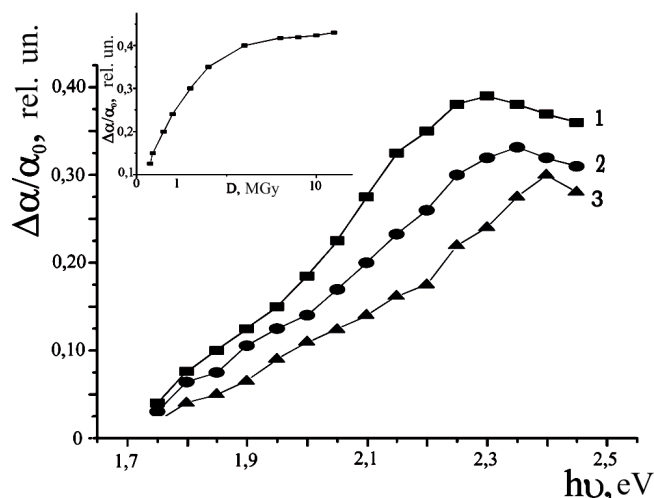

Fig. 2. Spectral characteristics of RICs in the optical absorption of the composition with $Z = 2.61$ in 24 hours (*1*), one month (*2*), and three months (*3*). The inset shows the dose dependence $\Delta\alpha/\alpha_0$ for glassy GeS_2

two components — the dynamic one attenuating with time and the static (residual) one that remains in irradiated samples for a long time. The dose dependence of the spectral characteristic of RICs of optical absorption for GeS_2 is given in the inset of Fig. 2. It demonstrates that the threshold of sensitivity to the electron irradiation for the investigated materials starts from the dose $D \sim 0.7 \times 10^5$ Gy and saturates at $D \sim 0.8 \div 0.9$ MGy depending on the alloy composition. It is known [20] that the density and the refractive index are interrelated quantities. We did not register any changes of the density of the investigated glasses under irradiation within the error limits. That is why the relative change of the refractive index Δn (Table 1) is evidently to be related to the variation of the electron polarization of the alloy components. Such a change of the polarization can be induced either by a topological reorientation of the defects existing before irradiation in the form of the so-called aliovalent pairs, including the switching of rigid covalent bonds, and by the electron-induced creation of new defects [7, 15–18].

The composition behavior of relative values of the total, dynamic, and static effects (Table 2) is determined by the mean coordination number. The analysis shows that the total contribution grows with increase in Z, and respectively, the dynamic component also decreases. Such a behavior can be related to a decrease of the energy barrier of the radiation-induced defect states in a glassy matrix with higher degrees of

T a b l e 1. **Optical pseudogap E_g^*, energy width of the edge E_0, static structural $E_0(X)$ and temperature $E_0(T)$ contributions, and a change of the refractive index Δn of Sb_2S_3 and $(GeS_2)_{0.5}(Sb_2S_3)_{0.5}$ glasses**

Parameters	Sb_2S_3		$((GeS_2)_{0.5}(Sb_2S_3)_{0.5}$	
	D0	D1	D0	D1
E_g^* (300 K), eV	1.651	1.671	2.37	2.34
E_0, MeV	56.0	68.3	61.2	74.7
$E_0(X)$	38.1	46.2	40.8	62.9
$E_0(T)$	17.9	22.0	20.4	11.8
$\Delta n \times 10^6$ (300 K)	–	17	–	21

T a b l e 2. **Composition dependence of electron-induced changes of the optical transmission of chalcogenide glasses of the Ge–Sb–S system**

Chemical composition	Z	Total effect		Static component		Dynamic component	
		$h\nu_{max}$, eV	ΔT_{max}, rel. un.	rel. un.	%	rel. un.	%
GeS$_2$	2.66	1.8	0.056	0.039	20	0.017	30
(GeS$_2$)$_{0.8}$(Sb$_2$S$_3$)$_{0.2}$	2.61	1.71	0.053	0.039	66	0.020	34
(GeS$_2$)$_{0.7}$(Sb$_2$S$_3$)$_{0.3}$	2.58	1.68	0.045	0.028	62	0017	38
(GeS$_2$)$_{0.5}$(Sb$_2$S$_3$)$_{0.5}$	2.53	1.59	0.021	0.09	43	0.012	57

delocalization of chemical bonds, which evidently results in a reduction of the concentration of these defects. The total effect of RICs and the ratio between the dynamic and static contributions also considerably depend on the compactness that favors the long-term stabilization of induced defects [11]. An important role in RICs is also played by the concentration of valence electrons $N_\nu = n_\nu/n_a$, where n_ν and n_a are the number of valence electrons and the number of atoms per formula unity, respectively. Indeed, for the studied glasses, $\gamma = (N_\nu - 4)/4 > 0$ and, according to the classification proposed in [19], these materials belong to defect ones, i.e. the efficiency of the processes of coordination defect formation is determined exactly by the imperfection of CGSs.

4. Conclusions

The performed studies of electron-induced changes of optical-refractometric parameters in CGSs of the Ge–Sb–S system show that the irradiation with doses in the range 0.7×10^5 Gy – 0.9 MGy induces the long-wavelength shift of the fundamental absorption edge and a change in the slope of its exponential region, which testifies to the induction of an additional structural disorder. The magnitude and the behavior of RICs considerably depend on the absorbed dose and the alloy composition. They are most pronounced in glasses enriched with Ge and decrease, as the content of Sb in alloys increases. The composition behavior of RICs of optico-refractometric parameters of the investigated glasses can be explained on the basis of the model of "switching" of homo- and heterogeneous chemical bonds of the CGS matrix.

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ЕЛЕКТРОННО-ІНДУКОВАНІ ЗМІНИ
ОПТИКО-РЕФРАКТОМЕТРИЧНИХ ПАРАМЕТРІВ
СКЛОПОДІБНИХ СПЛАВІВ СИСТЕМИ Sb_2S_3–GeS_2

М.М. Поп, М.О. Малец, І.І. Шпак, Д.Г. Семак

Р е з ю м е

Досліджено вплив електронного опромінення на зміну оптико-рефрактометричних (ОР) параметрів халькогенідних склоподібних сплавів системи Ge–Sb–S за розрізом Sb_2S_3–GeS_2. Проведено аналіз композиційних залежностей електронно-індукованих ефектів в досліджуваній системі. Отримані результати інтерпретовано в межах моделі "перемикання" гомо- та гетерохімічних зв'язків матриці ХСН.