

RADIATION-INDUCED OPTICAL EFFECTS IN $\text{Sb}_2\text{S}_3\text{-GeS}_2$ CHALCOGENIDE GLASSES

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INTRODUCTION

Chalcogenide vitreous semiconductors (ChVS), owing to the specific physical phenomena stimulated by external influences, remain interesting objects in the physics of disordered solids. Well-known γ -induced changes of ChVS physical properties are typical examples of these phenomena [1-11]. Such radiation-induced effects (RIE) were investigated, mainly, for the bulk samples of binary ChVS systems, which can be effectively used in industrial dosimetry [7,8]. At the same time, systematic study of RIE for ternary ChVS systems has not been carried out yet. Obtained results were rather incomplete and fragmentary [1,2,10,11].

One of interesting ChVS systems for the studying of RIE is Ge-Sb-S, which contains four-, three- and two-fold coordinated atoms and can be represented, for example, by the pseudobinary $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line. In the present paper, the influence of γ -irradiation on optical transmission spectra is investigated in details for the first time in these pseudobinary ChVS.

The previous considerations of photoinduced optical phenomena in the amorphous thin films and glasses of Ge-Sb-S system showed that the photostructural changes were more considerable in Ge-rich ChVS, characterised by the relatively large "free" volume [12-14]. In other words, the increasing of compactness of the structure and concentration of Sb-containing structural units led to the passivation of photoinduced effects. Analogously, one can assume that Sb will cause the decreasing of RIE in bulk glasses of $\text{Sb}_2\text{S}_3\text{-GeS}_2$ line and the "free" volume concept must play an important role in the interpretation of these effects.

Besides it, bearing in mind the possibility of redistribution of chemical bonds (as in the case of photoexposure [12,13]) and chemical bonds switching (as in the case of γ -irradiation and high-energy electron

irradiation [5,6,9,15]), we can suggest that RIE depend on the concentration of different types of chemical bonds, calculated according to the ordered bond network model (OBNM) [16].

EXPERIMENTAL

The ChVS samples from pseudobinary $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ($0.1 \leq x \leq 0.5$) line of the corresponded Ge-Sb-S diagram with the different values of average coordination number Z ($2.50 \leq Z \leq 2.63$) (calculated as the number of covalent chemical bonds per atom of the formula unit [17]) were selected for our investigation.

All glasses were synthesised from the high purity (99,9999 %) Ge, Sb and S elements by the method of melt quenching in the evacuated quartz ampoule [18]. Obtained samples were cut and polished to the 1-mm thickness disks of optical quality.

The radiation treatment of investigated ChVS was performed by γ -quanta in the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to the concentrically established ^{60}Co ($E=1.25$ MeV) sources. The power of exposure dose was near 20 Gy/sec; the total value of absorbed dose was equal to $3 \cdot 10^6$ Gy. No special measures had been used to prevent the uncontrolled thermal annealing of samples, but the maximum temperature in irradiating camera did not exceed 320-330 K during the whole period of radiation treatment.

The optical measurements were carried out using SPECORD M-40 spectrophotometer (200-900 nm). The spectral dependence of the optical transmittance differences (before and after γ -irradiation) $\Delta\tau(h\nu)$ ($h\nu$ - the photon energy) was chosen as the controlled parameter for investigated effects.

RESULTS

The radiation-induced long-wave shift of optical transmittance curve $\tau(h\nu)$ (the radiation-induced darkening) was observed for the majority of investigated samples in the fundamental absorption edge region (with the exception of compositions with high content of Sb). The same shift was proper for layer-like As_2S_3 glass, investigated previously [5,6].

The $\Delta\tau(h\nu)$ dependencies are plotted as the asymmetric bell-shaped curves with well-defined maximum $\Delta\tau_{\text{max}}$, corresponding to the fixed photon energy $h\nu_{\text{max}}$, the sharp high-energy and the extended low-energy "tails" (Fig.1). The radiation-induced darkening is unstable and restores gradually to some residual value after the period of 2-3 months. In other words, the total effect $\Delta\tau_{\Sigma}(h\nu)$ consists of two components - $\Delta\tau_{\text{dyn}}(h\nu)$ and $\Delta\tau_{\text{st}}(h\nu)$. The dynamic component

$\Delta\tau_{\text{dyn}}(h\nu)$ relaxes after γ -irradiation to the value of static part $\Delta\tau_{\text{st}}(h\nu)$, which remains stable for the long period of time after irradiation:

$$\Delta\tau_{\Sigma}(h\nu) = \Delta\tau_{\text{dyn}}(h\nu) + \Delta\tau_{\text{st}}(h\nu) \quad (1)$$

The spectral positions $h\nu_{\text{max}}$ of total and static RIE shift to the higher energies with increasing of Z in a strong accordance with the compositional dependence of optical band gap (Table 1 [19]).

The spectral characteristics of radiation-optical effects in the studied ChVS are presented in Table 2. The amplitudes $\Delta\tau_{\text{max}}$ of total, static and dynamic RIE reach the maximum values in the Ge-rich ChVS compositions with largest Z and decrease to zero at $Z=2.50$ ($x=0.5$).

It should be noted that the relative content of dynamic component into the total RIE decreases with Z , while the role of static part grows (Table 2). Beside it, as in the case of RIE in vitreous As_2S_3 [5,6], the residual effect disappears in the consequence of the thermal annealing at temperatures just below the glass transition. This means that the radiation-induced changes of ChVS optical properties are reversible.

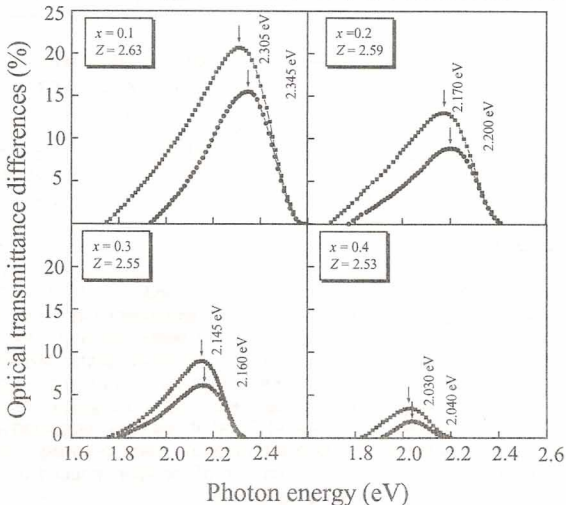


Fig.1. The spectral dependences of the γ -induced optical transmittance differences $\Delta\tau(h\nu)$ for the $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line of Ge-Sb-S system:

■ - next day after γ -irradiation; ● - two months after γ -irradiation

Table 1. The compositional dependence of density ρ [19], compactness of the structure δ and optical band gap energy E_g^o [19] for the $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line of Ge-Sb-S system

x	Z	ρ (g/cm ³)	δ (a.u.)	E_g^o (eV)
0.5	2.50	3.65	$-2.08 \cdot 10^{-2}$	2.38
0.4	2.53	3.50	$-3.54 \cdot 10^{-2}$	2.42
0.3	2.55	3.35	$-4.70 \cdot 10^{-2}$	2.62
0.2	2.59	3.15	$-6.94 \cdot 10^{-2}$	2.80
0.1	2.63	2.95	$-8.78 \cdot 10^{-2}$	2.92

Table 2. Spectral characteristics of radiation-induced changes of the optical transmittance $\Delta\tau(h\nu)$ for the $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line of Ge-Sb-S system

ChVS composition	Total effect, $\Delta\tau_{\Sigma}(h\nu)$			Static (residual) component, $\Delta\tau_{st}(h\nu)$			Dynamic component, $\Delta\tau_{dyn}(h\nu)$	
x	Z	$h\nu_{max}$ (eV)	$\Delta\tau_{max}$ (a.u.)	$h\nu_{max}$ (eV)	$\Delta\tau_{max}$ (a.u.)	(%)	$\Delta\tau_{max}$ (a.u.)	(%)
0.5	2.50	-	-	-	-	-	-	-
0.4	2.53	2.030	0.04	2.040	0.02	50	0.02	50
0.3	2.55	2.145	0.09	2.160	0.06	67	0.03	33
0.2	2.59	2.170	0.13	2.200	0.09	69	0.04	31
0.1	2.63	2.305	0.21	2.345	0.155	74	0.055	26

* In percents are presented the relative contents of static and dynamic components into the total effect ($\Delta\tau_{max}$).

DISCUSSION

“free” volume concept for the γ -induced optical effects

As it was mentioned above, the RIE were studied sufficiently well in the binary ChVS systems. The radiation-induced darkening effect for the vitreous As_2S_3 was connected with the chemical bond switching processes in a framework of the coordination defect formation model [5,6]. According to the previous investigations of photoinduced effects in the ternary Ge-Sb-S ChVS system [12-14], it could be suggested that one more factor such as effective formation of voids in glassy matrix plays the significant role in the mechanism of radiation-induced optical phenomena for these chalcogenide glasses.

It was found that the photoinduced changes of optical transmittance $\Delta\tau$ and reflectance Δr in the amorphous Ge-Sb-S layers and glasses proceed more effectively for the compositions with larger “free” volume

[12,13]. The Raman study of photostructural phenomena in the Ge-Sb-S thin films confirms this conclusion [14].

The measure of "free" volume is compactness of the structure δ , calculated according to the well-known formula [12-14]:

$$\delta = \frac{\sum_i V_i - V_{\text{exp}}}{V_{\text{exp}}} = \frac{\sum_i \frac{A_i x_i}{\rho_i} - \sum_i \frac{A_i x_i}{\rho}}{\sum_i \frac{A_i x_i}{\rho}}, \quad (2)$$

where V_i is the volume occupied by the atoms of i -th chemical element of glass; V_{exp} is the experimentally measured volume of glass; A_i , x_i and ρ_i are the atomic weight, the atomic fraction and the atomic density of i -th chemical element, respectively; ρ is the measured density of glass. The quantities δ can take the negative values, corresponding to larger "free" volume [12-14].

The calculated data of δ for $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ line are presented in Table 1. According to our estimations δ decreases (the "free" volume rises) with the increasing of Z . It can be connected with the specificity of network structure in the amorphous α -GeS₂. As known [20,21], the structure of α -GeS₂ contains the principal three-dimensional (3D) phase, which is characterised by the existence of voids due to the corner-sharing tetrahedral structural units, and the additional two-dimensional (2D) phase, formed by the edge-sharing tetrahedra. Really, the rise of GeS₂ concentration in $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ glasses leads to the increasing of "free" volume or the observed reduction of δ (Table 1).

The compositional trend of RIE in investigated ChVS agrees with the same dependencies of δ as it was observed earlier for the photoinduced effects in Ge-Sb-S system [12-14]. So, we find that RIE grow with the increasing of "free" volume and reveal maximum values in Ge-rich ChVS (Tables 1,2). This feature can be explained sufficiently well by the stabilisation of radiation-induced defects at the void structure. On the other hand, in more compact Sb-rich glasses the radiation-induced defects are less stable that leads to the relaxation of structural changes caused by the irradiation and the decreasing of defect population. In other words, the Sb-rich samples are characterised by the lower energy barrier for the formation of metastable radiation-induced defect states in comparison with the Ge-rich glasses and as the result, RIE are completely absent for ChVS glass composition with larger amount of Sb atoms. So, the relative content of dynamic (relaxing) component of RIE must increase in the direction of Sb-rich ChVS while static (residual) part must increase in the direction of Ge-rich ChVS that is observed really (Table 2).

Chemical bond approach to the γ -induced optical effects

Taking into account the model of photoinduced changes of optical properties in the amorphous As-S, Ge-S and Ge-Sb-S systems based on the redistribution of chemical bonds [12,13] and the model of coordination defect formation used for the explanation of radiation-induced transformations in the structure of vitreous As_2S_3 [5,6], we can assume that RIE are also dependent on the initial concentration of chemical bonds in the glass network. This feature can be expressed analytically as follows:

$$\chi_k = (\chi_k^{\text{ChB}}) \times (y^{\text{ChB}}), \quad (3)$$

where χ_k is the value of controlled parameter (that is $\chi_k = \Delta\tau$); (χ_k^{ChB}) is the row-matrix of the specific weight of chemical bonds (ChB) into radiation-induced change of controlled parameter; (y^{ChB}) is the column-matrix of the concentration of chemical bonds (ChB).

The concentration of chemical bonds was calculated according to the OBNM model [16]. In the case of studied Sb_2S_3 - GeS_2 pseudobinary system the main types of covalent chemical bonds are the heteropolar Sb-S and Ge-S ones. Thus, the Eq. (3) can be presented by the expression:

$$\chi_k = (\chi_k^{\text{Sb-S}} \chi_k^{\text{Ge-S}}) \times \begin{pmatrix} y^{\text{Sb-S}} \\ y^{\text{Ge-S}} \end{pmatrix} = \chi_k^{\text{Sb-S}} y^{\text{Sb-S}} + \chi_k^{\text{Ge-S}} y^{\text{Ge-S}}, \quad (4)$$

where $\chi_k^{\text{Sb-S}}$ is the coefficient representing the contribution of Sb-S bonds into the observed RIE and $y^{\text{Sb-S}}$ is the fraction of these bonds in ChVS composition; $\chi_k^{\text{Ge-S}}$ is the coefficient representing the contribution of Ge-S bonds into effect and $y^{\text{Ge-S}}$ is the fraction of these bonds. It is clear that $y^{\text{Sb-S}} + y^{\text{Ge-S}} = 1$.

According to the Eq. (5), having substituted $\Delta\tau_x$, $\Delta\tau_{st}$ or $\Delta\tau_{dyn}$ instead of controlled parameter $\Delta\tau$, using the data of Table 2, and taking into account the fraction of chemical bonds, we can obtain the contributions of Sb-S and Ge-S bonds into the RIE for any two chosen samples. Analogously, we can determine the contributions of these bonds for other combinations of samples. As the result, we calculated the average values of $\Delta\tau^{\text{Sb-S}}$ and $\Delta\tau^{\text{Ge-S}}$.

The following relations were obtained:

$$\begin{cases} \Delta\tau_x = 0.270y^{\text{Ge-S}} - 0.210y^{\text{Sb-S}} \\ \Delta\tau_{st} = 0.200y^{\text{Ge-S}} - 0.175y^{\text{Sb-S}} \end{cases} \quad (5)$$

The formula for $\Delta\tau_{dyn}$ parameter can be wrote according to the Eq. (1).

The negative coefficients show that corresponding chemical bonds assist the passivation of RIE. So, the smaller effect might be observed in the samples with larger concentration of Sb-S bonds (in the Sb-rich glasses).

According to our estimations (Eq. (5)) only hetepolar Ge-S bonds assist the occurrence of the RIE. Hence, the larger radiation-induced changes of the optical properties might be obtained in the ChVS with high amount of Ge-S bonds (in the Ge-rich glasses) that is observed really (Fig.1, Table 2).

Thus, the chemical bond approach for the interpretation of RIE in the investigated ChVS confirms the low sensitivity of compact Sb-rich glasses to γ -irradiation.

Mechanism of the γ -induced optical effects

The microstructural mechanism of the observed RIE can be explained by the coordination defects formation model based on the concept of covalent chemical bonds switching, proposed firstly for vitreous As_2S_3 [5,6,9]. The topological schemes of the coordination defects formation processes can be identified using the IR spectroscopy method in the range of vibrational bands corresponding to the own structural fragments ($400\text{-}200\text{ cm}^{-1}$).

In this paper we noted that analysis of radiation-induced changes of IR reflection spectra ($400\text{-}200\text{ cm}^{-1}$) in the investigated ChVS testifies about possibility of only one topological variant of radiation-induced destruction-polymerization transformation, shown in Fig.2, which is proper to Ge-rich glass compositions. It is connected with formation of heteroatomic (Ge_3^- , S_3^+) coordination defects pair owing to the switching of heteropolar Ge-S bonds on homopolar S-S bonds ($\text{Ge-S} \rightarrow \text{S-S}$). This transformation confirms by the chemical bond approach to the RIE.

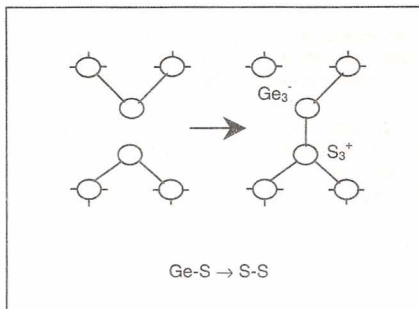


Fig.2. Topological variant of radiation- induced coordination defects formation processes in Ge-rich ChVS of the investigated line of Ge-Sb-S system

CONCLUSIONS

We established that ^{60}Co γ -irradiation of pseudobinary $\text{Sb}_2\text{S}_3\text{-GeS}_2$ glasses leads to the long-wave shift of their optical transmittance spectra in the fundamental absorption edge region for the majority of investigated samples. Radiation-induced changes of optical properties are unstable. They gradually restore to some residual value for the period of 2-3 months. Therefore, the RIE consists of the two components: dynamic (relaxing) and static (residual) ones. It is shown that RIE are larger in Ge-rich ChVS. The rise of Sb concentration in glass matrix results in the gradual decreasing of RIE. In Sb-rich samples the effects are completely absent.

The "free" volume concept logically explains the compositional trend of RIE and the origin of dynamic and static components in the investigated glasses. Observed effects can be also analytically described, taking into account the concentration of chemical bonds in glass matrix, calculated according to the OBNM model. Chemical bond approach confirms the low sensitivity of compact Sb-rich glasses to γ -irradiation and microstructural mechanism of the observed RIE, which is connected with formation of heteroatomic (Ge_3^- , S_3^+) coordination defects pair owing to the radiation-induced transformation of heteropolar Ge-S bonds.

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