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Effect of Co^{60} γ-irradiation on the optical properties of As–Ge–S glasses

V. Balitska [a], R. Golovchak [a], A. Kovalskiy [a], E. Skordeva [b], O.I. Shpotyuk [a,c,*]

[a] Lviv Scientific Research Institute of Materials of Scientific Research Company 'Carat', Stryjska str. 202, Lviv UA-79031, Ukraine
[b] Institute of Solid State Physics of Bulgarian Academy of Sciences, Tzarigradsko Chaussee 72, Sofia 1784, Bulgaria
[c] Institute of Physics of Pedagogical University, al. Armii Krajowej 13/15, Czestochowa 42200, Poland

Abstract

The influence of Co^{60} γ-irradiation on the optical properties of chalcogenide semiconducting glasses from As_2S_3–Ge_2S_3 cut-section is analyzed taking into account the accompanying spontaneous thermal annealing of the samples in the irradiation chamber. It is established that essential thermal heating of the investigated glasses during high-doses irradiation leads to the rough changes in compositional dependences of radiation-induced total (unrelaxed) and static (relaxed) optical effects. An attempt to describe dose dependence of the observed optical changes is made on the basis of stretched–exponential relaxation function.

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1. Introduction

Chalcogenide semiconducting glasses (ChSG) possess a number of unique features, such as dependence of their physical–chemical properties on high-energetic ionizing irradiation ($E > 1$ MeV). They are still remaining a topic of many investigations in last years. However, despite of a great progress in this field, some vital scientific problems remain unresolved. The well-known thermoradiation effects, consisting in mixed thermal and radiation influences on ChSG structure, are typical examples of the latter. These effects are shown to be very important in radiation-optical properties of oxide glasses [1]. Nevertheless, in the previous investigations of ChSG, they were not taken into account at all. As a result, the great inconsistencies appear in experimental results on radiation effects for the same glass compositions, irradiated in different (often uncontrolled) thermal conditions [2,3].

The present work is devoted to Co^{60} γ-irradiation dose effects revealed through optical properties changes of As_2S_3–Ge_2S_3 ChSG cut-section. The observed darkening effects in the fundamental optical absorption edge region are analyzed from the standpoint of simultaneous influence of high-dose γ-irradiation and spontaneous thermal annealing of the ChSG samples in the irradiation chamber.

* Corresponding author. Tel.: +380-322 63 83 03/63 10 65; fax: +380-322 63 22 28.
E-mail address: shpotyuk@novas.lviv.ua (O.I. Shpotyuk).

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2. Experimental

The As_2S_3–Ge_2S_3 samples of seven different chemical compositions with average coordination numbers Z [4], ranging from $Z = 2.48$ ($As_{32}Ge_8S_{60}$) up to $Z = 2.76$ ($As_4Ge_{36}S_{60}$), were selected for our investigations. It is supposed that all glasses with $Z < 2.67$ have a character layer-like 2D-structure proper to vitreous As_2S_3, and those with $Z > 2.67$ – a quasi three-dimensional cross-linked 3D-network proper to vitreous GeS_2 [5].

The investigated ChSG were synthesized from the constituent high-purity (99.9999%) elements by a standard melt-quenching method described in [6]. All samples were annealed additionally after synthesis at the temperatures of 20–30 K below softening point T_g to remove the mechanical strains.

The prepared ChSG samples were irradiated by γ-quanta ($E = 1.25$ MeV) at a few Gy/s exposure dose power. The accumulated doses Φ of 1.0 and 4.4 MGy were chosen as controlled ones, taking into account our previous investigations [6–8]. Radiation treatment was performed at the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to the concentrically established ^{60}Co sources. No special procedures were used to prevent the spontaneous thermal heating of the samples, but the temperature in Co^{60} cavity was controlled with ±5 K accuracy. It achieves the level of 320 K in the case of 1.0 MGy absorbed dose, and 390 K in the case of 4.4 MGy one. It should be noted that the temperature of 390 K is sufficient to anneal the radiation-stimulated optical changes in v-As_2S_3 [8].

Optical measurements were performed before and after γ-irradiation with 'Specord M-40' spectrophotometer (200–900 nm) at the ambient temperature using the high-quality polished disk samples of $d \approx 2$ mm thickness. The values of optical absorption coefficient α were obtained from the spectral dependences of optical transmission τ and reflection r using formula [9]

$$\alpha = (1/d)\ln((1 - r^2)/\tau). \quad (1)$$

The relative changes in absorption were taken as the descriptive parameter:

$$\Delta\alpha/\alpha_0 = (\alpha - \alpha_0)/\alpha_0, \quad (2)$$

where α_0 and α are the optical absorption coefficients at a fixed photons energy before and after γ-irradiation, respectively. The maximum value of the effect was near 40% and depended strongly on the glass composition.

3. Results

It was established previously that γ-irradiation of the investigated ChSG leads to the low-energetic shift of their fundamental optical absorption edge [6]. At that, the quantitative peculiarities of this effect for the samples, irradiated with 4.4 MGy absorbed dose of ^{60}Co γ-quanta, were discussed. The attention was paid mainly to the instability of radiation-induced changes of optical properties under natural conditions. The spontaneous heating effect was not separated during this consideration.

Particularly, it was shown that magnitudes of total (unrelaxed, measured just after γ-irradiation) and static (relaxed, measured two months after γ-irradiation) radiation-induced effects with 4.4 MGy absorbed dose in the investigated ChSG, defined as maximum fractional increase of optical absorption coefficient $(\Delta\alpha/\alpha_0)_{max}$ take the well-expressed minimum in the vicinity of $Z = 2.67$ (Fig. 1). However, the opposite character of these compositional dependences with the maximum (but not minimum) behaviour of the measured changes near $Z = 2.67$ should be expected taking into account the results of previously studied photoinduced optical effects in As_2S_3-Ge_2S_3 system [10]. But in the case of photo-exciting processes, the spontaneous heating is neglectfully small. In this connection we can suppose a large thermoradiation effect in the ChSG irradiated with 4.4 MGy dose.

In order to confirm the supposition on essential thermal contribution to the γ-induced optical changes, another γ-radiation treatment of the investigated As_2S_3–Ge_2S_3 glass samples has been carried out. The dose of irradiation was reduced to 1.0 MGy. The obtained results are shown in Fig. 1 too. As it was pointed out above, the temperature

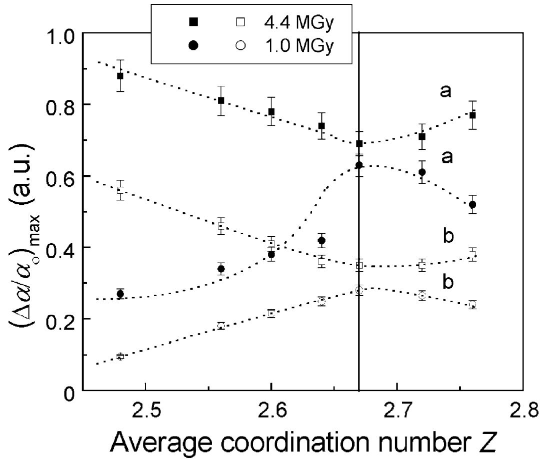

Fig. 1. Compositional dependence of total (curves a) and static (curves b) radiation-induced changes for As_2S_3–Ge_2S_3 glasses γ-irradiated with 1.0 and 4.4 MGy absorbed doses.

during irradiation in this case did not exceed 320 K. In consequence, the compositional dependences of total and static radiation-induced optical changes achieve maximum near $Z = 2.67$. The values of $(\Delta\alpha/\alpha_0)_{max}$ are lower than those observed at 4.4 MGy dose, and the shape of maximum changes after a period of natural storage (it becomes more smooth).

4. Discussion

It is clear, that thermal annealing under radiation treatment is sensitive to the structure of the ChSG and, consequently, reveals the peculiarity at the point $Z = 2.67$. It can be concluded, that the exact type of the observed extremum is strongly determined not only by the glass composition, but also by the dose level of irradiation and the correspondent temperature in the source cavity during radiation treatment. For this range of doses the higher the dose of γ-irradiation, the greater the absolute value of observed radiation-induced optical effect, but the more essential is also the influence of spontaneous thermal annealing of the samples during irradiation.

Earlier the dependence of γ-induced optical changes on the dose of irradiation was studied in details only for vitreous As_2S_3 [8]. Until now there were no attempts to describe this dependence analytically. If we consider that γ-irradiation leads to the formation of additional coordination defects (such mechanism is established elsewhere [11]), we can assume that spontaneous thermal heating favours their annihilation. Then the number of relaxation functions, used in [12] for characterization of time-dependent component of γ-induced optical changes, can be applied for analytical description of the dose dependence. In this connection, time dependence in the relaxation functions can be compared with dose dependence one due to the $\Phi(t)$ linearity. Such procedure was applied to the dose-dependence of γ-induced optical changes in vitreous As_2S_3 (Fig. 2). The best fitting results (minimum parameters and minimum χ-square value) were obtained for stretched–exponential DeBast–Gillard functional behaviour:

$$\chi = \chi_0\left(1 - e^{-(\Phi/\Phi_0)^k}\right), \tag{3}$$

where χ can be replaced with $(\Delta\alpha/\alpha_0)_{max}$, Φ is the accumulated dose, Φ_0, χ_0 and k are the fitting parameters.

It is not a surprise since great numbers of time-dependent relaxation processes in ChSG are well described by DeBast–Gillard function [13,14]. We

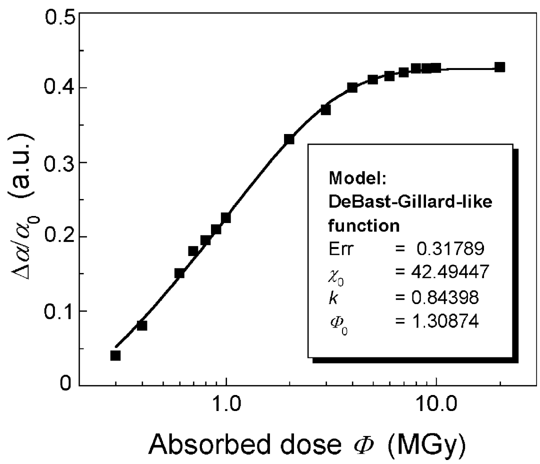

Fig. 2. Dose-dependence of γ-induced optical changes (registered at 600 nm wavelength) in vitreous As_2S_3 irradiated with ~5 Gy/s dose power and fitting parameters according with curve obtained from formula (3).

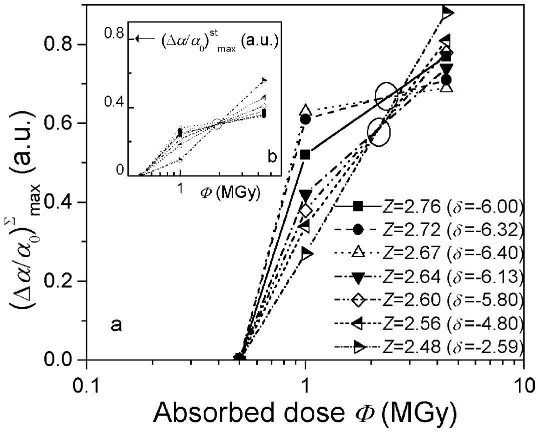

Fig. 3. Dose dependences of radiation-stimulated maximal relative changes of absorption $(\Delta\alpha/\alpha_0)_{max}$ for As_2S_3–Ge_2S_3 glasses: a – the total effect, b – the static effect (δ – atomic compactness [4]).

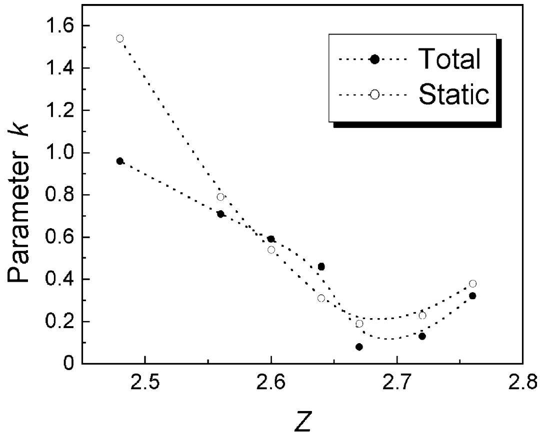

Fig. 4. Compositional dependences of parameter k from formula (3) in the investigated As_2S_3–Ge_2S_3 glasses.

used it for quantitative explanation of the observed peculiarities for investigated ChSG too. First of all, the interesting feature of dose dependences for the thermoradiation effects should be noted (Fig. 3). By straight connecting of the $(\Delta\alpha/\alpha_0)_{max}$ values for total 1.0 MGy dose effect with the correspondent values for total 4.4 MGy dose effect, two focal points can be distinguished on the cross-sights of these dose dependences. The first one at ~2.1 MGy is attributed to 2D-structured ($Z < 2.67$) ChSG, while the second focal point at ~2.2 MGy – to 3D-structured ($Z > 2.67$) cross-linked samples. In these points γ-induced effect does not depend on the ChSG composition. Practically the same happens when $\Phi = \Phi_0$ in Eq. (3). So, we can assume that Φ_0 plays the role of focal point position in the case of investigated ChSG. Using appropriate fitting procedure, we can find that $\chi_0 \approx 1$ for total radiation-induced effect independently on glass composition, but k parameter, likely to atomic compactness [4], exhibits strong dependence on the chemical composition (Fig. 4).

Two focal points for total radiation-induced effect in the investigated ChSG converge into single one (near 2.0 MGy) after a period of 2–3 months. The χ_0 value for this static effect reduces to ~0.5, but the same dependence on the glass composition for k parameter remains (Fig. 4).

By accepting the nature of the observed radiation-induced effects in strong correlation with non-equilibrium defect sub-system of the irradiated ChSG [11], we can explain the above features by different thermal stability of the created coordination topological defects. The microstructural picture of the correspondent atomic transformations needs more detailed investigations.

5. Conclusions

The quite different compositional dependences of the maximum relative changes of absorption $(\Delta\alpha/\alpha_0)_{max}$ in As_2S_3–Ge_2S_3 ChSG samples were obtained for 1.0 and 4.4 MGy accumulated absorbed doses of γ-irradiation. The maximum in the vicinity of $Z = 2.67$ for the first case and the minimum at this point for the second one were explained by the essential influence of spontaneous heating in the irradiation chamber. It is assumed that the effect of thermoradiation influence is connected with different thermal stability of coordination topological defects created under γ-irradiation, which, in turn, depends on structural peculiarities of ChSG. The combined influence of temperature and irradiation can be successfully described with stretched-exponential DeBast–Gillard function.

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