
Degradation of electron-induced dichroism in glassy $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3$

V.O. Balitska, O.I. Shpotyuk, M.M. Vakiv

Lviv R&D Institute of Materials of SRC "Carat", 202 Stryjska str., Lviv, 79031, Ukraine

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Abstract

Experimental results on time degradation of electron-induced dichroism in vitreous chalcogenide semiconductors $\text{As}_2\text{S}_3\text{-Sb}_2\text{S}_3$ are discussed. The adequate model for the quantitative description of this process can be developed on the basis of monomolecular relaxation function proper to annihilation of dipole-like coordination defects created on the basis of radiation-induced broken covalent chemical bonds.

Key words: glass, electron-irradiation, dichroism, degradation

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Introduction

Electron-induced dichroism (EID) was first observed in cubic samples of glassy $\text{g-As}_2\text{S}_3$ in a specific geometry of high-energetic (~ 3 MeV) electron irradiation [1]. It revealed itself as the differences between transmittance coefficients for linearly polarized sonde light with parallel and perpendicular orientations of the polarization plane (respectively to electron beam direction).

We discussed thermal stability, compositional dependence and microstructural mechanism of the EID for the quasibinary $\text{g-As}_2\text{S}_3\text{-Sb}_2\text{S}_3$ in our previous papers [2-4]. In this article we shall consider the problem on time-related degradation of the EID for the above glasses in details.

Experimental

The investigated $\text{g-(As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ ($x=0.7, 0.8, 0.9$ and 1.0) samples were synthesized from high-purity constituents (99.999%) in evacuated quartz ampoules by the direct melting method as was described

previously [1-4]. All investigated samples had cubic forms with 8-10 mm rib lengths and high-quality polished plane borders.

The irradiation was carried out with a beam of accelerated electrons with 2.8 MeV energy and $5 \cdot 10^{16} \text{ cm}^{-2}$ fluence directed perpendicularly to one of the specimen planes. The adjacent plane of the sample was chosen as the investigated one. The linearly polarized light beam had a diameter near 3 mm and passed perpendicularly through this plane at a distance of 2 mm from the irradiated plane. In such way we have distinguished two mutually orthogonal directions for the probe light with parallel (\parallel) and perpendicular (\perp) polarizations in respect to the electron beam direction. The estimated penetration depth of the 2.8 MeV electrons for our glasses was about 5 to 6 mm [5]. By this way, the investigated zone of the samples was really treated by absorbed electrons. The more detailed description of the geometrical sketch for the EID observation is presented in our previous papers [1-4].

All measurements were carried out in the region of the fundamental optical absorption edge of the samples using a “Specord M-40” spectrophotometer (200 to 900 nm). The magnitude of the EID was estimated by the parameter κ , determined by the expression:

$$\kappa = \Delta\alpha \cdot d = (\alpha_{\parallel} - \alpha_{\perp}) \cdot d = \frac{2(\tau_{\perp} - \tau_{\parallel})}{(\tau_{\perp} + \tau_{\parallel})}, \quad (1)$$

where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ ($\Delta\tau = \tau_{\perp} - \tau_{\parallel}$) is the difference of the optical absorption coefficients (the difference of the optical transmittance coefficients) for the probe light with perpendicular (α_{\perp} and τ_{\perp}) and parallel (α_{\parallel} and τ_{\parallel}) orientations of the polarization planes.

Results and discussion

It is known, that electron irradiation leads to a long-waved shift of the fundamental optical absorption edge of the chalcogenide vitreous semiconductors [6].

In the case under consideration, the linearly-polarized sonde light beam causes the splintering of the optical absorption edge of the electron-irradiated samples [1-4]. So, we obtain two different optical transmittance coefficients curves: $\tau_{\perp}(h\nu)$ and $\tau_{\parallel}(h\nu)$ ($h\nu$ - photon energy), shifted to the long-wave spectral region with respect to the initial $\tau(h\nu)$ curve for the non-irradiated samples. We can observe two different spectral characteristics of this effect - a bell-like $\Delta\tau(h\nu)$ curve with sharply expressed maximum EID at $h\nu_{max}^0$, as well as a monotonically increasing $\kappa(h\nu)$ or $\Delta\alpha(h\nu)$ dependences with two character quasi-linear regions. It is established that this effect is not stable and decays completely at ambient temperature within 5-10 days in dependence of the glass composition.

The time-dependent characteristics of the EID, estimated by κ and $\Delta\alpha$ parameters, calculated at $h\nu_{max}^0$ for each investigated sample are shown in Fig.1.

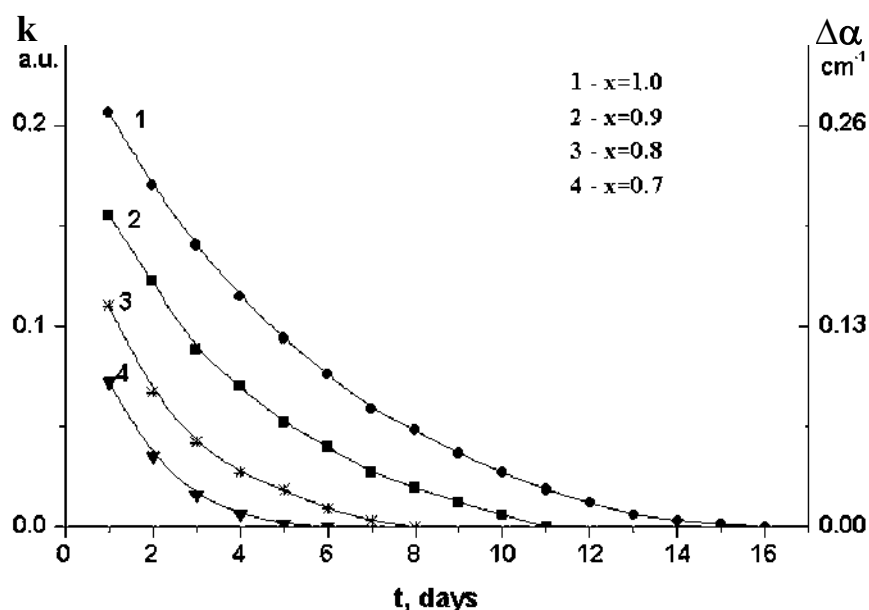


Fig.1. Time-dependent degradation of electron-induced dichroism effect ($\Phi=5 \cdot 10^{16} \text{ cm}^{-2}$, $E=2.8 \text{ MeV}$) in $(\text{As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses: 1 – $x=1.0$, $h\nu_{max}=1.93 \text{ eV}$; 2 – $x=0.9$, $h\nu_{max}=1.86 \text{ eV}$; 3 – $x=0.8$, $h\nu_{max}=1.83 \text{ eV}$; 4 – $x=0.7$, $h\nu_{max}=1.82 \text{ eV}$.

It is obvious that the substitution of As atoms by Sb ones in the $g\text{-(As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ (associated with x values decreasing) leads to the EID vanishing. This process reveals itself as sufficient decrease of the κ parameter with Sb_2S_3 content in the investigated system.

As was shown by us previously, the EID is connected with the existence of broken chemical bonds in the structural network of electron-irradiated chalcogenide glasses [5,7]. The atoms, formerly created covalent bonds, have smaller coordination (undercoordinated atoms) just after irradiation [8]. They appear in the glassy matrix owing to the displacements of the covalent-linked atoms at the bombardment by electrons in accordance with a threshold mechanism [9]. They are preferentially oriented along the direction of electron-beam propagation in the sample and, finally, they can be considered as the electrical dipoles producing the EID.

The process of EID degradation is determined mainly by annihilation of the above-mentioned defects. The rate of their annihilation dn/dt is expressed, in general, with a power-law dependence of the relaxation time t and of the actual defect concentration n [10]:

$$\frac{dn}{dt} = -\lambda n^\alpha t^\beta, \quad (2)$$

where α and β are the power indices ($\alpha > 0$,

$0 < \beta < 1$) and λ is some constant dependent on the glass composition.

It is clear, that the quantitative value of the EID (estimated by κ or $\Delta\alpha$ parameters) is proportional to the defect concentration n .

The solution of the above differential eq. (2) is the relaxation function (RF), which fulfills the following conditions for the EID observation:

$$\begin{cases} t \rightarrow 0 \Rightarrow n \rightarrow n_0 = \text{const} \\ t \rightarrow \infty \Rightarrow n \rightarrow 0 \end{cases}. \quad (3)$$

There are three physically real RFs, listed in Tabl.1, which satisfy these conditions (3).

The first RF corresponds to well-known monomolecular relaxation processes, expressed by simple exponential dependence on time t . If the degradation processes are caused by recombination of specific defect pairs (electrons and holes, vacancies and interstitials, etc.), the underlying kinetics is determined by bimolecular RF (the second RF in Tabl.1) [10]. The third RF in Tabl.1, describe stretched exponential relaxation processes in molecular and electronic glasses and is the most suitable for quantitative simulation of structural, mechanical and electrical degradations. This RF was introduced previously by DeBast and Gillard [11], as well as Williams and Watts [12].

Table 1. Calculated parameters for relaxation function of EID in $g\text{-(As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$

x	Monomolecular (exponential) RF			Bimolecular RF			Williams-Watts or DeBast-Gillard RF			
	$\chi = \chi_0 e^{-\frac{t}{\tau}}$			$\chi = \frac{\chi_0}{1 + \frac{t}{\tau}}$			$\chi = \chi_0 e^{-\left(\frac{t}{\tau}\right)^\lambda}$			
	χ_0	τ	err	χ_0	τ	err	χ_0	τ	λ	err
0.7	0.15	1.37	$1.7 \cdot 10^{-5}$	32.5	0.002	$2.9 \cdot 10^{-4}$	0.11	1.77	1.27	$1.2 \cdot 10^{-5}$
0.8	0.15	2.55	$1.72 \cdot 10^{-4}$	0.45	0.30	$5.5 \cdot 10^{-4}$	0.13	2.89	1.15	$1.6 \cdot 10^{-4}$
0.9	0.18	3.16	$7.3 \cdot 10^{-5}$		0.47	$1.3 \cdot 10^{-3}$	0.17	3.48	1.11	$5.9 \cdot 10^{-5}$
1.0	0.26	4.26	$5.22 \cdot 10^{-4}$	0.44	0.97	$5.8 \cdot 10^{-3}$	0.23	5.10	1.28	$2.4 \cdot 10^{-4}$
	err _{av} = $2.0 \cdot 10^{-4}$			err _{av} = $20.0 \cdot 10^{-4}$			err _{av} = $1.2 \cdot 10^{-4}$			

With the purpose of the adequate mathematical modeling of degradation kinetics in the studied $(\text{As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses, the quantitative values of χ_0 , τ and λ were calculated in such a way as to minimize the average square deviation err of the experimentally measured points from the chosen RF, listed in Tabl.1. It is established that this model can be satisfactorily developed with quite good accuracy at the basis of monomolecular RF. In this case, low values of err (near 10^{-4}) are achieved at a minimum number of fitting parameters (χ_0 and τ).

It is important to underline, that this monomolecular RF corresponds rigorously to annihilation kinetics of the defects created under electron irradiation. As was established, using the method of IR Fourier spectroscopy, that in the case of the g- As_2S_3 , these topological defects are undercoordinated atoms in the form of $(\text{As}_2^+, \text{S}_1^-)$, $(\text{As}_2^-, \text{As}_2^+)$ and $(\text{S}_1^-, \text{S}_1^+)$ pairs [2-4]. The charge of the defect centre is indicated by the superscript and the quantity of nearest neighboring atoms - by the subscript. With increasing of the concentration of Sb atoms in the investigated g- $(\text{As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ system, new types of topological defects do not appear owing to the low energetic barrier of the corresponding metastable state [8]. It means that the EID decreases in the investigated glasses in good accordance with our experimental results (Fig.1). Because of their instability these defects annihilate after electron irradiation at room temperature with a characteristic duration up to 15 days (in the Sb_2S_3 -riched glasses this process is shorter), explaining the time dependence of the EID. By this way, we obtained an additional confirmation on the nature of EID in g- As_2S_3 - Sb_2S_3 .

As to the DeBast and Gillard RF (see the third RF in Tabl.1), it is important to underline, that this RF corresponds strongly to the process of defect annihilation. But this fact is a small wonder, because this function describes satisfactorily almost all relaxation processes in the glasses due to the additional fitting parameter λ .

Conclusion

This paper presents experimental data on compositional and time-related dependences of the EID in the g- $(\text{As}_2\text{S}_3)_x(\text{Sb}_2\text{S}_3)_{1-x}$ ($x=0.7, 0.8, 0.9$ and 1.0) samples.

It is shown that the magnitude of EID is more pronounced in As_2S_3 -riched glasses (near $x=1.0$). This effect is unstable and disappears completely in the investigated glasses at room temperature within 15 days after electron-irradiation.

It is established that the adequate model for the quantitative description of the EID degradation can be developed at the basis of the monomolecular relaxation function proper to annihilation of the specific undercoordinated defects in the form of broken covalent bonds.

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