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Post- irradiation structural relaxation in quasibinary arsenic/antimony trisulphide glasses

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Abstract. Radiation – induced dynamic effects were studied in chalcogenide glasses of quasibinary $(As_2S_3)_{1-x}(Sb_2S_3)_x$ (0<x<0.3) system using optical spectrophotometry technique in the region of fundamental optical absorption edge. It was established that dynamical component of post – irradiation decaying gradually grows with Sb content in the studied glasses, the kinetics of the observed changes begin non-exponential tending towards monomolecular one. The observed changes were explained by compositional dependence of free volume in the studied system.

1. Introduction

Radiation induced effects in chalcogenide glassy semiconductors (ChGS) are in sphere of tight interests because of perspectives for their wide application in IR optics and photonics [1,2]. The first research on radiation-physical properties of ChGS was performed yet in the middle of the 60-s by I.A. Domoryad [3,4]. It was established, in part, that high energy γ-irradiation caused low-energetic shift in fundamental optical absorption edge of ChGSas as well as a number of other changes in their mechanical properties. The observed radiation-induced darkening effect was unstable [5,6]. It tended monotonically towards some residual value, showing a so-called dynamic component in contrast to static one, which kept mostly constant after irradiation. In Ge-based ChGS, this post-irradiation instability was shown to be quite prolonged up to 2-3 months. However, a detailed systematic study of these effects in other ChGS, especially in arsenic sulphides, has not been performed yet.

2. Experimental

In this work, we shall present the results on time degradation in radiation-induced optical darkening of quasibinary $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGs. The studied ChGS samples of four based compositions (x=0,0.1,0.2,0.3) were prepared by conventional melt quenching. The ingot was cut into discs of ~1 mm thickness and polished to high optical quality. To remove mechanical strains appeared after quick cooling, the samples were annealed during 1 hour at the temperature of 10-20 K below their glass transition temperature. Radiation treatment of the samples was conducted by γ-quanta with average energy of 1.25MeV and absorbed dose of 1.66 MGy in normal conditions of stationary radiation field created in closed cylindrical cavity surrounded by ^{60}Co sources. No special measures were taken to prevent uncontrolled thermal annealing of the samples, but maximum temperature in the irradaiating camera did not exceed 320-330K during prolonged γ-irradiation (more then 10 days). The spectral dependences of optical transmission τ of the samples were measured in 200-900 nm range in different time periods after irradiation (from 1 to 40 days) using "Specord M-40" device, the maximum error of measurements being no more 0.5%.

3. Results and discussion

The typical spectral dependence of radiation-induced optical darkening $\Delta\tau$ ($\Delta\tau=\tau_{in}-\tau_{irr}$,where τ_{in} is optical transmittance of initial non-irradiated sample, τ_{irr} is optical transmittance of irradiated sample measured in 1,2,3,5 and 40 day after irradiation, respectively) for vitreous As_2S_3 is shown in Figure 1.

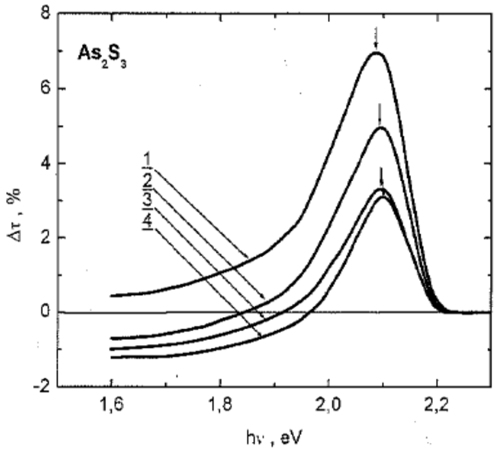

Figure 1. Spectral dependences of radiation induced optical darkening in vitreous As_2S_3 measured in the 1-st (1), 3-rd (2), 5-th (3) and 40-th day (4) after irradiation.

It is obvious that spectral dependence of $\Delta\tau$ has non-monotonic character with well expressed maximum $\Delta\tau_{max}$ at photon energies near 2.0 eV. With increase in time after irradiation, the low-energetic wing of this dependence shifts towards more negative $\Delta\tau$ values attaining a more symmetric shape (see Figure 1).

The similar spectral dependences were obtained for ChGS samples of the studied quasibinary $(As_2S_3)_{1-x}(Sb_2S_3)_x$ system (x=0.1,0.2 and 0.3). The only difference was decrease in the total value of measured radiation –induced effect with Sb content. Simultaneously, the spectral dependences of Sb-contained ChGS demonstrate shift towards negative $\Delta\tau$ values and increase in the photon energies corresponding to maximum $\Delta\tau_{max}$ values.

Thus, the character of dynamic post-irradiation effects in the studied $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS is determined mainly by their chemical composition (the positive $\Delta\tau$ value was only in vitreous As_2S_3 while with Sb_2S_3 content this parameter attained the negative values).

Compositional trends in static and dynamic components of radiarion – induced darkening effect in the studied ChGS at wavelength of maximal changes are well illustrated in Figure 2. The observed effect of post-irradiation decaying sharply enhanced with Sb content so that in ChGS with x=0.3 this effect was not detectable vanishing to small under-margin value.

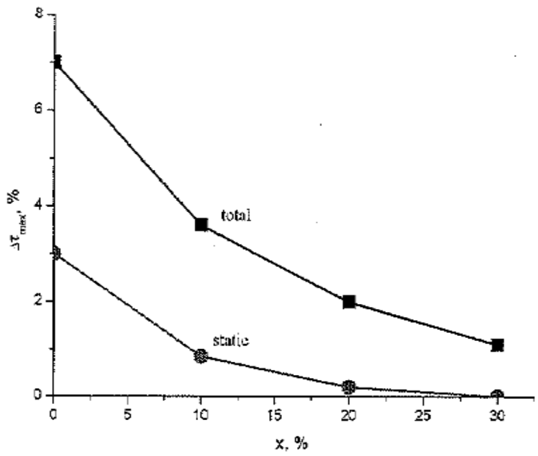

Figure 2. Compositional dependences of total and static components of radiation-induced optical darkening in $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS at the wavelength of maximal changes

The observed behavior of radiation – induced darkening effect in the studied ChGS samples correlates well with compositional dependence of free volume in this quasibinary system (see Fig.3). This feature allows us to put forward the hypothesis on decisive role of atomic compactness in the post-irradiation relaxation efficiency in ChGS. Dynamic tendency in radiation-induced changes significantly grows with Sb_2S_3 content in accordance to the observed rough decrease in molar volume.

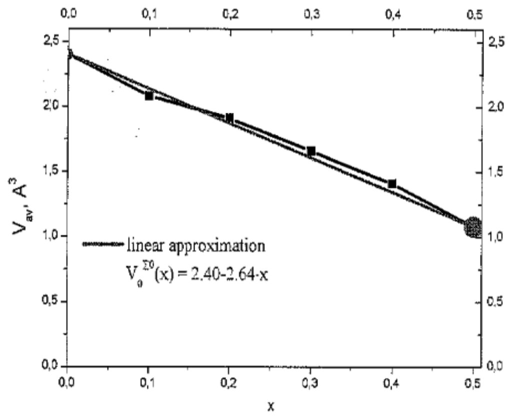

Figure 3 Compositional dependence of free volume per atom in $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS (bold circus denote values calculated as a comparison between atomic densities of isocompositional glasses and crystals, other points correspond to values estimated as input from As_2S_3 and Sb_2S_3 components

In order to quantitatively describe kinetics of the above post-irradiation instability effects, the possible mathematical variants of decay processes in ChGS were taken into account. In general, the rate of decaying in the control physical parameter $\chi(t)$ can be described due to known differential equqtion presented below [7,8].

$$\frac{dn}{dt} = -\lambda n^{\alpha} t^{\beta}, \quad (1)$$

where α and β are power indexes (α>0, 0<β<1) and λ is constant dependent on ChGS composition.

As it was pointed out in [7,8], there are five typical relaxation functions (RF), which can be simultaneously considered as possible partial solutions of Eq.(10 in dependence on numerical values of α and β parameters (Table 1).

Table 1. Degradation equations and corresponding RF for post-irradiation instability kinetics in ChGS

Degradation equation	RF type	RF parameters
$\frac{d\chi}{dt} = -\lambda\chi$	MonomolecularRF 1 $\chi = \chi_O e^{-\frac{t}{\tau}}$	$\chi_O = e^c, \tau = \frac{1}{\lambda}, \ c - const, \ \lambda \neq 0$
$\frac{d\chi}{dt} = -\lambda\chi^2$	Bimolecular RF 2 $\chi = \frac{\chi_O}{1 + \frac{t}{\tau}}$	$\chi_O = e^c, \ \tau = \frac{1}{\lambda},$ $c - const, \ \lambda \neq 0$
$\frac{d\chi}{dt} = -\lambda\chi^{\alpha}$	Party-polymerized RF 3 $\chi = \frac{\chi_O}{\left(1 + \frac{t}{\tau}\right)^{\kappa}}$	$\chi_O = c^{\frac{1}{\alpha - 1}}, \ \tau = \frac{c}{\lambda(\alpha - 1)},$ $\kappa = \frac{1}{\alpha - 1}, \ c - const, \ \alpha \neq 1, \ \lambda \neq 0$
$\frac{d\chi}{dt} = -\lambda\chi t^{\beta}$	Nonexponential RF 4 $\chi = \chi_O exp\left[-\left(\frac{t}{\tau}\right)^{\kappa}\right]$	$\tau = \left(\frac{1 + \beta}{\lambda}\right)^{\frac{1}{1 + \beta}}, \ \kappa = 1 + \beta,$ $\chi_O = e^c, \ c - const, \ \beta \neq -1, \ \lambda \neq 0$
$\frac{d\chi}{dt} = -\lambda\chi^{\alpha} t^{\beta}$	Generalized RF 5 $\chi = \frac{\chi_O}{\left(1 + \left(\frac{t}{\tau}\right)^{\kappa}\right)^{r}}$	$r = \frac{1}{\alpha - 1}, \ \kappa = 1 + \beta,$ $\tau = \left(\frac{c}{\lambda} \cdot \frac{1 + \beta}{\alpha - 1}\right)^{\frac{1}{1+\beta}}, \ \chi_O = c^{\frac{1}{1-\alpha}},$ $c - const, \ \alpha \neq 1, \ \beta \neq -1, \ \lambda \neq 0$

With a purpose of adequate mathematical description of the observed post-irradiation relaxation kinetics, the numerical values of fitting parameters of the above RF were calculated in such a way to minimize the mean-square deviation of the experimentally measured points from the chosen RF.

As a result (see Fig.4 and table 2), it was established that kinetics of the observed decaying was satisfactorily described on the basis of non-exponential RF 4, taken in the form of so-called suppressed-exponential RF with character non-exponential indexes of 1.8,2.2,3.0,3.5 days for $(As_2S_3)_{1-x}(Sb_2S_3)_x$ with x=0, 0.1,0.2 and 0.3, respectively. This kinetics tends towards single- exponential (or, alternatively, monomolecular) one with character time constants of 2.1,1.9, 1.6 and 1.4 days (for the above ChGS taken in the same sequence).

This result contradicts strongly to previus study on Ge-based ChGS [7], where bimolecular relaxation kinetics proper to annihilation of coordination topological defects was dominant. It means that other type of structural – relaxation processes at the level of medium range order is more essential in the glass under consideration. It should be supposed that in case of studied $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS the process of post-irradiation relaxation attains activation character owing to renovation of destroyed chemical bonds, being described by monomolecular RF 1 rather than bimolecular one. It is quite understandable that such process is quicker in time giving small values of character time constants.

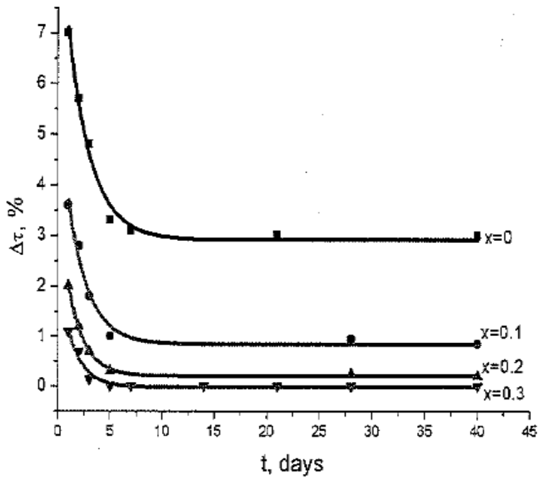

Figure 4. Time dependence of radiation – induced darkening $\Delta\tau_{max}$ in $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS(the bold lines correspond to modeling monomolecular RF)

Table 2. Main fitting parameters of post-irradiation relaxation in $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS

ChGS composition	Time constant in RF 1	Non-eponentiality index in RF 4
As_2S_3	2.1	1.8
$(As_2S_3)_{0.9}(Sb_2S_3)_{0.1}$	1.9	2.2
$(As_2S_3)_{0.8}(Sb_2S_3)_{0.2}$	1.6	3.0
$(As_2S_3)_{0.7}(Sb_2S_3)_{0.3}$	1.4	3.5

4.Conclusion

The process of post-irradiation structural relaxation in quasibinary $(As_2S_3)_{1-x}(Sb_2S_3)_x$ ChGS has an activation character owing to renovation of destroyed covalent chemical bonds, its kinetics being adequately described by suppressed-exponential RF tending towards monomolecular one. The observed compositional features in this decaying correlate well with known free volume tendencies.

Acknowledgements

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