

BIMOLECULAR BEHAVIOUR OF RELAXATION KINETICS IN RADIATION-OPTICAL PROPERTIES OF Ge-As(Sb)-S GLASSES

V. Balitska^{a,b}, O. Shpotyuk^{a,c*}

^aLviv Scientific Research Institute of Materials of SRC "Carat", 202, Stryjska str., Lviv, 79031, Ukraine

^bInstitute of Fire Safety, 35, Kleparivska str., Lviv, 79007, Ukraine

^cInstitute of Physics of Pedagogical University of Czestochowa, 13/15, al. Armii Krajowej, Czestochowa, 42201, Poland

The quantitative features of bimolecular decay relaxation kinetics are analysed for radiation-optical properties of chalcogenide glasses of ternary As_2S_3 - GeS_2 , Sb_2S_3 - GeS_2 and As_2S_3 - Ge_2S_3 systems in dependence on their chemical composition. It is shown, that the observed concentration dependences of relaxation parameters have monotonic character in the glasses of stoichiometric As_2S_3 - GeS_2 , and Sb_2S_3 - GeS_2 cut-sections, while anomalous extremum-like behaviour is observed in the point of expected 2D-3D phase transition in non-stoichiometric As_2S_3 - Ge_2S_3 glasses

1. Introduction

It is well known that a so-called bimolecular relaxation function (RF) $M_\eta(t)$, describing the relative change of control parameter η with time t as

$$M_\eta(t) = \frac{\eta_t - \eta_\infty}{\eta_0 - \eta_\infty} = \left(1 + \frac{t}{\tau}\right)^{-1}, \quad (1)$$

where τ is some material-related time constant,

η_0 is the initial amplitude of the control relaxation parameter ($\eta_0 = \eta_t$ when $t=0$),

η_∞ is the finite value of the control relaxation parameter ($\eta_\infty = \eta_t$ when $t \rightarrow \infty$),

often determines the degradation kinetics in different kinds of topologically-disordered solids [1-4]. In a more comprehensive way, this RF is introduced as exact solution of general degradation equation taken in a power-like form [1,3]

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

provided $\alpha=2$ and $\beta=0$. The latter condition means that relaxation rate of the chosen control parameter $\frac{d\eta}{dt}$ is independent on the time t . The same is proper also to monomolecular RF, giving a simple exponential behaviour in relaxation kinetics, but, in contrast, the relaxation rate of bimolecular degradation is directly proportional not to the first, but only to the second power in η . This bimolecular kinetics is proper to relaxation processes determined by recombination of specific defect centres of opposite nature – vacancies and interstitials, electrons and holes, over- and under-

* Corresponding author: shpotyuk@novas.lviv.ua

coordinated atoms, etc. [5]. It is well known that the bimolecular RF successfully describes the low-temperature decay kinetics of photoconductivity in solids (Vazer model) [6]. Sometimes, when the overall relaxation process can be decomposed on individual contributions from independent types of defects, the observed power-law decay behaviour can be explained in term of standard bimolecular kinetics too [5].

The decay kinetics observed in post-irradiation effects in glassy-like chalcogenide materials and revealed itself through time dependence of their radiation-induced properties (first of all, optical) can be mentioned as typical example of bimolecular relaxation [7,8]. Thus, in particular, it was established, that fundamental optical absorption edge of chalcogenide glasses (ChG) shifts in long-wave region in the result of corresponding decreasing in their band-gap energy, caused by irradiation of high energetic ($E > 1$ MeV) ^{60}Co γ -quanta. These so-called dynamic radiation-induced changes is not stable in time after irradiation in the normal conditions of samples storage, slowly decreasing during 2-3 months to some residual value in dependence on ChG composition [7,8].

The goal of this work is to analyse the compositional features of bimolecular decay relaxation kinetics for radiation-optical properties of ternary Ge–As(Sb)–S ChG taken along two typical glass-forming sections, the first one being restricted by stoichiometric arsenic (or antimony) trisulphide As_2S_3 (Sb_2S_3) and germanium disulphide GeS_2 , and the second one being restricted by stoichiometric As_2S_3 and non-stoichiometric Ge_2S_3 sulphides.

2. Experimental

The investigated ChG samples of As_2S_3 - GeS_2 , Sb_2S_3 - GeS_2 and As_2S_3 - Ge_2S_3 cut-sections characterised by average coordination number Z or, in other words, by number of covalent chemical bonds per one atom of glass-formula unit (in the supposition on full saturation of covalent bonding within glass-forming network), were chosen as follows:

- (As_2S_3) $_x$ (GeS_2) $_{1-x}$ at $x=0.1$ ($Z=2.63$), $x=0.2$ ($Z=2.59$), $x=0.4$ ($Z=2.53$) and $x=0.6$ ($Z=2.48$);
- (Sb_2S_3) $_x$ (GeS_2) $_{1-x}$ at $x=0.1$ ($Z=2.63$), $x=0.2$ ($Z=2.59$), $x=0.3$ ($Z=2.55$) and $x=0.4$ ($Z=2.53$);
- (As_2S_3) $_x$ (Ge_2S_3) $_{1-x}$ at $x=0.1$ ($Z=2.76$), $x=0.2$ ($Z=2.72$), $x=0.4$ ($Z=2.64$) and $x=0.8$ ($Z=2.48$).

The non-stoichiometric Sb_2S_3 - Ge_2S_3 chemical system was excluded from our consideration because of diminishingly small amplitude of the observed radiation-induced changes [9].

The above ChG samples of different chemical compositions were prepared from high-purity elemental constituents with direct synthesis in evacuated quartz ampoules. The standard rocking furnace technique followed by conventional melt-quenching route was applied [10]. After synthesis all ingots were air-annealed at a temperature of 20-30 K below T_g during 3-5 h to eliminate structurally-intrinsic imperfections (bubbles, cracks, incorporated strains and inclusions, etc.). Then they were cut into plates about 1-2 mm in thickness and 10-15 mm in diameter, the sample surfaces being polished to optical quality with 1 μm alumina. It was confirmed using X-ray diffraction and IR microscopy techniques that phase separation and crystallization processes did not occur in the investigated samples.

The value of atomic compactness δ calculated via the following formula [11]:

$$\delta = \frac{\sum_i \frac{\mu_i x_i}{\rho_i}}{V_a} - 1 = - \frac{V_o^\Sigma}{V_a}, \quad (3)$$

where x_i , μ_i , ρ_i – atomic part, mass and density of i -element within glass-forming network, respectively,

V_a – average molar volume (the ratio of molar weight M to experimental glass density ρ),

$V_o^\Sigma = V_a - \sum_i \frac{\mu_i x_i}{\rho_i}$ – average molar free volume,

was used as additional parameter for structural characterization of the prepared ChG. Apart from, the value of free volume per one atom of glass matrix V_o^A was estimated for each ChG to develop an adequate interpretation for microstructural origin of the observed relaxation phenomena. These parameters were calculated using known data on main physical-chemical properties of the investigated ChG [10,12].

The samples were irradiated with γ -quanta in the normal conditions of stationary radiation field, created in a closed cylindrical cavity by concentrically established ^{60}Co ($E=1.25$ MeV) radioisotope capsules. The accumulated dose for $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ChG was 2.2 MGy, for $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ChG was 1.0 MGy and for $(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$ ChG was 3.0 MGy, the absorbed dose power being at the level of a few Gy/s in all cases. The latter determined maximum temperature in glass bulk, which did not exceed 310-320 K during a whole period of γ -irradiation (from 2 to 6 weeks).

The optical transmission spectra of the investigated ChG were measured in the vicinity of fundamental absorption edge before, just after γ -irradiation and in some controlled moments during 3-months samples storage, using two-beam "Specord M-40" spectrophotometer (200-900 nm). Special marks were drawn on the sample surfaces in order to exclude errors caused by possible displacements in sample position respectively to probe light beam. As a result, the maximum error in optical transmission measurements did not exceed 0.5 %.

The observed radiation-optical effects reveal themselves clearly through long-wave (low-energetic) shift of fundamental optical absorption edge (darkening effect) [7-9]. So the value of relative increase in optical absorption coefficient $\Delta\alpha/\alpha_o$, was used as control relaxation parameter η in our experiments. The analytical description for relaxation kinetics was carried out taking maximal value of $\eta=(\Delta\alpha/\alpha_o)_{max}$. Since radiation-optical effects in the investigated ChG can be associated with specific structural defects having anomalous atomic coordination [6], the direct correlation exist between defect concentration and value of control relaxation parameter η . The observed decay kinetics in radiation-optical properties of ChG corresponds to annihilation of these defects after γ -irradiation switching-off [7-8].

3. Results

First of all, it should be emphasised once more that bimolecular RF is the most suitable one to describe adequately the decay relaxation kinetics in radiation-optical properties of ChG, when comparison is made with all other alternative resolutions theoretically possible for general differential equation of post-irradiation degradation [2-4].

The values of η_o and τ parameters proper to bimolecular RF describing decay kinetics in radiation-optical properties of the investigated ChG are presented in Table 1.

It is obvious that compositional dependencies of η_o and τ parameters have a smooth monotonical character for ChG of stoichiometric $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ and $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ systems. The time constant τ decreases in both cases, while η_o amplitude increases with Z for $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ and decreases for $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ChG.

At the same time, the anomalous character is observed in dependence of η_o and τ parameters on average coordination number Z for non-stoichiometric $(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$ system, the extreme values being observed near $Z \approx 2.7$ (in the point of possible 2D-3D topological phase transition [12-13]). Thus, the time constant τ and amplitude of relaxation parameter η_o reveal maximums in the vicinity of this point. This anomalous compositional behaviour is observed not only in radiation-optical, but other chemical-physical properties of the investigated ChG too [12-15].

Table 1. The values of η_0 and τ parameters of bimolecular RF, described decaying kinetics of radiation – optical properties in ternary $\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$, $(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$ and $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ ChG.

Structural-chemical parameters of ChG				Parameters of bimolecular RF	
x	Z	δ , %	V_o^A , \AA^3	η_0 , o.e.	τ , days
$(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$					
0.1	2.63	-11.4	3.16	0.36	112.7
0.2	2.59	-7.4	1.96	0.39	94.3
0.4	2.53	-6.7	1.73	0.43	73.7
0.6	2.48	-6.6	1.72	0.47	39.0
$(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$					
0.1	2.76	-7.4	1.97	0.54	20.0
0.2	2.72	-8.8	2.35	0.59	34.1
0.4	2.64	-9.2	2.46	0.43	54.1
0.8	2.48	-6.8	1.76	0.30	23.4
$(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$					
0.1	2.63	-8.78	2.42	0.72	197.5
0.2	2.59	-6.94	1.91	0.42	130.5
0.3	2.55	-4.70	1.28	0.28	126.6
0.4	2.53	-3.54	0.96	0.09	72.1

4. Discussion

It is well known that structural fragments of different dimensionality can co-exist simultaneously within covalent-bonded matrix of topologically-disordered solids like ChG. Thus, in part, 1D-dimensional or chain-like, 2D-dimensional or layered and 3D-dimensional or spatially cross-linked glass-forming blocks can be distinguished in ChG containing divalent two-fold coordinated chalcogen (S, Se or Te), trivalent three-fold coordinated pnictide (As, Sb or Bi) and tetravalent four-fold coordinated germanium Ge atoms in dependence on their composition [10,16]. That is why compositional effects in ChG are often revealed themselves through topological specifics of their glass-forming network. In other words, not only chemical, but also topological phase transitions are possible with composition change in ChG.

One of the above mentioned phase transition, which has a strict topological nature, is observed at $Z=2.4$, it being connected with “floppy-to-rigid” (or 1D-2D) structural transformation [17,18]. It is assumed for this case that average constraint per one atom is close to 3. When atomic system has a smaller constraint (less than 3), it is under-coordinated, when more – over-coordinated.

This approach K. Tanaka stretched on more structurally complicated ChG with 2D-dimensional layer-like and 3D-dimensional Ge-based units, fore seeing the possibility for analogous 2D-3D topological phase transition at $Z = 2.7$ [19]. He believed that quasi-layered 2D-dimensional structure is dominant at $Z < 2.7$, while in the case of $Z > 2.7$ the glass structure spontaneously transfers into 3D-dimensional spatially cross-linked network. Despite its simplicity, this version on the nature of $Z = 2.7$ phase transition cannot be accepted within Fillips-Thorpe rigidity concept as strict counterpart of mechanical “floppy-to-rigid” phase transition in the point of $Z = 2.4$ [18]. Therefore, chemical origin [14,15] or microphase separation processes [20,21] are often adopted to explain the above anomalous behaviour near $Z = 2.7$.

As to the investigated ternary Ge-As(Sb)-S systems, they are built mainly with 2D-dimensional pyramidal $\text{AsS}_{3/2}$ (or $\text{SbS}_{3/2}$) and 3D-dimensional tetrahedral $\text{GeS}_{4/2}$ complexes [10]. A small amount of Ge-enriched $\text{Ge}_2\text{S}_{6/2}$ structural groups appear only in non-stoichiometric As_2S_3 - Ge_2S_3 compositions at high Z values.

The studied stoichiometric As_2S_3 - GeS_2 and Sb_2S_3 - GeS_2 ChG have no any phase transitions in the whole Z range (Z values change from 2.4 to 2.67 for boundary compounds). The high saturation level of covalent chemical bonds in $\text{SbS}_{3/2}$ pyramids leads to the weakening of radiation-

induced defect formation processes within $(\text{Sb}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ system, while in $(\text{As}_2\text{S}_3)_x(\text{GeS}_2)_{1-x}$ systems the both components (As-based $\text{AsS}_{3/2}$ and Ge-based $\text{GeS}_{4/2}$) are sensitive to high-energetic γ -irradiation. As a result, the essential difference is observed in compositional dependencies of numerical parameters of bimolecular RF (η_0 and τ) for these ChG.

The time constant τ only decreases with average coordination number Z in both As_2S_3 - GeS_2 and Sb_2S_3 - GeS_2 systems, illustrating the common tendency to the stretching in decay relaxation kinetics with increase in the content of free volume (see Table 1). In other words, the duration of dynamic component of radiation-optical properties in the above stoichiometric systems increase with structural dimensionality of glass-forming network (rise in Z), presumably, owing to small atomic compactness δ (or, which is equivalent, owing to large content of free volume per one atom of glass matrix V_o^A). It should be noted that the higher absolute values of time constant τ are observed for stoichiometric Sb-based ChG in comparison with As-based ones, having the greater atomic compactness δ and smaller free volume V_o^A . So, the duration of the investigated decay relaxation process is determined by not only atomic compactness, but chemical nature of glass-forming network too.

The initial amplitude of the control relaxation parameter η_0 shows a monotonic growing dependence with Z for Sb_2S_3 - GeS_2 system and decaying one for As_2S_3 - GeS_2 system (Table 1). This behaviour is explained that both As- and Ge-related atomic subsystems are sensitive to radiation influence, while Sb-related subsystem leads to the weakening of radiation-induced changes owing to high metalisation level of covalent chemical bonds [22]. It should be noted that the observed monotonic character in compositional changes of relaxation parameters in the investigated stoichiometry systems agrees well with monotonic character in compositional dependences of atomic compactness δ and free volume V_o^A .

On the contrary, within non-stoichiometric ternary system $(\text{As}_2\text{S}_3)_x(\text{Ge}_2\text{S}_3)_{1-x}$, the character of radiation-induced processes essentially changes. Near $Z=2.67$ point, where the minimal atomic compactness δ and maximal free volume V_o^A are achieved, the greatest time constant τ is observed. So, despite stoichiometry of the investigated ChG, the greater free volume of glass-forming network, the higher value of time constant τ in post-irradiation relaxation process (see Table 1).

5. Conclusion

The observed bimolecular decay relaxation kinetics shows the monotonic compositional behaviour in stoichiometric As_2S_3 - GeS_2 and Sb_2S_3 - GeS_2 ChG, while extremum-like behaviour reveals in the vicinity of 2.7 average coordination number within non-stoichiometric As_2S_3 - Ge_2S_3 ChG. These features well correlate with compositional dependences of atomic compactness and free volume for all ChG systems.

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