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Radiation effects in physical aging of binary As–S and As–Se glasses

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Abstract Radiation-induced physical aging effects are studied in binary As_xS_{100-x} and As_xSe_{100-x} ($30 \leq x \leq 42$) glasses by conventional differential scanning calorimetry (DSC) method. It is shown that γ-irradiation (Co^{60} source, ~3 MGy dose) of glassy As_xS_{100-x} caused a measurable increase in glass transition temperature and endothermic peak area in the vicinity of glass transition region, which was associated with acceleration of structural relaxation processes in these materials. In contrast to sulfide glasses, the samples of As–Se family did not exhibit any significant changes in DSC curves after γ-irradiation. The observed difference in radiation-induced physical aging between sulfides and selenides was explained by more effective destruction-polymerization transformations and possible metastable defects formation in S-based glassy network.

Keywords DSC · Chalcogenide glass · Physical aging · Radiation effects

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Introduction

Chalcogenide glasses (ChG) are known as low-phonon energy materials transparent from the visible up to infrared perspective for IR telecommunication fiberoptic applications [1–3]. This feature of ChG is due to the heavier chalcogen atoms (S, Se, Te), which are the main constituents of their covalent networks. However, chalcogen-rich glasses possess a pronounced physical aging effect under ambient conditions hindering their wide use for several applications [4, 5]. The related structural relaxation processes are the reason for uncontrolled drift in the exploitation characteristics of ChG-based devices and can have extended kinetics from few hours up to tens of years depending on the glass composition and aging temperature [4, 5]. Their origin is associated with non-equilibrium metastable nature of the glassy state, which causes all glasses obtained by conventional melt-quenching route to approach the equilibrium structure of corresponding supercooled liquid over time [4–7]. To avoid this effect, the glasses with optimally-constrained covalent networks or almost saturated physical aging should be used in applications where the aging influence is detrimental on the desired glass properties [8, 9]. The first possibility demands substitution of twofold coordinated chalcogen atoms by chemical elements with higher coordination (i.e. As or Ge), increasing the number of constraints per atom (n_c) of the glass backbone, but simultaneously restricting the number of available compositions for practical application. The other option relies on the possibility to accelerate physical aging processes, having long-time kinetics under ambient conditions, into saturation by various external factors, such as thermal annealing at higher temperatures, sub-bandgap and bandgap photoexposure, radiation treatment, etc. [10–15].

Recently, it was shown that high-energy γ-irradiation was able to modify structural relaxation processes far below the glass transition temperature, T_g, in fragile ChG leading to their significant radiation-induced physical aging comparable with ~tens of years storage at the ambient conditions [13–15]. This effect has been comprehensively studied in Se-based glasses [13–15], whereas the impact of radiation treatment on physical aging processes in S-based ChG remained out of the scope. So far, these two chalcogenide glass systems exhibit different behavior of their optical properties in the fundamental optical absorption edge region on the influence of γ-irradiation [16, 17]. The arsenic sulfide glasses showed a well-expressed radiation-induced darkening associated with γ-induced chemical bonds switching and coordination topological defects formation, while radiation-induced changes in the fundamental optical absorption edge of arsenic selenide glasses were marginal [16, 17].

In the present paper, we compare the γ-induced physical aging effects in binary As–Se and As–S glasses as typical representatives of binary ChG widely used in photonics and optoelectronics.

Experimental

Glass samples of As_x (S, Se)$_{100-x}$ (x = 30, 33, 36, 40, 42) compositions were obtained by conventional melt-quenching technique. The mixture of high-purity precursors was melted in the evacuated quartz ampoules at 450–520 °C during 12–24 h in a rocking furnace. Then, the ingots were air quenched to a glassy state, which was confirmed visually by a character conch-like fracture and X-ray diffraction (XRD) data.

Before the experiment had started, all the samples were subjected to a rejuvenation procedure, which included heating of the samples ~50 °C above the onset of their calorimetric T_g, equilibrating of the obtained supercooled liquid and further its cooling with the rate $q > 5$ °C/min to room temperature. In such a way, it is possible to achieve a glassy state, which is close to the initial as-prepared state [18]. All the rejuvenated samples of each composition were divided into two batches. The first batch of samples was stored in hermetic plastic bags in the dark under controlled normal conditions, while the other one was disposed within the γ-irradiation chamber.

The γ-irradiation procedure was carried out at ambient conditions in a closed cylindrical cavity of concentrically established ^{60}Co sources (mean energy of 1.25 meV) with a few Gy/s dose rate, at a temperature not exceeding 28 °C. The total duration of γ-irradiation was 60 days and the accumulated dose was ~3 MGy. No special efforts were made to exclude the water/air influence during irradiation to minimize the difference between conditions of natural storage and radiation treatment of the investigated samples.

The samples of two batches were measured simultaneously using NETZSCH 404/3/F microcalorimeter before γ-irradiation (or storage) and just after γ-irradiation (or, consequently, after natural storage of the rejuvenated samples during the same period of time). The DSC curves were recorded in the ambient atmosphere with q = 5 °C/min heating rate. Three independent DSC measurements with samples of close masses were performed for each ChG composition to confirm the reproducibility of the results. T_g was determined from DSC heating data in cross-point of tangents at the beginning of glass-to-supercooled liquid transition (a so-called "onset" T_g value), using Proteus® software. Proteus® was also used for the determination of endothermic peak area A in the vicinity of glass transition. Statistical deviation of T_g for different samples of same prehistory did not exceed ±0.3 °C, while the error for peak area determination was about 2%.

Results and discussion

Structural relaxation of chalcogen-rich glass network through the glass-to-supercooled liquid transition interval normally results in a characteristic endothermic peak in the vicinity of T_g on the experimental DSC heating curves [4–6, 19]. It was shown that this endothermic peak also included the component associated with regaining of the entropy lost during natural storage [4, 5], photo or radiation influences [10–15], which were considered as signatures of physical aging effects caused by these factors. Schematic representation of the DSC curves and the corresponding behavior of configurational enthalpy (H) are shown in Fig. 1 as typical for the rejuvenated (as prepared) and aged Se-rich glasses. The area A under the endothermic peak (cross-hatched area in Fig. 1a) is directly proportional to the enthalpy losses (ΔH) caused by physical aging: the greater the A, the closer the glass is to the thermodynamic equilibrium state of the supercooled liquid (Fig. 1b). So, A was proposed as a control parameter for the quantitative description of physical aging effect induced by external factors [10–15]. In the case of fragile glasses, the accompanied increase in T_g values was commonly observed (Fig. 1a) [4, 5, 10–15].

It was shown recently that high-energy γ-irradiation stimulated additional physical aging in As_xSe_{100-x} ChG with $x < 30$ over the one produced by storage under ambient conditions [15]. This effect was expressed on DSC curves as an increase in T_g and A in the vicinity of glass transition region, like in Fig. 1a. At the same time, no measurable γ-induced changes in DSC curves were recorded for As_xSe_{100-x} ChG with $x \geq 30$ [15].

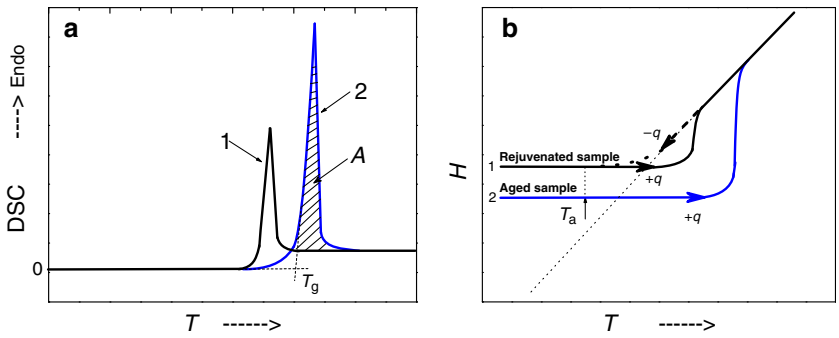

Fig. 1 Schematic representation of DSC curves (**a**) and configurational enthalpy *H curves* deduced from them (**b**) for Se-rich samples: 1 (*black*), just after the rejuvenation procedure; 2 (*blue*), after physical aging. *Dotted line* corresponds to the extrapolated glass equilibrium line of the supercooled liquid

Experimental DSC curves obtained for the rejuvenated, 60 days aged and γ-irradiated samples of the investigated As_xS_{100-x} ($30 \leq x \leq 42$) ChG are shown in Fig. 2a, c–f. Quantitative characteristics of the physical aging effects determined from DSC spectra as A and T_g values are plotted in Fig. 3a, b, respectively. The observed T_g values (Table 1) agree well with those in literature [20].

The A values just after the rejuvenation procedure do not exceed 0.9 J/g for all of the investigated glasses, which can be considered as a level of pure structural relaxation that occurred in these materials through a glass-to-supercooled liquid transition at given q [6, 19]. Like in the case of selenide glasses [15], no physical aging effect was observed in the investigated ChG of the As_xS_{100-x} compositional domain where $30 \leq x \leq 42$ after 60 days of storage at normal conditions. This result agrees well with the microstructural model of natural physical aging proposed recently on the basis of the investigations of this effect in long-term aged selenide glasses [21, 22]. This model considers physical aging as a complicated process, which consists of two components called short-term and long-term physical aging, respectively. The first one (short-term) is associated with the alignment of chalcogen polymeric chains consisting of three or more chalcogen atoms (can be alternatively understood as transition from *cis*- to *trans*-conformations of chalcogen atoms in chain within a

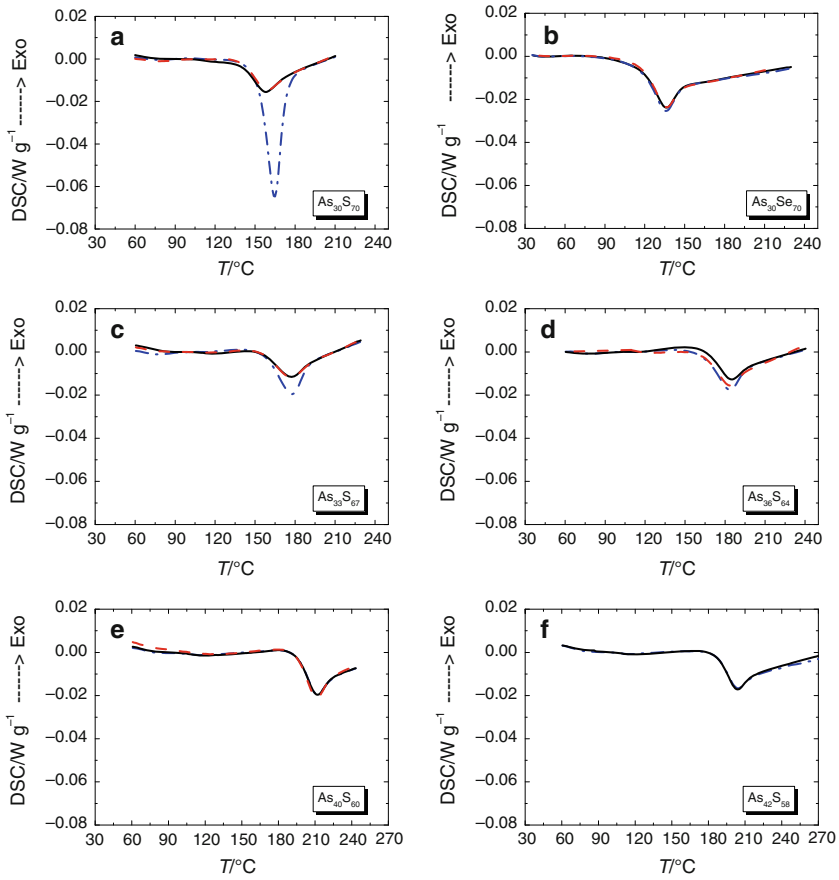

Fig. 2 (Color on-line) Heating ($q = 5$ °C/min) DSC curves of As_xS_{100-x} (**a**, **c**–**f**) and $As_{30}Se_{70}$ (**b**) ChG: rejuvenated or as prepared (*solid*, *black*), 60 days aged under normal (*dash*, *red*) and 60 days aged under Co^{60} γ-radiation conditions (*dash dot*, *blue*)

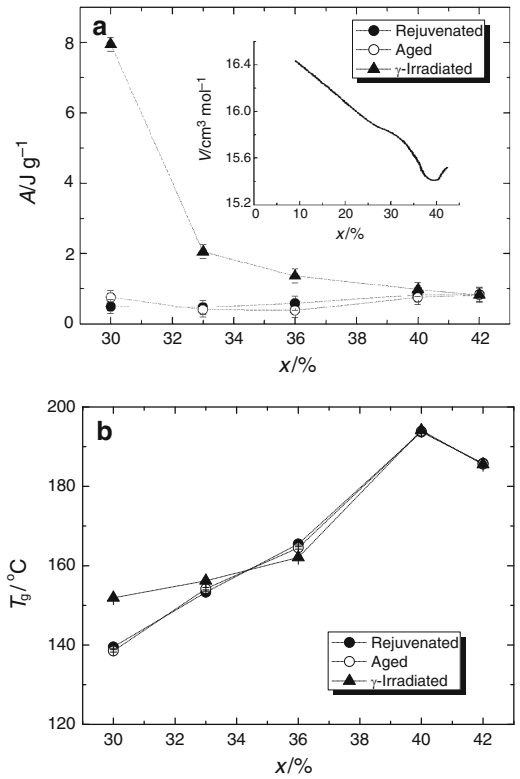

Fig. 3 Compositional dependences of the area A (**a**) and the glass transition temperature T_g (**b**) values for the rejuvenated, 60 days aged and γ-irradiated As_xS_{100-x} glasses, determined from corresponding DSC curves recorded with $q = 5$ °C/min. Inset shows compositional dependence of molar volume V [6]. The *lines* are drawn as guide for the eyes

so-called double-well potential) followed by a shrinkage of surrounding network [21]. This is a relatively fast process, which can be activated at room temperatures. We believe that it is responsible for a short-term physical aging effect observed in Se-rich As_xSe_{100-x} ($x < 25$), in which the glass backbone contains fragments with at least three Se atoms in the chain according to the "chains crossing" model, validated recently for these glasses [23]. The second component, long-term physical aging, is associated with prolonged overall shrinkage of an under-constrained glass network (i.e. $n_c < 3$), which can be accompanied by redistribution of chemical bonds [22]. Since sequences of three chalcogen atoms in a chain should fully disappear at a composition of As_xSe_{100-x} where $x \geq 25$ according to the "chains crossing" model formalism [23], the investigated under-constrained As_x (S, Se)$_{100-x}$ ($30 \leq x < 40$) glasses should be characterized solely by a long-term kinetics of physical aging, which requires >60 days of natural storage to be detected experimentally. Glasses of stoichiometric As_{40} (S, Se)$_{60}$ composition are expected to have optimally-constrained ($n_c = 3$) covalent network, which does not permit shrinkage. Therefore, these glasses should not exhibit conventional physical aging phenomenon at the ambient conditions [24].

Contrary to selenide glasses, a considerable radiation-induced physical aging effect was recorded for $As_{30}S_{70}$ and $As_{33}S_{67}$ compositions in the present experiment. The DSC curves of γ-irradiated ChG are shown by dashed–dotted (blue) lines in Fig. 2 for the investigated glasses of As_xS_{100-x} ($30 \leq x \leq 42$) and $As_{30}Se_{70}$ (Fig. 2b) as typical example of the investigated As_xSe_{100-x} glasses. Hence, 60 days of aging within the γ-radiation field conditions caused an increase in endothermic peak area A and T_g values for $As_{30}S_{70}$ and $As_{33}S_{67}$ compositions (Fig. 2a, c), while no effect was observed for $As_{30}Se_{70}$ and $As_{33}Se_{67}$ compositions of the investigated As_xSe_{100-x} glasses. This result correlates well with the previous investigations of γ-induced changes in the mechanical properties (shear modulus, microhardness) of binary arsenic-based ChG showing decay of the γ-induced changes in the compositional row $As_2S_3 \rightarrow As_2Se_3 \rightarrow As_2Te_3$ [25, 26]. To explain the different behavior of the glasses, which are expected to have similar structure of covalent networks, the processes under the influence of γ-radiation should be considered in more detail.

As a rule, three main mechanisms of the interaction of γ-rays with matter are considered: γ-quanta can lose their energy as a result of absorbing, Compton scattering, and creation of electron–positron pairs [27]. In the case of ChG and the energies of γ-quanta used (1.25 MeV), the main mechanism is related to Compton scattering [26]. Because of strong electron–phonon coupling associated with ChG

Table 1 Glass transition "onset" temperature values determined from DSC curves of rejuvenated (as prepared), 60 days aged and γ-irradiated As–S ChG and their statistical deviation

ChG composition	T_g-onset/°C		
	As prepared	Aged without radiation	Aged with γ-radiation
$As_{30}S_{70}$	139.5 (±0.3)	138.5 (±0.3)	151.9 (±0.3)
$As_{33}S_{67}$	153.3 (±0.3)	154.2 (±0.3)	156.2 (±0.3)
$As_{36}S_{64}$	165.5 (±0.3)	164.5 (±0.3)	162.1 (±0.3)
$As_{40}S_{60}$	193.7 (±0.3)	193.9 (±0.3)	194.1 (±0.3)
$As_{42}S_{58}$	185.8 (±0.3)	185.6 (±0.3)	185.5 (±0.3)

[6], the Compton photoelectron produces specific destructive structural transformations. They are associated with chemical bonds breaking/switching, which can be accompanied, in part, by coordination defect formation [28]. In the case of selenide glasses, these processes decay rapidly without conservation of any coordination defects, which is evident from the absence of significant changes in optical properties of these materials after γ-irradiation.

A drastically different situation is expected for sulfide glasses. On the basis of optical studies, it is shown that γ-induced covalent bonds switching in these materials is accompanied by the formation of metastable topological coordination defect pairs, such as diamagnetic positively-charged, over-constrained and negatively-charged under-constrained atoms [16, 28]. Their concentration decays to some residual value during few days/months after radiation treatment depending on glass composition [16, 29]. So, we can assume that γ-stimulated structural transformations (broken or switched covalent bonds, topological coordination defect pairs, in the first approximation) are more stable and appropriate to sulfide networks giving additional possibility for reorientation of constituent structural units and more extended structural fragments under irradiation conditions. Along with structural rearrangements associated with topological coordination defects themselves, these processes provide an additional effective channel for the release of free volume, which is frozen during melt quenching and, thus, contribute to general shrinkage of the glass backbone.

On the other hand, the structural network of As_xS_{100-x} (as well as As_xSe_{100-x}) ChG approaching stoichiometric composition at $x = 40$ becomes more rigid, being built mostly of the optimally-constrained ($n_c = 3$) phase made of corner-shared pyramids, which are resistant to shrinkage processes [23]. Moreover, compositional dependence of molar volume V exhibits a minimum at $As_{40}S_{60}$ composition (see insert to Fig. 3a) [6], testifying also a minimum value of free volume available for relaxation in this glass within the whole As_xS_{100-x} vitreous system. Therefore, it is quite consistent with these data that γ-induced changes in DSC curves decrease rapidly toward stoichiometric $As_{40}S_{60}$ composition (Fig. 3a).

It should be noted here that under γ-radiation conditions, the relaxation of the network sites can be achieved even if it would never occur during very long natural storage because of spatial constraints. This process is possible due to the destruction of covalent bonds under γ-irradiation, which makes it different from the natural physical aging effect where only conformations of the network are considered. So, we can achieve a more thermodynamically stable equilibrium state with γ-irradiation than is achievable after many years of natural storage, provided γ-stimulated excitations do not decay rapidly. Therefore, the use of γ-radiation is an alternative way to achieve a thermodynamic quasi-equilibrium state of glass for a short period of time (days) at much lower (room) temperatures, at which relaxation rate normally is very slow (tens of years).

Conclusions

It is shown by the conventional DSC technique that binary As_xS_{100-x} and As_xSe_{100-x} ChG of $30 \leq x \leq 42$ compositions stored at normal conditions during 60 days do not exhibit any significant physical aging effect. However, despite structural similarity of main constituent building blocks (pyramids and chalcogen chains), the As_xS_{100-x} ChG possessed completely different compositional behavior of physical aging under γ-irradiation than As_xSe_{100-x} glasses. Contrary to selenide glasses, γ-irradiation of As_xS_{100-x} ChG with $x < 40$ caused a measurable increase in the endothermic peak area in the vicinity of the glass transition region. Using the analogy with natural and γ-induced physical aging effects in As_xSe_{100-x} ChG with $x < 30$, it is concluded that the structural network of these γ-irradiated As_xS_{100-x} ChG relaxes under irradiation to a new thermodynamic state, which is closer to equilibrium of supercooled liquid exhibiting a well-pronounced γ-induced physical aging. Owing to metastable coordination defects formation possible in sulfide glasses, the nature of the observed phenomenon is assumed to be associated with additional possibility for shrinkage of glassy backbone under γ-radiation conditions due to more effective destruction-polymerization transformations.

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