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Structural-relaxation phenomena in As–S glasses as probed by combined PAL/DBAR technique

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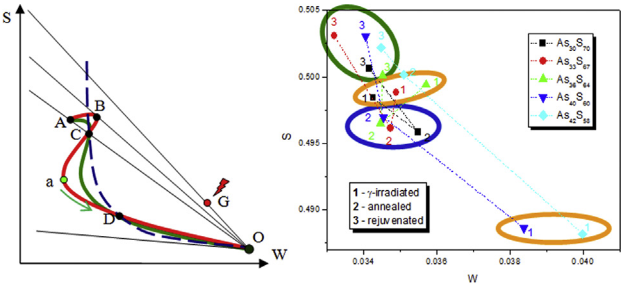
HIGHLIGHTS

- Combined optical, PAL and DBAR probes to study structural relaxation in As–S glasses.
- Void agglomeration, fragmentation and disappearing are main stages of physical aging.
- Radiation-induced coordination defects are important in near-stoichiometric As–S.
- Proposed model describes free-volume evolution in the void structure of As–S glasses.

GRAPHICAL ABSTRACT



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ABSTRACT

Experimental techniques exploring phenomena of positron–electron interaction, namely the positron annihilation lifetime spectroscopy and Doppler broadening of annihilation radiation, are shown to be very informative tools to study radiation- and thermally-induced phenomena in chalcogenide glasses of binary As–S system. Time-dependent processes of free-volume voids agglomeration (expansion), fragmentation (refining) and disappearing (contraction) are identified as main stages of physical aging in S-rich glasses, while a competitive channel of coordination topological defects formation associated with void charging becomes significant in a vicinity of near-stoichiometric glass compositions under γ-irradiation. The data of combined positron lifetime and Doppler broadening of annihilation radiation measurements are correlated with radiation-induced shift of fundamental optical absorption edge of the studied glasses. The meaningful model for γ-induced and relaxation-driven evolution in free-volume void structure of As–S glasses giving a unified insight on their structural-chemical nature is proposed.

1. Introduction

Glassy compounds of chalcogen atoms (S, Se or Te) with elements of fourth and fifth groups of Periodic table, known also as chalcogenide glasses (ChG), are still in a focus of researchers because of their transparency in the mid- and far-infrared region

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[1]. Form the other hand, their unique functionality is determined by a possibility to occupy different metastable states under the external influences (absorbed light, thermal annealing, high-energy irradiation, etc.) [2–4]. This ability is proper to network solids like ChG because of a specific type of structural transformations associated with induced covalent chemical bonds redistribution. These redistribution processes called also in the beginning of the 1970-s as *destruction-polymerization transformations* (DPT) [5] don't change the average covalent bonding of a glassy network (defined by overall number of bonds), but significantly modify energetic characteristics of a glass backbone due to the changes in the bond type (switching of weaker into stronger bonds, for example), producing measurable shift in the fundamental optical absorption edge as well as a number of other noticeable effects [2–5]. In fact, the DPT involves destruction of single covalent bond followed by formation of a new one, this switching being considered as an elementary precursor for new metastable state, which is characterized by two atoms in a glass network with abnormal local coordination beyond *8-N* rule [3]. The created over- and under-coordinated atoms form diamagnetic pair of charged coordination topological defects (CTD), where positive and negative charges are localized on over- and under-coordinated atoms, respectively. Alternatively, the DPT can proceed as more complicated non-defect structural rearrangement, when two covalent bonds simultaneously switch into two others without changes in the charge and local coordination of the participating atoms [6,7].

The first experiments on direct evidence of DPT in ChG were conducted yet in 1980-s involving reversible photo- [6–8] and radiation-induced [9] structural changes in amorphous arsenic trisulphide As_2S_3. In the earliest 2000-s, these experiments were followed by remarkable theoretical works [10–12] justifying the CTD-related origin of induced effects in ChG through quantum-chemical modeling of different disturbed configurations in $AsS_{3/2}$-pyramid-like network. Then, the CTD concept has been revised many times. The most often, this concept was challenged because of low intrinsic concentration of CTD frozen during initial melt quenching procedure [13], estimated at the level of ~10^{17}–10^{18} cm^{-3} [4,6]. This is definitely not enough to produce meaningful changes in physical properties of ChG. Nevertheless, the possibility of CTD formation in more significant concentrations as a result of external influences was still accepted as a reasonable way to explain such changes in physical properties of irradiated ChG [4].

However, recent reports questioned even this possibility [14–17]. In particular, these authors have challenged the possibility of DPT in g-As_2S_3 [15,17], which is considered as one of the model objects for induced effects, where CTD concept is relatively well justified [6–9]. At the same time, a certain number of flaws in the works [14–17], like absence of direct experimental evidence for radiation-induced effect itself (transmission data in the fundamental optical absorption edge region, which usually provide a direct evidence through radiation-induced darkening effect, were not provided), inaccuracy of the experimental techniques due to *ex-situ* measuring protocol (as in a case of positron annihilation measurements [17]), neglecting role of the samples' prehistory (experimental samples were treated in multiple irradiation-annealing cycles, irradiated more than 7 years before the measurements, etc.), do not allow one to make an unambiguous conclusion on the validity of CTD concept for radiation-induced effects in ChG.

In our research, we have studied comprehensively the radiation-induced DPT followed by eventual CTD formation in ChG of binary As–S system including stoichiometric g-As_2S_3 as model object by positron annihilation lifetime (PAL) and Doppler broadening of annihilation radiation (DBAR) techniques as ones of the most suitable and powerful tools for investigation of solids at the different levels of their structural hierarchy [18–21]. In fact, PAL and DBAR methods were used for defect spectroscopy investigations, as a source of both qualitative and quantitative information about defects on an atomic scale. The radiation-induced effect itself was controlled by optical transmission in the range of fundamental optical absorption edge routinely at all stages of the experimental measurements, e.g. just after γ-irradiation, near-T_g thermal annealing and rejuvenation procedures. This ensures that PAL and DBAR measurements reflect the real effect of irradiation on all studied objects.

2. Experimental

The samples of glassy g-As_xS_{100-x} with $x = 30, 33, 36, 40, 42$ were prepared by conventional rocking-melting-quenching technique as was described elsewhere [22]. The samples were synthesized using respective quantities of high-purity elemental constituents (no worse than three nines) in evacuated and sealed fused quartz ampoules. The mixture was melted in a rocking furnace at 720–790 K for 12–24 h. The ingots were air-quenched to a glassy state, which was confirmed by X-ray diffraction data. The samples were additionally annealed during 1–2.5 h at the temperature 30–40 K below the glass transition temperature to relieve the residual mechanical stresses. Before the experiments, the samples were cut into plane-parallel plates of 1.5 mm in thickness and polished to high optical quality.

The γ-irradiation treatment was carried out at the ambient conditions in a closed cylindrical cavity of concentrically established ^{60}Co sources (the mean energy of γ-quanta was 1.25 MeV) with 0.7 kGy/h dose rate at the temperature not exceeding 300 K. The overall duration of γ-irradiation treatment was 6 months and total accumulated dose during this period was ~3 MGy. After γ-irradiation, part of the irradiated samples were annealed at 30–40 K below glass transition temperature T_g (for a few hours) and then rejuvenated above T_g in a heating–cooling cycle (the values of annealing and rejuvenation temperatures were chosen based on the results [23]). Such a protocol allowed us to perform the investigations in a so-called *backward measurement chronology* during short period of time after γ-irradiation, excluding most of the inaccuracies associated with instrumentation and measurement procedures.

Optical transmission spectra in the fundamental optical absorption edge region were recorded one month after γ-irradiation using *AvaSpec-2048* spectrometer (*Avantes*, Netherlands) with an accuracy not worse than ±1% as was described elsewhere [24,25]. Annealing and rejuvenation of the γ-irradiated samples were performed directly in the optical chamber of the spectrometer, using air-flow heating and cooling system with ±0.5 K accuracy of temperature control, and a constant 5 K/min heating/cooling rate. The optical spectra were recorded *in-situ* before, during and after thermal treatment of γ-irradiated ChG samples, which position was kept the same in respect to the probe light beam during a whole experiment. It is noteworthy to underline that such *in-situ* protocol allows to exclude inaccuracies associated with samples installation in multiple measuring cycles, as well as to distinguish “pure” radiation- and thermally-induced effects.

Under this methodological route, three different structural states were studied in g-As_xS_{100-x}: the annealed and γ-irradiated (state 1), additionally annealed after γ-irradiation (the post-irradiation state 2) and rejuvenated (the post-irradiation state 3). Our investigation is grounded on the prerequisite that the rejuvenation procedure restores as-prepared state of ChG [26], and below-T_g thermal annealing fully erases reversible part of γ-induced changes [3,4]. So the evolution of void structure

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