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Compositional anomalies in Se-rich As-Se glass-forming system as revealed from positron annihilation lifetime spectroscopy and *ab initio* cluster modeling

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ABSTRACT

Positron annihilation lifetime spectroscopy in high-measurements statistics supported by *ab initio* quantum chemical modeling developed within cation-interlinking network cluster approach were used to examine compositional peculiarities of free-volume evolution in Se-rich As-Se glasses. Existence of some anomalies in the studied glasses observed as jump in the defect-related positron lifetime near average coordination $Z \approx 2.33$ and strong growing trend approaching $Z = 2.40$ is justified. These features correspond to evolution of glassy network due to free-volume elements based on solid angle free of bond charge associated with Se atoms in a vicinity of heteropolar chemical bonds. The results are explained within structural models of optimized network of As-Se glasses composed of $AsSe_{3/2}$ pyramids interlinked by variable-length Se-chains.

1. Introduction

Chalcogenide glasses (ChG), i.e. vitreous compounds based on chalcogens (either sulfur S or selenium Se, sometimes tellurium Te, but not oxygen O), have been in a focus of extensive research during last decades, due to their excellent IR-transmitting properties and possibility of numerous applications in modern photonics (chalcogenide photonics) [1–4]. The glassy arsenic selenides As-Se prepared by melt-quenching route are typical representatives of ChG, showing strong glass-forming ability in a wide range of chemical compositions corresponding to average coordination numbers Z from pure Se ($Z = 2.00$) to almost $Z \cong 2.70$ [5–8].

One of most characteristic features of ChG, which is really important from practical implementation point, is their structural metastability connected with transition from frozen supercooled liquid to more thermodynamically equilibrium state [9,10]. This process known as physical aging [9,11] results in elimination of excess of configurational enthalpy or free volume in spatial distribution of glass-forming units available for relaxation [11,12].

Compositionally, the ChG demonstrate three network-forming structural domains in respect to physical aging, these being (i) under-constrained or floppy networks, which are undergoing on pronounced natural physical ageing, (ii) optimally constrained (rigid but stress free) networks, which are most attractive for applications because of theirs non-aging ability, and (iii) over-constrained or stress-rigid networks, which are susceptible to ageing but only at higher temperatures [13,14]. The compositional range of optimally constrained elastic phase (in which the number of Lagrangian constrains per atoms equals space dimensionality) forms the reversibility window (RW). In respect to Phillips-Thorpe rigidity theory [15,16], the RW boundaries in covalent network glass-formers (like As-Se glassy system) are expected to be compositionally narrowed and close to stoichiometry $Z = 2.40$ [17]. In contrast, the experimental temperature-modulated DSC measurements revealed the RW in these ChG at much lower atomic coordination ($Z = 2.29$–2.37), i.e. essentially shifted towards chalcogen-rich compositions and too extended in glass chemistry ($\Delta Z = 0.08$).

Recently, the glass-forming tendency in chalcogen-rich arsenic selenides As-Se was examined through *ab initio* quantum chemical modeling in respect to a row of network-forming clusters (NFC) built within cation-interlinking network clusters approach (CINCA) [18–21]. It was shown [20,21], these NFC demonstrate some anomalies near the lower limit of the RW previously announced in [22–24], but it was unclear whether these anomalies could be accepted as realistic signatures of the RW boundaries.

The ChG belonging to the RW are imagined as self-organized network glass-formers non-affected to physical ageing in view of their minimal free-volume available for relaxation. Therefore, effective methods to probe compositional variations in such

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systems are those, which are selectively sensitive to their atomic-deficient free-volume sub-system. One of such methods is positron annihilation lifetime (PAL) spectroscopy [12,25–27], the method grounded on space-time continuum determination for electron annihilating with its antiparticle, the positron. Because different types of open-volume defects occur in amorphous materials (open-volume holes, inner pores, vacancies or vacancy-like clusters and their agglomeration), they usually form trapping sites for positrons [25–31]. Respectively, the lifetimes of positrons trapped in open-volume defects are longer in comparison to lifetime of free annihilating positrons. The known two-state positron trapping model [12,25,27] allows parameterization such annihilation processes in semiconductor materials. Within this model two lifetime components τ_1 and τ_2 of PAL spectrum are accepted, where the second (the longer) is correlated with defect-related one [12,28,31]. Further, it was shown [32] that decisive role in the correlation between defect-related lifetime τ_2 and corresponding radius of free-volume positron traps in ChG plays chemical environment of free-volume voids possessing an effective negative charge owing to difference in electronegativities of chemical bonds belonging to neighboring network-forming units (such as $AsSe_{3/2}$ pyramids in As-Se glasses).

In this work, the compositional dependencies of defect-related positron annihilation lifetime τ_2 in As-Se ChG are discussed in the light of modeling results for two-cation NFC, based on CINCA simulation algorithm for network covalent solids [18–20].

2. Methods description

The glasses of As_xSe_{100-x} system (x = 10, 20, 24, 28, 30, 33, 35, 36, 38 and 40) were experimentally tested with PAL technique. The tested samples were prepared by conventional melt-quenching route as it was describes in more details elsewhere [20,21].

The PAL spectroscopy measurements were carried out with an ORTEC spectrometer with FWHM (full-width at half-maximum) of 230 ps. The ^{22}Na radioisotope with ~50 kBq activity was used as a source of positrons. This source was placed between two identical samples, forming a "sandwich" system. The PAL spectra were collected at room temperature under high-measurement statistics involving near $\sim 5 \times 10^6$ elementary annihilation events. All spectra were treated with LT 9.0 program [33], taking into account the FWHM and source correction.

The network-forming tendencies in binary As-Se glasses were simulated with known algorithm described in [20]. The As_2Se_m NFC with m = 3–7 (corresponding to Z = 2.22, 2.25, 2.29, 2.33, 2.40) were built in full agreement with CINCA procedure [20,21]. They were constructed of two separate trigonal pyramids $AsSe_{3/2}$ interlinked through common length-variable Se bridges of = As—Se_n—As = type suitable to the chosen glass composition (i.e. n = 1 for single-atom Se chain, and/or $n \geq 2$ for respectively longer multi-atomic Se chains). In general, atomic clusters with both integer and fractional steps determined by m values are possible. However, the fractional m parameters correspond to larger asymmetric atomic clusters (with inter-cluster legs of different length). Such clusters cannot be simply modeled within CINCA approach, therefore they are not considered in this paper.

The *ab initio* quantum chemical calculations were performed with Hyper Chem Release 7.5 program using RHF/6311G* basis set [34,35]. The basis-set was chosen as reliable for all atomic clusters despite their length and symmetry. The geometrical optimization and single-point energy calculations were carried out with the Fletcher-Reeves conjugate gradient method until root-mean-square gradient of 0.1 kcal/Å·mol was reached. The E_f value of cluster forming energy was calculated for optimized NFC (terminated by H atoms) as the forming energy normalized to the energy of single $AsSe_{3/2}$ pyramid (−72.309 kcal/mol) [20].

3. Results and discussion

The best results of raw PAL spectrum reconstruction for As-Se glasses were achieved with two-component fitting procedure, proving existence of two components [12,25]. Therefore, two-state positron trapping model with τ_1 and τ_2 lifetimes and I_1 and I_2 intensities (under normalization condition $I_1 + I_2 = 1$), was accepted as valid for studied As-Se glasses. The first (the shortest) positron lifetime was fixed at τ_1 = 0.200 ns independently on ChG to minimize deviations in the defect-related components between close glass compositions [36]. The same chemical environment in all ChG, consisting of corner shared $AsSe_{3/2}$ pyramids with Se-chain bridging, fully justifies this assumption.

The values of defect-related positron annihilation lifetime τ_2 and I_2 intensity as a function of As content in As-Se system (determined by average atomic coordination Z) are depicted in Fig. 1.

As it follows from Fig. 1a, the defect-related positron lifetime τ_2 does not substantially differ in Se-rich compositions within Z range of 2.10–2.33. Then, as tending towards As_2Se_3 stoichiometry, this parameter increases rapidly starting from $Z \approx 2.33$. Simultaneously, the I_2 intensity (Fig. 1b) corresponding to longer lifetime component in the measured PAL spectrum also demonstrates a growing tendency (I_2 reaches ~0.66 for Z = 2.10–2.24; ~0.69 for Z = 2.28–2.38, and ~0.75 for Z = 2.40).

Let's look yet at the values of positron trapping rate κ_d, as one of decisive parameters in two-states positron trapping model, which can be calculated as [12,25]:

$$\kappa_d = I_2\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) \quad (1)$$

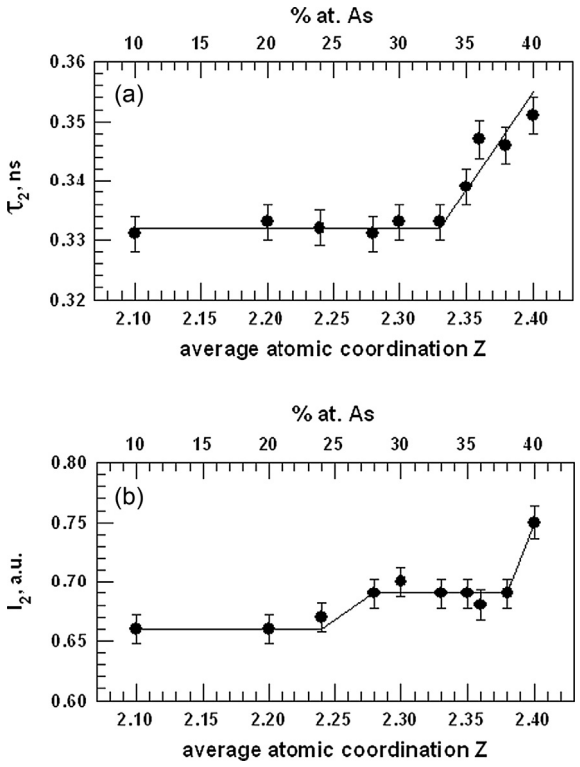

Fig. 1. Defect-related positron annihilation lifetime τ_2 (a) and I_2 intensity (b) as a function of average atomic coordination Z in As-Se system.