Journal of Non-Crystalline Solids 392–393 (2014) 1–5

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Long-term natural physical aging in glassy Ge_5Se_{95} as probed by combined NMR and PAL spectroscopy

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ARTICLE INFO

Article history:
Received 28 January 2014
Received in revised form 18 March 2014
Accepted 24 March 2014
Available online xxxx

Keywords:
Chalcogenide glasses;
Nuclear magnetic resonance;
Positron annihilation;
Physical aging

ABSTRACT

Structural rearrangements associated with long-term natural physical aging in glassy Ge_5Se_{95} are studied using combined methods of solid state ^{77}Se nuclear magnetic resonance and positron annihilation lifetime spectroscopy. *Ab initio* quantum chemical calculations with RHF/6-311G* basis set was performed to justify the character of the observed destruction–polymerization transformations possible during long-term natural storage of Ge_5Se_{95} glass. It is shown that some amount of directly corner-shared $GeSe_{4/2}$ tetrahedrons present in as-prepared glasses slowly transform under prolonged physical aging in a more uniform glassy network composed by nearly-equal Se chains between neighboring $GeSe_{4/2}$ tetrahedrons. These transformations are accompanied by atomic shrinkage with character fragmentation of free-volume voids typical for chalcogen-rich glasses. The observed effect in Ge_5Se_{95} glass is compared with similar changes in long-term aged As–Se glasses having short ($As_{30}Se_{70}$) and long ($As_{10}Se_{90}$) selenium chains.

1. Introduction

Physical aging (PhA) occurring as a result of structural relaxation below the glass transition temperature T_g (referred also as *below-*T_g *structural relaxation*) is a permanent feature of different network glass-formers, including oxide and chalcogenide glasses (ChG) [1–4]. In particular, strong PhA effect caused by prolonged storage in natural conditions (natural PhA) and under different external influences (thermal heating, high-energy irradiation, absorbed light photoexposure) was detected in Se-based ChG of binary As–Se [5–7], Ge–Se [8–10] and ternary Ge–As–Se [11] systems. The nature of this effect is associated with the Johari–Goldstein β-relaxation [2] involving two stages of structural perturbations [12,13]. The first stage relies on the elementary relaxation events (twisting) of inner Se atoms within double-well potentials associated with high flexibility of chalcogen bonds (presumably viewed as *cis–trans* reconformations) [12–14], which serve as precursors for spontaneous densification (alignment) of local Se-rich regions. This initial process leads to a partitioning of the system into loosely and more densely packed regions (confirmed recently by simultaneous positron annihilation lifetime (PAL) spectroscopy and differential scanning calorimetry (DSC) measurements [15]), which then collapse decreasing density fluctuations. In the second stage, the above relaxation processes are assumed to happen at a larger scale in sequence and/or parallel way, leading to an overall shrinkage of the glass backbone, which can be attributed to the Johari–Goldstein β-relaxation facilitating α-relaxation events [13].

During overall shrinkage, the bond-changing structural rearrangements are also possible in ChG as a minor process. Thus, it is shown recently for glassy g-$As_{30}Se_{70}$ that some of the two neighboring $=\!As-Se-Se-As\!=$ bridge-like structural units switch into short $=\!As-Se-As\!=$ and long $=\!As-Se-Se-Se-As\!=$ fragments as a result of long-term natural PhA [16]. This possibility is confirmed by our modeling within cation-interlinked network cluster approach (CINCA), showing energetic preference for directly corner-shared $AsSe_{3/2}$ pyramids in the structure of binary As–Se glasses with short chalcogen (Se) chains (like g-$As_{30}Se_{70}$) [16]. Therefore, long-term natural PhA in these glasses can be accompanied by changes in bonds statistics, deviating from predictions of the uniform "chains crossing" model [17].

In case of longer Se chains interconnecting rigid cation-centered structural units, however, it was established previously at the example of g-$As_{10}Se_{90}$ that chemical bond distribution is almost held during structural transformations associated with long-term PhA [12]. The natural question then arises: does it hold for all the Se-rich ChG, or maybe there are some peculiarities due to the nature of cation-centered structural units?

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.03.025
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To answer this question, we have studied chemical ordering and atomic-deficient (void) structure of Ge_5Se_{95} glass, which is characterized by an average coordination number of 2.1 (similar to g-$As_{10}Se_{90}$) subjected to long-term natural PhA for more than two decades. The results are compared to ones obtained for rejuvenated samples of the same composition, which is assumed to be in a state close to the as-prepared virgin glass.

2. Experimental

Glassy g-Ge_5Se_{95} samples were prepared by conventional melt-quenching route more than two decades ago (in 1990) [18]. The mixture of high-purity precursors (not worse than three nines) was melted in an evacuated quartz ampoule at 973 K for 5 h in a rocking furnace. Then, the ingots were air-quenched from 900 K to achieve a glassy state. After synthesis, each of the samples was stored in a dark place at controlled room temperature before the present measurements were carried out. The amorphous state of the samples was inferred from data of differential scanning calorimetry and X-ray diffractometry.

Before the experiments, part of the aged samples was rejuvenated in order to achieve the structural state close to the initial as-prepared one [4,10]. This procedure implied heating of the samples above their glass transition temperatures (T_g), waiting equilibrium at ($T_g + 30$) K and subsequent cooling in the chosen regime at the same cooling rate ($q = 5$ K/min).

The ^{77}Se ($I = 1/2$) nuclear magnetic resonance (NMR) measurements were carried out at room temperature on Avance 300 Bruker spectrometer operating at 57.3 MHz with a 2.5 mm Magic Angle Spinning probe rotating at 22 kHz. Due to the breadth of the NMR lines for glasses, a Hahn spin echo sequence was applied to refocus the whole magnetization. The Fourier transforms were performed on the whole echoes to increase the signal-to-noise ratio and to directly obtain some absorption mode line shapes. Because of slow longitudinal relaxation, the recycle time was equal to 300 s and numbers of scans were about 1000 meaning around 3 days for each measurement. The experimental spectra were simulated with Dm2000nt version of the Winfit software [19].

The PAL spectra were recorded with fast–fast coincidence system (ORTEC) of 230 ps resolution (FWHM of a single Gaussian, determined by measuring ^{60}Co isotope) at the room temperature and relative humidity $RH = 35\%$, provided by special climatic installation. Two identical aged or rejuvenated g-Ge_5Se_{95} samples were used to arrange a sandwich structure needed for PAL measurements. Statistical averaging was performed for three independent PAL probes assembled with samples of the same thermal prehistory. Each spectrum was measured with a channel width of 6.15 ps (covering 8000 channels) and contained ~10^6 coincidences in a total, which can be considered as a necessary precondition for normal measurement statistics. Isotope ^{22}Na of ~50 kBq activity was used as a source of positrons (prepared from aqueous solution of ^{22}NaCl, wrapped by Kapton® foil of 12 μm thickness and sealed), which was sandwiched between two identical glassy samples. The source correction due to special calibration tests performed with Ni and Kapton® foil was applied to all raw PAL spectra in order to compensate an additional input originating from annihilation in source itself and covering Kapton® foil.

The registered PAL spectra of the investigated g-Ge_5Se_{95} were processed with standard LT 9.0 computer program [20]. The variance of *FIT* determined as statistically weighted least-squares deviation between experimental points and theoretical curve reconstructed for two independent components (with τ_1, τ_2 positron lifetimes and I_1, I_2 intensities) was taken into account to select the best result. The obtained fitting parameters agreed well with each other within an experimental error-bar of ±0.005 ns in positron lifetimes and ±0.01 in the corresponding intensities.

The average positron lifetime τ_{av} was determined as a center of mass of whole lifetime spectrum in respect to known expression:

$$\tau_{av} = \sum_i I_i \tau_i, \tag{1}$$

where τ_i and I_i denote lifetime and intensity of the corresponding components, respectively.

Then, the positron trapping modes in g-Ge_5Se_{95}, *e.g.* the positron lifetime in "defect-free" bulk τ_b, and positron trapping rate in "defects" κ_d, were calculated using a formalism of two-state positron trapping model ($I_1 + I_2 = 1$) [21–25]:

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}, \tag{2}$$

$$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right). \tag{3}$$

To perform cluster modeling for different network-forming atomic configurations proper to g-Ge_5Se_{95} and confirm, in such a way, the possible structural transformations during prolonged PhA, the PC-aided simulation procedure known as CINCA (cation-interlinking network cluster approach) [26] was utilized. The *ab-initio* quantum chemical modeling was performed using HyperChem Release 7.5 program package based on restricted Hartree–Fock (RHF) self-consistent field method using split-valence double-zeta basis set with single polarization function 6-311G* [27,28]. The final geometrical optimization and single-point energy calculations for selected molecular precursors of network-forming clusters were performed employing the Fletcher–Reeves conjugate gradient method until the root-mean-square gradient of 0.1 kcal/(Å·mol) was reached. The obtained energy of clusters were corrected on H atoms according to the procedure well developed elsewhere [29–31].

3. Results and discussion

In respect to NMR spectra shown in Fig. 1a, the aged g-Ge_5Se_{95} demonstrate nearly ideal "chain-crossing" model [17]: 80% of Se atoms occupy positions between two other Se atoms (–Se–**Se**–Se– chains or rings) and 20% of Se atoms occupy positions between Se and Ge atoms (–Se–**Se**–Ge≡ fragments). The corresponding NMR spectra on Fig. 1a can be well reconstructed with two Gaussian peaks located at ~850 ± 10 ppm (peak A of nearly 200 ppm width, which corresponds to Se–**Se**–Se environment) and ~580 ± 10 ppm (peak B of nearly 250 ppm width, which corresponds to preferential Se–**Se**–Ge environment) with 80:20 ratio (the peak intensities was determined with an error of nearly ±3%) [32–35]. As shown in [35], the origin of B line can also be attributed to additional input from edge-sharing Ge–Se–Ge environment. But edge-sharing tetrahedrons were not confirmed in this sample with high-resolution XPS [18] and the existence of such a high percentage (20%) of direct edge-sharing bridges between tetrahedrons is not consistent with initial glass composition, so it seems more plausible attribution this line to preferential Se–**Se**–Ge environment.

The above 80:20 distribution between –Se–**Se**–Se– and –Se–**Se**–Ge≡ structural fragments in the aged g-Ge_5Se_{95} is disturbed after rejuvenation, as it testified from NMR results depicted in Fig. 1b for non-aged samples. The reconstructed NMR spectrum of this rejuvenated g-Ge_5Se_{95} shows clear broadening at the low chemical shift and additional peak C of ~300 ppm width has to be introduced at ~380 ± 10 ppm to achieve an acceptable goodness of fit. This new contribution can be decidedly attributed to bridging ≡Ge–**Se**–Ge≡ environment [32–35]. The observed changes are relatively weak, involving ~7% of