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Medium range order and structural relaxation in As–Se network glasses through FSDP analysis

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HIGHLIGHTS

- Aged and non-aged As–Se glasses are studied with XRD and neutron scattering.
- Compositional and temperature dependences of FSDP are analyzed.
- FSDP parameters are correlated with (non)isothermal structural relaxation data.

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ABSTRACT

Synchrotron X-ray diffraction and neutron scattering studies are performed on As–Se glasses in two states: as-prepared (rejuvenated) and aged for ~27 years. The first sharp diffraction peak (FSDP) obtained from the structure factor data as a function of composition and temperature indicates that the cooperative processes that are responsible for structural relaxation do not affect FSDP. The results are correlated with the composition dependence of the complex heat capacity of the glasses and concentration of different structural fragments in the glass network. The comparison of structural information shows that density fluctuations, which were thought previously to have a significant contribution to FSDP, have much smaller effect than the cation–cation correlations, presence of ordered structural fragments or cage molecules.

1. Introduction

Correlation between the medium-range order (MRO) [1–7] and structural relaxation [8] in network glasses is one of the least studied and most controversial problems in solid state physics. According to S.R. Elliott [1], MRO is defined as a higher level of structural organization beyond the short-range order (SRO) in amorphous (glassy) materials, extending up to ~20 Å from a given atom. It is common to classify MRO into three categories [1–6]: the short-range MRO (~3–5 Å), which indicates mutual orientation of neighbored coordination polyhedra comprising the glass network; the intermediate-range MRO (5–10 Å), which originates from triplet correlations between network forming units (correlations between pairs of dihedral angles, which is usually associated with clusters formation); and the long-range MRO (~10–20 Å), which is assumed to be determined by local dimensionality (1D, 2D or 3D) of glass network.

From this perspective, the chalcogenide glasses (ChG) can be considered as unique model objects, where all of these types of MRO can be purposefully realized. Thus, for example, different kind of network-forming units (pyramids on the basis of three-fold co-ordinated P, As, Sb or Bi; tetrahedra on the basis of four-fold coordinated Si, Ge or Ga cations; polymeric chains on the basis of S, Se, Te atoms) can result in MRO focusing on a short-range or intermediate-range scales; degree of dimensionality of the network can be easily modified by varying the composition of a glass (e.g. by

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increasing/decreasing the content of two-fold coordinated chalcogen atoms) leading to a controlled modification of long-range MRO, etc. [9,10]. In addition, high purity ChG can be obtained with SRO of relatively simple structural units that can be unambiguously derived from conventional structural probe data and verified by theoretical models, giving a possibility to link the observed regularities directly with the structural features [11,12]. Also, a very large database on various physical–chemical properties of these materials is available in scientific literature, which can be used as additional information for validating the interpretations of data [9–12].

Structural relaxation occurs as a result of thermodynamic forces driving the non-equilibrium glassy system towards a state of thermodynamic equilibrium of supercooled liquid [8]. The associated enthalpy losses (ΔH) can be measured with differential scanning calorimetry (DSC) by heating the glass through the glass-to-supercooled liquid transition [13]. Degree of structural relaxation depends on the waiting time below the glass transition temperature (T_g), the relevant processes being known as physical ageing (excludes any chemical reactions, crystallization or phase separation) [13,14]. The greater ageing duration, the greater is the enthalpy loss (ΔH) expressed through the endothermic peak at T_g in DSC scans [13]. In general, the ΔH follows a sigmoidal time dependence, which is defined by a choice of ageing temperature T_a in respect to T_g (increasing T_a accelerates structural relaxation kinetics) [8]. For glasses with low T_g, significant enthalpy losses can be observed at room temperature over a short period of time, while for glasses with higher T_g, longer periods of storage are needed to observe physical ageing at room temperature [15–17]. The investigated arsenic selenide glasses show decrease in the value of physical ageing at room temperature towards the stoichiometric As_2Se_3 composition [17], which has the highest T_g among all As–Se glasses [9,11].

Different theoretical and experimental methods have been used so far to elucidate structural transformations during physical ageing in ChG. Most popular experimental techniques include Raman spectroscopy, nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), high-resolution X-ray photoelectron spectroscopy (XPS) and positron annihilation lifetime spectroscopy (PALS) [14–18]. However, the data from these techniques show insignificant difference between the SRO structural parameters of the aged and non-aged glasses. The SRO remains practically invariant during physical ageing. Although some minor structural transformations were detected, like 5–7% redistribution of Se atoms between different structural fragments [14–16], they could not explain the large changes in T_g value and enthalpy losses (ΔH) observed with thermal analysis technique after prolong storage [17], as well as plateaus and steep regions in long-term kinetics of enthalpy relaxation [13]. Therefore, significant changes at MRO were anticipated. The deviations from monotonic linear temperature dependence of nearest neighbor distance and Debye-Waller factor found recently with quick EXAFS [19] had created additional reasoning for such expectations.

To study possible correlations between the MRO in ChG and their structural relaxation (physical ageing), the same as-prepared (rejuvenated) and aged samples should be investigated with the probes sensitive to the changes at MRO and those giving the magnitude of structural relaxation or physical ageing effect. However, contrary to structural relaxation processes, which can be conveniently characterized with thermal analysis techniques, the experimental investigation of MRO is a non-trivial task. Traditional structural probes such as X-ray, neutron or electron diffraction are sensitive to pair correlations between atoms, and therefore provide very limited information on MRO features. On the other hand, vibrational spectroscopies such as IR or Raman are more sensitive to the mutual correlations between coordination polyhedra, but usually they are suffered from the ambiguities in the interpretation of experimental spectra due to a great number of different possible vibrational modes that overlap. The information on MRO, which can be obtained using diffraction methods, is believed to be contained in the so-called first sharp diffraction peak (FSDP) [1–7]. It is observed as a prominent low-Q ($0.8 < Q < 1$–1.6 Å^{-1}) feature in the structure factor $S(Q)$ of network glasses. Although FSDP has been a subject of extended interest in the last three decades, its origin is still debated [20–25]. It is clear that FSDP can arise for various reasons in different systems [20,23,25], but in general it reflects features of the glass network at both the MRO and SRO length scales, for example, homopolar bonds, cage molecules, random/nonrandom distribution of the network-forming clusters, prevailing structural motif, etc. [3,23,25]. A characteristic length scale associated with the FSDP position typically implies 2–4 interatomic distances (~3.5–10 Å), which correspond to the intermediate MRO. It was found earlier that the FSDP is distinguished from other $S(Q)$ peaks by at least two anomalies relative to the usual behavior of $S(Q)$ in solids: (i) it remains invariant with increasing temperature (sometimes may even become more intense and narrower) in contrast to the thermal broadening of usual peaks in $S(Q)$ [26–28], and (ii) its amplitude decreases with increasing pressure, again contrary to the response of other $S(Q)$ peaks [29,30]. The models used to explain the FSDP rely on the existence of layer-like structures in the glass network or regularities in the void distribution [1–5,31]. Others have recently proposed the FSDP as having a topological origin, arguing for a structural origin of the so-called topological "intermediate phase" in As_xSe_{1-x} glasses [24]. The neutron diffraction with isotopic substitution and anomalous X-ray scattering clearly show that the main contribution to the FSDP in network glasses usually comes from network-forming cation–cation (metal–metal) correlations [21,22], although the physical picture of these correlations in real glass structure remains unclear. A review of the theories of the FSDP for amorphous materials is given by Moss & Price [31] and Wright [3].

To determine the potential of FSDP analysis in application to MRO and structural relaxation in network glasses, we have studied FSDP compositional trends in As_xSe_{1-x} glasses ($0 < x < 0.55$) with complementary X-ray diffraction (XRD) and neutron scattering techniques. Samples aged over a long period of time are compared to rejuvenated (thermal prehistory is erased by the annealing above the glass transition temperature T_g) samples derived from the same aged material, to investigate the influence of isothermal structural relaxation. Some of the aged Se-rich samples are additionally studied with neutron scattering *in-situ* during their heating through the glass transition interval, to study the effect of non-isothermal structural relaxation. The obtained evolution of FSDP parameters with composition and temperature is correlated with isothermal and non-isothermal structural relaxation data of temperature modulated DSC (TMDSC).

2. Experimental

The samples of binary As_xSe_{100-x} ($x = 0, 2, 5, 10, 20, 28, 30, 40, 45, 50, 53, 55$) were prepared in 1985 by conventional melt-quenching route in evacuated quartz ampoules from a mixture of high purity (99.999%) As and Se precursors. The furnace was rocked to obtain highly homogeneous melt. All ingots were quenched by switching off the furnace. Amorphous state of the as-prepared chalcogenide glasses was established visually by a characteristic conch-like fracture as well as by X-ray diffraction. All the samples were then sealed in hermetic plastic bags and stored in the dark, under ambient conditions for ~27 years before the measurements. The purity and the composition of the samples after the storage