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Local structure of room-temperature superionic Ag–GeSe$_3$ glasses

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ABSTRACT

Anomalous X-ray scattering experiments on amorphous Ag$_{0.5}$(GeSe$_3$)$_{0.5}$ at the *K* absorption edges of each constituent element have been performed to investigate the local- and intermediate-range structure in this material. This method can provide insight into the structural properties enabling the effect of superionic conductivity in the amorphous phase. The experimental results were analyzed with reverse Monte Carlo modeling, providing the partial structure factors and the corresponding partial pair-distribution functions. A nanometer range phase separation tendency of the Ag atoms over a background of a GeSe$_4$ tetrahedral network is observed, which may confirm the view of Ag conduction pathways forming in this phase.

1. Introduction

Superionic conducting materials are of growing interest in fundamental and applied materials science, as they can e.g. be employed as solid electrolytes in solid-state batteries. Superionic glasses with a high ionic conductivity of $10^{-6} - 10^{-2}$ S/cm are promising materials for such applications. It is well-known that superionic behavior in Ag containing chalcogenide glasses is observed at room temperature, such as for Ag–GeSe$_3$ alloys, in contrast to high temperatures needed in crystalline superionic conductors. Another advantage of these glasses as electrolytes is that the glassy state can easily be obtained in a wide concentration range by simple water or even air-quenching.

In the system Ag$_x$(GeSe$_3$)$_{1-x}$, a sharp jump in the electrical conductivity is observed at Ag concentrations of $x > 0.3$, where a superionic conducting phase is formed [1]. For low contents of Ag, the structural properties of this system have been studied extensively by Piarristeguy and coworkers by standard X-ray diffraction [2,3] and neutron diffraction [4]. For the superionic conducting phase, Ohara, Kumara and coworkers analyzed the structure by means of high-energy X-ray scattering, neutron diffraction, and extended X-ray absorption fine-structure (EXAFS) [5,6]. These data were analyzed using reverse Monte Carlo (RMC) modeling, and three-dimensional atomic configurations were obtained, where chain-like fragments of Ag atoms were observed.

However, a detailed analysis of the intermediate range order (IRO), such as the Ge-Se network in Ge$_x$Se$_{1-x}$ [7], is difficult to achieve by EXAFS and total scattering data alone, as pointed out by Waseda [8]. On the other hand, the IRO is known to be a dominant feature in the structure of chalcogenide glassy systems. To achieve a more detailed insight into the structure of the superionic phase on an intermediate-range length scale, we have carried out anomalous X-ray scattering (AXS) experiments on Ag$_{0.5}$(GeSe$_3$)$_{0.5}$ near the X-ray energies close to the Ge, Se and Ag *K*-absorption edges, and analyzed the data using RMC.

2. Principle of anomalous X-ray scattering

Anomalous X-ray scattering (AXS) utilizes the anomalous variation of the atomic form factor f of a specific element near an X-ray absorption edge, which is given as a function of energy E and momentum transfer Q:

$$f(Q,E) = f_0(Q) + f'(E) + if''(E), \tag{1}$$

where $f_0(Q)$ is the usual energy-independent term, and $f'(E)$ and $f''(E)$ are the real and imaginary parts of the anomalous term, respectively. In general, only when the incident X-ray energy approaches an absorption edge

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of a constituent element, the energy-dependent terms $f'(E)$ and $f''(E)$ become important. In fact, $f'(E)$ has a large negative minimum and $f''(E)$ shows an abrupt jump near the absorption edge energy. The resulting intensity contrast $\Delta_k I$ between two scattering functions close to an absorption edge of element k can be expressed as

$$\begin{aligned}\Delta_k I(Q,E_1,E_2) \propto\ & \Delta_k\left[\left\langle f^2\right\rangle - \langle f\rangle^2\right] \\ & + \Delta_k\left[\langle f\rangle^2\right]\Delta_k S(Q).\end{aligned} \tag{2}$$

Here, $\Delta_k[\,]$ indicates a difference of values in the bracket at energies of E_1 and E_2 close to an absorption edge of the k-th element, typically some 100 eV and some 10 eV below the edge, respectively, and $\langle\rangle$ represents the chemical average. Similar to a total scattering function $S(Q)$, these differential structure factors, $\Delta_k S(Q)$, can be expressed by a linear combination of partial correlations $S_{ij}(Q)$ as

$$\Delta_k S(Q) = \sum_{i=1}^{N}\sum_{j=1}^{N} W_{ij}(Q, E_{\text{far}}, E_{\text{near}}) S_{ij}(Q) \tag{3}$$

with the weighting factors W_{ij}'s given as

$$W_{ij}(Q, E_{\text{far}}, E_{\text{near}}) = x_i x_j \frac{\Delta_k\left[f_i f_j^*\right]}{\Delta_k\left[\langle f\rangle^2\right]} \tag{4}$$

where x_i and f_i are the concentration and the atomic form factor of i-th element, respectively. Since the number of $S_{ij}(Q)$'s rises as $N(N+1)/2$, with N denoting the number of elements, many scattering experiments with different W_{ij}'s are, in principle, necessary to obtain a complete set of $S_{ij}(Q)$ for a multicomponent non-crystalline material. Thus, AXS is very useful to increase the number of the scattering data with different W_{ij}'s. Further details on the theoretical and experimental background of AXS can be found elsewhere [7–11].

3. Experimental procedure

3.1. Sample preparation

The amorphous sample of $Ag_{0.5}(GeSe_3)_{0.5}$ was prepared by water-quenching from the sealed mixture of the respective ratios of Ag, $GeSe_2$ and Se into a silica tube under vacuum. The obtained glass was pressed into a round pellet with a flat surface of about 13 mm in diameter. The concentrations and homogeneity were examined by X-ray diffraction and differential thermal analysis at several positions of the quenched samples.

3.2. AXS experiments

The AXS measurements were carried out in reflection geometry at the beamline BM02 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The diffraction experiments were performed using a standard ω-2θ diffractometer installed at the beamline at two incident X-ray energies (-20 for Ge and Se or -30 eV for Ag, and -200 eV for all) below the K absorption edges of each constituent element. To obtain the $\Delta_k S(Q)$ in a high statistical quality, we used a bent graphite crystal energy-analyzer combined with a long (1 m) detector arm carrying a photomultiplier with a NaI scintillator to grant a good energy resolution capable to discriminate elastic signals from spurious inelastic contributions (i.e. mainly K_β fluorescence or "resonant Raman" signals and Compton scattering) as well as a reasonable number of detected photons during the collection time. Details of the experimental setup are given elsewhere [10,11].

For the AXS data analysis, theoretical values for the anomalous terms f' and f'' tabulated by Sasaki [12] and theoretical values for the term f_0 [13] were employed. Following a procedure outlined e.g. in [7,9,10], $\Delta_k S(Q)$'s were calculated for each K edge.

As can be observed from $W_{ij}(Q)$'s, this method enhances the edge-related partial contributions $S_{ij}(Q)$ to $\Delta_k S(Q)$, and other partials are highly suppressed. Exemplary, the W_{ij} values at 2 Å^{-1} near the $S(Q)$ maximum position are tabulated in Table 1; the variation with Q is comparably small.

3.3. RMC modeling

In the RMC modeling procedure, the obtained three $\Delta_k S(Q)$'s for each element and one total $S_{ij}(Q)$ obtained at 25.215 keV, i.e. 200 eV below the K edge of the highest measured energy, were included as experimental reference data. We employed the RMC_POT program package by Gereben et al. [14,15].

We chose an input configuration of 10,000 atoms with proper stoichiometry, randomly distributed in a cubic box corresponding to the number density of 0.03802 atoms/Å^{-3} and defined minimum atomic distances to avoid unphysical configurations as 2.9, 3.3, 2.3, 3.3, 2.1, and 2.1 Å for the Ag–Ag, Ag–Ge, Ag–Se, Ge–Ge, Ge–Se, and Se–Se distance, respectively. After confirming a coordination number of about 4 for the Ge–Se bond, a weak bond angle constraint has been applied subsequently to ensure a tetrahedral bonding coordination of Se around Ge atoms.

4. Results

The total and differential structure factors calculated from the experimental data together with the best fits obtained from the RMC simulation are displayed in Fig. 1. The total structure factor obtained in this experiment agrees well with the $S(Q)$ data from other experiments, e.g. high-energy X-ray diffraction [16]. In the low-Q region, a small first sharp diffraction peak (FSDP) can be seen at $Q_1 = 1.05$ Å^{-1}, and there are two peaks of nearly similar intensity located at $Q_2 = 2.0$ Å^{-1} and $Q_3 = 3.4$ Å^{-1}. The last comparably pronounced peak is situated broadly around $Q_4 = 5.45$ Å^{-1}. For values above $Q = 3$ Å^{-1}, a similar behavior is observed in the $\Delta_{Se}S(Q)$ and $\Delta_{Ag}S(Q)$ functions. In the region below 3 Å^{-1}, a relative increase in the peak located at 2 Å^{-1} compared to $S(Q)$ can be observed on both differential structure factors.

A major difference is the behavior of the FSDP, which is similar between the total structure factor and $\Delta_{Se}S(Q)$, but basically missing in $\Delta_{Ag}S(Q)$. On the other hand, the features in $\Delta_{Ge}S(Q)$ are largely different to all other structure factors: The FSDP is much more pronounced, there is a minimum at the Q_2 position, and the Q_4 peak is shifted to slightly higher Q-values. The features of the $\Delta_{Se}S(Q)$ and the $\Delta_{Ge}S(Q)$ closely resemble the corresponding functions in the pure $GeSe_3$ [7], except that the FSDP in the $\Delta_{Se}S(Q)$ there is only visible as a small shoulder of the first structure factor peak.

Fig. 2 shows the $S_{ij}(Q)$'s obtained by the RMC modeling, respectively. Using the $S_{ij}(Q)$'s, a differentiation of the signals in the experimental data by individual pair correlations is possible: The peak at Q_2 consists mainly of the three homopolar bonds, dominated by Se–Se, whereas the third peak around $Q_3 = 3.4$ Å^{-1} comprises contributions from all correlations. Interestingly, the FSDP consists only of Ge–Se and Ge–Ge correlations — similar to the pure $GeSe_3$ phase, where there is also no indication of a FSDP in the Se–Se partial correlation. Being majorly

Table 1
Weighting factors W_{ij} of $S_{ij}(Q)$ for each dataset at $Q = 2.0$ Å^{-1} near the first peak position in $S(Q)$.

Dataset	AgAg	AgGe	AgSe	GeGe	GeSe	SeSe
$S(Q)$	0.059	0.088	0.280	0.033	0.209	0.331
$\Delta_{Ag}S(Q)$	0.234	0.184	0.582	0.000	0.000	0.000
$\Delta_{Ge}S(Q)$	0.003	0.251	0.034	0.138	0.516	0.058
$\Delta_{Se}S(Q)$	0.001	-0.005	0.298	-0.004	0.182	0.528