

Local Structure of Superionic Glass $\text{Ag}_x(\text{GeSe}_3)_{1-x}$, $x=0.565$

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Abstract. To investigate relation between inhomogeneous structure of $\text{Ag}_x(\text{GeSe}_3)_{1-x}$ superionic glass and conduction path formation, x-ray diffraction, neutron diffraction and EXAFS measurements on *K*-edges for each constituent were performed. Reverse Monte Carlo structural modelling based on these experimental data revealed that Ag conduction paths are formed in random glass media of GeSe_4 tetrahedral network. The first sharp diffraction peak (FSDP) located at 1.1 \AA^{-1} is mainly contributed by GeSe_4 network, while an observed intense small angle scattering is contributed also by Ag-Ag as well as GeSe_4 network.

1 Introduction

Noble metals as an additive in glassy media have attracted widespread interest in relation with superionic behavior of noble-metal ions and its potential application as solid electrolytes in new devices. The interest in $\text{Ag}_x(\text{GeSe}_3)_{1-x}$, ternary alloy based on chalcogenide glass, stems from the extensive compositional range of bulk glass forming [1], and from the rapid enhancement in ionic conductivity from 10^{-14} to 10^{-4} S/cm of these glasses at Ag concentration of $x=0.3$ with increasing Ag content [2].

In our previous paper, temperature variation of structure for $x=0.5$ was studied associating with formation of ionic conduction path from molten state [3]. It was revealed that the Ag distribution in $\text{Ag}_{0.5}(\text{GeSe}_3)_{0.5}$ has a tendency of forming chain-like fragments even in the molten state, which is characteristic feature in the Ag based superionic melts such as AgI [4] and Ag_2Se [5]. The grown-up of medium-range order with decreasing temperature is related to the process of Ag ionic conduction path formation in the molten and super-cooled liquid states [3]. However, micro phase separation has been recently reported by several researchers [6-8]. Although our analysis suggests heterogeneous structure

of this material, the model should be interpreted as an average structure consisting of Ag-rich phase and chalcogenide glass phase almost without Ag.

This time we found that $\text{Ag}_x(\text{GeSe}_3)_{1-x}$ with $x=0.565$ exhibits intense small angle scattering in the wavenumber region below 0.3 \AA^{-1} suggesting the presence of nanometer range inhomogeneties. To understand the structural background of small angle scattering we try to construct a structural model reproducing both small- and wide angle X-ray scattering as well as neutron diffractions and extended X-ray absorption fine structure (EXAFS) measurement at the Ge *K*-, Se *K*- and Ag *K*-edges.

2 Experimental procedure

2.1 Sample preparation

The amorphous samples of $\text{Ag}_x(\text{GeSe}_3)_{1-x}$ Ag concentration $x = 0.565$ were prepared by water-quenching from the sealed mixture of Ag, Se and Ge into a silica tube under vacuum.

2.2 High energy x-ray diffraction

X-ray diffraction measurements for $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature were carried out using a two-axis diffractometer installed at the BL04B2 beamline [9] in the third-generation synchrotron radiation facility Spring-8, Hyogo, Japan. The incident X-ray beam was 113.26 keV in energy and 0.1093 Å in wavelength from a Si(1 1 1) monochromator with the third harmonic reflection. A sample was sealed in a fused silica capillary with an inner diameter of 2.5mm and wall thickness 0.2 mm.

2.3 Neutron diffraction

Neutron diffraction was carried out using the two-axis diffractometer 7C2 located at the hot source of the reactor Orphée in Laboratoire Léon Brillouin, Saclay, France [10]. The neutron beam monochromatized by Cu(1 1 1) reflection. The wavelength of incident neutrons was 0.72 Å. Powder sample was filled into a thin-walled vanadium can. Scattered neutrons were detected by the multi PSD (position sensitive detector) array where 640 cells filled by $^{10}\text{BF}_3$ cover a scattering angle 2θ from 1.25° to 128° . The accessible useful momentum transfer, Q , is ranged from 0.4 to 16 \AA^{-1} .

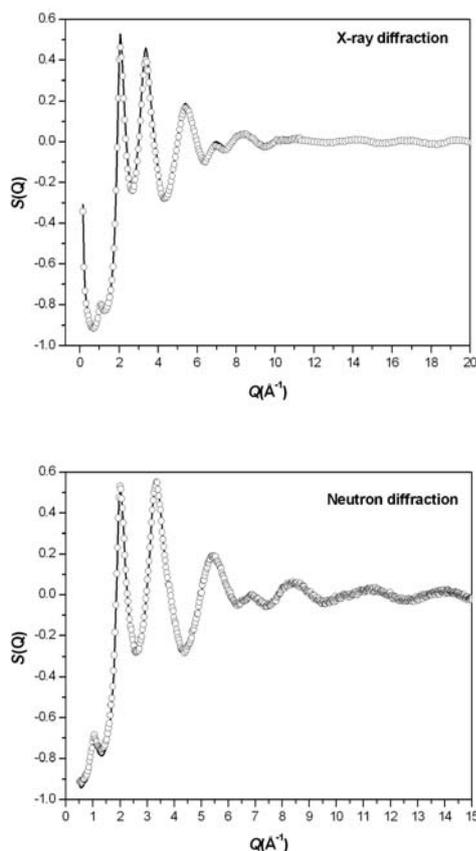


Fig. 1. Experimental (open circle) and RMC (solid line) total structure factors of superionic glass $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature obtained by X-ray diffraction (upper) and neutron (lower) diffraction.

2.4 Extended x-ray absorption fine structure

EXAFS measurements on the K -edges of Se, Ge and Ag were performed using 3C1 beamline of Pohang Accelerator Laboratory, Pohang, Korea [11]. Spectra were recorded in transmission mode. Powder samples were placed between Scotch tapes together with a spacer. The intensity of the incident and transmitted x-ray beams were monitored by ionization chambers. To extract the EXAFS oscillation, $\chi(k)$ (k is the wave number of the photoelectron) from the observed absorption spectrum, μt , the extrapolated pre-edge background absorption was subtracted first. The resulting curved was then normalized by dividing the jump of absorption at the edge.

3 Results

Figure 1 shows the total structure factors obtained by X-ray and neutron diffractions. The differences between neutron and x-ray total structure factors are small but distinct. For example, the intensity of the first sharp diffraction peak (FSDP) at around $Q = 1.1 \text{ \AA}^{-1}$ is larger in the neutron structure factor and ratios of the height of the first peak locating at around $Q = 2.05 \text{ \AA}^{-1}$ to that of the second at around $Q = 3.0 \text{ \AA}^{-1}$ are quite different as well. These differences originate from the different x-ray and neutron scattering powder of the components. The coherent scattering lengths of Ge and Se (Ge:8.185fm, Se:7.970fm) are larger than that of Ag (5.922fm) so the scattering intensity emphasizes the glassy network structure composed of Ge and Se. On the other hand, the number of electrons in the Ag atom is larger than that in Ge and Se atoms (Ag:47, Ge:32, Se:34) thus x-ray diffraction is more sensitive to correlations including Ag ions.

Figure 2 shows the EXAFS spectra weighted by k^3 for (a) Ge K -, (b) Se K - and (c) Ag K -edges which was Fourier-filtered in the r range of $1.5 < r < 2.8 \text{ \AA}$, $1.5 < r < 2.8 \text{ \AA}$ and $1.8 < r < 3.2 \text{ \AA}$, respectively.

4 Structural modelling

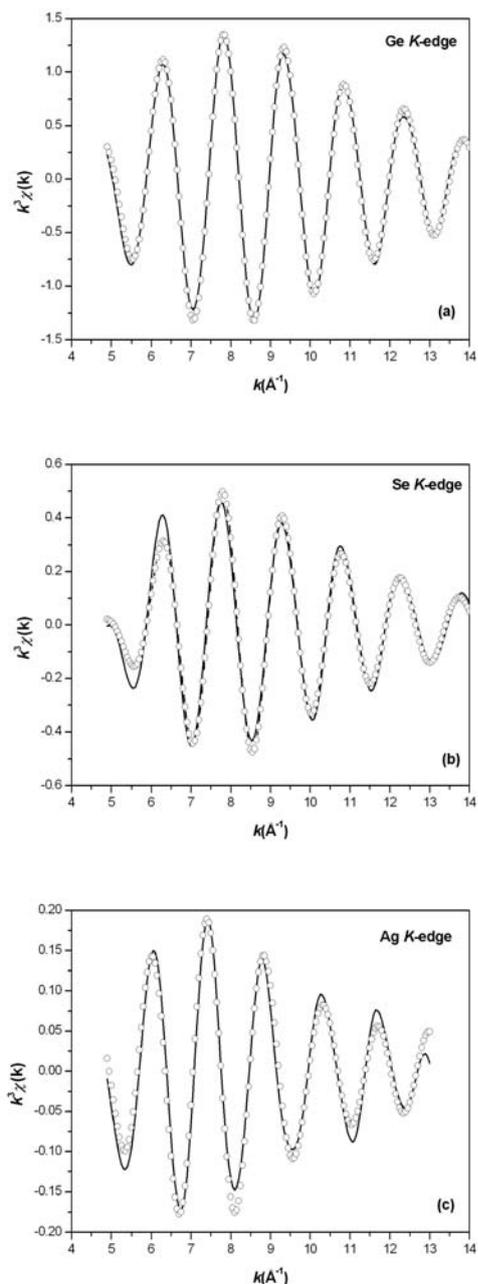


Fig. 2. Experimental (open circle) and RMC (solid line) of EXAFS spectra, $k^2\chi(k)$, of superionic glass $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature on the Ge (upper), Se (middle) and Ag (lower) K-edges.

To see the atomic distribution of $\text{Ag}_{0.5}(\text{GeSe}_3)_{0.5}$ in detail, reverse Monte Carlo (RMC) structural modeling [12,16] was carried out using x-ray and neutron diffraction structure factors as well as EXAFS datasets simultaneously as input data. The simulation box contained 18000 particles with proper stoichiometry. EXAFS backscattering factors needed to calculate model $\chi(k)$ curves were obtained by the feff 8.4 code [17]. The minimum interatomic distances (cut-off) were 3.2, 2.1, 3.1, 2.1, 2.3 and 2.7 Å for Ge-Ge, Ge-Se, Ge-Ag, Se-Se, Se-Ag and Ag-Ag pairs, respectively. The cut-off distances of Ge-Se, Se-Se and Ag-Se correlations were chosen from the corresponding atomic distances (2.36 Å

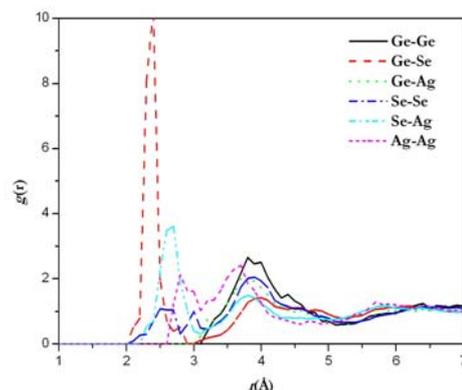


Fig. 3. Partial pair correlation functions of superionic glass $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature obtained by X-ray diffraction (upper) and neutron (lower) diffraction.

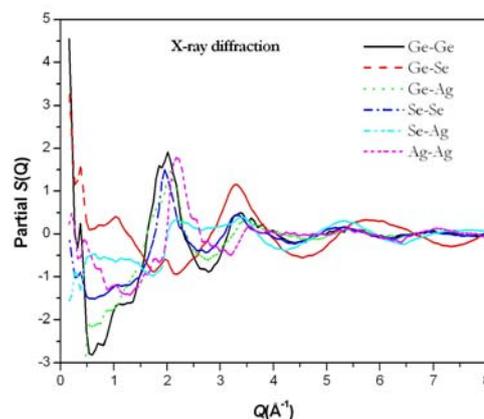


Fig. 4. Partial structure factors of superionic glass $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature obtained by X-ray diffraction (upper) and neutron (lower) diffraction.

for Ge-Se, 2.34 Å for Se-Se and 2.6 Å for Ag-Se) in the reference materials of crystalline GeSe_2 [13], amorphous Se [14] and glassy $\text{Ag}_4\text{Ge}_3\text{Se}_9$ [15]. The cut-off distances of Ge-Ge and Ag-Ge were set around the deep valley in $g(r)$. The Ag-Ag cut-off was first 3.2 Å but it had to be reduced to 2.7 Å to reproduce the Ag K-edge EXAFS data. Two coordination number constraints were also used: 1. each Ge atom was forced to have 4 Se neighbours 2. Se atoms were allowed to have at most 2 Ge neighbours. Thus it was assumed that Ag bonds mostly to Se and the Se-Ge coordination number found in GeSe_3 glass (4/3) cannot increase upon alloying it with Ag. The above constraints were satisfied by at least 90% of the atoms. The resulting X-ray and neutron diffraction and EXAFS model curves are compared with the experimental datasets in figures 1 and 2.

5 Discussion

From the structural model generated by RMC, the partial pair correlation functions are deduced as shown in figure 3. Ge-Se, Se-Ge, Se-Ag, Ag-Se and Ag-Ag coordination numbers calculated to the first minimum of the corresponding pair correlation function are 3.7, 1.2, 0.9, 2.2 and 0.6 respectively. There is a pronounced peak at 2.34 Å in Ge-Se correlations which corresponds to the Ge-Se covalent bond. Since Ge-Ge correlations has a broad distribution centered at 3.8 Å, Ge(Se_4) $_{1/2}$ tetrahedral network is more or less preserved by adding Ag. Se-Se correlation has a peak at around 2.5 Å which is slightly

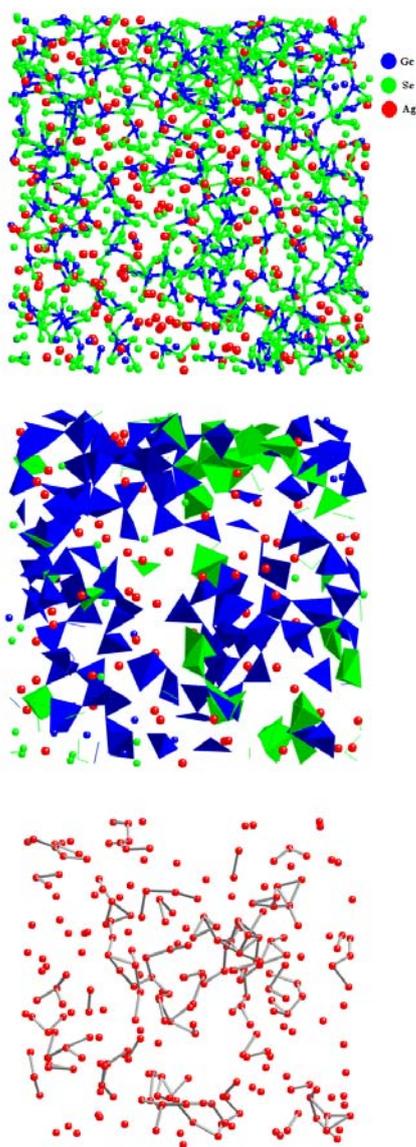


Fig. 5. Structural model of superionic glass $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ at room temperature deduced by RMC based on X-ray and neutron diffractions and EXAFS data on the Ge, Se and Ag K-edges.

longer than Se-Se covalent bond in pure liquid or glassy Se. Even assuming that a Se⁻ ion is connected to Se atom of Ge(Se_4) $_{1/2}$ tetrahedron, this bond length of Se-Se⁻ is unexpected. When we push out Se-Se bond by elongating

Se-Se cut-off distance to 3.0 Å, the reproducibility of experimental data by RMC fitting is almost similar to the present model. Therefore, we cannot decide at this stage whether Se-Se covalent bonds exist or not.

Ag-Ag correlation has a peak in the region of 2.8 - 2.9 Å, whose distance is almost similar to that of molten AgI. Since Ag-Ag collective motion is expected in molten AgI from chain-like fragments seen in atomic configuration model [4], it is plausible that such fast conduction of Ag ions occurs even in molten phase of Ag-Ge-Se alloy and then conduction path of Ag ions in molten phase is quenched into random media of chalcogenide glass (see figure 5). The second neighbor of Ag-Ag is broadly distributed around 3.2 - 4.0 Å with peak at 3.6 Å.

Figure 4 shows the partial structure factors by RMC structural modeling. The FSDP at 1.1 Å⁻¹ is mainly contributed by Ge-Ge and Ge-Se correlations. This means that medium-range order of this material is driven from the Ge-Se tetrahedral network. In the small angle region below 0.5 Å⁻¹, Ag-Ag correlation also contributes to intense scattering observed in X-ray diffraction, as well as the Ge-Se network.

The obtained atomic configuration model is shown in figure 5. One can see inhomogeneity of the glass structure in the upper figure. There are 'network regions' and Ag-rich regions surrounded by Se atoms. Ge-Se network and Ag distributions are separately visualized in the middle and lower figures, respectively. In the Ag distribution, one can see short chain-like fragments, which is similar to Ag distribution of molten AgI. Taking into account of glass forming process of Ge-Se network by quenching from molten state, it is natural to consider that the conduction paths of Ag ions have already existed in molten state.

6 Conclusion

The structure of $\text{Ag}_{0.565}(\text{GeSe}_3)_{0.435}$ superionic glass has been investigated by fitting simultaneously X-ray and neutron diffraction and Ge-, Se- and Ag K-edge EXAFS data. Satisfactory fits could be obtained by assuming only Ge-Se, Se-Ag and Ag-Ag bonds in the glass. It has been observed that the distribution of Ag ions in the GeSe $_{4/2}$ tetrahedral network is inhomogeneous suggesting the presence of Ag conduction paths in the covalent network.

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References

1. M. Mitkova, Yu Wang and P. Boolchand, *Phys. Rev. Lett.* 83 (1999) 3848.
2. M. Kawasaki, J. Kawamura, Y. Nakamura and M. Aniya, *Solid State Ionics* 123 (1999) 259.
3. K. Ohara, L.S.R. Kumara, Y. Kawakita, S. Kohara, M Hidaka, S. Takeda, *J. Phys. Soc. Jpn.* 79 (2010) Suppl. A 141.
4. Y. Kawakita, S. Tahara, H. Fujii, S. Kohara, S. Takeda, *J. Phys.:Condens. Matter* 19 (2007) 335201.
5. S. Tahara, H. Ueno, K. Ohara, Y. Kawakita, S. Takeda, S. Kohara, S. Ohno, *J. Phys. Soc. Jpn.* 79 (2010) Suppl. A 133.
6. J. Kawamura, N. Kuwata, K. Hattori, J. Mizusaki, *Rep. Inst. Fluid Sci., Tohoku Univ.* 19 (2007) 67.
7. A. Piarristeguy, M. Ramonda, A. Ureña, A. Pradel, M. Ribes, *J. Non-Cryst. Solids* 353 (2007) 1261.
8. M. A. Ureña, M. ontana, A. Piarristeguy, B. Arcondo, *J. Alloy. Comp.* 495 (2010) 305.
9. S. Kohara, M. Itou, K. Suzuya, Y. Inamura, Y. Sakurai, Y. Ohishi, M. Takata, *J.Phys. Condens. Matter* 19 (2007) 506101
10. LLB 7C2
11. PAL 3C1
12. R.L. McGreevy and L. Pusztai, *Mol. Simul.* 1 (1988) 359.
13. G.Dittmar, H.Schafer, *Acta Crystallogr.* B32 (1976) 2726.
14. D.Hohl, R.O. Jones, *Phys. Rev.* B43 (1991) 3856.
15. R.Dejus, S.Susman, K.Volin, D.Montague, D.Price, *J.Non-Cryst. Solids* 143 (1992) 162.
16. Rmcpp: O. Gereben, P. Jóvári, L. Temleitner, L. Pusztai, *J. Optoelectron. Adv. Mater.* 9(2007)3021.
17. Feff: A.L. Ankudinov, B.Ravel, J.J Rehr and S.D. Conradson *Phys. Rev. B* 58 (1998)7565