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Conduction pathways in AgI-doped chalcogenide glasses

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Introduction

Superionic conducting glasses containing Ag ions have received much attention because of scientific interests in their conduction mechanism as well as their application in solid-state electrochemical devices[1]. Although many different kinds of glass systems have been structurally investigated, especially in silver oxysalt systems, the ionic diffusion mechanism is not yet fully understood. In addition, there has been a lack of information concerning physical properties and detailed microscopic structure for AgI-doped 'non-oxide' glass systems. The present report describes results of the EXAFS analysis in AgI-As_2Se_3 glasses, in order to discuss the conduction mechanism in AgI doped non-oxide glasses.

Experimental procedure

Appropriate amounts of AgI, As and Se, with those compositions expressed as $(AgI)_x(As_2Se_3)_{1-x}$ with $x \leq 0.6$, were sealed within an evacuated quartz ampoule and thoroughly mixed in a rocking furnace at 700 °C. Then, the melts were quenched rapidly in an ice-water mixture.

EXAFS studies for amorphous samples were carried out at BL-10B (for Ag and I K-edges) stations in KEK-PF. The intensity of the incident beam, I_0, and that of the transmitted beam, I, were measured using ionization chambers.

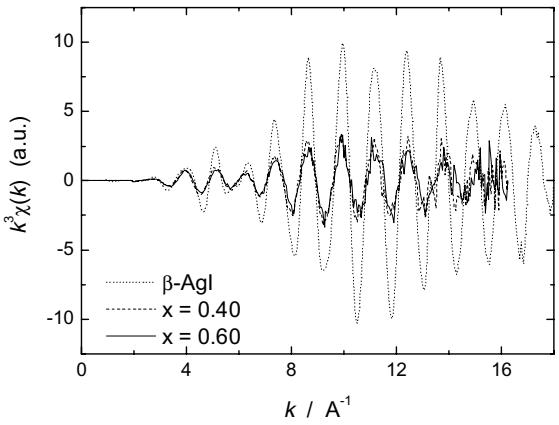

Fig. 1 I K-edge EXAFS functions for $(AgI)_x(As_2Se_3)_{1-x}$ glasses

Results

Figure 1 shows the EXAFS oscillations observed around the I K-edge for $(AgI)_x(As_2Se_3)_{1-x}$ glasses together with those for β-AgI. Because of the structural disorder of the glasses, signal intensities for the glasses were weaker compared with that for β-AgI. Nevertheless, reasonably good signals were obtained up to 16 Å^{-1}. The corresponding Fourier transforms $F(R)$ has one main peak at round 2.5 Å for the glasses (Fig. 2), the position of which is very similar to the case of β-AgI, although a slight disagreement in the signal phase between glasses and β-AgI can be seen in $k^3\chi(k)$. It is worth remarking that the peak of a second coordination shell, which is clearly observed at around 4.3 Å in $F(R)$ for β-AgI and corresponds to the I-I correlation of sub-lattices, completely vanished in the glass state. This fact seems to be attributed to the structural disorder of the I-I sub cages in the glasses.

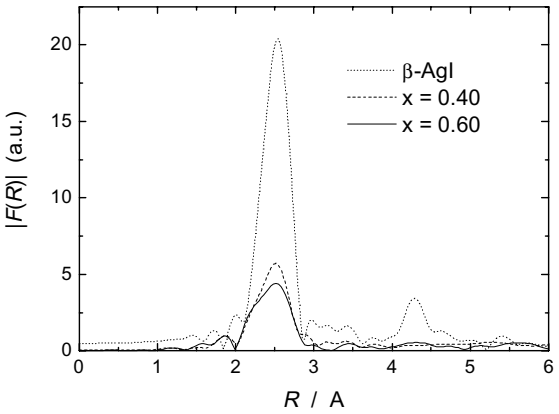

Fig. 2 I K-edge distribution functions for $(AgI)_x(As_2Se_3)_{1-x}$ glasses

The results of a least-squares fitting analysis for the EXAFS data including Ag, As and Se K-edges[2] allow us to predict that the structure model for AgI-As_2Se_3 glasses can be proposed to be a pseudo-binary mixture of the $As(Se_{1/2})_3$ network matrix and AgI-related conduction pathways, which would be responsible for the high mobility and diffusivity of Ag^+ in the present glass system.

References

[1] T. Minami, K. Imazawa, M. Tanaka, J. Non-Cryst. Solids 42 (1980) 469.
[2] T. Usuki, K. Nakajima, T. Furukawa, T. Nasu, M. Sakurai, PF Activity Report 2003 #21 Part B (2003) 170.
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