10B,12C/2001G289

Coordination environment in noble metal chalcogenide glasses

Takeshi USUKI*[1], Kohei NAKAJIMA[1], Takaaki FURUKAWA[1], Ryoki UEJO[1], Toshio NASU[2], Masaki SAKURAI[3]
[1]Depertment of Material and Biological Chemistry, Yamagata Univ., Yamagata 990-8560, Japan
[2]Faculty of Education, Yamagata Univ., Yamagata 990-8560, Japan
[3]Institute for Materials Research, Tohoku Univ., Sendai 980-8577, Japan

Introduction

Superionic conducting glasses containing noble metal ions have received much attention because of scientific interests in their conduction mechanism as well as their application in solid state electrochemical devices. Although extensive studies have been carried out to investigate their ionic transport mechanism in silver oxysalt systems, such as MI-M_2O-M_xO_y (M: Cu, Ag) [1], an obvious explanation of the conduction mechanism has not yet emerged from the literature. In addition, there has been a lack of information concerning physical properties and detailed microscopic structure for MI doped non-oxide glass systems.

The present report describes results of the EXAFS analysis in MI-As_2Se_3 glasses, in order to discuss the conduction mechanism in MI doped non-oxide glasses.

Experimental procedure

Appropriate amounts of MI, As and Se, with those compositions expressed as $(MI)_x(As_2Se_3)_{1-x}$ 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-12C (for Cu, As, Se K-edges) and 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.

Results

A functional form of the EXAFS oscillations $k^3\chi(k)$ for both the As and Se K-edges changes only slightly at any x for all of the present glass systems containing Ag and/or Cu iodides. The As and Se K-edges Fourier filtered experimental signals have been well simulated by fitting structural parameters in a single shell model (As surrounded only by Se atoms, and vice versa). The quantitative analysis shows that, whatever the glass composition, the three-fold local coordination of $AsSe_{3/2}$ pylamidal units with the As-Se interatomic distance of 2.42 A do not change significantly in the present glasses.

Figure 1 shows the the EXAFS oscillations observed around the Cu K-edge for $(CuI)_x(As_2Se_3)_{1-x}$ glasses together with those for γ-CuI. A decrease of the signal intensity, compared with that of γ-CuI, at low k region (2 - 6 A^{-1}) followed by an obvious disagreement in the signal phase at high k region (>10A^{-1}) can be seen in the figure. The peak position of the Fourier transform moduli, similar for all of the CuI doped glasses, is significantly lower than that for γ-CuI. This feature may be directly related to the presence of short-distance Cu-Cu correlations in the first coordination shell besides Cu-I ones, which is the most striking characteristic of α-CuI. Thus, a curve fit with a two subshells model, including both Cu-I and Cu-Cu correlations, has been performed for $(CuI)_x(As_2Se_3)_{1-x}$ glasses (Table).

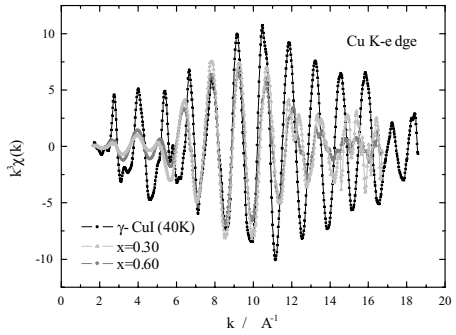

Fig. 1 EXAFS functions for $(CuI)_x(As_2Se_3)_{1-x}$ glasses

Table: structural parameters in $(CuI)_x(As_2Se_3)_{1-x}$ glasses

	As_2Se_3	x=0.30	x=0.60	γ-CuI
r_{As-Se}	2.41	2.42	2.42	-
r_{Se-As}	2.41	2.41	2.41	-
r_{Cu-I}	-	2.58	2.58	2.59
r_{Cu-Cu}	-	2.41	2.40	-

According to our previous study of physical properties for $(CuI)_x(As_2Se_3)_{1-x}$ glasses, an incorporation of CuI into As_2Se_3 glass is responsible for a pronounced increase in the total electrical conductivity, which varies exponentially with increasing CuI content. Their ion transport properties are strongly associated with the local structure proposed as the pseudo-binary mixture of $AsSe_{3/2}$ network matrix and dispersed CuI clusters.

The structure model for $(AgI)_x(As_2Se_3)_{1-x}$ glasses can also be proposed as the pseudo-binary mixture of the $AsSe_{3/2}$ network matrix and dispersed AgI clusters, where the addition of a large amount of AgI does not significantly affect the short-range order of both the network former and modifier atoms.

References

[1] T. Minami, K. Imazawa, M. Tanaka, J. Non-Cryst. Solids 42 (1980) 469.

* usuki@sci.kj.yamagata-u.ac.jp