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Ionic conduction and disordered structure in glassy ionic conductors

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1 Introduction

Glasses with high ionic conductivity have been called great scientific attraction due to their potentiality as solid electrolytes. Recently, it was demonstrated that glassy AgI-As_2Se_3 samples were successfully obtained by the mechanical milling method and their ionic conductivity increased rapidly at the early stage of the milling [1]. This paper will present results of XAFS experiments and discuss the local structure in fast ionic conductive AgI-As_2Se_3 systems.

2 Experiment

$(AgI)_x(As_2Se_3)_{100-x}$ (x = 40 and 60) samples were prepared at room temperature by means of the mechanical milling method (milling time = 0, 0.5, 1, 2, 10, 20 and 40 hours) using a planetary ball mill equipment.

XAFS studies were carried out at BL-12C (for As and Se K-edges) and NW10A (for Ag and I K-edges) stations in KEK. The intensity of the incident beam, I_0, and that of the transmitted beam, I, were measured using ionization chambers. The sample temperature was set to be 30K.

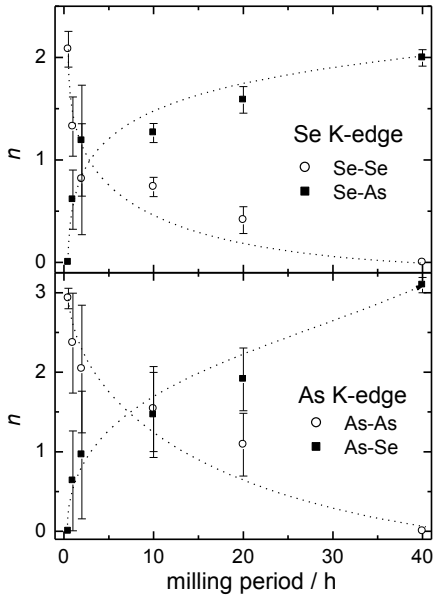

Fig. 1 Milling time dependence of coordination numbers around As and Se atoms in the $(AgI)_{40}(As_2Se_3)_{60}$ system.

3 Results and Discussion

Figure 1 shows the milling time dependences of the coordination numbers around As and Se atoms in the $(AgI)_{40}(As_2Se_3)_{60}$ system. These parameters were calculated under an assumption that the main peaks of $|F(R)|$ were constructed by As-As and As-Se bonds for the As edge data and Se-Se and Se-As bonds for the Se edge data, respectively. The coordination number of As-As and Se-Se bonds decreases with increasing milling time, whereas that of As-Se bonds increases due to the formation of the As-Se bonds. The construction of $AsSe_{3/2}$ networks occurs more rapidly in the 40 mol% AgI system compared to the case of 60 mol% AgI samples.

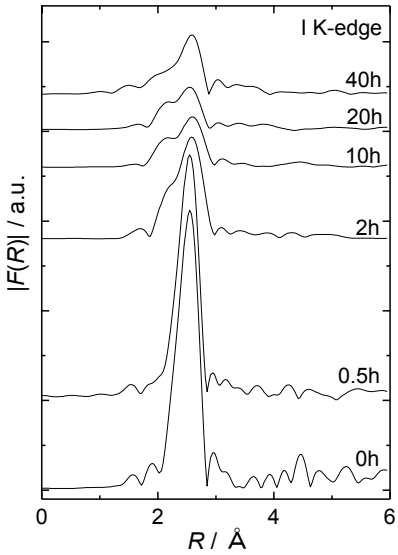

Fig. 2 Magnitude of Fourier transformation of the EXAFS oscillation function at the I K-edge for the $(AgI)_{40}(As_2As_3)_{60}$ system.

Figure 2 provides the magnitude of the Fourier transformation, $|F(R)|$, of the EXAFS oscillation function at the I K-edge for the $(AgI)_{40}(As_2Se_3)_{60}$ samples at the different milling stages. The intensity of the main peak significantly decreases, implying the decrement of the coordination number of mobile Ag ions around I ions. These tendencies are reasonably confirmed by the result for the Ag K-edge EXAFS data. The milling time dependences of the interatomic distance, $r_{Ag\text{-}I}$, and the coordination number, $n_{Ag\text{-}I}$, of Ag-I pairs decrease clearly with increasing milling time in both 40 and 60 mol% AgI samples. The apparent decrease of coordination number of Ag-I pairs corresponds to the disordering of Ag ions in the glass (or distortion of AgI units in the glass matrix), which might be strongly related to the appearance of fast ion conduction in the present glass system.

References

[1] M. Sekine, Y. Suzuki, H. Ueno, Y. Onodera, T. Usuki, T. Nasu, S. Wei: J. Non-Cryst. Solids **353** (2007) 2069.

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