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Appearance of fast ionic conduction in AgI-doped chalcogenide glass powders prepared by mechanical milling

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Abstract

$(AgI)_x(As_2Se_3)_{1-x}$ glass powders were successfully obtained up to 70 mol% AgI content by the mechanical milling method. Electrical conductivities, which show the exponential increase with addition of AgI, are comparable to the values of the corresponding melt-quenched glasses. The conductivity of 60 mol% AgI-doped glass shows great increase at the early period of the milling. A DSC signal for the β–α phases transition of crystalline AgI becomes weak at the medium stage of the milling, whereas glass transition appears clearly. EXAFS measurements at Ag, I, As, and Se K-edges have been carried out for $(AgI)_{0.6}(As_2Se_3)_{0.4}$ glasses with different period of the milling. The amorphization process of $(AgI)_{0.6}(As_2Se_3)_{0.4}$ system was accompanied by a decrease of the nearest neighboring coordination number of Ag at the medium stage of the milling. These results suggest that the structural disordering of AgI units in the glass matrix would be strongly related to the appearance of fast ionic conduction.

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Keywords: Amorphous metals, metallic glasses; Conductivity; Fast ion conduction; Chalcogenides

1. Introduction

Superionic conducting glasses have attracted much attention for the last few years because of their high ionic conductivity (more than 10^{-4} S cm^{-1} at room temperature), which is applicable to the solid-state batteries, fuel cell technologies and other electrochemical devices in place of liquid electrolytes [1–4]. A variety of silver-containing chalcogenide glasses, which is one of the high ionic conducting glasses, have been prepared by using the melt quenching method [2]. Electrical conductivities and physical properties measurements have been performed for MI-doped As-chalcogenide glasses (M: Ag or Cu) over a wide composition range up to 60 mol% MI [1,2]. High-energy X-ray diffraction [5], neutron diffraction [5,6] and extended X-ray absorption fine structure (EXAFS) studies [5] have also been carried out for MI-As_2Se_3 glasses prepared by the melt-quenching method and then discussed the relationship between glass structure and ionic conduction in the MI-doped chalcogenide glass systems. However, the conduction mechanism in these glasses is not yet fully understood.

A mechanical milling technique has been recently used for a preparation of glassy solid electrolyte powders [7]. It has the advantage of directly obtaining amorphous fine powders under room temperature and normal pressure. It is also a good method for making these glass powders of different milling periods to investigate the properties and structural changes.

This paper will present results of X-ray diffraction, electrical conductivity, DSC measurements, and EXAFS studies for the systems $(AgI)_x(As_2Se_3)_{1-x}$ prepared by using the mechanical milling method, and discuss the conduction

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mechanism dependent on a variation of milling stages in the system.

2. Experimental

$(AgI)_x(As_2Se_3)_{1-x}$ samples were prepared by the mechanical milling method using the planetary ball mill (Fritsch Pulverisette 7) with the powder mixture of the high purity starting materials of crystalline AgI, arsenic and selenium. The stating materials were charged into the agate vial with a ball-to-powder weight ratio of 30:1 under dry Ar atmosphere. The rotation speed of the milling was set to be 350 rpm. X-ray diffraction (XRD) measurements (Cu Kα) were carried out for the samples with different milling periods. The total electrical conductivity measurements were performed on the pelletized samples using an a.c. impedance technique (NF LCZ2340) with a frequency range of 10–1.2×10^6 Hz at room temperature. Both side of the pelletized sample were deposited with gold. DSC measurements were performed using Shimadzu DSC-60 with 10 K/min. EXAFS measurements at As, Se, Ag and I K-edges for the pelletized sample of the present powders with BN fine powders were carried out at BL-10B, PF-KEK (Tsukuba, Japan) and NSRL-USTC (Hefei, China). Measurement temperature was set to be 20 K. Data analyses for EXAFS measurements are identical to those described elsewhere [8].

3. Results

Glass samples were successfully obtained up to 70 mol% AgI content using the mechanical milling method. Halo patterns, which are characteristic nature of glassy samples, were observed in all compositions investigated, and are very similar to those of the corresponding melt-quenched glasses [2]. The electrical conductivities, which show the exponential increase with addition of AgI, are also comparable to the values of the corresponding melt-quenched glasses. The ion transport number is almost unity, that is, the contribution of electrons to the conductivity is found to be negligibly small.

Fig. 1 shows a variation of XRD patterns of $(AgI)_{0.6}$-$(As_2Se_3)_{0.4}$ powder samples mechanically milled for the different milling periods (0, 0.5, 1, 2, 10, 20, and 40 h) at room temperature. Debye lines corresponded to the AgI, As and Se crystals are observed in the starting mixture (0 h). After milling for 0.5 h, the intensities of all Debye lines become weaker. The peaks due to the crystalline Se are disappeared

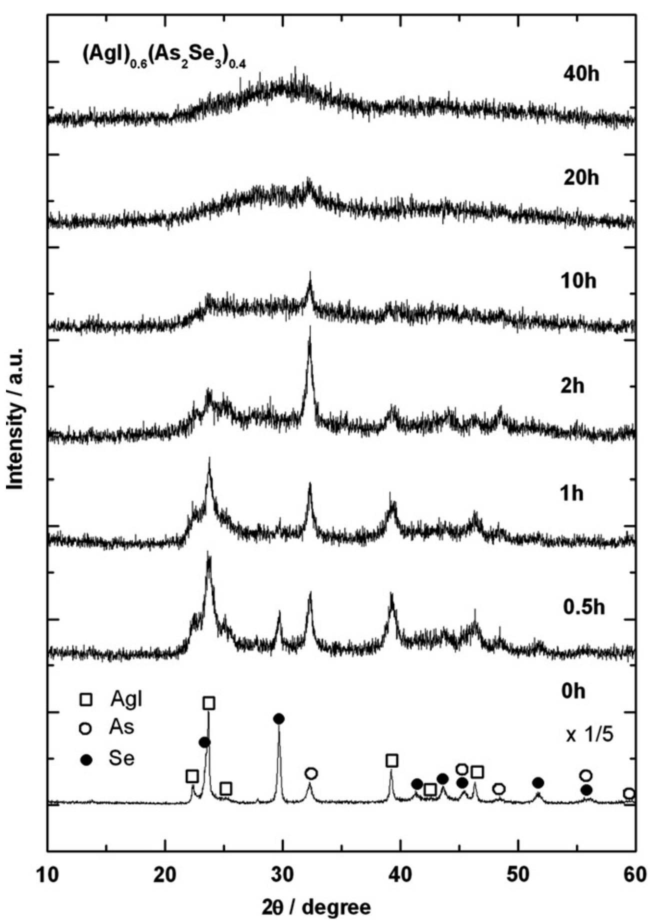

Fig. 1. X-ray diffraction patterns for $(AgI)_{0.6}(As_2Se_3)_{0.4}$ systems with the different milling period.

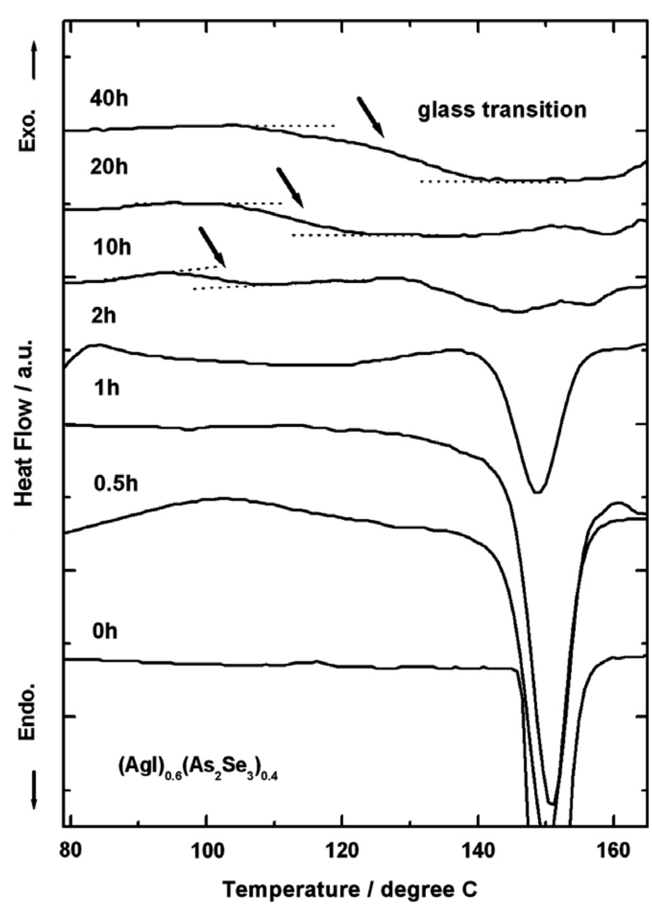

Fig. 2. Trace of the DSC measurements for $(AgI)_{0.6}(As_2Se_3)_{0.4}$ systems with the different milling period.