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Nanoscale phase separation of CuI–Cu_2MoO_4 superionic conducting glass studied by analytical transmission electron microscopy

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ABSTRACT

Microstructures of CuI–Cu_2MoO_4 superionic conducting glasses have been studied by analytical transmission electron microscopy equipped with high angle annular detector dark field (HAADF) detector and energy dispersive X-ray spectroscopy (EDS). Structural inhomogeneities of 5–10 nm in size are observed from HAADF images in the glass. Deference of composition between bright and dark contrast regions is clearly confirmed by EDS experiments. The nanoscale phase separation of 5–10 nm in size has been clarified by HAADF and EDS experiments.

1. Introduction

The class of solids usually called by superionic conducting glasses exhibits an extraordinarily high ionic conductivity [1–3]. Superionic conducting glasses have attracted much attention because of the technological needs for solid electrolytes and academic interests of understanding the ionic transport mechanism. In particular, glasses composed of AgI or CuI and some kinds of oxy-anionic species are known to show a high ionic conductivity up to 10^{-2} S/m at room temperature [2,3]. The dependence of the conductivity on the local atomic-scaled structure corresponding to the coordination environment was studied by various techniques, such as infrared spectroscopy [2–4], Raman scattering [5–7], Brillouin scattering [8], neutron scattering [9–13] and NMR [14]. For a long time, correlation between the glass structure and the anomalous high ionic conductivity has been discussed to clarify the mechanism of the ionic conductivity [1–19].

For the development of future applications, it is indispensable to advance a fundamental understanding of the microstructures and overall results of them on the macroscopic properties. The ionic conductivity generally decreases accompanied with crystallization [15]. On the other hand, an increase of the conductivity has been observed during the early stages of crystallization processes, whereas the completely crystallized samples exhibit a reduced ionic conductivity for a few oxide glass systems [16–19]. Transmission electron microscopy (TEM) is one of the most powerful tools for studying microstructures of materials at a nanoscopic level [18,19]. In our previous reports [18,19], we have performed thermal analysis and analyzed the microstructure of $(CuI)_x$–$(Cu_2MoO_4)_{1-x}$ superionic conducting glasses. In the reports, we have confirmed finely dispersion of nano-crystalline CuI of 2–3 nm in diameter in $x = 0.52$ sample annealed at 463 K by high-resolution TEM [18]. As a result, the conductivity increases by about 50% [18]. On the other hand, the conductivity of $x = 0.57$ as-quenched sample is much lower than that of $x = 0.52$ sample as-quenched one, in spite of the increase of the CuI concentration and existence of CuI nano-crystals [19]. We need further information to clarify the correlation between the nanoscale inhomogeneities and the ionic conductivity in detail. Recently, nanoscale phase separation has been observed in LaF_3 containing aluminosilicate glass [20] and metallic glasses [21] by high angle annular detector dark field scanning transmission electron microscope (HAADF-STEM) techniques. In HAADF-STEM images, the contrast is obtained predominantly by elastically scattered electrons, through high angles. The scattering is almost incoherent and the intensity is roughly proportional to the square of the atomic number of the scatterer [22]. Therefore, the image is sensitive to the compositional fluctuation. In this paper, we have studied the structural inhomogeneities in $(CuI)_x$–$(Cu_2MoO_4)_{1-x}$ glasses by analytical transmission electron microscopy equipped with HAADF-STEM and energy-dispersive X-ray spectroscopy (EDS).

2. Experiment

The starting materials were CuI (purity 99.5%), Cu_2O (purity 99.5%) and MoO_3 (purity 99.99%) powders. The as-quenched sample was prepared as follows. A mixture of the raw materials was capsuled in quartz tubes in a purified Ar atmosphere and quenched in ice water from the melt at 973 K. The phase identification and macroscopic homogeneity were examined by conventional powder X-ray diffraction using an X-ray diffractometer (Rigaku) with CuKα incident beam. In

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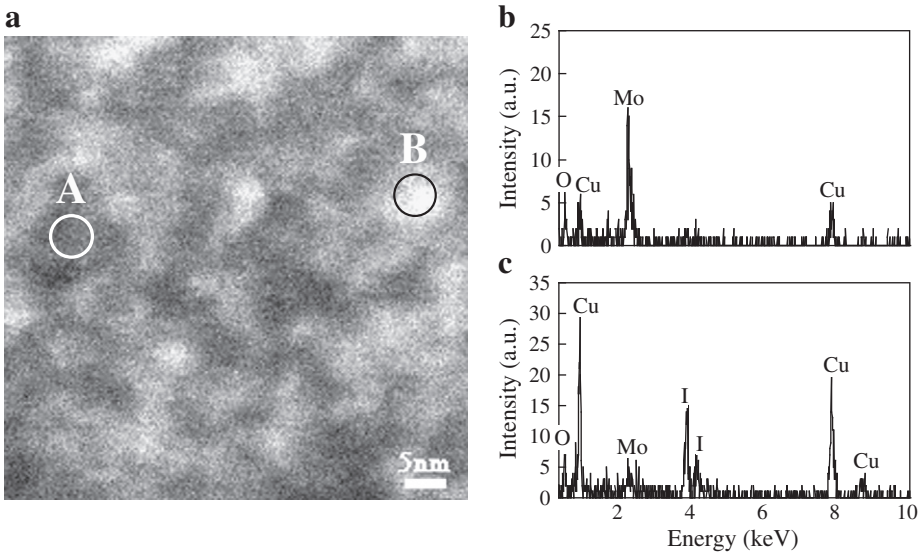

Fig. 1. (a) A HAADF-STEM image and (b), (c) representative EDS spectra obtained from regions A and B for $(CuI)_{0.52}$–(Cu_2MoO_4) as-quenched sample. Regions A and B are shown in (a).

$0.40 \leqq x \leqq 0.52$, X-ray diffraction patterns show that the specimens are fully amorphous phase. Thermal analysis was performed by a differential scanning calorimeter, DSC (Seiko Instrument; DSC220) at a heating rate of 0.333 K/s under an argon gas atmosphere.

Observation of TEM was performed with a JEOL JEM-3000F microscope operating at 300 kV equipped with HAADF-STEM and EDS. There are both merits and demerits to observe TEM specimens by crushing method and ion milling techniques. In this study, we observed specimens by them. To observe the morphology of specimens at a low magnification, we had to ensure a wide observation area. Thus, specimens were prepared by the standard ion milling techniques using a Fischione Model 1010 at an accelerating voltage of 3.0 kV. In addition, we observed specimens by the crushing method. Because we had to confirm that the specimens are not affected during the ion milling processes at a local area. Bulk specimens were crushed into fine pieces and put onto microgrids covered with carbon films. EDS analysis was performed with an electron probe of 1 nm in diameter. For EDS analysis, Cu and oxygen were detected using the K_α lines at 8.040 and 0.525 keV, respectively. Mo and I were detected using the L_α lines at 2.293 and 3.937 keV, respectively.

3. Results

Initially, we analyze the structure for the as-quenched sample of $(CuI)_{0.52}$–$(Cu_2MoO_4)_{0.48}$ by HAADF-STEM. Fig. 1 shows a HAADF-STEM image and representative EDS spectra obtained from regions A and B. Regions A and B are shown in Fig. 1(a). In Fig. 1(a), bright and dark contrast regions of 5–10 nm in size are clearly observed. To analyze the chemical composition quantitatively, we estimated the Cu/Mo and Mo/Cu atomic ratios in the bright and dark contrast regions, respectively. In Fig. 1(b), quantitative EDS analysis shows that the Mo/Cu atomic ratio is about 5 in the dark regions. On the other hand, the Cu/Mo atomic ratio is nearly 2.2 in the bright contrast regions in Fig. 1(c). The EDS spectra show that the bright and dark contrast regions correspond to Mo-poor and Mo-rich matrices, respectively. In HAADF-STEM images, the contrast is obtained predominantly by elastically scattered electrons, through high angles. The scattering is almost incoherent and the intensity is roughly proportional to the square of the atomic number of the scatterer [22]. One of the most important factors to characterize HAADF-STEM images is the atomic number of the elements contained in materials. Among all elements contained in this glass, iodine has the highest atomic number ($Z = 53$), while Mo($Z = 42$), Cu($Z = 29$), and O($Z = 8$) possess smaller atomic numbers than I. Therefore, bright contrast regions correspond to I-rich environments, while dark contrast regions correspond to Mo-rich environments.

Next, we study the microstructure with different compositions at a nanoscopic level by HAADF-STEM. Fig. 2 shows HAADF-STEM images for $(CuI)_{0.40}$–$(Cu_2MoO_4)_{0.60}$ and $(CuI)_{0.57}$–$(Cu_2MoO_4)_{0.43}$ as-quenched

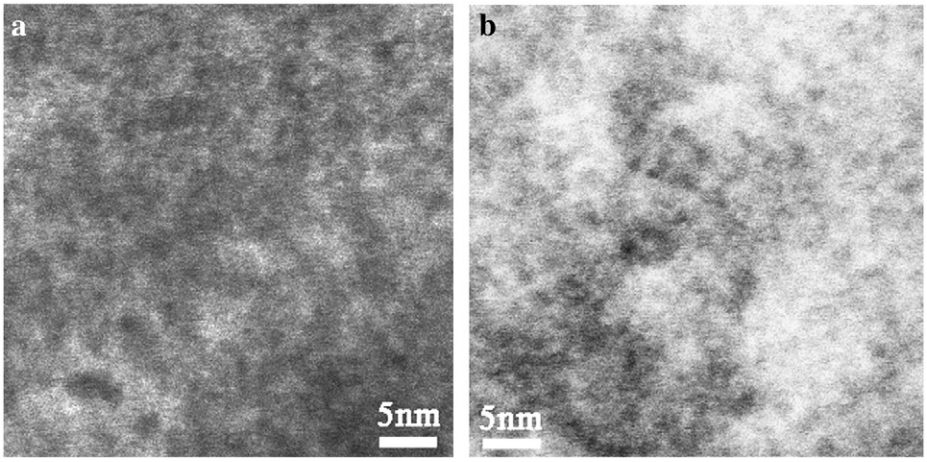

Fig. 2. HAADF-STEM images for (a) $(CuI)_{0.40}$–$(Cu_2MoO_4)_{0.60}$ and (b) $(CuI)_{0.57}$–$(Cu_2MoO_4)_{0.43}$ as-quenched samples.