Liquid Phase Separation and Precipitation of α -AgI Nano-Crystallites from AgI-Ag₂O-B₂O₃ Melt

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The dc electrical conductivity, σ_{dc} , was measured for liquid $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ ($x = 0.7-0.9$; $y = 0.05-0.2$) by using an ac impedance method in particular concern with the precipitation mechanism in the α -AgI precipitated glass, which was prepared by a rapid quenching technique due to a twin-roller apparatus. The temperature dependence of σ_{dc} exhibits two inflexion points. The existence of two liquid phase separation was confirmed by the electrical conductivity measurements with the use of specially designed cell. In addition, the X-ray diffraction and the SEM (Scanning Electron Microscope) experiments were performed for the rapidly quenched samples. The α -AgI precipitated glass was obtained by adopting the higher holding temperature even for the composition for which the β -AgI precipitated glass was prepared in the case of a lower holding one. These results indicate the role of two liquid phase separation on the preparation process of nano α -AgI crystallites in the glass matrix.

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1. Introduction

The superionic conductors are expected from many fields due to their high ionic conductivity particularly in battery materials and sensors. The representative of such materials is α -AgI, which shows very high ionic conductivity only over 420 K. Therefore, the effort has been done to provide the good ionic conductors at the room temperature. One of such materials is α -AgI precipitated glass, which is prepared by the rapid quenching technique.¹⁾ The ionic conductivity of α -AgI precipitated glass is considerably high. However, up to date, the understanding is insufficient for the precipitation process of α -AgI in the glass matrix. In this study, in order to gain an insight into the mechanism of the precipitation of α -AgI, the electrical conductivity was measured for the starting materials of α -AgI precipitated glass, $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ ($x = 0.7-0.9$; $y = 0.05-0.2$) in the liquid state. The evidentiary base for the two liquid phase separation was observed on the temperature dependence of the electrical conductivity.²⁻⁵⁾ The mechanism of precipitation of α -AgI crystallites was discussed with the relation between this two liquid phase separation and the quality of rapidly quenched samples which was investigated by the X-ray diffraction and SEM analysis.⁶⁾

2. Experimental

At first, the explanation is given for the method for the preparation of α -AgI precipitated glass. The reagents, AgI, Ag₂O and B₂O₃, were mixed in a mortar with the use of pestle. The AgI used was the special grade (over 99%) from Kojundo Chemical Laboratory Co. Ltd. The Ag₂O and B₂O₃ used was also the special grade (over 99%) from Wako Pure Chemical Co. Ltd. These were melted together and were held at 923 K in a silica glass tube with one open end. Then, the

melts were quenched by a twin-roller rapid quenching apparatus. The higher holding temperature, 1223 K, was adopted for some experiments in order to investigate the effect of the holding temperature. The concentration range studied was $x = 0.7-0.9$ and $y = 0.05-0.2$ for $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$. X-ray diffraction analyses were performed for the rapidly quenched samples at room temperature using the Rigaku MultiFlex with Cu K- α radiation. The microstructures of these samples were observed by using a SEM (JEOL JSM-5800LV) on an Al cell plate.

Impedance measurements were performed by an ac two-probe method. As shown in Fig. 1(a), the cell used was U-type with capillary on its bottom.²⁾ Two tungsten wires were used as electrodes. The melts of the samples in the cell were evacuated at 373 K in an electrical furnace, and then were kept under Ar atmosphere of 0.3 atm to prevent the samples from the evaporation.⁷⁾ The temperature of the melt

Fig. 1 The schematic figures of U-type (A) and H-type (B) cell; a: tube for sheathed thermocouple; b: tungsten electrode.

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Fig. 2 Typical X-ray diffraction patterns; nano α -AgI precipitated glasses, B: $(\text{AgI})_{0.82}-(\text{Ag}_2\text{O})_{0.14}-(\text{B}_2\text{O}_3)_{0.06}$, C: $(\text{AgI})_{0.80}-(\text{Ag}_2\text{O})_{0.14}-(\text{B}_2\text{O}_3)_{0.06}$, and D: $(\text{AgI})_{0.79}-(\text{Ag}_2\text{O})_{0.14}-(\text{B}_2\text{O}_3)_{0.07}$; β -AgI precipitated glass, A: $(\text{AgI})_{0.88}-(\text{Ag}_2\text{O})_{0.09}-(\text{B}_2\text{O}_3)_{0.03}$; homogeneous glass, E: $(\text{AgI})_{0.73}-(\text{Ag}_2\text{O})_{0.18}-(\text{B}_2\text{O}_3)_{0.09}$.

Fig. 3 The SEM image of the cross-section of sample $(\text{AgI})_{0.80}-(\text{Ag}_2\text{O})_{0.14}-(\text{B}_2\text{O}_3)_{0.06}$ (quenched at 923 K) at the room temperature. The fine particles and the dark background indicate the precipitated α -AgI and the glass matrix respectively.

samples was measured by the immersion of sheathed Almel-Chromel thermocouples into the melt samples in the vertical part of U-tube, as shown Fig. 1. The thermocouples were calibrated using the melting temperatures of pure Pb, Sn and Zn. The measurements of σ_{dc} were performed in an electrical furnace during cooling from 873 K. The dc part of the electrical conductivity, σ_{dc} , was extracted from the measured impedance by the conventional method. The impedance measurements were performed by using HIOKI 3532-20High Tester in the frequency range from 47 Hz to 5 MHz.

3. Results

Figure 2 shows a typical X-ray diffraction pattern of the rapidly quenched samples. We confirmed the existence of the crystallite phases with Bragg peaks and the glassy phase with halo pattern. Figure 3 shows the SEM (Scanning Electron Microscope) photograph of α -AgI precipitated glass. A large number of fine white spots were dispersed on the dark continuous phase for the sample in which only the Bragg

Fig. 4 The phase diagram representing the existing phases; $\circ$: the phase of α -AgI precipitated glass; $\bullet$: the phase of β -AgI precipitated glass; $\triangle$: the glass phase with both α - and β -AgI precipitates; $\blacksquare$: the homogenous glass phase.

Fig. 5 The SEM images of the cross-section of the sample of $(\text{AgI})_{0.85}-(\text{Ag}_2\text{O})_{0.07}-(\text{B}_2\text{O}_3)_{0.08}$; (A) the sample quenched at 923 K (white coarse dots correspond to β -AgI crystal); (B) the sample quenched at 1223 K (white fine particles correspond to α -AgI crystallites).

peak of α -AgI was observed in the halo pattern. Therefore, Fig. 3 indicates the fine particles of α -AgI as fine white particles and the glass matrix as dark color matrix.

Figure 4 represents the phase diagram for the existing phases, which were determined by using the X-ray diffraction analyses. We noticed some important features in this phase diagram: 1) the composition range of homogenous glasses was less than 75 mol%AgI; 2) the rapidly quenched samples with more than 85 mol%AgI showed only the Bragg peak of β -AgI crystal; 3) α -AgI precipitated glass exists between 75 mol%AgI and 85 mol%AgI.

Figure 5 shows the comparison of SEM microstructure between the rapidly quenched sample with lower holding

Fig. 6 The typical example of the dc electrical conductivity, σ_{dc} , of the melt of $(\text{AgI})_{0.88}-(\text{Ag}_2\text{O})_{0.09}-(\text{B}_2\text{O}_3)_{0.03}$ as a function of temperature, T .

Fig. 7 The concentration dependence of the inflexion temperatures of the dc electrical conductivity as a function of AgI mole fraction, x .

temperature (923 K) and that with higher one (1223 K). When the melt of $(\text{AgI})_{0.85}-(\text{Ag}_2\text{O})_{0.07}-(\text{B}_2\text{O}_3)_{0.08}$ was quenched rapidly from 923 K, the SEM image of rapidly quenched sample shows coarse white particles of a few micro meter [Fig. 5(A)]. These particles correspond to the β -AgI crystallites judging from the X-ray diffraction analysis. The melt of the same composition showed the precipitation of α -AgI crystallites when it was quenched from 1223 K, as shown in the SEM image of Fig. 5(B).

Figure 6 depicts a typical example of the measured dc conductivity, σ_{dc} , of $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ system in the liquid state as a function of temperatures. The temperature dependence of σ_{dc} showed two inflection points. Figure 7 represents the dependence of these inflexion points on the mole fraction of AgI. It can be seen that there are two kinds of lines, one is a horizontal line at 567 K and the other is an upwardly convex curve with a maximum at 0.84 as the mole fraction of AgI.

4. Discussions

Here we discussed the mechanism of the precipitation of

Fig. 8 The typical example of the temperature dependences of dc electrical resistivity, σ_{dc} , for $(\text{AgI})_{0.80}-(\text{Ag}_2\text{O})_{0.15}-(\text{B}_2\text{O}_3)_{0.5}$ melt by using U-type cell and H-type one respectively.

α -AgI on the rapid quenching process in terms of the behavior of the electrical conductivity. At first, we note the fact that the composition range of AgI for α -AgI precipitated glass in Fig. 4 is situated beyond the solubility limit of AgI in the homogenous glass phase and less than 85 mol% AgI over which only the β -AgI precipitated glass appears. The certain amount of glass content is important as well as the large amount of AgI to obtain the α -AgI precipitated glass at the room temperature. Taking into account of volume expansion at the transition from α -AgI to β -AgI, the role of glass matrix around α -AgI crystallites is to keep the volume of α -AgI constant in spite of the volume expansion on the transition from α -AgI to β -AgI, which is most stable at the room temperature. The spherical shapes of precipitated crystallites of α -AgI shown in the SEM image of the rapidly quenched samples (Fig. 3) may suggest that the crystallites of α -AgI with white color do not appear as a result of the diffusion in the solid state but appear as AgI droplets in liquid state.

It is important to note the physical properties in the liquid state of starting material for the α -AgI precipitated glass. As already described, on cooling, the temperature dependence of the dc electrical conductivity for $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ showed two inflection points. In addition, the concentration dependence of these inflexion temperatures reminds us the phase diagram of miscibility gap systems, such as Bi-Ga, Li-Na, etc. In Fig. 7, the lower inflection points in the range, $x = 0.6-0.7$, are lower than those in the range, $x = 0.8-0.9$ (x : the mole fraction of AgI). Probably this depression is caused by the supercooling due to the increase of the viscosity of melt with the increase of Ag₂O and B₂O₃ contents. Therefore, we studied directly the possibility of two liquid phase separation for the starting material of rapid quenching. The σ_{dc} in the liquid state was measured in range of the α -AgI precipitation for $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ system. This measurement was performed by using a H-type Pyrex cell with capillary on its

middle, as shown in Fig. 1(B). This cell is suitable for measuring the σ_{dc} of the upper part of the melt when the separation into two-liquid phases occurs. In this respect, the U-type cell, already described, can measure the σ_{dc} of its lower part. Figure 8 is a typical example of the comparison between the result of the H-type cell and that of the U-type one. Clear difference of σ_{dc} between H-type and U-type appeared below 795 K. This may indicate the results of separation into two liquid phases, which consist of the AgI melt and the melt of glass components. In the $(\text{AgI})_x-(\text{Ag}_2\text{O})_y-(\text{B}_2\text{O}_3)_{1-(x+y)}$ system in the liquid state, the dc electrical conductivity in the AgI rich range with no networks may be larger than that in the $\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$ range with some network structures. The larger dc conductivity of U-type cell may indicate the occupation of AgI rich liquid on the bottom part of the cell.

Figure 5 provides another ground for the role of the two liquid phase separation on the mechanism of α -AgI precipitation. When we quench the melt from 1223 K, we may freeze the state with smaller degree of two liquid phase separation; α -AgI with the small size is surrounded by the sufficient amount of glass phase and can be kept even at the room temperature. However, when the melt is quenched from 923 K, the state with well developed AgI liquid is frozen; α -AgI with the large size is surrounded by the insufficient amount of glass phase and may be changed into β -AgI due to the insufficient restriction to the phase transition (from α to β) with the volume expansion.

5. Conclusion

The appearance of α -AgI precipitated glass depends not only on the composition but also on the melt state at the instant of quenching. The existence of the two-liquid phase separation is important to understand the precipitating process of α -AgI precipitated glass.

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