

Ionic Conductivities of Molten CuI and AgI-CuI Mixtures

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Abstract. Ionic conductivities σ for molten CuI and AgI-CuI mixtures were measured in the temperature ranges of approximately 580-800 and 500-850 °C, respectively. The value of σ for molten CuI in the range is smaller than that for molten CuBr and CuCl. σ for molten AgI-CuI mixtures decreases with increasing CuI-concentration. The activation energies E_a for molten AgI-CuI system were determined from the analysis of temperature dependence of σ by using the Arrhenius type equation. E_a for molten AgI-CuI gradually increase with increasing CuI-concentration.

1 Introduction

AgI and CuI are well known as superionic conductors. In these materials, Ag and Cu ions can migrate through the interstitial space of the sublattice formed by I ions in high temperature solid phase under the melting point [1-3]. It is also known that AgI-CuI mixtures form solid solutions, and both Ag and Cu ions can migrate through the anion sublattice in the high temperature superionic phase [4,5]. In the superionic phase of AgI-CuI mixtures, I ions form lattice, and the lattice type depends on the cationic concentration (b.c.c. for Ag-rich region and f.c.c. for Cu-rich region) [4,5]. Although the structure and ionic conductivity of AgI-CuI solid solutions have been investigated by several scholars using experimental and simulation techniques [5-7], those in molten phase have not been investigated yet.

In the present study, we report the ionic conductivities of molten CuI and molten (AgI)_{1-x}(CuI)_x mixtures measured by the four-probe method, and discuss the detailed information on ionic conduction with activation energies.

2 Experimental

AgI and CuI powder samples were purchased from Wako Pure Chemical Industries. Samples of (AgI)_{1-x}(CuI)_x ($x = 0.2, 0.5, 0.8$) mixtures were prepared by mixing powder materials of AgI and CuI. A mixture sample was put into an original quartz cell with 4 mm

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inner diameter, and four carbon electrodes were inserted in small tapered holes of the cell [8,9]. The four carbon electrodes were fastened by nickel bands to prevent a leakage of the liquid sample at higher temperature. Each nickel band has a lead wire made of tungsten to connect each carbon electrode to the 3532-80 Chemical Impedance Meter (HIOKI E. E. Corporation). The sample was heated and melted by kanthal electric heating wire up to approximately 900°C. Ionic conductivity measurements were performed by four-probes technique under during the cooling process, where the measurement current was supplied to the two outside electrodes, and resulting voltage drop along the sample was measured across the two inside electrodes. Before the measurement, the cell constant of each original sample-cell was determined by using a standard aqueous solution of potassium chloride (76.5829 g-KCl/kg-H₂O). The original cell with the sample was put in a process chamber of stainless steel and alumina, where the conductivity measurements were carried out under an argon atmosphere to prevent oxidation of tungsten electrode wires. Bubbles forming in a liquid sample during the measurements were removed by stirring it with a silica rod.

3 Results and discussion

3.1 Molten CuI

Figure 1 shows the temperature dependence of the ionic conductivity $\sigma(T)$ for CuI together with the literature values of molten CuCl [10] and CuBr [11]. The σ for CuI rapidly increases with the phase transition from superionic to liquid phase around the melting point 605 °C, which is different from the behaviour of σ for AgI and CuBr. In cases of superionic AgI and CuBr, σ decreases when these materials melt, which has been interpreted as that the random distribution of anions in liquid phase disturbs the cationic conduction. Such a difference in the behaviour of σ over the melting point may be associated with the structure-type of anion-sublattice in the superionic phase. Specifically, anions in the superionic phase of AgI and CuBr form a b.c.c. lattice, while I ions in α -CuI form a f.c.c. lattice.

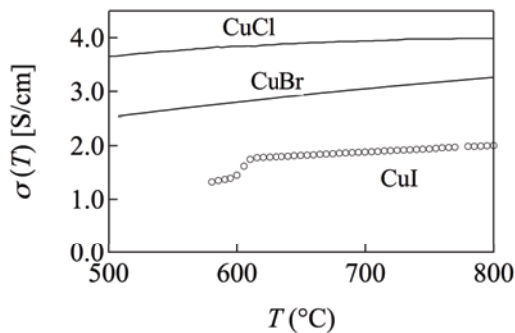


Fig. 1. Temperature dependence of the ionic conductivity σ for CuI (open circles) together with literature values (solid line) for molten CuCl [10] and CuBr [11] (solid lines).

The value of σ for molten CuI is smaller than that for molten CuBr and CuCl in the observed temperature range, which could be affected by the slower diffusion of I ions compared to Br and Cl ions due to the large ionic size and mass. The temperature dependence of σ for molten CuI was fitted by an Arrhenius type equation

$$\sigma T = A \exp(-E_a / k_B T) \quad (1)$$

to estimate the activation energy E_a , where A and k_B are a pre-exponential factor and the Boltzmann constant, respectively [11]. The estimated E_a for molten CuI is 0.14 eV.

3.2 Molten AgI-CuI mixtures

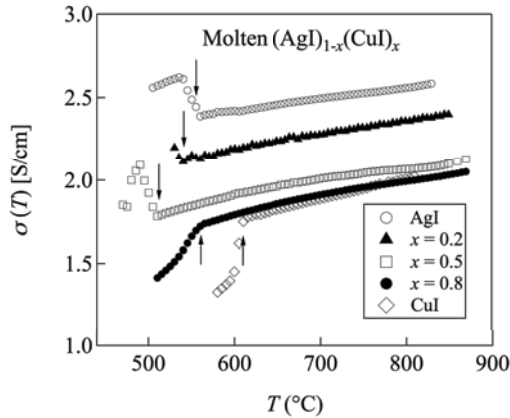


Fig. 2. Temperature dependence of the ionic conductivities for molten $(\text{AgI})_{1-x}(\text{CuI})_x$ mixtures. The arrows denote melting points [4].

The temperature dependence of the ionic conductivities $\sigma(T)$ for molten $(\text{AgI})_{1-x}(\text{CuI})_x$ are shown in Fig. 2. The value of $\sigma(T)$ for pure AgI rapidly decreases at the melting point T_m ($= 555^\circ\text{C}$) in the heating process as already reported by the literature [1]. The $\sigma(T)$ for the molten phase of AgI gradually increases with increasing temperature, which also shows a good agreement with the literature [1]. The $\sigma(T)$ for the mixtures of $(\text{AgI})_{1-x}(\text{CuI})_x$ in a small x region ($x \leq 0.5$) around the melting point rapidly decreases with increasing temperature, while the $\sigma(T)$ in a large x region ($0.5 < x$) rapidly increases. As written in Sec. 1, I ions in superionic phase of $(\text{AgI})_{1-x}(\text{CuI})_x$ mixture form b.c.c. and f.c.c. lattice in the small and large x regions, respectively. Therefore, the cationic diffusion in the melting process would be affected by the type of anion-sublattice. In all of the CuI-concentrations, the value of σ for the molten phase gradually increases with increasing temperature.

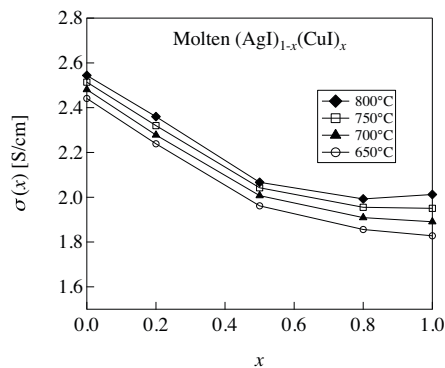


Fig. 3. Composition dependence of the ionic conductivities for molten $(\text{AgI})_{1-x}(\text{CuI})_x$.

The concentration dependence of the ionic conductivities $\sigma(x)$ for molten $(\text{AgI})_{1-x}(\text{CuI})_x$ at several temperatures is shown in Fig. 3. The value of $\sigma(x)$ rapidly decreases with increasing CuI-concentration in a small x region ($x < 0.5$), suggesting that the relative slow conduction

of Cu ions in comparison with Ag ions contributes to the decrease of $\sigma(x)$. On the other hand, the concentration dependence of $\sigma(x)$ is small in a large x region ($0.5 \leq x$), suggesting that Ag ions diffuse as slow as Cu conduction in this concentration region.

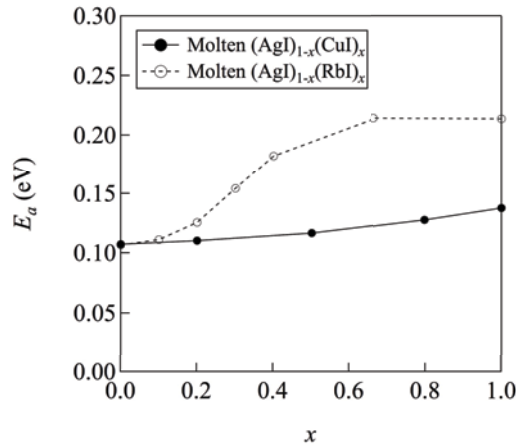


Fig. 4. Concentration dependence of the activation energies E_a for molten molten $(AgI)_{1-x}(CuI)_x$ together with those for molten $(AgI)_{1-x}(RbI)_x$ system [9].

The concentration dependence of E_a for molten $(AgI)_{1-x}(CuI)_x$ mixtures obtained by eq. (1) is shown in Fig. 4 together with that for molten $(AgI)_{1-x}(RbI)_x$ reported in the earlier paper [9]. The E_a for molten $(AgI)_{1-x}(RbI)_x$ rapidly increases in the range of $0.2 < x < 0.4$, suggesting that a large energy is needed to move large and heavy Rb ions, and Rb ions would obstruct the Ag-conduction path in the high RbI-concentration [9]. On the other hand, the E_a for molten $(AgI)_{1-x}(CuI)_x$ mixtures gradually increases with increasing CuI-concentration. It is difficult to explain why the E_a for molten CuI is larger than that for AgI by considering the difference in the ionic size and mass between Ag and Cu, because an Ag ion is larger and heavier than a Cu ion, which seems to be a disadvantage for the ionic diffusion. Furthermore, the valence charges of Ag and Cu ions are almost the same [12,13]. However, the concentration dependence of E_a for $(AgI)_{1-x}(CuI)_x$ mixtures observed in this study would not be the error, because the similar behavior has also been reported for the solid solution of AgI-CuI system [5]. As also discussed in Ref. 5, the activation energy is sometimes not directly related to the ionic size and mass. Therefore, other reasons except for the size, mass, and valence charge of cations have to be considered in this case. For example, a relative strong covalency for Ag-I and Cu-I pairs has been found in molten AgI and CuI by *ab-initio* calculations. Furthermore, weak covalencies of cation-cation pairs have also been reported [14,15], and finally the resulting first correlation lengths of cation-cation and cation-I correlations are different for molten AgI and CuI [16]. Moreover, it has been reported that the electric field generated from the dipole-moment of anions affects the liquid structure and cationic diffusion in molten Ag and Cu halides [12,13,17-19]. These complex properties of Ag and Cu halides compared to typical molten salts might be associated with the activation energy in AgI-CuI system.

4 Conclusion

The electrical conductivities due to the ionic conduction in molten CuI and $(AgI)_{1-x}(CuI)_x$ mixtures were measured in the temperature ranges of approximately 580-800 and 500-

850 °C, respectively. The conductivity of molten CuI in the range was found to be smaller than that of molten CuBr and CuCl previously reported. Moreover, the activation energy of molten CuI was determined as $E_a = 0.14$ eV by the analysis of the temperature dependence of the conductivity. The conductivity and energy of molten $(\text{AgI})_{1-x}(\text{CuI})_x$ mixtures decreases and gradually increases with increasing CuI-concentration, respectively, which is similar behaviour to the AgI-CuI solid solutions. The concentration dependence of the activation energy for molten $(\text{AgI})_{1-x}(\text{CuI})_x$ cannot be explained by considering only the mass, ionic size, and valence charge of Ag and Cu ions. The complex interactions between cation and anion and between cations might affect the activation energies also.

This study was supported by JSPS KAKENHI Grant Number 16K17766.

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