Concentration Effects of Silver Ions on Ionic Conductivities of Molten Silver Halides

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Abstract. Ionic conductivities of molten (RbX),,(AgX),c (X = Cl and I) mixtures were measured to clarify the concentration effects of silver ions on ionic conductivities of molten silver halides. It is found that the addition of RbX to molten AgX rapidly reduces the ionic conductivity with 0 ≤ c ≤ 0.4. It suggests that strong Ag-Ag correlation is necessary to fast conduction of Ag ions in molten state. The absolute values of ionic conductivity for (RbCl),,(AgCl),c are larger than those for (RbI),,(AgI),c mixtures at all compositions. These differences might relate to difference of diffusion constant between Cl− and I− and difference of effective charge carried by an ion between molten AgCl and AgI.

1 Introduction

Ionic conductivities, σ, of silver halides at solid and molten phases have been reported by many earlier works [1-11]. It is well known that σ of superionic σ-AgI (high temperature solid phase of AgI) is as large as that of molten salts, while σ of crystal AgBr and AgCl under the atmospheric pressure are small even at high temperature [10, 11]. Above the melting point, these silver halides show larger σ than typical alkali halides [12]. Taking into account of the fact that Ag diffusion constants are more than twice as large as those of anions, fast diffusion of Ag ions even in molten phase causes high ionic conductivity [13-15]. Such a feature is very interesting, because Ag is heavy compared with alkali metals.

In our previous papers on structure of molten silver halides by high-energy x-ray diffraction, neutron diffraction and structural modelling by Reverse Monte Carlo modelling [16-18], revealed that Ag distribution of molten AgI has large fluctuations where one-dimensional streams consisting of several Ag ions are formed. These results correspond to Ag-Ag partial pair distribution functions (pdf). The first peak of Ag-Ag pdf of molten AgCl shows penetration into the first coordination shell of Ag-I pdf, and a similar penetration is also reported by results of ab-initio molecular dynamics (MD) simulation [19]. It might suggest collective motions of Ag ions. On the other hand, Ag distribution of molten AgCl shows relatively a uniform-like feature [16-17]. However, it is still quite different from cation distribution of molten alkali halides in an extremely flat structure of the Ag-Ag pdf [20]. An empirical MD simulation using the polarizable ion model based on Vashishta-Rahman potential reasonably reproduced the flat structure of Ag-Ag pdf [13]. This structure-less of Ag-Ag pdf implies that correlations between Ag ions in molten AgCl might be weak like gas. The differences in Ag distribution between AgI and AgCl originate from effective charge carried by an ion and covalency of bonding between Ag and halogens. Much drastic changes of structure and transport properties are expected by varying Ag concentration. It is consider that Ag concentration variation is virtually possible by mixing Ag halides with alkali halides.

In this study, ionic conductivity of molten (RbI),,(AgI),c and (RbCl),,(AgCl),c mixtures which have eutectic concentration at c = 0.3 and 0.4 [21-23], respectively, were measured. The (RbI),,(AgI),c mixtures have stoichiometric compound RbAgI₄ which shows the superionic phase even at room temperature [23-27], and its structure factor at molten phase has the largest scale of medium-range order in the molten (RbI),,(AgI),c system [28]. We have two motivations in this study. First, whether dose the weakening of the strong Ag-Ag correlation of molten AgI with decreasing Ag concentration affect ionic transport, or not? Second, are there differences between molten (RbI),,(AgI),c and (RbCl),,(AgCl),c mixtures according to the difference in Ag distribution between AgI and AgCl?
2 Experimental procedure

Samples of \((\text{RbI})_c(\text{AgI})_{1-c}\) (\(c = 0, 0.1, 0.2, 0.3, 0.4, 0.667, 1\)) and \((\text{RbCl})_c(\text{AgCl})_{1-c}\) (\(c = 0, 0.1, 0.2, 0.4, 0.667, 1\)) mixtures were prepared by mixing powder materials of AgI and RbI, or AgCl and RbCl in sealed quartz tube. Ionic conductivity measurements were performed by four-probes method using 3532-80 Chemical Impedance Meter (HIOKI E. E. Corporation) under a cooling process. A sample was put into quartz cell with 4 mm inner diameter where four small tapered holes are located with each 28 mm interval to insert carbon electrodes [29]. The carbon electrodes were fastened by nickel bands to prevent a leak of liquid sample. Each nickel band has a lead wire made of molybdenum to connect each electrode to 3532-80 Chemical Impedance Meter (HIOKI E. E. Corporation). Current was supplied to outside two electrodes, and voltage was measured at inside two electrodes. Cell constant was determined by using a standard aqueous solution of potassium chloride (76.5829 g-KCl/kg-H2O). The measurements were carried out under an argon atmosphere to prevent oxidation of molybdenum wires and vaporization of samples. Bubbles forming in a liquid sample during the measurements were removed as possible as we can by stirring it with a silica rod. The temperature was measured by using four chromel-alumel thermocouples immediately above the electrodes.

3 Experimental results

Figure 1 shows temperature dependences of \(\sigma\) of molten \((\text{RbI})_c(\text{AgI})_{1-c}\) and \((\text{RbCl})_c(\text{AgCl})_{1-c}\) mixtures, respectively. We confirmed that the present ionic conductivities of molten AgI, AgCl, RbI and RbCl are in good agreement with those of earlier works [1-9, 30-31]. The increase of \(\sigma\) of AgI at a phase transition from molten phase to the superionic \(\alpha\)-phase, is also reported by earlier works [3-5, 7]. This increase of \(\sigma\) relates to higher Ag conductivities in the superionic phase than those in molten phase at immediately around \(T_m\). From experimental and theoretical studies on a self-diffusion constant of Ag, \(D_{Ag}\), of AgI beyond the transition point from \(\alpha\)-phase to molten phase, \(D_{Ag}\) in molten phase shows smaller value than that in superionic phase at around \(T_m\) [32-34]. The addition of RbI into molten AgI reduces \(\sigma\) in the RbI concentration region less than 0.667. The \(\sigma\) of molten \((\text{RbI})_{0.3}(\text{AgI})_{0.7}\) is comparatively large at a low temperature and becomes small in a high-temperature region.
The $\sigma$ of RbI-Agl mixtures below $T_m$ might receive some influence of Ag conduction of $\alpha$-RbAgI and $\alpha$-AgI. $\sigma$ of molten (RbI),(AgI)$_{1-e}$ shows similar temperature and concentration dependence as molten (RbI),(AgI)$_{1-e}$ except of a little higher conductivity of AgCl and rapidly decrease of $\sigma$ by solidification. Although a gradual increase of the slope by adding RbCl is not observed, the ratio of temperature coefficient to the $|\sigma|$ of molten AgCl is still smaller than that of molten RbCl.

The concentration dependence of $\sigma$ of molten (RbI),(AgI)$_{1-e}$ and (RbCl),(AgCl)$_{1-e}$ mixtures are shown in Figs. 2(a) and 2(b), respectively. The $\sigma$ rapidly decreases with increasing concentration of RbCl from $c = 0$ to 0.4, and then the $\sigma$ becomes almost constant at $0.4 \leq c \leq 1$. These features are reported for molten KI-AgI, KCl-AgCl systems, and so on [6]. The decrease of $\sigma$ with increasing concentration of AgX, becomes more rapid as temperature decrease for molten (RbI),(AgI)$_{1-e}$, which is associated with small temperature dependence of $\sigma$ for molten AgI.

4 Discussion

The ionic conductivity is generally written by an Arrhenius expression

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

where $E_a$, $A$, and $k_B$ are the activation energy, the pre-exponential factor, and the Boltzmann constant, respectively [35-37]. In general, $E_a$ is estimated by fitting a linear function to the Arrhenius plot (ln|$\sigma$T) vs. 1/T). The Arrhenius plot of molten (RbI),(AgI)$_{1-e}$ mixtures is shown in figure 3.

Figure 4 shows the concentration dependence of activation energy, $E_a$, which is estimated by fitting a linear function to Arrhenius plot within the measured temperature region of each composition. The estimated $E_a$ of molten AgI, AgCl, RbI, and RbCl are 0.107, 0.114, 0.213, and 0.215 eV, respectively. $E_a$ of molten AgX are smaller than that of molten RbX, which is consistent with the fact that the diffusion constant of Ag ions in molten AgX is higher than that of Rb in molten RbX [13, 15, 38]. The $E_a$ increases in the concentration region from $c = 0.2$ to 0.4 where the melting point exhibits minimum. The $E_a$ of molten AgI is slightly small compared with that of molten AgCl. It is in good agreement with earlier work [8].

To compare the ionic transport properties between (RbI),(AgI)$_{1-e}$ and (RbCl),(AgCl)$_{1-e}$ precisely, the conductance per 1 mole-cubic which includes 1 mole molecules, $\sigma_{mol}$, was deduced to normalize by carrier density. $\sigma_{mol}$ was estimated by

$$\sigma_{mol} = \sigma \cdot (S/L) = \sigma \cdot V^{2/3} = \sigma \cdot (N_A/\rho)^{2/3}$$

where $V$ is the molar volume of materials. $L$ and $S$ are the side length of the 1 mole-cubic ($L = V^{1/3}$) and the side area of the cubic ($S = L^2 = V^{2/3}$), respectively. $N_A$ and $\rho$ are the Avogadro constant and the number density of molecules, respectively. Estimated $\sigma_{mol}$ for molten (RbX),(AgX)$_{1-e}$ mixtures at 750ºC are shown in the figure 5. $\rho$ of molten (RbX),(AgX)$_{1-e}$ ($c = 0.1 \sim 0.667$) mixtures was estimated from linear combination of molar volume between AgX and RbX [12].

The $\sigma_{mol}$ for molten (RbI),(AgI)$_{1-e}$ mixtures decreases rapidly with increasing RbI with $0 \leq c \leq 0.4$, and then settles to be almost constant with $0.4 \leq c \leq 1$. Taking into account of the fast collective migrations of Ag in molten AgI, the collective motion of Ag rapidly decreases with increasing RbI concentration. Since such collective dynamics is ruled by the second power of the number density or higher order of the power, the rapid decrease of $\sigma_{mol}$ by adding RbI supports reasonably this dynamical model suggested from the static structural model. On the other hand, it is surprising that the concentration dependence for molten (RbCl),(AgCl)$_{1-e}$ shows a similar tendency with that for molten (RbI),(AgI)$_{1-e}$. It suggests that the diffusion of Ag ions in molten AgCl is also
The property of Cl ions. Structural investigation of molten bonding character which may also cause polarizable measured the structure of molten (RbI) anomalous Ag migration in molten AgI. We have already may be reduced through a covalent property of Ag-Cl interactions by high density of Ag ions, carrying charge carrying charge from ±1 to ±0.68. To avoid repulsive effect, inspite of weak Ag-Ag partial correlations. The concentration dependence of \( \sigma_{\text{mol}} \) which was normalized by carrier density for molten (RbCl),(AgCl)\(_{1-c}\) mixtures. It suggests that the diffusion of Ag ions in molten AgCl is also regulated by many-body effect, inspite of weak Ag-Ag partial correlations. The concentration dependence of \( \sigma_{\text{mol}} \) between (RbCl),(AgCl)\(_{1-c}\) and (RbI),(AgI)\(_{1-c}\) would be differences of diffusion constants between Cl and I ions. In addition, differences of an effective charge carried by an Ag ion in molten AgCl and AgI also may contribute to the differences of \( \sigma_{\text{mol}} \) between (RbCl),(AgCl)\(_{1-c}\) and (RbI),(AgI)\(_{1-c}\).

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### References

2. M. C. Bell and S. N. Flengas, J. Electrochemical soc. 111 575 (1964)
32. C. Tubandt and E. Lorentz: Z. Phys. Chem. 87 513 (1914)