Dynamical Behavior and Phonon Propagation in Superionic AgBr-CuBr System

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Molecular dynamics simulation (MD) has been performed to investigate the partial dynamical structure factors $S_{\alpha\beta}(k,\omega)$ of the superionic phases for $(Ag_{x}Cu_{1-x})Br$ of $x = 0.1$, which contains two kinds of mobile cations, $Ag^+$ and $Cu^+$. From the obtained $S_{\alpha\beta}(k,\omega)$, the longitudinal acoustic (LA), the longitudinal optical (LO), and the transverse acoustic (TA) modes have been observed. All these modes are propagated mainly by Br ions. The interaction between ions is also discussed using the model based on the plasma frequency.

Key words: molten AgBr-CuBr, molecular dynamics, dynamic structure factor, transverse acoustic mode

1. INTRODUCTION

There is a group of substances called superionic conductor (SIC) or solid electrolyte, which conductivities are comparable to those of liquid electrolytes. SIC’s are applied to various practical devices, e.g. solid state batteries, fuel cells, optical devices etc [1]. AgI and CuBr are typical examples of noble metal halides which have a SIC phase. AgBr and AgCl, however, do not show superionic conduction until their melting point. The mixed systems of these two different type noble metal halides are of particular interest.

Though the distributions of cations in the SIC phase of noble metal halides have been studied in detail, these studies have been executed mainly in the systems which contain one kind of cation, i.e. $Cu^+$ or $Ag^+$. The cations are supposed to distribute mainly around the tetrahedral 12(d) site of halogen bcc lattice. According to the recent experimental study, however, cations $Cu^+$ and $Ag^+$ distribute mainly around the octahedral 6(b) site in the superionic $(Ag,Cu_{1-x})I$ [2]. In addition to the interest of physical chemistry on the interaction between $Cu^+$ and $Ag^+$ ions, there would be an advantage for practical application, because the mixed ionic conductor may lower the transition temperature to the SIC phase.

Under these circumstances, we have investigated the SICs and their melt, which also contain two kinds of mobile cations [3]. In the previous study, we have carried out the molecular dynamics (MD) simulation to examine the structural properties of the SIC phase of $(Ag,Cu_{1-x})Br$ for $x<0.1$. The MD results were quite noteworthy, i.e. the different distribution between $Ag^+$ and $Cu^+$ ions in SIC phase has been detected. For $x_{Ag} = 0.10$, $Cu$ ions mainly distribute around the tetrahedral 12(d) site; whereas the significant distribution of Ag ions are found around the octahedral 6(b) site. This fact contradicts to the generally accepted view. In other words, there is a phase separation tendency between $Ag^+$ and $Cu^+$ in the SIC phase of $(Ag,Cu_{1-x})Br$. This structural feature may affect the dynamical properties of this system.

Furthermore, in the previous articles [4], MD have been performed in the molten phase of RbAg$_{4}$I$_{5}$, which is known as a SIC at room temperature. From the obtained $S_{\alpha\beta}(k,\omega)$, the longitudinal acoustic (LA), the longitudinal optical (LO), and the transverse acoustic (TA) modes have been observed. It is noteworthy that they are propagated mainly by the different ions; LA and LO modes by I ions, TA modes by Ag ions.

The recent experimental study has proved the existence of TA mode in liquid Ga [5]. This fact also provides a motivation of the study of dynamical features and phonon propagation in multi-component systems.

On the theoretical point of view, in SIC phase, e.g. $\alpha$-AgI, LA and LO modes are observed in the peaks of $S_{\alpha\beta}(k,\omega)$ of anion sublattice [6]. However, as far as we know, the propagation mechanism of phonon modes in the multi-component SIC systems has not been discussed in detail.

Considering these circumstances mentioned so far, as a continuous work, we have calculated the partial dynamical structure factors $S_{\alpha\beta}(k,\omega)$ in superionic $(Ag,Cu_{1-x})Br$ for $x<0.1$ to investigate the correlation between ions in detail.

2. DETAILS OF SIMULATION PROCEDURE

The essential procedure of MD simulations is same as our previous works [3,4], which we briefly describe as follows. The Rahman, Vashishta and Parrinello (RVP) type pair potentials are used [7], which is expressed as,

$$V_{ij}(r) = \epsilon_{ij} [1/(\sigma_{ij}^r) - 1]$$

where $i$ and $j$ stands for anions or cations; the first term is the repulsion between ions; the second term is the Coulomb interaction; the third term is charge-dipole interaction; the last term is the van der Waals interaction. We have neglected the forth term for simplicity. The used potential parameters are taken from literature, which have been determined by fitting to the solid-state properties [8,9]. The interaction parameters between Ag and Cu are obtained using the Lorentz-Berthelot combining rules [10]. We adopt the power $n_{ij}$ of $r$ for the first term for CuBr, because the
purpose of MD simulation is to examine the Cu rich superionic side. The used potential parameter sets are listed in the Table 1 in the previous paper [3]. We postulate that the effective charge $z_i$'s have the equal value 0.48 as in CuBr to preserve the charge neutrality condition of the whole cell. The periodic boundary condition is used. Coulomb interaction is calculated using the Ewald method.

The MD calculations have been performed in $(\text{Ag}_{x}\text{Cu}_{1-x})\text{Br}$ system for $x=0.10$ with 864 ions ($43\text{Ag} + 389\text{Cu} + 432\text{Br}$) and 500 ions ($25\text{Ag} + 225\text{Cu} + 250\text{Br}$) to increase the number of the wave vectors $k$, which is expressed as $(2\pi/a)(\iota/n, \mu/n, \nu/n)$ corresponding to the set of integer $(\iota, \mu, \nu)$, and the lattice constant $a$. In our MD, $n$ takes the value 6 and 5 for 864 and 500 ions, respectively, because a unit cell includes $2(\text{Ag}_{0.1}\text{Cu}_{0.9})\text{Br}$ [10]. The conditions of the temperature and the molar volume of the system for MD are 773K and 48.2Å$^{-3}$, respectively, which is estimated from the experimental density data of $\alpha$-CuBr postulating the similar temperature dependence to that in $\beta$-CuBr [11].

By the MD conditions and potentials described so far, SIC phase has been reproduced, and the transport properties, thermodynamic properties and structure factors have been obtained properly by MD [3]. Therefore the accuracy of the potentials are thought to be confirmed.

The dynamic structure factors for binary molten salts have also been obtained by MD [6]. In this section, we wish to show the extension of the method to the multi-component systems, i.e. molten $(\text{Ag}_{0.1}\text{Cu}_{0.9})\text{Br}$. The Fourier component of the density of the ion $\xi$ is,

$$\rho_\xi(k, t) = \sum_{i=1}^{N_\xi} e^{i k r_\xi i (t)}$$

where $\xi$ stands for Ag, Cu, and Br. $N_\xi$ and $r_\xi i (t)$ are the number of ion $\xi$ and the position of $i^{th}$ $\xi$ ion, respectively. The partial dynamic structure factors are defined as the spectrum of the density correlation between $\xi$ and $\eta$ ions ($\xi, \eta = \text{Ag, Cu, Br}$), as,

$$S_{\xi\eta}(k, \omega) = \frac{1}{2\pi(\omega)} \int_0^\infty e^{i\omega t} \langle \rho_\xi (k, t) \rho_\eta (k, 0) \rangle \, dt$$

where the brackets denote an ensemble average, which is interpreted as an average over time in MD. Though the convergence of the correlation function is slow in the case that a vibrational mode has a long lifetime, the direct calculation of the power spectrum can avoid this difficulty. The raw dynamical structure data have been convoluted with a Gaussian window function which has a full width at half maximum (FWHM) of 1.5(ps)$^{-1}$ to eliminate the statistical noise. The obtained dynamic structure factors are expressed as the normalized form as,

$$\bar{S}_{\xi\eta}(k, \omega) = S_{\xi\eta}(k, \omega)/S_{\xi\eta}(k)$$

where $S_{\xi\eta}(k)$ is the static structure factor. The sum rule has been assumed to obtain $S_{\xi\eta}(k)$, as,

$$S_{\xi\eta}(k) = \int_{-\infty}^{\infty} S_{\xi\eta}(k, \omega) \, d\omega$$

The MD has been performed in the molten phase, where the system expected to be isotropic. Therefore the dynamic structure factor is a function of only the absolute value of $k$.

![Fig. 1](image-url) $\bar{S}_{\xi\eta}(k, \omega)$'s of longitudinal modes for Br-Br, Cu-Cu and Ag-Ag. Plasma frequency $\omega_p$ is shown.
Fig. 2 \( S_{\psi}(k, \omega)'s \) of transverse modes for Br-Br, Cu-Cu and Ag-Ag.

Fig. 3 The \( \omega-k \) dispersion relations for LA, LO and TA modes.
3. SIMULATION RESULTS AND DISCUSSION

The normalized dynamic structure factors $\tilde{S}_{\omega}(k,\omega)$ obtained by MD are shown in Fig.1 and Fig.2, where the calculation has been performed to the [100] direction of the unit cell, therefore $k = k_0$ is presented in these figures. As seen in Fig.1, some subsidiary peaks have been observed in $\tilde{S}_{\omega}(k,\omega)$ in the high $k$ region, which may be attributed to the vibration of cations in the anion bcc sub-lattice. This feature of $\tilde{S}_{\omega}(k,\omega)$ stands in marked contrast to the smooth profile of that of molten RbI-Agl [4]. In order to investigate the phonon modes of $\tilde{S}_{\omega}(k,\omega)$, the curve fitting has been tried. The $\tilde{S}_{\omega}(k,\omega)$ profiles have been reproduced to some extent by the sum of three Lorentzian functions corresponding to the Rayleigh line, the Brillouin line or LA mode, and LO mode.

The LA modes are clearly observed in $\tilde{S}_{\omega}(k,\omega)$. This fact suggests that the vibration of the bromide ions strongly correlate with the LA modes, i.e. the LA modes are mainly carried by Br ions. The small humps can be observed in $\tilde{S}_{\omega}(k,\omega)$ corresponding to the LA modes in $\tilde{S}_{\omega}(k,\omega)$, which indicates the weak correlation of Cu ions with Br ions. The LA peaks move to the higher $\omega$ position as the absolute value of the wave vector $k$ increases. The LO modes also can be observed in $\tilde{S}_{\omega}(k,\omega)$ at higher $\omega$ in Fig.1.

The dispersion relations of $k$ and $\omega$ obtained from the peak position of LA and LO modes are shown in Fig.3. As seen in Fig.3, $\omega$ in LA modes increase almost linearly up to 0.46 Å$^{-1}$. On the other hand, LO modes are almost constant.

Next, we investigate the TA modes. The calculation method is essentially similar to that used in the SIC phase [6]. In the calculation of $\tilde{S}_{\omega}(k,\omega)$ for TA modes, the wave vector $k$, which appears as $k r_{ij}$ in $\rho_{ij}(k,\omega)$, is expressed as $k = q + K$, where $q$ is the wave vector in the first Brillouin zone, $K$ is the reciprocal-lattice vector perpendicular to $q$. In the calculation in the superionic phase of AgI, the configurations of cations are supposed to be affected by the structure of anions at the bcc lattice points. Therefore the normalized dynamic structure factors of cation-cation and anion-anion, or $\tilde{S}_{c,c}(k,\omega)$ and $\tilde{S}_{c,a}(k,\omega)$, have peaks for $K$, e.g. $K=(2\pi/\alpha)(0,2,0)$, then TA modes can be discussed using $\tilde{S}_{\omega}(k,\omega)$ [6,12].

The obtained $\tilde{S}_{\omega}(k,\omega)$’s for $k = q + K$ are shown in Fig.2. As seen in Fig.2, TA modes also can be observed as the pronounced peaks in $\tilde{S}_{\omega}(k,\omega)$ similar to LA modes which have been observed mainly as peaks in $\tilde{S}_{\omega}(k,\omega)$ in Fig.1. The TA modes in SIC phase of AgBr-CuBr are in marked contrast with those in molten RbAgAl$_3$, where LA are observed in $\tilde{S}_{\omega}(k,\omega)$, whereas TA are found in $\tilde{S}_{\omega}(k,\omega)$[4]. The dispersion relations between $k$ and $\omega$ of TA modes are also shown in Fig.3. The TA modes appear at the similar frequencies to LA modes up to 0.55 Å$^{-1}$. Then TA modes seem to begin to decrease. In the $\tilde{S}(k,\omega)$ for liquid Ga obtained by an inelastic x-ray scattering experiment, the TA phonons have been observed at the first pseudo-Brillouin-zone boundary as the quasi-transverse branch of LA modes. The mixing of LA and TA modes has been occurred in the viscoelastic or fast-sound regime for LA phonons [5]. In the present case of SIC AgBr-CuBr, the first pseudo-Brillouin-zone boundary is 0.69 Å$^{-1}$, from where TA modes are expected to separate from LA modes.

Next we consider the ionic plasma frequency to understand the distribution of the peak positions in $\tilde{S}_{\omega}(k,\omega)$ in relation to the microscopic ionic motion. In the case of ionic liquids or SIC, there are two important features in common; (a) the macroscopic and microscopic charge neutrality; (b) the presence of mobile charge carriers. The existence of mobile ions in combination with Maxwell’s equations and hydrodynamic equations leads to the long-wavelength charge fluctuation, which gives rise to the high frequency collective modes of cations and anions similar to the charge oscillations found in plasmas [10].

To the best of the author’s knowledge, the ionic plasma in SIC phase and ionic melt have been studied mainly for binary systems [10]. We extend the consideration to the ternary system, SIC AgBr-CuBr. The simple model for plasma frequency in molten phase is expressed as,

$$\omega_p = \frac{4\pi \rho f^2}{\varepsilon_0 M}$$

where $\rho$ is the density of cations; $f$ is the ionization parameter, which is assumed to be equal to the effective charge $z_e$; $\varepsilon_0$ is the dielectric constant obtained by experiment [13]; $M$ is the reduced mass of components, which is expressed as

$$\frac{1}{M} = \frac{1}{m_{Ag}} + \frac{c_{Ag}}{m_{Cu}} + \frac{1}{m_{Br}}$$

where $c_{Ag}$ and $c_{Cu}$ are 0.1 and 0.9, respectively [9]. Similar to AgI, the obtained plasma frequency 21.5 ps$^{-1}$ is very close to the peak of LO mode observed around 21–23ps$^{-1}$ in Fig.1. This fact suggests that the origin of the LO modes is attributed to the plasma frequency, i.e. cation-anion interaction. On the other hand, LA and TA modes, which are found at the frequencies less than 10ps$^{-1}$, are not the plasma frequency. In other words, the TA modes are supposed to be raised by the cage effect by the surrounding ions. This result also agrees with the fact that the peaks of TA modes are also found in $\tilde{S}_{AgAg}(k,\omega)$ and $\tilde{S}_{CuCu}(k,\omega)$ in Fig.2, though their frequencies are different from that in $\tilde{S}_{BrBr}(k,\omega)$, which suggests the existence of a kind of resonance between LA and TA modes.

4. SUMMARY

The dynamic structure factors $\tilde{S}_{\omega}(k,\omega)$ have been obtained for SIC AgBr-CuBr by MD using the RVP type potentials. The LA, LO and TA phonon modes have been detected. The LA, LO modes and the TA modes are mainly propagated by Br ions. The calculated plasma frequency is very close to that of the LO mode. These facts suggest that the origin of the TA modes is not the cation-anion interaction, but the cage effect by the surrounding ions.

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REFERENCES

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