Structural Features of Superionic Phase in AgBr-CuBr System by Molecular Dynamics Simulation

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Abstract. Molecular dynamics simulation has been performed to investigate the structural properties of superionic phase for \((\text{Ag}_{x}\text{Cu}_{1-x})\text{Br}\) of \(x<0.5\), which contains two kinds of cations, \(\text{Ag}^+\) and \(\text{Cu}^+\). \(\text{Ag}^+\) and \(\text{Cu}^+\) ions show different distribution in superionic phase. Concentration dependence also can be observed in the distribution of cations and their pair distribution functions.

1. Introduction
There has been a lot of study of a group of substances with high ionic conductivity though they are still in solid phase. Such substances are called superionic conductors or solid electrolytes, which conductivities are comparable to those of liquid electrolytes. Superionic conductors are applied to various practical devices, e.g. solid state batteries, fuel cells, memory devices etc [1].

The silver and copper halides, e.g. AgI and CuBr, are typical examples of superionic conductors in their \(\alpha\) phase. However, AgBr and AgCl do not show superionic conduction in their rock salt structure until their melting point. Therefore it is of particular interest to investigate the pseudo binary mixture of these two different type noble metal halides. The distribution of cations in the superionic phase of noble metal halides and their mixtures has been studied in detail. These studies, however, have been executed mainly in the systems with one kind of cation [2,3,4,5]. The studies dealing with the structure of the superionic conductors with two kinds of cations have been performed mainly in AgI-CuI system [6,7,8]. In AgBr-CuBr system, detailed experimental analysis has been done especially in Ag rich side [9], however the discussion in Cu rich side in higher temperature or superionic phase seems not to be sufficient. Therefore, in this study, we perform molecular dynamics (MD) study to examine AgBr-CuBr system in its superionic phase as an example of the pseudo binary mixtures with two kinds of cations \(\text{Cu}^+\) and \(\text{Ag}^+\).

2. Simulation Procedure
The essential procedure of MD simulations is same as our previous works [5]. The Rahman, Vashishta and Parrinello (RVP) type pair potentials are used [10], which are expressed as, \(V_{ij}(r) = \frac{H_{ij}}{r^{n_{ij}}} + z_i z_j e^2/r - P_{ij}/r^4 - C_{ij}/r^6\), where \(i\) and \(j\) stands for anions or cations; the first term stands for the repulsion between ions; the second term is the Coulomb interaction; the tired term is charge-dipole interaction; the last term is the van der Waals interaction. We neglected the forth term for simplicity. The used potential parameters are taken from literature [11,12]. The interactions between cations are estimated by the definition of the parameters. Though the RVP potentials for AgBr are different from those for CuBr in the power \(n_{ij}\) of \(r\) in the first term, we adopt the value for CuBr,
because the purpose of MD simulation is to examine the superionic state, i.e. Cu rich side. For the same reason, we postulate that the effective charge \( z_i \)'s have equal value 0.48 as in CuBr, because the charge neutrality condition must be preserved when Ag and Cu ions move around the whole cell. The used potential parameter sets are listed in Table 1.

Table 1. The unit of energy is \( e^2/\AA = 14.39 \text{eV} \); the unit of length is \( \text{\AA} \); \( n_{ij} = 7 \) for all ion pairs.

| \( H_{ij} \) | Ag-Ag | Ag-Br | Br-Br | Cu-Cu | Cu-Br | Cu-Ag |
|------------|--------|--------|--------|--------|--------|--------|
| H          | 0.4205 | 16.842 | 186.35 | 0.00538 | 6.014 | 0.0664 |
| \( p_{ij} \) | 0.0    | 0.5210 | 1.0419 | 0.0    | 0.5210 | 0.0    |

The MD calculations are performed in \((\text{Ag}_{0.1}\text{Cu}_{0.9})\text{Br}\) system with 864 ions, for \( x_{\text{Ag}} = 0.10 \) (43Ag + 389Cu + 432Br) ions, and for \( x_{\text{Ag}} = 0.40 \) (173Ag + 259Cu + 432Br) ions. The lattice constant \( L \) is estimated from the experimental density data of CuBr [13] postulating the similar temperature dependence as in the \( \beta \) phase. The periodic boundary condition is used. Coulomb interaction is calculated using the Ewald method. At first, the ions are allocated to the crystal structure of \( \alpha \) phase; Br ions are placed on the bcc lattice site, Cu and Ag ions are randomly placed on the tetrahedral (12d) site. Initial velocities of ions are allocated to the Maxwellian distribution of specified temperature, which is kept constant for 3000 time steps to equilibrate the system. In the MD calculation, we have used the algorithm of Verlet with one time step \( \Delta t = 2.0 \times 10^{-15} \text{s} \).

3. Results
As mentioned in the section 1, one of the main purpose of this study is to investigate the structural properties of the superionic phase of \((\text{Ag}_{x}\text{Cu}_{1-x})\text{Br}\) system. There is a superionic phase in the phase diagram of AgBr-CuBr system in the concentration range approximately \( x_{\text{Ag}} < 0.60 \). To examine the distribution of cations and their concentration dependence in superionic phase, we perform the MD simulation for \( x_{\text{Ag}} = 0.10 \) and 0.40.

Figure 1 (a) Br (left), (b) Cu (centre), (c) Ag (right) ion trajectories for \((\text{Ag}_{0.1}\text{Cu}_{0.9})\text{Br}\) at 773K.

Figure 2 (a) Br (left), (b) Cu (centre), (c) Ag (right) ion trajectories for \((\text{Ag}_{0.4}\text{Cu}_{0.6})\text{Br}\) at 603K.
Figure 1(a)–(c) show the trajectories of (a) 432Br, (b) 389Cu, (c) 43Ag ions in the same MD cell for (Ag0.1Cu0.9)Br at 773K. Figure 2(a)–(c) show (a) 432Br, (b) 259Cu, (c) 173Ag ions trajectories for (Ag0.4Cu0.6)Br at 603K. The trajectories are obtained by marking the positions of ions at 20 Δt intervals for the period of 5000Δt (figure 1(c) 10000Δt) with dots, which are projected on to the same basal plane. In figure 1 and 2, it is obviously seen that Br ions move around the bcc lattice points, while Cu and Ag ions make diffusive motion. The characteristic pattern or structure can be seen in the trajectories of cations. A little disarray of Br lattice can be seen in (Ag0.4Cu0.6)Br in figure 2(a). The Ag ions movement and lack of uniformity of distribution in figure 2(c) may give rise to the disarray of Br lattice, because the mass of Ag is much heavier than those of Cu or Br. A sort of buckled structure has also observed by XAFS experiment in AgBr0.6Cl0.4[14]. Further more, Cu ions are observed to be more diffusive than Ag ions, which may be caused by the difference in masses and interactions of Ag and Cu ions. The partial pair distribution functions $g_{\alpha\beta}(r)$ of this ternary system are defined as,

$$\langle n_{\alpha\beta}(r) \rangle \Delta r = 4\pi r^2 \rho_{\beta} g_{\alpha\beta}(r),$$

where $n_{\alpha\beta}(r) \Delta r$ denotes the number of β-type particles around an α-type particle between spherical shells of radii r and r+Δr. The bracket $\langle \rangle$ stands for the thermal average as well as the average over all α-type particles. $\rho_{\beta}$ is the mean number density of the β-type particles.

In figure 3, $g_{\alpha\beta}(r)$’s for (a) (Ag0.1Cu0.9)Br at 773K and (b) (Ag0.4Cu0.6)Br at 603K are shown. $g_{\text{BrBr}}(r)$ has relatively sharp peaks as in a thermal agitated crystal. The first peak positions in $g_{\text{BrBr}}(r)$ represent the first nearest neighbour distance of bcc cation lattice. In both of figure 3(a) and (b), however, $g_{\alpha\beta}(r)$’s of cation-cation pairs have broad peaks similar to molten state. These facts indicate that these (a) and (b) are in superionic phase. The difference between $g_{\text{CuBr}}(r)$ and $g_{\text{AgBr}}(r)$ can be observed in (a) and (b), which means the distributions of Cu and Ag around Br are different. Further more, the obvious difference can be seen between corresponding $g_{\alpha\beta}(r)$’s in (a) and (b).

Next, to examine the detailed structural difference of cations, we obtain the density distributions of cations on (1,0,0) plane of thickness L/10, L being the lattice constant. In figure 4, (Ag0.1Cu0.9)Br at 773K, and figure 5, (Ag0.4Cu0.6)Br at 603K, the density distributions of (a) Cu and (b) Ag are shown. For $x_{\text{Ag}} = 0.10$ in figure 4(a), Cu ions are mainly distributed around tetrahedral 12(d) site with the wide distribution in a belt along <1,0,0> direction. On the other hand, the significant distribution of Ag ions around the octahedral 6(b) site can be seen in figure 4(b), though the belt like distribution along <1,0,0> direction also can be observed. For $x_{\text{Ag}} = 0.40$ in figure 5(a), however, Cu ions are mainly distributed around the octahedral 6(d) site with the distribution in a belt along <1,0,0> direction. In figure 5(b), Ag ions distribution around octahedral 6(b) site is more enhanced than their distribution in $x_{\text{Ag}}=0.10$, figure 4(b). These differences in cation distribution correspond to the difference in the pair distribution functions in figure 3.

Figure 3. $g_{\alpha\beta}(r)$’s for (a) (left) (Ag0.1Cu0.9)Br; (b) (centre) (Ag0.4Cu0.6)Br. Figure 4(a) (right) Cu distribution for (Ag0.1Cu0.9)Br on (1,0,0) plane.

Figure 4(a) (right) Cu distribution for (Ag0.1Cu0.9)Br on (1,0,0) plane.
Figure 4(b) (left) Ag distribution for $(\text{Ag}_{0.1}\text{Cu}_{0.9})\text{Br}$; Figure 5(a) (centre) Cu, 5(b) (right) Ag distributions for $(\text{Ag}_{0.4}\text{Cu}_{0.6})\text{Br}$ on $(1,0,0)$ plane.

4. Conclusions
The MD simulations have been performed in the superionic phase of $(\text{Ag}_{x}\text{Cu}_{1-x})\text{Br}$, for $x_{\text{Ag}}=0.10$ and 0.40. The trajectories of ions, pair distribution functions, density distribution of cations have been obtained. The distribution difference of Cu and Ag ions around Br ions has been observed in $g_{ij}(r)$. The concentration dependence of cation distribution has also been detected both in $g_{ij}(r)$ and the density distributions. It has been observed that the main distribution point of Cu has changed from the tetrahedral 12(d) site to the octahedral 6(d) site as the concentration changes from $x_{\text{Ag}}=0.10$ to 0.40. On the other hand, distribution of Ag at the octahedral 6(d) site has been enhanced as the concentration changes from $x_{\text{Ag}}=0.10$ to 0.40. Though the difference of $g_{ij}(r)$’s of cation-anion pairs have been reported in AgI-CuI, the clear image of the structure has not been proposed [7]. Our study might be the first report of the detailed distribution difference and their concentration dependence of two kinds of mobile cations in superionic phase of AgBr-CuBr by MD, as far as we know. It is expected that other properties in superionic phase, e.g. the transport properties, are also affected by these structural difference of cations. We are now investigating on this point at issue.

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