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MOLECULAR DYNAMICS SIMULATION OF THE PHASE BEHAVIOR OF $AgI_{1-x}Cl_x$

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The temperature and pressure dependencies of the structure and transport properties of $AgI_{1-x}Cl_x$ are studied by means of molecular dynamics. From the results of the calculations, the P–T phase diagram for the $AgI_{0.8}Cl_{0.2}$ system has been obtained. The phase diagram indicates that the superionic phase transition temperature increase with the application of pressure. It is also pointed out that $AgI_{1-x}Cl_x$ has a tendency of phase separation.

Keywords: *$AgI_{1-x}Cl_x$, molecular dynamics, phase diagram, superionic conductors*

Introduction

AgI has a rich phase diagram. By increasing the temperature at ambient pressure, it transforms to the superionic phase at T=420 K. The superionic α-phase is characterized by its high ionic conductivity of an order of $(\Omega\ \mathrm{cm})^{-1}$. This magnitude of the ionic conductivity is usually found in molten salts. However, in the superionic phase, the large ionic conductivity is due to the movement of one kind of ions between sites provided by the immobile ion sublattice [1–3].

AgI has been always considered as a prototype of superionic conductors [1–3]. Many studies, both theoretical and experimental have been performed on AgI after the discovery of its superionic conduction [1–22]. However, the explanations to the unusual properties that AgI and the superionic conductors in general exhibit are still unsatisfactory. Concerning this point, one of the authors has suggested the need of electronic theory to understand the classical problem of ion transport in condensed matter [6–8].

Regarding the pressure effects [9–14], at ambient temperature AgI shows a structural phase transition from the wurtzite (β-phase) or zinc-blende (γ-phase) structures to the rocksalt structure by the application of pressure of about 0.3 GPa. It has been also reported that the melting curve of AgI has a temperature maximum at about 1.0 GPa, which suggests the existence of dense liquid phase above this pressure [11]. Concerning the pressure effect on ion transport properties, it has been reported that the ionic conductivity in the non-superionic phase increases by the application of pressure [12–14]. The behaviors that the superionic materials exhibit under the action of pressure, have provided key concepts to understand the mechanism of superionic conduction [6].

The effect of substitution of one part of ions in AgI with other ions has been widely studied [23–30]. For instance, it has been reported that the substitution of Cl ions for I ions in AgI leads to a substantial decrease in the superionic transition temperature, and also to a large increase in the ionic conductivity in the non-superionic phase [24]. The system $AgI_{1-x}Cl_x$ has been also studied by the molecular dynamics method [25, 29]. However, in these studies the pressure dependence has not been investigated. In the present paper, the temperature and pressure dependencies of the transport properties in $AgI_{1-x}Cl_x$ are studied by the molecular dynamics method. From the results of the calculation, a rough phase diagram is constructed.

Method of calculation

In our study, the atomic motion was calculated within the NPT ensemble by the reversible integrators [31], and the electrostatic interactions were calculated by the Ewald method. We used a system consisting of 864 ions, which includes 432 cations and 432 anions. In the initial configuration, the anions formed a body-centered cubic lattice, whereas two cations were randomly located in the 12d sites [5] of the cube faces of the unit cell. The iodine and chlorine atoms in the anionic positions were randomly placed.

The size of the initial MD box, to which the periodic boundary conditions are applied, was determined so as to reproduce the experimental lattice constant at 470 K and ambient pressure [5]. The time

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Table 1 The values of the parameters in the interaction potentials, H_{ij} and W_{ij} are given in e^2/Å

$Z_I = -0.6e$	$n_{AgAg}=11$	$W_{AgAg}= 0$
$Z_{Cl} = -0.7e$	$n_{AgI}=9$	$W_{AgI}= 0$
$H_{AgAg}=0.014804$	$n_{AgCl}=11$	$W_{AgCl}= 0$
$H_{AgI}=114.64$	$n_{II}=7$	$W_{II}= 6.9832$
$H_{AgCl}=127.645$	$n_{ICl}=7$	$W_{ICl}= 2.11074$
$H_{II}=446.64$	$n_{ClCl}=11$	$W_{ClCl}= 2.11074$
$H_{ICl}=266.317$	$\alpha_{Ag}=0$	
$H_{ClCl}=17152.23$	$\alpha_I=6.52\ 10^{-3}$ mm^3	
	$\alpha_{Cl}=3.45\ 10^{-3}$ mm^3	

integrations were performed with the time step of 5 fs. After a long initial aging of the system which was about 5 ns, the calculations extending over 50 ps were used to analyze the properties of the system. This simulation time is longer by 1 or 2 orders of magnitude than those used in previous studies [15–22, 25, 29, 30, 32].

The interaction potential used in the calculation was of the Born-Mayer-Huggins type, which consists of Coulomb, repulsive, charge-dipole and van der Waals interactions. This type of potential has been used by Vashishta and Rahman [15] and Parrinello *et al.* [16] in their pioneering molecular dynamics studies of superionic AgI. The form of the interaction potential used in the calculation is given by

$$V_{ij} = \frac{Z_i Z_j}{r} + \frac{H_{ij}}{r^{n_{ij}}} - \frac{P_{ij}}{r^4} - \frac{W_{ij}}{r^6} \tag{1}$$

where r is the interionic distance, Z_i is the effective charge of the i^{th} ion, H_{ij} and n_{ij} are the parameters describing the repulsion caused by the overlap of electron shells, and W_{ij} is the van der Waals interaction parameter. The parameters describing the charge-dipole interactions are given by,

$$P_{ij} = \frac{1}{2}(\alpha_i Z_j^2 + \alpha_j Z_i^2) \tag{2}$$

where α_i is the electron polarizability of the i^{th} ion. The values of the parameters were those used in previous reports [15, 16, 24, 29] and are listed in Table 1. The charge of the silver cations was chosen based on the condition of the electrical neutrality.

We used the same values set of parameters to study the pressure effects. Strictly speaking, the interatomic interactions are expected to change with the application of pressure. However, in the pressure range considered in our study, the functional forms of the interatomic interactions are not expected to change. The application of pressure is reflected mainly in the value of the interatomic distance r. The appropriateness of this statement has been verified by Tallon for the case of AgI [18]. Tallon used the potential proposed by Parrinello *et al.* [16] and reproduced quite well the P-T phase diagram known experimentally. Since the potential parameters used in this study incorporate the potential used by Tallon when x=0, we assumed the validity of the potential at different pressures also for the case of $AgI_{1-x}Cl_x$. Related to this point, in the literature we can find many examples [18, 33, 34] that use the interaction potential determined at ambient pressure to study the properties of high pressure phases.

Results and discussion

We performed the molecular dynamics simulations in $AgI_{1-x}Cl_x$ for three different compositions. Namely x=0.0, 0.1 and 0.2. In Fig. 1, the temperature dependencies of the mean square displacements (MSD) at P=0 GPa are shown. We can see clearly that at T=200 K the system is in the non-superionic state. At T=500 K the system is in the superionic state, because only Ag ion exhibits appreciable slope in the MSD. The diffusion coefficient of Ag ion at T=500 K was estimated to be D=1.0 10^{-5} cm^2 s^{-1}. At T=1000 K, we can see that all the curves exhibit slopes whose diffusion coefficients are larger than 5.6 10^{-6} cm^2 s^{-1}, so the system may be considered to be in the molten phase. From the figure, we can also see that the iodine ion is more mobile than chlorine ion.

In Fig. 2 we show the pressure dependencies of the MSD calculated at T=600 K. We can see that the ion transport is inhibited by the application of pressure. At P=0 GPa the system may be considered to be in the molten phase, because the diffusion coefficient for Cl is estimated to be 6.7 10^{-7}cm^2 s^{-1}. At P=1 GPa, the system is in the superionic phase, and at P=2 GPa it is in the non-superionic phase.

The partial radial distribution functions $g_{\alpha\beta}$ calculated at T=600 K and P=1 GPa is shown in Fig. 3. It is seen that the oscillations in $g_{\alpha\beta}$ at large distance are damped in the $g_{\alpha\beta}$ containing Ag, whereas the oscillations of other $g_{\alpha\beta}$ remain over 14 Å. This is a structural manifestation that the system is in the superionic state.

In Fig. 4 the composition dependencies of the MSD at T=800 K and P=0 GPa is shown. We can con-

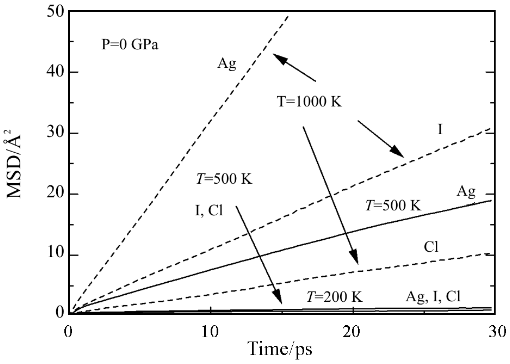

Fig. 1 Temperature dependencies of the mean square displacements, MSD at P=0 GPa in $AgI_{0.8}Cl_{0.2}$

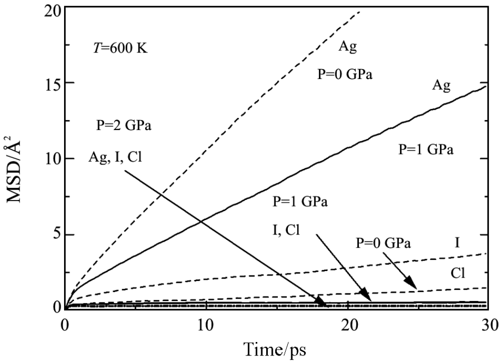

Fig. 2 Pressure dependencies of the mean square displacements, MSD at T=600 K in $AgI_{0.8}Cl_{0.2}$

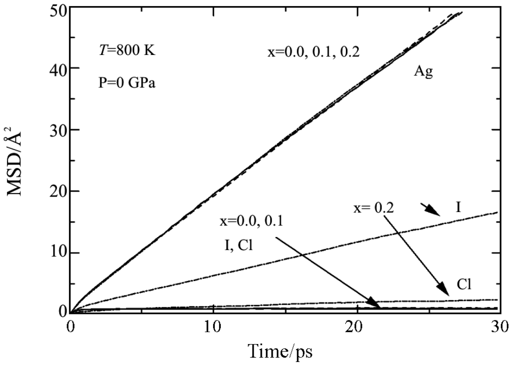

Fig. 4 Composition dependencies of the mean square displacements, MSD at T=800 K and P=0 GPa in $AgI_{1-x}Cl_x$

firm that at x=0, the system is in the superionic phase as is usually known from the phase diagram of AgI. Figure 4 indicates that the diffusion coefficient of Ag in $AgI_{1-x}Cl_x$ does not depend on the amount of substituted Cl ions. However, in the calculation performed at T=500 K, we have observed a composition dependence in the diffusion coefficient. The result obtained at T=800 K is in contrast with the molecular dynamics simulation performed by Ivanov-Shitz *et al.* [29]. Their results reported at 700 K infer a concentration dependence of the diffusion coefficient. The origin of this disagreement is not clear at present. However, it must be mentioned that they used a system of 256 ions, whereas we used 864 ions. In addition, it seems that the form of the charge-dipole interaction that they used is different from the form given in Eq. (2). From Fig. 4 we can also see that the effect of composition appears noticeably in the transport property of I ions. By increasing the concentration of Cl ions from x=0.1 to x=0.2, it is found that the diffusion coefficient of I ions estimated form the slopes of the MSD increases by about 10^6. This result indicates that the melting temperature, and probably also the superionic transition temperature will decrease with the increase of x. This observation is in accord with the experimental phase diagram of $AgI_{1-x}Cl_x$ [35] and the Bond Fluctuation Model of superionic conductors [6–8], which predicts that the superionic phase is induced by the appearance of local bond fluctuations. In the system $AgI_{1-x}Cl_x$, such fluctuation is induced by the addition of Cl ions, which tend to form more strong Ag–Cl ionic bond than Ag–I.

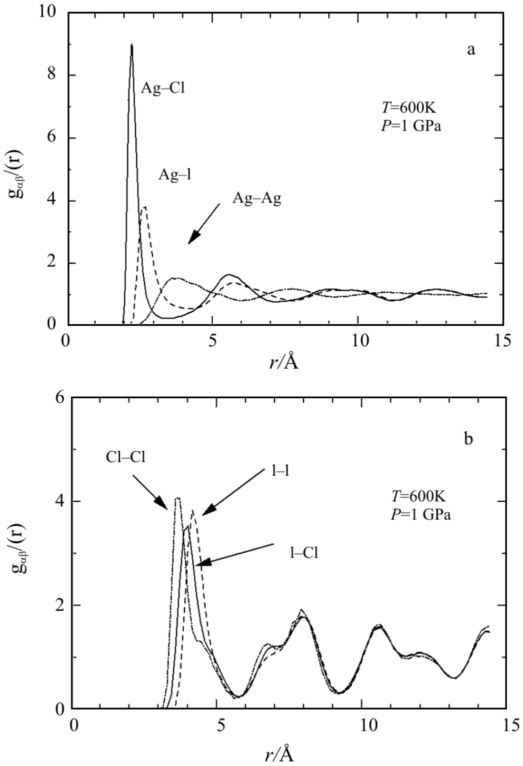

Fig. 3 Partial radial distribution functions $g_{\alpha\beta}(r)$ at T=600 K and P=1 GPa in $AgI_{0.8}Cl_{0.2}$

The results shown above are portions of the calculations. A summary of the calculations is shown in Fig. 5 as a phase diagram for the case of $AgI_{0.8}Cl_{0.2}$. We can recognize that the superionic transition temperature increases with the increase in pressure. The rough phase diagram suggests that the melting temperature will also increase with the pressure. However, for a definitive conclusion a detailed study is required, because pure AgI exhibits an interesting pressure dependence of the melting point [11]. An important aspect that must be mentioned in the phase diagram of Fig. 5 is that it has been calculated by increasing the temperature and pressure. In the determination of phase diagram by computer simulation there is the hysteresis effect. That is, the phase boundary determined by increasing and decreasing the external variables are usually different. In Fig. 5, it seems that the superionic phase transition and the melting temperatures are somewhat high when compared with the phase diagram of AgI. The reason may be due to the hysteresis effect. Another effect that we have found, but not discussed in the present paper, is that the system in consideration exhibits the tendency of phase

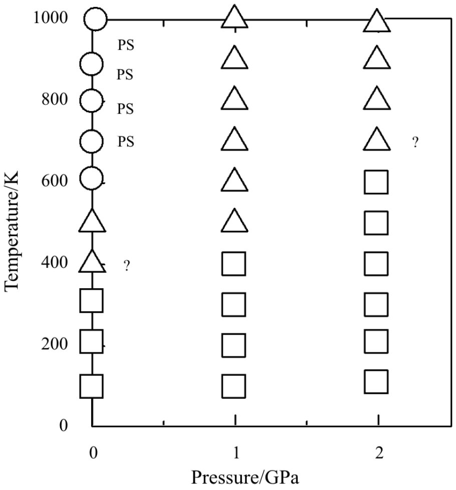

Fig. 5 *P–T* phase diagram of $AgI_{0.8}Cl_{0.2}$. The symbols indicate □ – non-superionic, △ – superionic and ○ – molten phases. ? – ambiguous phase, PS means the phase that we have found the tendency of phase separation

separation. We have also found that this tendency is suppressed by the application of pressure. In Fig. 5, the phases where we have found the tendency of phase separation are indicated also. Concerning the phase separation behavior, the results will be reported elsewhere.

As far as the authors are informed, this is the first phase diagram reported for the $AgI_{1-x}Cl_x$ system. In the course of our study, we were informed on the composition dependence of the phase diagram measured at ambient pressure [35]. We are planning to extend our calculations for x>0.2 in order to compare the phase diagram with the measured results.

Conclusions

In the present paper, we have studied the transport properties in $AgI_{1-x}Cl_x$, (x=0.0, 0.1, 0.2) by means of the molecular dynamics method. We have shown how the mean square displacements of different ions depend on temperature, pressure and concentrations. From the results of the calculation, a rough phase diagram has been constructed for the $AgI_{0.8}Cl_{0.2}$ system. The phase diagram indicates that the superionic phase transition temperature increases with the application of pressure. The phase diagram also suggests that the melting temperature will increase with the pressure. The tendency of phase separation that this system exhibits is also pointed out.

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