

## Chemical bonding of Ag ions in AgI-based superionic conducting glasses

Y. Kowada<sup>\*</sup>, M. Okamoto<sup>\*</sup>, I. Tanaka<sup>\*\*</sup>, H. Adachi<sup>\*\*</sup>, M. Tatsumisago<sup>\*\*\*</sup>, and T. Minami<sup>\*\*\*\*</sup>

*\*Hyogo University of Teacher Education, Yashirocho, Kato-gun, Hyogo 673-1494, Japan*

*\*\*Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan*

*\*\*\*Department of Applied Materials Science, Osaka Prefecture University, Sakai 599-8531, Japan*

*\*\*\*\* Osaka Prefecture University, Sakai 599-8531, Japan*

*e-mail address : [ykowada@sci.hyogo-u.ac.jp](mailto:ykowada@sci.hyogo-u.ac.jp)*

The electronic state of AgI-based superionic conducting glasses was calculated by the DV-X $\alpha$  cluster method. We have adopted several model clusters with different conduction paths of Ag ions. The electronic state of the similar clusters using Na ions was also calculated for comparison. The net charge of moving cations and the total bond order between the moving cation and the other ions in these model clusters were used for discussion of chemical bonding of the moving cation. The total bond order of the moving Ag ion was decreased with the movement and had a minimum at the middle of the path. The variation of the total bond order of the Ag ion was much smaller than that of the Na ion in any conduction paths. On the other hand, the change of the net charge of the Ag ion with the movement was almost the same as that of the Na ion. These results suggest that the smaller change of the total bond order of the Ag ion should play an important role in the fast ion conduction in AgI-based superionic conducting glasses, rather than the change of the net charge of cations.

Topic: superionic conducting glasses, Ag ion, molecular orbital calculation, chemical bonding, DV-X $\alpha$  method

## 1. Introduction

AgI-based superionic conducting glasses are important solid state electrolytes. The ionic conductivity of AgI-based glasses, which contain more than 60 mol% of AgI such as 60AgI•30Ag<sub>2</sub>O•10B<sub>2</sub>O<sub>3</sub>, 80AgI•20Ag<sub>2</sub>MoO<sub>4</sub>, and 85AgI•15Ag<sub>4</sub>P<sub>2</sub>O<sub>7</sub> glasses, has reached near  $10^{-2} \text{ Scm}^{-1}$  at room temperature. [1-4] Such high ionic conductivity of AgI-based superionic conducting glasses might be originated from the local structure of these glasses. Generally the local structures around moving Ag ions in AgI-based superionic conducting glasses should be similar to that of the  $\alpha$ -AgI crystal, which has high Ag ion conductivity near  $1 \text{ Scm}^{-1}$ . Unfortunately the  $\alpha$ -AgI crystal is stable only above 147°C and transforms to  $\beta$ -AgI at lower temperature. In the  $\alpha$ -AgI crystal the unit cell contains 2 iodide ions located on body centered cubic lattice sites. On the other hand there are two Ag ions in the unit cell and they should be located at two sites among 24 of trigonal sites, 12 of tetrahedral sites and 6 of octahedral sites by iodide ions.

Several computational simulation studies, such as the molecular dynamics calculation [5-8] and the Monte Carlo calculation [9] were reported to explain the anomalously high ion conductivities. They suggested that the potential of the Ag and I ions were very important to reproduce the experimental results. These results means that the detail of chemical bonding of the Ag ion with I ions is necessary to understand the high ionic conductivities of the AgI-based superionic conducting glasses.

Usually it is difficult to calculate electronic state of the models containing heavy elements like Ag and I ions. Among them, the DV-X $\alpha$  cluster method is one of the most appropriate methods to operate the chemical bonding of Ag ions in the AgI-based superionic conducting glasses. This method has been widely applied to the electronic state calculations in the fields of metals, ceramics, glasses and so on. [10-16]

In the present study we have calculated the electronic state of AgI-based superionic

conducting glasses by the DV-X $\alpha$  cluster method. We used a model cluster which contains different kinds of the estimated conduction paths. The variation of chemical bonding of Ag ions with the movement in AgI-based superionic conducting glasses has been discussed.

## 2. Calculation method

The DV-X $\alpha$  cluster method has been used to calculate the electronic state of the AgI-based superionic conducting glasses. This method is one of the linear combination of atomic orbital (LCAO) molecular orbital methods. In this method the exchange potential [17]  $V_{XC}$  is described by

$$V_{XC}(r_{\uparrow}) = -3\alpha \left[ \frac{3}{4\pi} \rho_{\uparrow}(r) \right]^{\frac{1}{3}}$$

Where  $\rho$  is the electron density of the cluster and  $\alpha$  is a constant.  $\alpha$  is fixed to be 0.7 throughout the present work, which was found empirically as the most appropriate.[18] The Mulliken population analysis was used for the evaluation of the net charge of each atom and the bond overlap population between atoms.

In the  $\alpha$ -AgI crystal structure, there are three kinds of stable positions for Ag ions. The first is the tetrahedral site coordinated by four I ions. This position should be the most stable site for Ag ions from X-ray diffraction studies. The second is the octahedral site and the third is the trigonal site. Usually Ag ions are moving from a tetrahedral site to the other tetrahedral site through either an octahedral site or a trigonal site. Then there are

several kinds of the conduction paths for Ag ions in the  $\alpha$ -AgI crystal. In the present study, two kinds among the conduction paths were adopted. Fig. 1 shows a schematic diagram of the model cluster,  $M_{20}I_{20}$ , used in the present work. In this figure solid lines show tetrahedral and octahedral sites as the guide to the eye. This model contains two kinds of the moving paths. In the first path, path A which is shown by the small gray spheres, an Ag ion moves from a tetrahedral site to the other tetrahedral site through a trigonal site, a tetrahedral site, an octahedral site, a tetrahedral site, and a trigonal site. This path might be the most probable path among several conduction paths from X-ray diffraction measurements. The second is a path from a tetrahedral site to the other tetrahedral site through a trigonal site, an octahedral site, and a trigonal site.

Usually it is very difficult to calculate the electronic state of a model cluster with the moving ions, because the common electronic state calculation methods adopt Born-Oppenheimer approximation. Then we have simulated the movements of Ag ions by using several model clusters changed the position of an Ag ion. We regard the electronic state of each model with various position of an Ag ion as that with the movement, so that the movement of electrons is much faster than that of the Ag ions.

As described above, only one among 20 Ag ions moves in the cluster in order to neglect the influence of the variations of movements of many Ag ions. On average only two Ag ions are included in the unit cell of the  $\alpha$ -AgI crystal. Then more than three Ag ions hardly approach together. However, the number of the second neighboring Ag ions at the center of the octahedral site becomes two if we have adopted all the Ag ions in the  $\alpha$ -AgI crystal structure. This excess number of the neighboring Ag ions against the moving one might cause excess estimation of the Ag-Ag interaction. To avoid this, one of the second neighboring Ag ion near the center of the octahedral site has removed and the number of the second neighboring Ag ion is kept to one during the movement of the Ag ion in the model

cluster.

In order to obtain the bonding state of the moving Ag ions, Mulliken population analysis has been achieved for each model clusters. Bonding nature of the moving Ag ion is discussed using of bond overlap population (BOP), which is the measure of covalency and net charge (NC), which is the measure of ionicity of the bondings.

We have adopted Na ions, which are the typical monovalent ion, to compare the results with that for the Ag ions because the ionic radius of the Na ion is similar to that of the Ag ion.

### 3. Results and Discussion

Fig. 2 shows the change of BOP of a moving M ion along with path A (4-3-4-6-4-3-4). In this figure, circles show the results of the Ag ion and squares show the results of the Na ion. Ordinate shows total BOP (TBOP) and abscissa shows the position of the moving cation, which is shown as the projection of the normalized position of the moving Ag ion to the x axis in the model cluster. Then the value of 0 means the center of the initial tetrahedral site, 0.5 means the center of the octahedral site, and 1 means the center of the final tetrahedral site.

Here TBOP means the summation of bond overlap populations between the moving Ag ion and all the other ions.

In the case of the Na ion, TBOP at the starting position  $x = 0$  is 0.79 and decreased with the movement of the Na ion. TBOP has a local minimum at  $x = 0.167$  and increased toward  $x = 0.333$ . After  $x = 0.333$  the TBOP is decreased again and has a minimum at  $x = 0.5$ . The difference between the minimum and the maximum is 0.23 for the Na ion.

In the case of the Ag ion, TBOP is 1.03 at  $x = 0$  and slightly decreased with the

movement of the ion. At  $x = 0.5$ , the center of the octahedral site, TBOP becomes smaller, 0.97. After  $x = 0.5$ , TBOP changes a little with the movement and the smallest value, 0.951, is observed at  $x=0.825$ . The difference of TBOP of the Ag ion between at the initial tetrahedral site and at the center of the octahedral site is 0.06, which is much smaller than that of the Na ion. This smaller change of TBOP of the Ag ion was caused by the covalent interaction between the moving Ag ion and the second neighboring Ag ion near the center of the octahedral site. There are few reports about the interaction between Ag ions in Ag ion conductors by the experimental method, since it is very difficult to detect the interaction.[19]

The change of TBOP is corresponding to the change of the covalent bonding energy. The smaller change of TBOP of the Ag ion means the smaller activation energy of the movement than that of the Na ion during the movement.

On the other hand, ionicity of the moving cation is also very important properties to discuss the ionic conductivities of super ionic conductors. The ionicity of the cation is evaluated by the net charge of the cation.

Fig. 3 shows the net charges of the Ag and Na ions with their movements. At the starting point, the net charge of the Na ion is 0.43 and is increased with the movement. There is the maximum at  $x = 0.5$  and the net charge becomes 0.57. The difference between the maximum and the minimum values is 0.14.

The similar tendency is observed in the net charge of the Ag ion. At  $x = 0$ , the Ag ion has the charge of 0.04. The charge becomes larger with the movement of the Ag ion and takes a maximum values, 0.17 at  $x = 0.5$ . The difference between the maximum and minimum values of the net charge is 0.13. The change of the net charge of the Ag ion is very similar to that of the Na ion. This result suggests that the ionic interaction of the moving Ag ion is almost the same as that in the case of the Na ion. So there are no characteristics in the change of the ionic interaction of the moving Ag ion.

Fig. 4 shows TBOP of the Ag ions moved along with the path A ( circles ) and the path B ( triangles ). The TBOP of the moving Ag ion with the path A is decreased with the movement. The change of the TBOP, however, is very small during the movement. The difference of the TBOP of the Ag ion between at the initial tetrahedral site and the center of the octahedral site is only 0.06.

In the case of the path B, the TBOP of the moving Ag ion is decreased with the movement of the Ag ion and has local minimum near  $x = 0.333$ , which is the intermediate position between the trigonal and the octahedral sites. The TBOP is slightly increased at  $x = 0.5$ , which is the center of the octahedral site. The change of the TBOP of the Ag ion in the path B is 0.13 and is much smaller than that in the path A. This result suggests that the Ag ion should prefer to move along with the path A since the change of the TBOP is much smaller than that of the path B, while the distance of the path A is longer than that of the path B.

## 5. Conclusion

Electronic state of AgI-based superionic conducting glasses was calculated by the DV- $X\alpha$  cluster method. We have proposed two kinds of conduction paths of Ag ions. The electronic state of the similar clusters using Na ions was also calculated for comparison. In the path A, the variation of TBOP of the Ag ion was much smaller than that of the Na ion in any conduction paths. On the other hand, the change of the net charge of the Ag ion with the movement was almost the same as that of the Na ion, while the absolute values of the net charge of the Na ion is larger than that of the Ag ion.

As the result of comparison between paths A and B, the variation of TBOP of the Ag ion in path A was smaller than that of path B. The covalent interaction between the moving Ag ion and the other Ag ions became large near the center of the octahedral site.

This Ag-Ag covalent interaction is the reason of the smaller change of the TBOP in path A.

The results obtained in the present work suggest that the smaller change of TBOP of the Ag ion should play an important role for the fast ion conduction in AgI-based superionic conducting glasses.

## References

- [1] T. Minami, *J. Non-Cryst. Solids* 56 (1983) 15.
- [2] T. Minami, *J. Non-Cryst. Solids* 73 (1985) 273.
- [3] T. Minami, *J. Non-Cryst. Solids* 95/96 (1987) 107.
- [4] K. Hariharan, R. Kaushik, *J. Mater. Sci.* 22 (1987) 3335.
- [5] P. Vashishta, A. Rahman, *Phys. Rev. Lett.* 40 (1978) 1337.
- [6] W. Andreoni, J. C. Phillips, *Phys. Rev. B: Condens. Matter* 23 (1981) 6456.
- [7] W. Andreoni, *J. Phys. C* 14 (1981) 4017.
- [8] M. Parrinello, A. Rahman, P. Vashishta, *Phys. Rev. Lett.* 50 (1983) 1073.
- [9] Y. Hiwatari, A. Ueda, *Solid State Ionics* 3/4 (1981) 111.
- [10] R. Ninomiya, H. Yukawa, M. Morinaga, K. Kubota, *J. Alloys Comp.* 215 (1994) 315.
- [11] H. Yukawa, Y. Takahashi, M. Morinaga, *Intermetallics* 4 (1996) S215.
- [12] Y. Matsumoto, M. Morinaga, T. Nambu, T. Sakaki, *J. Phys.: Condens. Matter.* 8 (1996) 3619.
- [13] I. Tanaka, H. Adachi, *Phil. Mag.* B72 (1995) 459.
- [14] N. Takao, I. Tanaka, H. Adachi, *Intermetallics* 4 (1996) S113.
- [15] Y. Kowada, H. Adachi, M. Tatsumisago, T. Minami, *J. Non-Cryst. Solids* 192/193 (1995) 316.
- [16] Y. Kowada, K. Morimoto, H. Adachi, M. Tatsumisago, T. Minami, *J. Non-Cryst.*



Solids 194 (1996) 204.

[17] J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 4 (McGraw-Hill, New York, 1974)

[18] E. J. Baerends and P. Ros, Chem. Phys. 2 (1973) 52.

[19] M. Tansho, C. A. Fyfe, H. Grondy, T. Markus, H. Wada, Solid State Ionics 132 (2000) 87.

## Figure captions

Fig. 1 Schematic diagram of the  $M_{20}I_{20}$  model cluster (a) path A, (b) path B.

Fig. 2 The relationship between the position and the total bond overlap population for the moving M ion with path A. The lines are drawn as a guide to the eye.

Fig. 3 The relationship between the position and the net charge of the moving M ion with path A. The lines are drawn as a guide to the eye.

Fig. 4 The relationship between the position and the total bond overlap population of the moving Ag ion in both paths A and B. The lines are drawn as a guide to the eye.









