

Electronic state of sulfide-based lithium ion conducting glasses

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Abstract

Electronic states of the sulfide-based lithium ion conducting glasses were calculated by the DV-X α cluster method. The cluster models were constructed by the coordination number reported by experimental methods and the bond length estimated from the ionic radii of each ion. The movement of the Li ion was simulated by several model clusters with different positions of the moving ion. The relationship between ionic conductivity and the differential total bond overlap population (DBOP) was discussed for the sulfide-based glasses in the systems Li₂S–SiS₂–Al₂S₃ and Li₂S–SiS₂–P₂S₅. In these glasses, the DBOP with the movement of the lithium ion had good negative correlations with the ionic conductivities and positive correlations with the activation energies obtained by the experimental measurements. In any cases, the smaller change of the total bond overlap population of the moving cations played an important role for the fast ion movement in the superionic conducting glasses. This bonding state of the moving cations is one of the characteristics of the electronic state in the sulfide-based lithium ion conducting glasses.

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1. Introduction

Recently about 10 years, we have paid attention to the relationship between fast ion movement and covalent bonding in the super ionic conducting materials [1–4]. In the AgI-based superionic conducting glasses, there was a certain covalent bonding between the moving Ag ion and the neighboring Ag ions. This bonding interaction made the moving Ag ion stable and the change of the covalent interaction between the moving Ag ion and the surrounding ions was very small in the course of the movement through the path. This result was the characteristic of the AgI-based superionic conducting glasses.

In the present work, we have tried to estimate the relationship between the ionic conductivity and chemical bond-

ing of the moving Li ions in the sulfide-based superionic conducting glasses. Usually it is difficult to calculate electronic state of inorganic materials. Among various calculation techniques, the DV-X α cluster method is one of the most appropriate methods to analyze the chemical bonding of Li ions in the sulfide-based superionic conducting glasses [5]. This method has been widely applied to the electronic state calculations in the fields of metals, ceramics, glasses and so on [6–9].

In the present study we have calculated the electronic state of sulfide-based superionic conducting glasses by the DV-X α cluster method.

2. Calculation method

The DV-X α cluster method has been used to calculate the electronic state of the sulfide-based superionic conducting glasses. This method is one of the linear combination of

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atomic orbital (LCAO) molecular orbital methods. In this method the exchange potential [10] V_{XC} is described by

$$V_{XC}(r_1) = -3\alpha \left[\frac{3}{4\pi} \rho_1(r) \right]^{\frac{1}{3}},$$

where ρ is the electron density of the cluster and α is a constant. α is fixed to be 0.7 throughout the present work, which was found empirically as the most appropriate. [11] The Mulliken population analysis was used for the evaluation of the bond overlap population between atoms.

In order to calculate the electronic state of the Li ion in the sulfide-based superionic conducting glasses, there is a hurdle to construct a model cluster, since it is difficult to obtain the details of the structure around Li ions in the glasses by experimental methods. The coordination number of sulfide ions to the Li ion and the distances between the Li ion and the first neighboring ions were reported about several kinds of the sulfide glasses [12–14]. As based on these studies, we have modeled a tetrahedral structure and estimated the bond length from the ionic radius of each ion reported by Shannon [15], to calculate electronic state near Li ions. Fig. 1 shows a schematic diagram of the model cluster to calculate the electronic state around the Li ion in the present work. In this model, a lithium ion is located in the center and four sulfide ions are coordinated to the center atom. Each sulfide ion forms a SiS_4 unit, which has regular tetrahedron structure. The outside sulfide ions of SiS_4 units are terminated by lithium ions. The distances of Si–S, Li–S, P–S, and Al–S are 2.10, 2.43, 2.01, and 2.23 Å, respectively. Near the center tetrahedral unit, three lithium ions are located on the outside to keep the cluster neutral. The movement of the center Li ion was simulated by shifting the Li ion to different positions of the five clusters. The Li ion is moved along with the conduction path through a face of the tetrahedron of sulfide ions coordinated to the Li ion. The length of the movement of the Li ion was 0.810 Å. The SiS_2 content was changed with exchange of Si in SiS_4 units with the other elements, such as Al and P. In this case, the neutrality of the model clusters was adjusted by the number of the outside Li ions. Then the contents of Al and P in the clusters could become

25, 50, 75, and 100 mol% in the present work. To compare the theoretical results with the experimental ones, the bond overlap population calculated for the composition corresponding to the experimental samples was obtained by interpolation of the results of these four compositions.

As previously reported, the covalency of bonding nature between the moving cations and surrounding ions were very important to realize the fast movement of the ions. We investigated the total bond overlap population to estimate total of covalent interactions of moving cations and it was suggested that the cations, which could move easily, had small change of the total bond overlap population in the course of the movement. In the present work we would like to introduce differential total bond overlap population (DBOP), to evaluate the relationship between the covalent interaction and the fast movement of the moving Li ions. DBOP is obtained by subtracting the minimum from the maximum of the total bond overlap population throughout the movement of the lithium ion along the path. Though the net charge of the moving Li ion is also very important to discuss the ionic conductivity, the changes of the net charge of the moving Li ions were very small in all systems. Then we have omitted for the page limitation. In this study the electronic state of the moving lithium ions were calculated in the systems $\text{Li}_2\text{S}-\text{SiS}_2-\text{Al}_2\text{S}_3$ and $\text{Li}_2\text{S}-\text{SiS}_2-\text{P}_2\text{S}_5$ to compare with the ionic conductivity.

3. Results

The composition dependences of the DBOP and the ionic conductivity at 25 °C in the system $\text{Li}_2\text{S}-\text{SiS}_2-\text{Al}_2\text{S}_3$ are shown in Fig. 2. In this figure, closed diamonds show the results of ionic conductivity reported in Ref. [16] and closed rectangles show DBOP in the $60\text{Li}_2\text{S} \cdot 0.4(x\text{AlS}_{1.5} \cdot (100-x)\text{SiS}_2)$ glasses. The ionic conductivity is decreased with an increase in the compositional parameter x up to $x = 50$ and then gradually decreased with further increase in x . On the other hand, the DBOP shows opposite tendency with the Al_2S_3 content. The DBOP at $x = 0$ is 0.017 and shows increasing tendency with the Al_2S_3 content to 0.057 at $x = 100$. As mentioned above, the faster

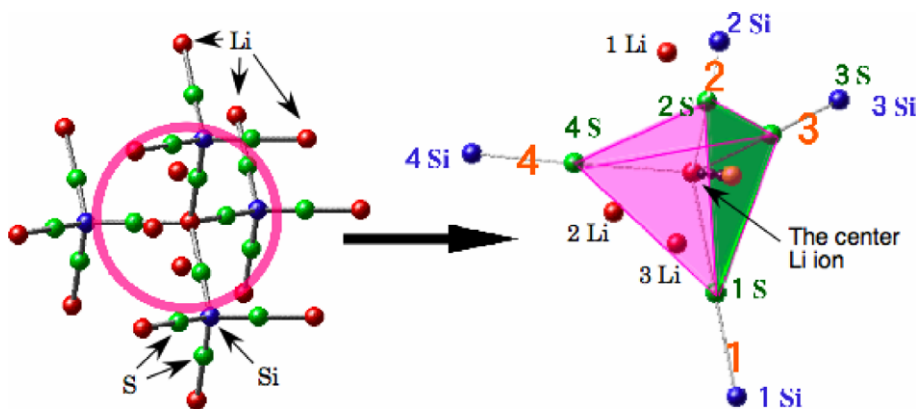


Fig. 1. Schematic diagram of the $\text{Li}_{16}\text{Si}_4\text{S}_{16}$ model cluster.

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