Lithium-Ion Conduction Analysis in LISICON by First-Principles Calculations

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Toward the development of next-generation all solid rechargeable batteries, it is essential to further improve ionic conductivity of solid electrolytes. The name LISICON, which stands for Lithium Super Ionic Conductor, is a member of the solid solution, $Li_{2+2x}Zn_{1-x}GeO_4$ ($0 \leq x \leq 1$) [1,2]. $Li_{3.5}Zn_{0.25}GeO_4$ (x=0.75) has high ionic conductivity, 0.125 S/cm at 300°C. LISICON is one of the classical Li^+ ion conductors. However, theoretical investigation has not been done enough yet. The crystal structure of γ-Li_4GeO_4 (x=1) is shown in Fig. 1. Oxide ions are arrayed as distorted hexagonal close packing. Cations occupy one-half of the tetrahedral sites. Moreover, excess Li^+ ions partially occupy the interstitial octahedral sites in x>0 for composition. There are γ, β and Li_4SiO_4-form as crystalline polymorph according to temperature and stoichiometry. The difference between their structures is characterized by orientation of a [GeO_4] tetrahedron. In this work, we employ the first-principles method to predict accurately relationship between spatial atomic configurations and energy surface, and to clarify Li^+ ion conduction mechanism.

First-principles calculations were performed using the projector augmented wave method with generalized gradient approximation as implemented in the VASP code. First, we calculated total energies for non-equivalent spatial configurations of Li^+ ions in Li_4GeO_4 (x=1). The unit cell which includes 36 atoms for the γ-form, 18 atoms for the β-form and the Li_4SiO_4-form was employed as a calculation model. All internal positions and lattice constants were relaxed. The optimization procedure was truncated when the residual forces on the relaxed atoms became smaller than 0.02 eV/Å. Second, potential barriers for Li^+ ion conducting were evaluated by the nudged elastic band (NEB) method. The supercell which includes 144 atoms was employed as a calculation model.

Fig. 2 shows total energies which were calculated systematically for 1748 atomic configurations in Li_4GeO_4. The lowest energy configuration is obtained from the Li_4SiO_4-form and agrees to the low-temperature phase of Li_4GeO_4 reported experimentally [3]. Li^+ ion conductivity of the ground state structure is expected to be very small because the energy difference between the most stable structure and the second stable one is large, 0.43 eV / $Li_8Ge_2O_8$. On the other hand, because each Li^+ ion configuration of the γ-form or the β-form has similar potential energy, Li_4GeO_4 with the γ-form or the β-form probably have high ionic conductivity. Furthermore, we found that excess Li^+ ions preferentially occupy interstitial octahedral sites which have edge sharing with [GeO_4] tetrahedrons.

The migration paths for Li^+ ion conducting were evaluated using the lowest energy configuration of the γ-form by the NEB method. We found an interstitialcy

mechanism. In this mechanism, excess Li^+ ion at an octahedral site jumps to a tetrahedral site and another Li^+ ion at the tetrahedral site simultaneously jumps to another octahedral site. Fig. 3 shows potential energy profile when Li^+ ion jumps to a neighbor site. The potential barrier of this interstitialcy mechanism is much lower than those of an direct interstitial mechanism.

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References

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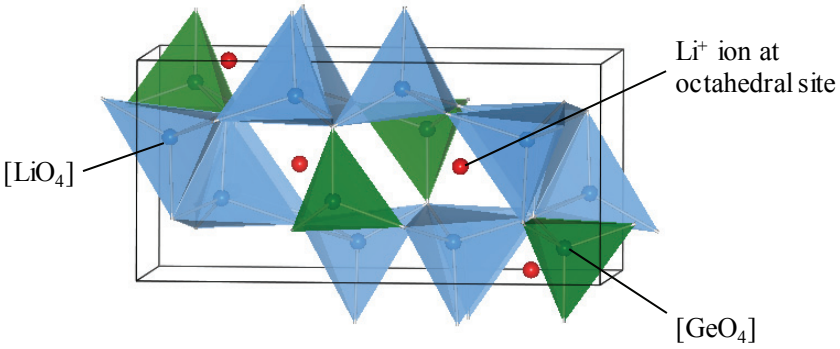

Fig. 1 Unit cell of γ-Li_4GeO_4

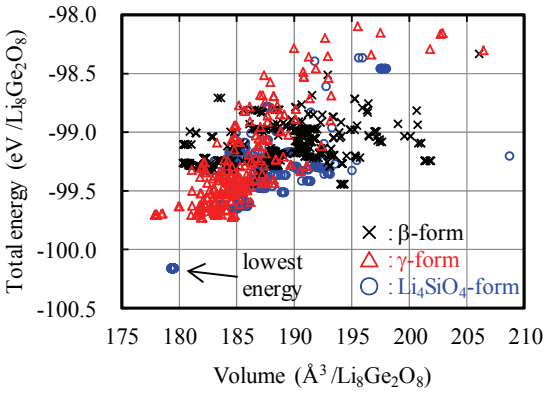

Fig. 2 The relationship between volume and energy of atomic configurations in Li_4GeO_4.

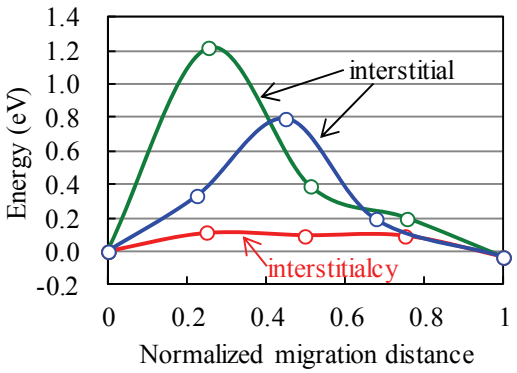

Fig. 3 Energy profile of Li^+ ion jump paths in γ-Li_4GeO_4.