

Order-disorder transition of Li ions at octahedral site in LISICON-type oxides

Akifumi Sumitani¹, Takafumi Moriasa¹, Kazuki Shitara¹, Atsuto Seko¹,
Yukinori Koyama¹ and Isao Tanaka^{1,2}

¹Department of Materials Science and Engineering, Kyoto University,
Yoshida, Sakyo, Kyoto 606-8501, Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Atsuta, Nagoya 456-8587, Japan

Toward development of all-solid-state lithium ion batteries, it is essential to find a solid-state lithium ionic conductor with high conductivity and chemical stability. $\text{Li}_{3.5}\text{Zn}_{0.25}\text{GeO}_4$, which is called LISICON (Lithium Super Ionic Conductor), has been investigated for a few decades[1]. However, the conductivity needs to be improved when application to the solid electrolyte of rechargeable batteries is considered. The atomic structure of $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$ is shown in Fig. 1. This is $\gamma\text{-Li}_3\text{PO}_4$ type structure in which oxide ions are arrayed as distorted hexagonal close packing. Cations in $\gamma\text{-Li}_3\text{PO}_4$ occupy tetrahedral sites within the oxygen sublattice. When the number of cations exceeds the number of the tetrahedral sites as in $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$ ($x>0$), the excessive lithium ions occupy the octahedral sites of the oxide-ion sublattice. They are expected to contribute to the high Li-ion conductivity. However, most of LISICON-type compounds show much lower conductivity at room temperature than that is expected from the chemical composition. Phenomenologically, the low conductivity can be ascribed to the presence of a deflection point in the Arrhenius plot of the conductivity. However, the atomistic mechanism of the deflection has not been revealed yet. In the group of the present authors', theoretical prediction of the lithium conductivity of the LISICON-type oxides was systematically made by combining a large set of density functional theory (DFT) calculations and machine learning of experimental data [2]. The mechanism of the deflection was assumed to be the order-disorder transition of the octahedral Li ions. The present study aims at validating the hypothesis by experiments.

Samples were prepared by a solid-state reaction method. A mixture of starting materials was calcined at 1023 K for 2 h. After pulverizing the product, pressed pellets were sintered at 1273 K for 12 h. All samples were characterized by powder X-ray diffraction (XRD). The temperature dependence of the ionic conductivity was then measured using AC impedance method.

All samples exhibit $\gamma\text{-Li}_3\text{PO}_4$ type structure by XRD. Diffraction peaks move to

lower angles with the increase of x . This is natural when P ions are replaced by Ge ions having larger ionic radius. Figure 2 shows Arrhenius plots of the conductivity. With the increase of x , meaning excess Li, the conductivity increases. The deflection of the ionic conductivity can be found at all of three compositions. Experimental deflection temperatures show reasonable agreement with the theoretical order-disorder transition temperature[2], implying the experimental deflection is related to the order-disorder transition.

Acknowledgments

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References

- [1] H. Y-P. Hong, Mater. Res. Bull., **13**, (1978) 117.
- [2] K.Fujimura, et al., Adv. Energy Mater., **3**, (2013) 980.

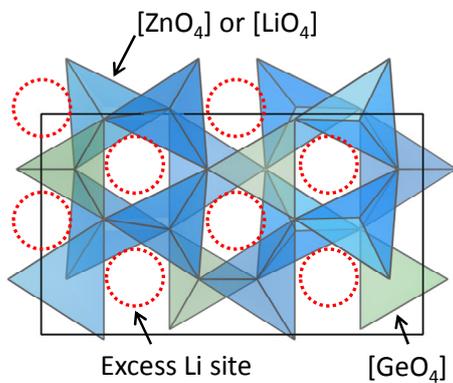


FIG. 1. Atomic structure of γ - $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$. Circles with red broken lines show the excess Li sites.

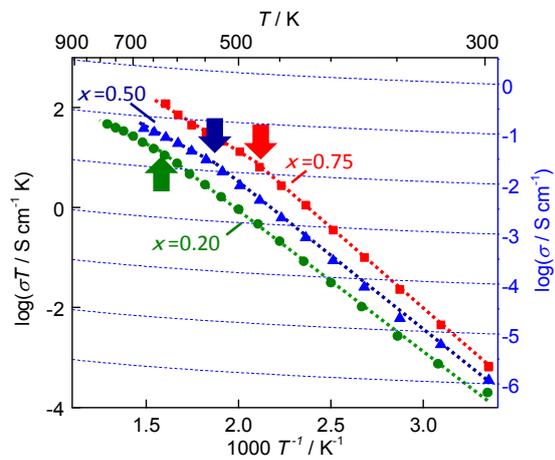


FIG. 2. Temperature dependence of conductivity, σ , for three $\text{Li}_{3+x}\text{Ge}_x\text{P}_{1-x}\text{O}_4$ samples. Arrows show deflection points.