Mechanistic study of $Li_{10}GeP_2S_{12}$ superionic conductor based on neutron diffraction data on single crystal

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1. Introduction

A superionic conductor $Li_{10}GeP_2S_{12}$ (LGPS), showing the Li conductivity over 10 mS cm^{-1}, is a possible candidate for a separator used in the all-solid-state battery, which potentially promises improved power and safety characteristics in the future [1, 2]. Due to its surprisingly high conductivity value, LGPS is suitable for the mechanistic study of ionic conduction. Understanding of the Li migration in the crystal lattice attracts much attention as the prediction or simulation for the Li ionic conductor is more widely studied.

The purpose of our study is to understand the relationships between crystal structure of LGPS and its high ionic conductivity. In this study, we aimed to obtain neutron diffraction data using single-crystal sample and analyze the structure.

2. Experiment

The time-of-flight (TOF) neutron-diffraction measurement was performed at SENJU diffractometer with the beam power of 400 kW. The synthesized single-crystal sample having an approximate size of 1 x 1 x 1 mm^3 was fixed to a special sample attachment, as shown in Figure 1. To prevent a moisture attack when mounting the sample on diffractometer, epoxy was thinly coated on the crystal. Measurements were carried out at 10 K and 298 K. The data were collected in seven directions for the wavelength range from 0.4 to 4.4 Å, and two directions from 4.6 to 8.8 Å, respectively.

3. Results

We analyzed the data using JANA2006 software [3]. The lattice parameters were determined in the space group $P4_2/nmc$ at both 10 K and 298 K. Lattice parameters at 298 K , a = 8.704 Å and c = 12.6148 Å, are in good agreement with those reported for measurements of powder samples. Figure 2 shows the framework structure, which consists of PS_4 and $(Ge/P)S_4$ tetrahedra, and is also consistent with that in the literatures [2, 4].

Figure 3 illustrates the Li atoms in the LGPS crystal at 10 K based on the analysis of diffraction data in this study. We tried several models for Li sites. In the model that provided the lowest R factors, the Li3 site, which was considered as a single site (8*f*) previously, was found to be split; 16*h* site at 298 K, and 8*f* and 16*h* sites at 10 K, respectively. We defined the new 16*f* site at 10 K the Li5 site. In this structure model, Li atoms distribute more uniformly in the crystal, or have more significant degree of spatial disorder. Since Li distribution influences ion conduction, this structure model will provide a clue for the Li conduction mechanism via the Li3 site.

4. Conclusion

In this study, we obtained the neutron diffraction data for a single-crystal LGPS for the first time. On the basis of the data, we suggested a new structure model. In the model, Li sites are uniformly distributed. For further understanding of the relationships between LGPS-type structure and its high ionic conductivity, it is necessary to simulate ion migration using molecular dynamics based on the structural data in this study.

Figures

Figure 1 LGPS single-crystal on the sample attachment for SENJU diffractometer.

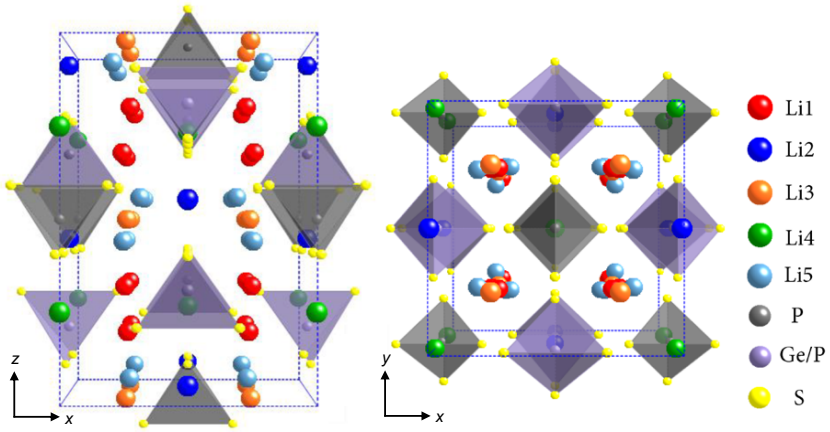

Figure 2 Framework of LGPS crystal. Tetrahedra represents $(Ge/P)S_4$ or PS_4 units. Li sites, including the Li5 site, are represented by sphere.

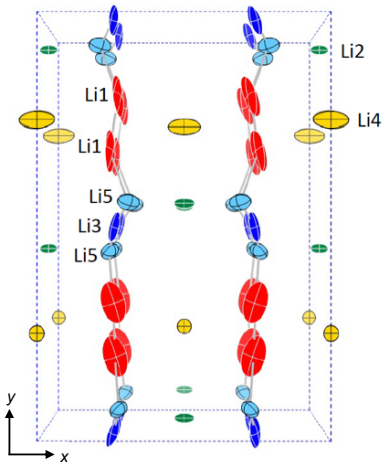

Figure 3 Li sites in the LGPS crystal at 10 K. Each Li sites are represented by ellipsoids. The size and shape of ellipsoids respectively indicates the degree and direction of positional disorder for each Li sites.

References

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