Local structure change around germanium due to crystallization of LiGe$_2$(PO$_4$)$_3$ with NASICON-type structure

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1 Introduction
Rechargeable lithium ion batteries using non-aqueous liquid electrolytes are applied for many electronic devices because of large energy density. However, these liquid electrolytes generally consist of flammable organic solvents. To improve the safety of rechargeable lithium ion batteries, superior solid lithium ion conductors with high lithium ionic conductivity and high stability should be developed.

The sodium (Na) super ionic conductor (NASICON)-type LiGe$_2$(PO$_4$)$_3$-based compounds have been reported to exhibit the high stability in air and non-reactivity with lithium metal. Many efforts have been dedicated to increase the lithium ionic conductivity of LiGe$_2$(PO$_4$)$_3$-based compounds. It has been reported that the lithium ionic conductivity of the crystal phase of LiGe$_2$(PO$_4$)$_3$ systems is much larger than that of the glass phase which can be obtained by the quenching of molten glass [1]. Thus, it is meaningful to compare the structure of the crystal phase with that of the glass phase in LiGe$_2$(PO$_4$)$_3$ systems. However, structure of the glass phase of LiGe$_2$(PO$_4$)$_3$-based systems is not completely understood yet. In this study, the local structure around germanium atoms of the glass and crystal phases of LiGe$_2$(PO$_4$)$_3$ was investigated by X-ray absorption fine structure (XAFS) measurements.

2 Experiment
The mixture of chemicals such as Li$_2$CO$_3$, GeO$_2$ and NH$_4$H$_2$(PO$_4$)$_3$ was melted in a platinum crucible at 1673 K for 10 min in air. In order to obtain glass specimen, the melt was quenched onto a copper plate and then immediately pressed by a copper block. The crystal specimen with the NASICON structure was prepared by annealing the glass specimen at 1123 K for 6 h.

The XAFS measurements were carried out at the Ge K absorption edge (11.1036 keV) using the synchrotron radiation facility at the beam line station BL-7C of the Photon Factory, Tsukuba, Japan. To obtain the adequate intensity, appropriate amounts of the specimens were finely ground and mixed with BN powders, and then their X-ray absorption spectra were measured in the transmission mode. The X-ray absorption spectra were analyzed by the program REX2000.

3 Results and Discussion
Radial structure functions (RSFs) around germanium atoms obtained by Fourier transform of extended X-ray absorption fine structure spectra are presented in Fig. 1. The RSF of the glass specimen exhibits a correlation peak which is attributable to the coordination of oxygen. It is well known that the Ge-O atomic distance in the crystalline GeO$_2$ is closely related with the coordination number [2]. The Ge-O atomic distance of the quarts like GeO$_2$ with a four-fold coordination has been reported to be located at the shorter atomic distance side in comparison with that of the rutile like GeO$_2$ with a six-fold coordination. It should be noted that the Ge-O correlation peak in the RSF of the glass specimen is located at a longer distance side in comparison with that of the crystal specimen. Accordingly, the change of coordination number of germanium is probably caused by the crystallization of the NASICON-type LiGe$_2$(PO$_4$)$_3$ compound from the glass phase.

Fig. 1: Radial structure functions (RSFs) around germanium atoms of the glass and crystal specimens of LiGe$_2$(PO$_4$)$_3$.

References

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