Explore of the Lithium Ion Conductor Having Spinel Structure

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Summary

Ionic conductivity of solid is one of the most promising subject for the development of fuel cell and lithium-ion secondary batteries. Although ionic conductivity of solid is lower than the liquid state, solid electrolytes are expected to be advance materials for these electrochemical devices.

We have reported superionic phase transition for Li$_3$InBr$_6$. A quite similar superionic phase transition was observed for LiInBr$_4$. (Fig. 1) The Rietveld analysis on LiInBr$_4$ suggested that the crystal belong to a cubic spinel structure with a space group $Fdar{3}m$ or a trigonal structure with space group $R-3m$. Fig. 2 shows structural model with a space group $R-3m$. The octahedron corresponds to an InBr$_6$ unit in which In$^{3+}$ occupies one half. This structure could be also described as a defect NaCl structure, because bromide ions keep a cubic closest packing similar to LiBr. Therefore, we have planed to synthesize a solid-solution between LiBr and InBr$_3$ according to the following equation,

$$3\text{Li}^+ \rightarrow \text{In}^{3+} + 2\square \quad (1)$$

The synthesized Li$_{1-x}$In$_x$Br$_3$ (x = 0.1) showed a quite similar X-ray powder pattern above 330 K to that of LiBr, suggesting a formation of the homogenous solid-solution. Preliminary conductivity measurement supported a superionic character of this material above 330 K. $^{115}$In NMR supported the incorporation of In$^{3+}$ into a rock salt structure.

![Fig.1 Conductivity of LiInBr$_4$ together with Li$_3$InBr$_6$.](image1)

![Fig. 2 Crystal structure of LiInBr$_4$.](image2)