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主 論 文 の 要 旨

論文題目 **Synthesis and Characterization of
Anti-Perovskite Structured Li⁺ Conducting
Solid State Electrolyte**
(アンチペロブスカイト型構造を有する
Li⁺伝導性固体電解質の合成と評価)

氏 名 **SUGUMAR Manoj Krishna**

論 文 内 容 の 要 旨

Lithium-rich anti-perovskite structured material, commonly known as LiRAP, is a candidate as a superior oxide-based Li⁺ conductive solid electrolyte for all-solid-state batteries because they are soft and possibly high Li⁺ conductive materials. Researches for improving the total ionic conductivity of LiRAP is classified as follows.

1. Cation doping
2. Halogen species control, including mixed halogen effects
3. H amount

Among them, the most serious problem is the control of hydrogen amount in LiRAP. Most of the preparation methods apply a heating process for fabricating LiRAP, and then it is not easy to suppress the removal of H during the fabrication. Thus, a better way is to fabricate LiRAP at lower temperatures and then clarify how the total ionic conductivities are influenced by other factors considering the H amount. Based on the

above motivations, the author has focused on the preparation of LiRAP at room temperature and then investigate their ionic conductivities.

In chapter 2, cubic-phase anti-perovskite-structured Li_2OHBr was synthesized at room temperature just by a dry ball-milling process. The starting materials LiOH and LiBr, were mixed in equal molar ratio and ball-milled in a planetary micro mill at a rotation speed of 700 RPM in an argon atmosphere at room temperature for 48 hours. The resultant Li_2OHBr sample had a lattice constant of 4.046 Å and a total ionic conductivity of $1.1 \times 10^{-6} \text{ S cm}^{-1}$, which was in good agreement with the past work, and the synthesis process was a straightforward method to fabricate Li_2HOBr . Since no heating was required, this was an effective method to control the hydrogen amount, as discussed in chapter 5 in detail.

In chapter 3, Li_2OHCl was synthesized by room temperature dry ball-milling process. Li_2OHCl generally forms an orthorhombic phase at room temperature, but the resultant material formed a cubic phase and then showed one order higher ionic conductivity than previous reports. The starting materials LiOH and LiCl, were mixed in equal molar ratio and ball-milled in a planetary micro mill at a rotation speed of 700 RPM in an argon atmosphere at room temperature for 72 hours. Variable-temperature synchrotron powder X-ray diffractions studied the phase transition temperature. During the heating process, the orthorhombic phase gradually changed to the cubic phase between 36 and 40 °C, whereas the cubic phase changed to the orthorhombic phase between 34 and 30 °C during the cooling process. This metastable cubic-phase formation was believed to be originated from the smaller-sized crystallites uniquely formed through mechanochemical synthesis.

In chapter 4, anion-exchanged LiRAP were prepared to improve total Li^+ conductivity. $\text{Li}_2\text{OHBr}_{1-x}\text{X}_x$ ($\text{X} = \text{Cl}, \text{I}$) mixed halogen samples were prepared at room temperature by a dry ball-milling process. In anti-perovskites, structural manipulations are possible by chemical substitution, e.g., by replacing small Br^- anions at the dodecahedral site with large I^- anions, mixed halogen samples can be prepared. These mixed halogen samples have a higher tolerance factor, which indicates a large lattice constant and less distortions. This helps to achieve higher Li-ion conduction via Frenkel interstitial transport. The starting materials, LiOH , LiBr , LiCl , and LiI , were mixed in different molar ratios and ball-milled as with the condition in chapter 2. Both the solid solution formation range and total ionic conductivity were studied. In this chapter, by substituting smaller ionic radius Cl^- in place of Br^- the lattice constant decreased whereas, substituting larger ionic radius I^- in place of Br^- the lattice constant increased and total ionic conductivity increased. The $\text{Li}_2\text{OHBr}_{0.9}\text{I}_{0.1}$ sample had the largest lattice constant of 4.060 \AA with the highest total ionic conductivity of $4.9 \times 10^{-6} \text{ S cm}^{-1}$.

In chapter 5, Li-excess and Li-deficient anti-perovskite structured $\text{Li}_{2+x}\text{OH}_{1-x}\text{Br}$ were prepared at room temperature by dry ball-milling process, and their effects on total ionic conductivity are discussed. The starting materials $\text{LiOH}\cdot\text{H}_2\text{O}$, LiOH , LiBr , and Li_2O were mixed in different molar ratios and ball-milled as with the chapter 2. In order to increase the Li concentration, Li-excess $\text{Li}_{2+x}\text{OH}_{1-x}\text{Br}$ samples were synthesized by doping Li_2O which, increased the lattice constant and helped to improve the total ionic conductivity. The $\text{Li}_{2.2}\text{OH}_{0.8}\text{Br}$ sample with a lattice constant of 4.056 \AA has a total ionic conductivity of $3.6 \times 10^{-6} \text{ S cm}^{-1}$. The rotational assistance of OH for improving total ionic conductivity did not play an important role in Li_2OHBr probably because of the larger lattice constant compared with Li_2OHCl .

In conclusion, this doctoral dissertation proposes a novel low-temperature synthesis method that can control the H content, which affects the ionic conductivity of LiRAP, and investigates the high ionic conductivity of LiRAP from the viewpoints of the specificity of the synthesized nanocrystals, halogen substitution, and hydrogen substitution, and proposes a mechanism for the high ionic conductivity. These results have been summarized in four scientific papers, one of which is under review. The results are important for developing large-sized all-solid-state lithium batteries and will contribute greatly to its engineering development.