論文 / 著書情報
Article / Book Information

題目(和文)	岩塩・ペロブスカイト・逆蛍石型構造を有する酸化物系リチウムイオン導電体の合成、構造と電気化学特性
Title(English)	Synthesis, structures and electrochemical properties of lithium ion conducting oxides with rock-salt, perovskite and anti-fluorite structures
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電子科学　　　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（　理学　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Chapter 1: In this thesis, novel lithium ion conducting oxides were developed using reported structural frameworks, rock-salt, perovskite, and anti-fluorite-types. Base compositions for these structures are $LiScO_2$, $(Li_xLa_{1-x/3})ScO_3$, and $Li_{5+x}(Fe_{1-x}Zn_x)O_4$, respectively. Aliovalent cation doping to improve lithium ion conductivity was examined for $LiScO_2$ and $(Li_xLa_{1-x/3})ScO_3$. These oxide-based materials were synthesized by ambient pressure or high-pressure synthesis method to obtain target composition and structure. Structure analysis and electrochemical evaluation were conducted to understand their relationship and achieve further improvements in the electrochemical properties of the lithium ion conductors.

Chapter 2: The powder samples were synthesized by either solid-state reaction in air at 900−1350°C (Chapter 3, $LiScO_2$ system), 650−750°C (Chapter 5, Li_5FeO_4 anti-fluorite system) or high-pressure synthesis method at 900−1250 °C with a pressure of 1−2 GPa (Chapter 4, $LaScO_3$ perovskite system). Obtained samples were subjected to X-ray and synchrotron X-ray diffraction analyses for structure determination. Diffraction data was analyzed by Rietveld refinement method using Rietan-FP program. Ionic conductivity was measured by the AC-impedance method using frequency response analyzers (Solartron 1260); the samples were placing under flowing Ar gas, and the measurements were performed over the temperature range from 25 to 450 °C and the frequency range from 0.1 Hz to 10 MHz. Gold pastes were painted onto both sides of each sample for the measurements as the blocking electrodes.

Chapter 3: The lithium containing oxides, rock-salt type $LiScO_2$ and $Li_{1-y}Sc_{1-x}M_xO_2$ (M = Zr^{4+}, Nb^{5+} and Ta^{5+}) were synthesized. The highest conductivity of 7.94×10^{-6} S cm^{-1} at 350 °C for the sample doped with 10% Zr^{4+} was confirmed, which was improved by two orders of magnitude than that of $LiScO_2$. Enhanced ionic conductivities were achieved by the introduction of vacancies in the structure by doping with tetra-valent cations (Zr^{4+}) at Sc-site.

Chapter 4: The perovskite type $(Li_xLa_{1-x/3})ScO_3$ and M-doped $(Li_xLa_{1-x/3})ScO_3$ (M = Ce^{4+}, Zr^{4+}, Nb^{5+}) were synthesized and their lithium ion conductive properties were investigated. A-site doping (M = Ce^{4+}) improved the conductivity of $(Li_xLa_{1-x/3})ScO_3$, while the presence of B-site doping (M = Zr^{4+}, Nb^{5+}) did not contribute its improvement. An optimal compound $(Li_{0.4}Ce_{0.15}La_{0.67})ScO_3$ shows the maximum ionic conductivity of 1.06×10^{-3} S cm^{-1} at 350 °C, which is nearly two orders of magnitude improved comparing to that of the optimal composition $(Li_{0.45}La_{0.85})ScO_3$ in $(Li_xLa_{1-x/3})ScO_3$ system. The crystal structure analyses and ionic conductivity measurements indicate the ionic conductivities of $(Li_xLa_{1-x/3})ScO_3$ could be improved because

of the introduction of lithium-ion and lithium-ion interstitials in the structure by doping with a tetra-valent cation (Ce^{4+}) at A^{3+}-site.

***Chapter 5*:** $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ forms solid solutions in $0 \leq x \leq 0.1$ and $0.1 < x \leq 1$ for α− and β−phases, respectively. The phases are reported to be obtained by quenching process. However, a dominant factor in determining the conductivity and conductivity jumped at high temperature region (~430 °C) are still unclear. To solve these problem and obtain a direction of novel material design, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ are investigated in this chapter. $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ formed solid solutions in $0 \leq x \leq 0.3$ and $0.5 \leq x \leq 1$ for α− and β−phases, respectively by a solid state synthesis method with a slow cooling process. The α−phase obtained in this study, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ (x = 0.2, 0.3) showed lower ionic conductivity than reported β-phase with the same composition. The fact indicates the phase-type is the dominant factor for higher ionic conductivity than the composition. The formation of LiOH by a decomposition of this material due to reaction with water in the atmosphere was detected, indicating the conductivity jump is contributed to the liquid phase of LiOH at the high-temperature. High-temperature β-phase with anti-fluorite structure could be good candidates as solid electrolyte while controlling the atmosphere is required for this material.

***Chapter 6*:** In this chapter, the conclusion of this study is mentioned. The ionic conductivities of rock-salt type $LiScO_2$ and perovskite-type $LaScO_3$-based materials were improved by doping of lithium vacancy or interstitial, respectively. Optimizing the solid solution formation region with suitable doping/substitution elements and synthesis methods, and understanding the conductive mechanism and structure characteristics of the materials are valuable knowledge for developing new groups of solid lithium ion conductors that can be used in practical applications as solid electrolytes or electrodes for all-solid-state lithium batteries.