題目(和文)	
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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

系・コース： Department of, Graduate major in	応用化学 系 エネルギー コース	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 ）

In **Chapter 1**, research background is provided. Superionic conductor $Li_{10}GeP_2S_{12}$ (LGPS) and its structural derivatives show high lithium conductivity reaching to 10 mS cm^{-1} at room temperature, and they are potentially used in all-solid-state batteries (ASSB), which is an attractive alternative for lithium ion batteries, owing to its expected safety improvement. To meet the demand of high power density and high energy density for ASSBs by finding further high-performance solid electrolytes, this study performed a material search in the Li–*M*–P–S–*X*–O (*M* = Si, Ge, Sn; *X* =F Cl, Br, I) systems for LGPS-type phase with high conductivity, and in the Li–P–S system for high electrochemical stability. The relationships between composition, structure and properties were investigated in both systems.

Chapter 2 described the experimental methods in this study. All the experimental procedures were performed under inert atmosphere. In synthesis, raw materials in the targeted molar ratio were mixed by planetary ball milling, and then heated at synthesis temperature. Phases were identified by powder X-ray diffusion (XRD) method, and the crystal structures were analyzed by Rietveld method using synchrotron X-ray and/or neutron diffraction data. The ionic conductivity values were measured using the alternating current impedance method for the compressed powder at 298 K, or at low temperature measurements between 170 and 233 K.

In **Chapter 3**, the effects of oxygen substitution for the $Li_{10}GeP_2S_{12}$ (LGPS)-type $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ (LSiPSCl) were investigated. The structural analysis using synchrotron X-ray diffraction measurements showed a decrease in the lattice parameters with increased oxygen substitution over the range of $0 < z \leq 0.6$ in $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7-z}Cl_{0.3}O_z$ ($LSiPSClO_z$), which indicate the formation of solid solution. XRD measurements indicated the introduction of O atoms enhanced purity of the LGPS-type phase in synthesized product in the Li–Si–P–S–Cl system. The oxygen-substituted samples exhibited higher ionic conductivities than the original LSiPSCl for their cold-pressed samples, with a calculated bulk conductivity of 28 ± 3 mS cm^{-1} being determined for $LSiPSClO_{0.3}$. All-solid-state cells containing $LSiPSClO_{0.6}$ as the separator electrolyte, and a Li–In alloy anode and $LiNbO_3$-coated $LiCoO_2$ cathode, exhibited a high discharge capacity retention of 97% after 20 cycles, which was significantly higher than that obtained for the cell containing LSiPSCl as its electrolyte counterpart. This study proposed possibility of simultaneously improvements of ionic conductivity and electrochemical stability upon oxygen substitution for sulfide superionic conductors.

In **Chapter 4**, a series of anion and cation substitution effects for LGPS-type Li–*M*–P–S–*X*–O (*M* = Si, Ge, Sn; *X* =F, Cl, Br, I) was investigated. The phase-pure LGPS-type phase was obtained at the composition of $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Br_{0.3}O_{0.6}$ ($LSiPSBrO_{0.6}$). The structural analysis showed a larger lattice parameter of $LSiPSBrO_{0.6}$ compared to $LSiPSClO_{0.6}$, which supports that Cl locates in the crystal structure of LSiPSCl, as well as indicates that the Cl atom was substituted by Br atom. For achieving higher conductivity, the Si atoms in $LSiPSBrO_{0.6}$ were further partially substituted by larger Ge or Sn atoms; solid electrolytes were synthesized according to the chemical composition formula of $Li_{9.54}(Si_{1-\delta}M_{\delta})_{1.74}P_{1.44}S_{11.1}Br_{0.3}O_{0.6}$ ($LSiM_{\delta}PSBrO$, *M* = Ge and Sn). The single LGPS-type phases and a gradual increase in lattice parameters with higher δ values were observed in the range of $0 < \delta \leq 0.5$ for $LSiGe_{\delta}PSBrO$, and $0 < \delta \leq 0.4$ for $LSiSn_{\delta}PSBrO$, which may correspond to the solid solution limits for each system. The synchrotron XRD Rietveld analysis confirm the Ge and Sn atoms substitutes the Si atoms. At the compressed powder state, Ge-substituted samples show total ionic conductivities of 11.3–13.8 mS cm^{-1}. The bulk conductivity was estimated to be 37.4 mS cm^{-1} for $LSiGe_{0.4}PSBrO$. The value was higher than those for $LSiPSClO_z$. These results imply simultaneous substitution for anion and cation in LGPS-type phase potentially provide even more conductive phases.

In **Chapter 5**, the Li–P–S system was investigated for finding solid electrolyte with electrochemical stability. A phase with a new crystal structure was obtained at the nominal composition of $Li_{3.2}PS_4$. The contamination of O atoms from raw material and/or moisture during synthesis resulted in transformation from the new crystal to LGPS-type structure, which may cause the low phase purity for $Li_{3.2}PS_4$. The structure analysis indicates the new-structure-type $Li_{3.2}PS_4$ with a hexagonal unit cell and space group of $P3_1$. Based on the direct-space method and Rietveld method, the crystal was found to have layered PS_4 units and P_2S_7 units. The solid-state-cell with $LiNbO_3$-coated $LiCoO_2$ cathode and Li–In anode using the new $Li_{3.2}PS_4$ phase as a separator showed high capacity-retention of 98% after 20 cycles, indicating high electrochemical stability of this phase. This study deepened understanding of composition–phase–property relationships in the Li–P–S system.

Chapter 6 summarized the study in this thesis. In conclusion, the relationships between composition, phase and electrochemical property were elucidated in both Li–*M*–P–S–*X*–O system and Li–P–S system. Two types of solid electrolytes with a respective advantage were discovered; highly conductive LGPS-type LSiGePSBrO and electrochemically stable hexagonal $Li_{3.2}PS_4$. These two types of solid electrolytes can be complementarily applied in an all-solid-state cell with bilayer solid electrolytes configuration. For both Li–*M*–P–S–*X*–O and Li–P–S systems, contaminated or introduced oxygen affected the final product phase and its property. This study demonstrated consideration of oxygen amount and possible double substitution in synthesis composition is an effective approach for finding novel sulfide superionic conductors.