論文 / 著書情報
Article / Book Information

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種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 エネルギー 系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 (理学) Doctor of
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要旨（英文 800 語程度）

Thesis Summary（approx.800 English Words ）

The development of all-solid-state lithium (Li) metal batteries having high energy density and safety requires solid electrolytes with high Li-ion conductivity and electrochemical stability to Li metal. Fast Li ion conductors that are synthesized in the Li_2S–P_2S_5–LiX (X = Cl, Br, I) pseudo-ternary system and categorized into glass-ceramics are promising candidates for such solid electrolytes. However, monophasic compositions and crystal structures of these compounds have been unknown, due to lack of understanding of relationships between structures and compositions on the pseudo-ternary diagram. The present study aimed to address this fundamental issue. The thesis presents results obtained by solving the issue, including the discovery of new Li conductors based on refined crystal structures, and the understanding of properties of identified Li conductors by experiments and fast principles calculations using obtained structural information as the input.

In Chapter 1, research background is described with emphasis on research problems of glass-ceramics in the Li_2S–P_2S_5–LiX compositional system. Chapter 2 presents procedures of experiments and calculations, as well as both theoretical bases that are necessary for understanding results and discussions described in the following chapters.

Chapter 3 describes the solid-state synthesis and phase identification for samples with the composition of $(100–p–q)Li_2S$–pP_2S_5–qLiX. For the system containing chlorine (X = Cl), results are summarized in Appendix. The composition–phase relationships were elucidated to obtain monophasic glass-ceramics which show a high ionic conductivity and contain crystalline phases of $Li_{10}P_3S_{12}Br$ (LPSBr) and $Li_{10.25}P_3S_{12.25}I_{0.75}$ (LPSI). Rietveld analyses for their synchrotron X-ray or neutron diffraction data revealed that their crystal structure is respectively analogous to a lithium superionic conductor $Li_{10}GeP_2S_{12}$ (LGPS), in terms of the space group, lattice constants, and framework tetrahedral units. Interest structural difference is additional anion positions with 2a or 4c Wyckoff positions, which are present in LPSBr and LPSI but not present in the original LGPS. By the substitution with oxygen for sulfur in refined LGPS-type structures, two series of new Li conductors of LGPS-type $Li_{10}P_3S_{12–x}BrO_x$ (LPSBrO_x) and $Li_{10.25}P_3S_{12.25–y}I_{0.75}O_y$ (LPSIO_y) were synthesized.

Chapter 4 is about temperature-dependent phase changes revealed by both experiments and theoretical calculations for the two series of Li conductors that are described in the previous chapter. In experiments, the high-temperature X-ray diffraction measurement and differential thermal analyses were performed. In first principles calculations, the energy above hull (E_{hull}), which represents relative stability, was calculated using solved structures as the initial input. Linking of each result revealed that both series of LGPS-type LPSBrO_x and LPSIO_y phases show E_{hull} values from 0.027 to 0.068 eV atom^{-1} and upon a temperature elevation they change into phases that are present on the respective pseudo- ternary or quaternary diagram and have lower E_{hull} values down to 0 eV atom^{-1}. From these results, it was concluded that the two series of LGPS-type phases are metastable compared with competitive phases surrounding each of them on the respective pseudo- ternary or quaternary diagram.

Chapter 5 presents composition-dependent changes in ionic conductivity at room temperature for the two series of LGPS-type LPSBrO_x and LPSIO_y phases, which are described in Chapter 3. With increase in oxygen molar ratio, conductivity tends to decrease after notable improvements up to 7.6 mS cm^{-1} in LPSBrO_x from 5.8 mS cm^{-1} for LPSBr as well as to 12.8 mS cm^{-1} in LPSIO_y from 9.1 mS cm^{-1} for LPSI. The structural parameters relating to bottlenecks for ionic conduction pathways for the two phase-series were analyzed to clarify the mechanism of conductivity changes depending on anion species added to the base composition in the Li–P–S system. For LGPS-type LPSBrO_x phases, *ab initio* molecular dynamic (AIMD) simulation was performed to elucidate ion dynamics. These two approaches indicated that the conductivity tends to decrease when ionic conduction in paths along c-axis is impeded. It was also proposed that in such situation unfavorable for ionic conduction, conductivity still increases when conduction is facilitated in paths over ab-plane by expanding their bottlenecks via a proper degree of the substitution with oxygen for sulfur.

This study identified and developed derivatives of LGPS in the Li–P–S–X–O (X = Br, I) system that had not been fully investigated to elucidate composition–crystal-structure relationships. The ionic conductivity and thermal stability for these compounds, which are promising solid electrolytes for all-solid-state batteries, were elucidated by measuring monophasic samples with minimized influences from secondary phases. By combining experiments and first-principles calculations based on the solved structural information, this study deepened the understanding of phase stability and ionic conductivity of LGPS-type phases in the Li–P–S–X–O (X = Br, I) system.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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