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論文 / 著書情報
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種別(和文)	論文要旨
Type(English)	Summary

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（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	
学生氏名： Student's Name	Wenze Huang		

申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of (Science)
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

1. Introduction

All-solid-state batteries with non-flammable solid electrolytes are proposed to solve fundamental safety problems associated with lithium batteries. P_2S_5-based sulfide conductors have recently been among the most highly sought after and promising candidates for all-solid-state batteries because of superionic conductivities (10^{-4}–10^{-2} S cm^{-1}). However, the volatility of P_2S_5 prevents the syntheses of these conductors at atmospheric pressure, with well-designed sealed pressure vessels required. Therefore, in this study, aliovalent substitutions of P^{5+} with Al^{3+} and Si^{4+} was introduced, and the synthesis of novel materials in the Li–Al–Si–S based system was conducted. Cost-effective and earth-abundant Al_2S_3- and SiS_2-based solids have been reported to be more flexible for synthesis applications than their volatile P_2S_5-based counterparts, although the crystalline compounds discovered in these systems have relatively low ionic conductivities. However, a large proportion of this system remains unexplored; consequently, promising structures with high ionic conductivities such as those found in the phosphorus system, can be expected. Following a systematic materials search, many kinds of phosphorus-free lithium superionic conductors were synthesized in this study. The relationship between ionic conductivity and the structure of the lithium-ion conductors in this system was elucidated.

2. Experimental

All of the experiments were conducted in Ar-filled environment. Li_2S, Al_2S_3, Si_2S, and Li_2O were the starting materials. These powders were weighed in stoichiometric ratios and then mechanically mixed using a vibration milling apparatus. The obtained mixtures were pelletized, placed and sealed in a quartz tube, followed by annealing at 400–1000 °C, after which they were slowly cool down or quenched in ice water. Powder X-ray diffraction, Synchrotron X-ray diffraction, and Neutron diffraction measurements were conducted to identify the synthesized phases. Lattice and structural parameters were refined using the Rietveld method. The morphologies and elemental distributions of the synthesized samples were examined by SEM and EDS. The ionic conductivity of each sample was determined by the AC-impedance method. All-solid-state batteries were constructed and evaluated using the solid conductors synthesized in this study.

3. Synthesis and Electrochemical Properties of Thio-LISICONs in the $Li_{4+x}Al_xSi_{1-x}S_4$ System

The thio-lithium superionic conductors of $Li_{4+x}Al_xSi_{1-x}S_4$ system were synthesized by a solid-state method. Two thio-LISICON phases Li_5AlS_4 and Li_4SiS_4 with γ-Li_3PO_4-type structure appeared in most of the synthesized samples. On the other hand, a novel thio-LISICON appeared in the nominal composition of

$Li_{4.5}Al_{0.5}Si_{0.5}S_4$ (x = 0.5), which was obtained by pre-heating at 400 °C for 8 h, followed by annealing at 550 °C for 8 h. It has a similar but not identical structure to that of Li_4SiS_4. The ionic conductivity, $\sigma_{r.t.}$ = 2.05×10^{-6} S cm^{-1} of this novel conductor is at least one order magnitude higher than the previously reported solid solutions in the $Li_{4+x}Al_xSi_{1-x}S_4$ system.

4. Superionic Lithium Conductor with a Cubic Argyrodite-type Structure in the Li–Al–Si–S System

Novel phosphorus- and halide-free superionic lithium conductors were synthesized in the quasi-ternary Li_2S–Al_2S_3–SiS_2 system. Both HT- and LT-argyrodite type $Li_{4+x}Al_xSi_{1-x}S_4$ (LASS) materials were produced by quenching at an x value of around 0.1. The HT-LASS exhibited a high ionic conductivity of 2.54×10^{-4} S cm^{-1} at room temperature, which is three orders of magnitude higher than those previously reported for thio-LISICONs in the Li–Al–Si–S system. This HT-LASS was identified to be a promising material for application as a solid electrolyte in an all-solid-state battery.

5. Phase Diagram of the Pseudo-binary Li5AlS4–Li4SiS4 System

The pseudo-binary Li_5AlS_4−Li_4SiS_4 system was studied by DTA and XRD techniques. A phase diagram displaying the thio-LISICONs (α, β, γ) and argyrodite-type phases (HT-A, LT-A) of this system was constructed based on the results of **Chap. 3** and **Chap. 4**. It reveals that the α, β, and γ-type phases are the stable thermodynamic phases at room temperature, and thus can be obtained by conventional solid-state reaction. But the argyrodite phases exist in a narrow solid-solution region around x = 0.1 at high temperature. They cannot be obtained by slow cooling from reaction temperature, but by fast quenching on the basis of the kinetic effect. This study provides an insight view of the thermodynamic properties and the structural relationships of the superionic conductors in the pseudo-binary Li_5AlS_4−Li_4SiS_4 system.

6. The Effect of Oxygen Substitution on Lithium Argyrodite in the Li–Al–Si–S–O System

The effect of oxygen substitution on the novel lithium argyrodite synthesized in the Li–Al–Si–S–O system was investigated. Cubic argyrodite-type $Li_{6.15}Al_{0.15}Si_{1.35}S_{6-x}O_x$ (LASSO) materials were obtained by quenching at an x value from 0.4 to 0.8. The oxygen substitution in the LASSO system not only stabilizes the cubic argyrodite-type structure but also creates anion site-disorder lowering down the activation barrier for Li ions diffusion. The $Li_{6.15}Al_{0.15}Si_{1.35}S_{5.4}O_{0.6}$ exhibited a bulk ionic conductivity of 4.3×10^{-3} S cm^{-1} at 25 °C with a low activation energy of 37 kJ mol^{-1}. This material is a serious competitor for application as a solid electrolyte in an all-solid-state battery.

7. Summary

These results indicate that systematic study based on phase diagram helps to clarify the relationship of structure and ionic conductivity for superionic conductors. Li–Al–Si–S based system is like a gold mine of solid electrolytes providing numerous promising materials, such as the thio-LISICON-type and argyrodite-type conductors for all-solid-state batteries.

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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