論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Synthesis of crystalline lithium ion conductors based on the Li-Ge-P-S-O and Li-Sn-Si-P-S systems: phase relationships, structures and electrochemical properties
著者(和文)	SunYulong
Author(English)	Yulong Sun
出典(和文)	学位:博士（理学）, 学位授与機関:東京工業大学, 報告番号:甲第10296号, 授与年月日:2016年9月20日, 学位の種別:課程博士, 審査員:菅野 了次,平山 雅章,原 正彦,川路 均,松下 伸広,中村 二朗
Citation(English)	Degree:, Conferring organization: Tokyo Institute of Technology, Report number:甲第10296号, Conferred date:2016/9/20, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質電子化学　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　理学　）
学生氏名： Student's Name	Yulong Sun	指導教員（主）： Academic Advisor(main)	菅野　了次
		指導教員（副）： Academic Advisor(sub)	平山　雅章

要旨（英文 800 語程度）

Thesis Summary（approx.800 English Words ）

In this thesis, material searches based on quasi-ternary phase diagram in Li_2S-MS_2-P_2S_5 system (M=Si, Sn) are carried out. As the beginning point of this study, original LGPS composition is focused. Using the high ionic conductive property and structure of LGPS, enhancement of electrochemical stability is demonstrated by partial oxygen substitution for sulfur; $Li_{10}GeP_2S_{1-x}O_x$. Given that the chemical bonds between Ge/P-O are stronger than those of Ge/P-S, oxygen substitution would be expected to enhance thermodynamic stability. In addition, in term of cost, ion conductors constructed by cheap and earth-abundant elements might be promising as solid electrolytes for practical application. Therefore, Li_4MS_4-Li_3PS_4 tie line is examined as following composition of $Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$, which could provide LGPS type solid solution. Finally, unexplored region in the phase diagram, deviated from the tie line, is investigated with a composition of $(Li_{3.45+\beta-4\alpha}Sn_\alpha)(Si_{0.36}Sn_{0.09})(P_{0.55-\beta}Si_\beta)S_4$.

The structures, electrochemical properties and phase relationship of obtained crystalline lithium ion conductors in in the Li-Ge-P-S-O and Li-Sn-Si-P-S systems were also investigated.

Chapter 3: For the lithium super-ionic conductor $Li_{10}GeP_2S_{12}$, the partial substitution of sulfur by oxygen is achieved *via* a solid-state reaction. The solid-solution range of oxygen is found to be $0 \leq x < 0.9$ in $Li_{10}GeP_2S_{12-x}O_x$. Structure refinements using synchrotron X-ray diffraction data confirm the preference for oxygen substitution in the PS_4 tetrahedra. The local structural change in the $P(S/O)_4$ tetrahedra upon substitution is also indicated by Raman spectroscopy. High ionic conductivities are maintained even after the oxygen substitution in $Li_{10}GeP_2S_{12}$; the ionic conductivity of $Li_{10}GeP_2S_{12-x}O_x$ ($0.3 \leq x \leq 0.6$) ranges from 1.03×10^{-2} to 8.43×10^{-3} S cm^{-1} at 298 K. No redox current is observed by cyclic voltammetry from nearly 0 to 10 V versus Li/Li$^+$ except for that due to the lithium deposition/dissolution reactions. All-solid-state batteries using $Li_{10}GeP_2S_{12-x}O_x$ (x = 0.3 and 0.6) as solid electrolytes with Li metal anodes show discharge capacities exceeding 100 mAh g^{-1} and better cycling performance compared to batteries using the original $Li_{10}GeP_2S_{12}$. The partial substitution of oxygen for sulfur in $Li_{10}GeP_2S_{12}$ affords a novel solid electrolyte, $Li_{10}GeP_2S_{12-x}O_x$, with high conductive properties and electrochemical stability.

Chapter 4: Solid solutions of Sn-Si derivatives with the LGPS-type structure were synthesized by a solid-state reaction in the Li_3PS_4-Li_4SnS_4-Li_4SiS_4 quasi-ternary system. The monophasic region of the LGPS-type structure deviated from the tie line between $Li_{10}SiP_2S_{12}$ and $Li_{10}SnP_2S_{12}$, and the composition of the solid solution was determined to be $-0.1 \leq \delta \leq 0.5$ and $0 \leq y \leq 1.0$ in $Li_{10+\delta}[Sn_ySi_{1-y}]_{1+\delta}P_{2-\delta}S_{12}$ ($0.50 \leq x \leq 0.7$ and $0 \leq y \leq 1.0$ in $Li_{4-x}[Sn_ySi_{1-y}]_{1-x}P_xS_4$). The solid solution was formed by a double substitution that changed the Sn/Si ratio and the M^{4+} (Sn^{4+} and Si^{4+})/P^{5+} ratio, which adjusted the sizes of the lithium conduction tunnels and the lithium concentration, and contributed to the optimal conductivity value. The highest ionic conductivity value of 1.1×10^{-2} S cm^{-1} was achieved for the composition of

$Li_{10.35}[Sn_{0.27}Si_{1.08}]P_{1.65}S_{12}$ ($Li_{3.45}[Sn_{0.09}Si_{0.36}]P_{0.55}S_4$) at 298 K, which is close to the value for the original LGPS compound (1.2×10^{-2} S cm^{-1}). The Ge-free solid electrolyte could be suitable for practical applications in all-solid-state batteries.

Chapter 5: Crystalline lithium ionic conductors were explored in the Li_2S-SnS_2-SiS_2-P_2S_5 system. LGPS-type phase, $Li_{3.25}Sn_{0.19}Si_{0.56}P_{0.35}S_4$, deviating conventional $Li_{4-x}M_{1-x}PS_4$ (M = Si, Ge, Sn) formula and argyrodite phases and $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ were discovered. Interestingly, the compositions of $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ far deviateed from the conventional Li_7PS_6 argyrodite, and the $Li_{3.14}[Sn_{0.74}Si]P_{0.38}S_6$ argyrodite was stable at room temperature.

Material search based on LGPS structure and the quasi-ternary phase diagram in Li_2S-MS_2-P_2S_5 system (M=Si, Sn) provided novel materials with various structure, composition and electrochemical properties. Detailed tuning of the composition, which contributes to ionic conductivity and electrochemical stability, for the developed materials is expected to achieve solid-electrolyte materials for practical use in the all-solid-state battery system.