

## Lithium ion conductive oxysulfide, $\text{Li}_3\text{PO}_4\text{--Li}_3\text{PS}_4$

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### Abstract

Ionic conductivity of  $\text{Li}_3\text{PS}_4$  was enhanced by the two ways: quenching method and addition of  $\text{Li}_3\text{PO}_4$ . The quenching method froze its high-temperature phase partially down to room temperature and increased its ionic conductivity by three times. Addition of  $\text{Li}_3\text{PO}_4$  resulted in the formation of a new metastable phase, the composition of which was considered to be around  $0.25\text{Li}_3\text{PO}_4\text{--}0.75\text{Li}_3\text{PS}_4$ . Its conductivity at room temperature was  $7.3 \times 10^{-5} \text{ S cm}^{-1}$ , which was about 100 times higher than that of  $\text{Li}_3\text{PS}_4$ .

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### 1. Introduction

Lithium ion conductive solid electrolytes attract much attention for their application to lithium batteries, because they will give a fundamental solution for the safety issue of the lithium batteries due to the flammable organic solvent used in their electrolytes. Requirements for the solid electrolytes are not only their high ionic conductivities but also their high electrochemical stabilities. These requirements had made only sulfide glasses [1–4] candidates for the application to solid state batteries for a long time. For example, although some oxide materials, e.g.,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  [5] and  $\text{La}_{0.51}\text{Li}_{0.34}\text{TiO}_{2.94}$  [6], have ionic conductivities of the order of  $10^{-3} \text{ S cm}^{-1}$ ,  $\text{Ti}^{4+}$  ions in them are easily reduced in contact with reducing anode materials to give electronic conduction. Consequently, only sulfide glasses with ionic conductivities of the order of  $10^{-3} \text{ S cm}^{-1}$  had been candidates to be used in solid state lithium batteries.

Recently, two kinds of crystalline materials have been found as alternative candidates; one is  $\text{Li}_2\text{S--GeS}_2\text{--P}_2\text{S}_5$  [7], and another is  $\text{Li}_2\text{S--P}_2\text{S}_5$  glass-ceramics [8,9]. The former is categorized into thio-LISICON family, in which many highly conductive compounds have been found [7,10–12]. The highest conductivity in the  $\text{Li}_2\text{S--GeS}_2\text{--P}_2\text{S}_5$  system was observed at a composition of  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  [7], and the other systems in the family also showed high ionic conductivities at the compositions near  $\text{Li}_3\text{PS}_4$  [12]. The composition of the highly conductive glass-ceramics was  $0.8 \text{ Li}_2\text{S--}0.2 \text{ P}_2\text{S}_5$ , the composition of which was also close to  $\text{Li}_3\text{PS}_4$ . These findings suggest that new highly conductive solid electrolytes may be found at compositions around  $\text{Li}_3\text{PS}_4$ .

$\text{Li}_3\text{PS}_4$  [13] was reported to have an ionic conductivity of  $10^{-7} \text{ S cm}^{-1}$ , and its high-temperature phase is lower in the activation energy for conduction than its low-temperature phase [14]. Therefore, stabilization of its high-temperature phase down to room temperature is expected to be a promising way to synthesize a solid electrolyte with high ionic conductivity.

Stabilization of high-temperature phase may be achieved in glass matrices. For example,  $\alpha\text{-AgI}$ , which is a high-temperature phase of  $\beta\text{-AgI}$  showing high ionic conduction,

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was frozen in a glass matrix of  $\text{Ag}_3\text{BO}_3$  [15]. In the present study,  $\text{Li}_3\text{PO}_4$ , which may act as a glass network former, was added to  $\text{Li}_3\text{PS}_4$  in order to enhance its ionic conductivity.

## 2. Experimental

Quenched (Q-)  $(1-x)\text{Li}_3\text{PS}_4-x\text{Li}_3\text{PO}_4$  was prepared from  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$ , and  $\text{Li}_3\text{PO}_4$  by a quenching method. The mixture of the starting materials was sealed in a silica tube, inside of which was coated with pyrolytic carbon, and heated at  $950^\circ\text{C}$  for 1 h. The molten mixture was quenched by putting the tube in water. Slow-cooled (SC-)  $\text{Li}_3\text{PS}_4$ , i.e.,  $x=0$ , was also prepared by a slow cooling method as a comparison. The mixture of the starting materials was heated at  $500^\circ\text{C}$  for 48 h and cooled down to room temperature at a cooling rate of  $10^\circ\text{C}/\text{h}$ .

Crystal structures of the samples were investigated by powder X-ray diffraction (XRD) and Raman spectroscopy. The sample was put into an airtight sample holder with an Al window for the XRD measurement. The XRD data were collected on an X-ray diffractometer (RAD-2B, Rigaku) using  $\text{Cu-K}\alpha$  radiation. The samples were sealed in evacuated Pyrex tubes for the Raman spectroscopy. Raman spectra were obtained in a backward microconfiguration using a 514.5 nm line from an  $\text{Ar}^+$  laser ( $\approx 0.1$  mW). The scattered light was dispersed by a subtractive triple spectrometer (T64000, Jobin-Yvon/Atago Bussan) and collected with a liquid-nitrogen-cooled charge-coupled device (CCD) detector.

Ionic conductivity was measured for a cold-pressed pellet of the sample by an ac impedance method using a frequency response analyzer (Solartron 1260). The sample was ground into powder and then pressed into a pellet with graphite electrodes attached onto its both faces. The ac impedance of the cell was measured in heating and cool processes, which were repeated twice, by applying 100mV in a frequency range from  $10^6$  Hz to  $10^{-1}$  Hz.

Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (DSC 111, Setaram). Each sample was sealed in an evacuated Pyrex tube. It was heated and cooled between  $50^\circ\text{C}$  and  $400^\circ\text{C}$  twice at heating and cooling rates of  $2^\circ/\text{min}$ . Alumina powder was used as a reference.

## 3. Results and discussion

Fig. 1(a) shows the ionic conductivities of SC- and Q- $\text{Li}_3\text{PS}_4$  as a function of reciprocal temperature. Q- $\text{Li}_3\text{PS}_4$  showed a conductivity of  $7.0 \times 10^{-6}$   $\text{S cm}^{-1}$  at  $25^\circ\text{C}$ , which was three times higher than that of SC- $\text{Li}_3\text{PS}_4$  ( $2.3 \times 10^{-6}$   $\text{S cm}^{-1}$ ). The conductivity of Q- $\text{Li}_3\text{PS}_4$  increased obeying Arrhenius law upon the heating. However, it deviated from the Arrhenius law at  $70^\circ\text{C}$  to

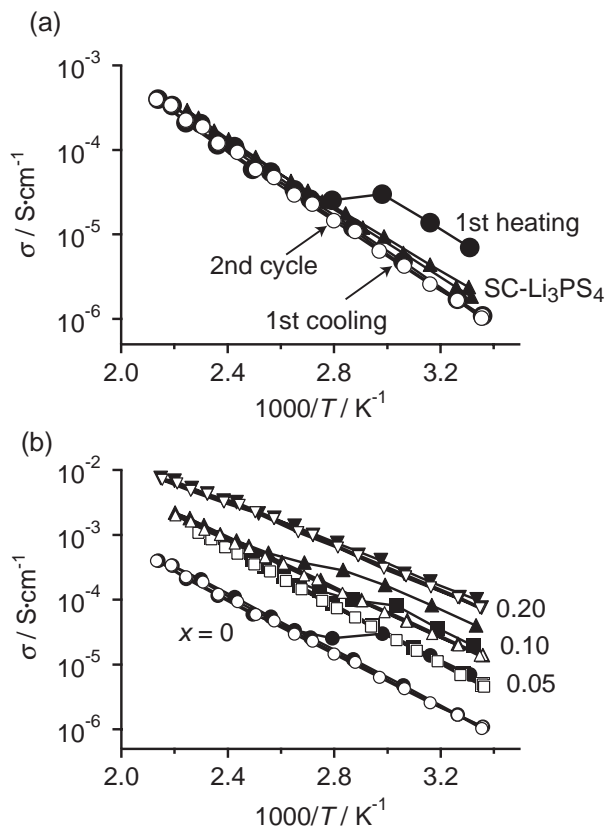


Fig. 1. Ionic conductivities ( $\sigma$ ) of the samples as a function of reciprocal temperature. Ionic conductivities of the Q- $(1-x)\text{Li}_3\text{PS}_4-x\text{Li}_3\text{PO}_4$  in the 1st and the 2nd cycles are indicated by closed and open symbols, respectively. Those of SC- $\text{Li}_3\text{PS}_4$  are by triangles. Panel (a) compares  $\sigma$  between SC- $\text{Li}_3\text{PS}_4$  and Q- $\text{Li}_3\text{PS}_4$ .  $\sigma$  for Q- $(1-x)\text{Li}_3\text{PS}_4-x\text{Li}_3\text{PO}_4$  with  $0 \leq x \leq 0.2$  are indicated in panel (b).

approach those of SC- $\text{Li}_3\text{PS}_4$ . Its conductivities in the 1st cooling process and the second cycle were also the same as those of SC- $\text{Li}_3\text{PS}_4$ . This result suggests that the high-temperature (HT-) phase, which is highly conductive, was maintained down to room temperature by the quenching method and transformed to the low-temperature (LT-) phase in the 1st heating process.

This idea was supported by the DSC curves shown in Fig. 2 and the XRD patterns in Fig. 3. The DSC curve of Q- $\text{Li}_3\text{PS}_4$  had endothermic (A) and exothermic (A) peaks at around  $310^\circ\text{C}$  and  $240^\circ\text{C}$ , respectively; which were similar to those observed for SC- $\text{Li}_3\text{PS}_4$  (see the two DSC curves on the top in Fig. 2). In addition, the enthalpy ( $\Delta H$ ) of  $54.9$   $\text{J g}^{-1}$  in the endothermic peak (A) observed for Q- $\text{Li}_3\text{PS}_4$  agreed well with that for SC- $\text{Li}_3\text{PS}_4$  ( $53.2$   $\text{J g}^{-1}$ ). However, it showed an additional exothermic peak (B) between  $150^\circ\text{C}$  and  $250^\circ\text{C}$  only in the 1st heating process, which disappeared in the 2nd cycle. These results suggested that the HT phase in Q- $\text{Li}_3\text{PS}_4$  was transformed to the LT phase during the heating, and the  $\Delta H$  in the exothermal peak B was the difference of enthalpy of formation between high- and low-temperature phases.

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