Chemical and structural changes of $70Li_2S$-$30P_2S_5$ solid electrolyte during heat treatment

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The sulfide solid electrolyte composed of $70Li_2S$-$30P_2S_5$, known as $Li_7P_3S_{11}$, is promising material for all-solid-state battery, due to its high ion conductivity. It is synthesized by ball-milling processing and obtained as amorphous phase. Through heat treatment, it crystallizes and shows high ion conductivity[1]. So, analyzing chemical structure of sulfide solid electrolyte during heat treatment is important for development of higher ion conductive material. In this study, we have investigated the chemical changes and crystallization of $70Li_2S$-$30P_2S_5$ with heat treatment, using *in situ* Raman spectroscopy, and *in situ* X-ray diffraction, *in situ* outgas analysis (TPD-MS: temperature programmed desorption MS)[2].

$70Li_2S$-$30P_2S_5$ glass sample was synthesized from a mixture of 70 mol% Li_2S (Mitsuwa Chemical Co. Ltd.) and 30 mol% P_2S_5 (Sigma-Aldrich Corp.). The mixture was milled mechanically using a planetary ball-milling apparatus (P-6; Fritsch Japan) about 30 hours at 400 rpm under Ar atmosphere.

Figure 1 shows the temperature dependence of gas generation from $70Li_2S$-$30P_2S_5$ glass sample. H_2S, deriving from impurities, was detected from around 160-220 °C, and S compounds, generating with change in the chemical structure of $70Li_2S$-$30P_2S_5$, were also detected around 220-260 °C, and the second generation maximum was around 350-400 °C. To investigate what happened during each gas generation process, Raman spectra in the temperature region 1-4 were obtained (Figure 2). The observed Raman bands are assigned to PS stretching of PS_4^{3-} and $P_2S_7^{4-}$ structure. Comparison of the spectra in the temperature region 2 (Figure 2(a)), intensity ratio of $P_2S_7^{4-}$ against PS_4^{3-} was increased, and it suggested that PS_4^{3-} anion was changed to $P_2S_7^{4-}$ anion. In the temperature region 4 (Figure 2(b)), $P_2S_6^{4-}$ anion was detected after 375 °C heat treatment. The details will be discussed in the presentation considering the data of *in situ* XRD diffraction patterns.

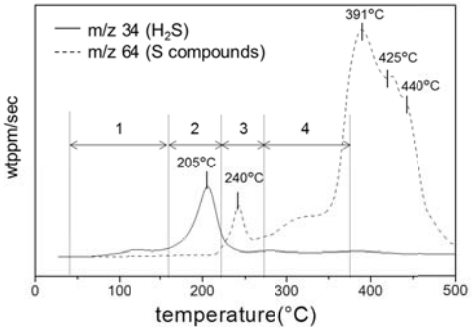

Figure 1 Gas generation from $70Li_2S$-$30P_2S_5$ glass sample during heat treatment

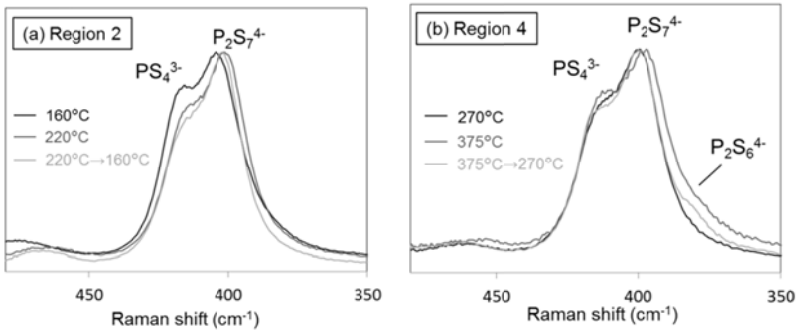

Figure 2 Raman spectra in the temperature from 160°C to 220°C (a) and from 270°C to 375°C (b)

References:

[1] F. Mizuno, A. Hayashi, K. Tadanaga, M. Tatsumisago, Adv. Mater. 17 (2005) 918-921.

[2] Y. Aoki, K. Ogawa, T. Nakagawa, Y. Hasegawa, Y. Sakiyama, T. Kojima, M. Tabuchi, Solid State Ionics, 310 (2017) 50-55