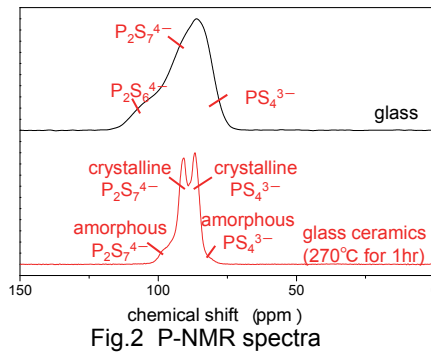
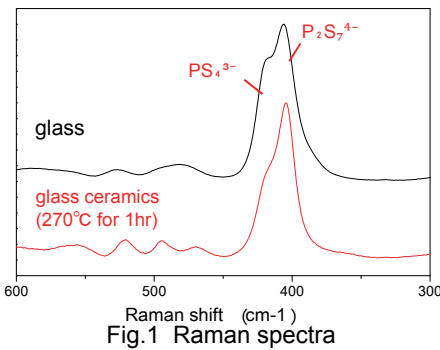


Structural analysis of sulfide solid-state electrolytes - Next-generation battery material -

Heating of sulfide solid electrolyte results in the changes of its chemical structure, crystallinity and Li-ion mobility. Raman, Solid-state NMR, Outgas analysis and XRD provide these information and are useful for developing new solid electrolytes and evaluating their performance.

Sample: $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ ($\text{Li}_2\text{S} : \text{P}_2\text{S}_5 = 70 : 30$) supplied by Dr. Tabuchi, AIST Kansai

Structural change by heat treatment



	Relaxation time T_1 (s) of ^7Li
Glass	11.2
Glass ceramics	3.7

Table 1. Relaxation time of ^7Li (by NMR)

- Change in Raman and P-NMR spectral shapes => Increase in crystallinity by heat treatment
- Decrease in T_1 of lithium => Increase in mobility of Li ions

It is crucial to know changes in chemical and crystalline structures with heat treatment for understanding the relation between ion conductivity and chemical structures.

Structural change during heat treatment

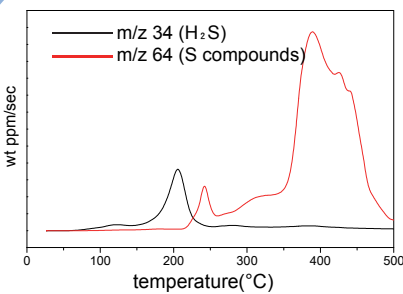


Fig.3 Outgas with rising temperature

Outgas and Raman spectral change during heating:

- Outgas analysis showed that sulfur was generated above 200°C.
- Raman analysis also showed a band of sulfur.

=> Sulfur desorption started at about 200°C in the heat treatment process.

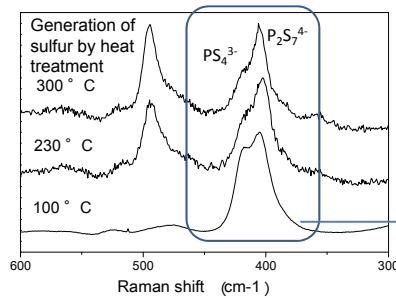


Fig.4 Raman spectral change with rising temperature

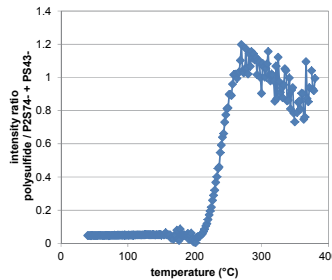


Fig.5 Relative intensity of polysulfide against $\text{P}_2\text{S}_7^{4-}$ and PS_4^{3-}

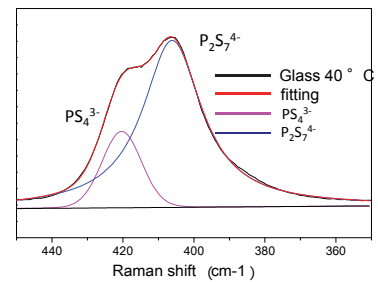


Fig.6 Peak separation of Raman bands

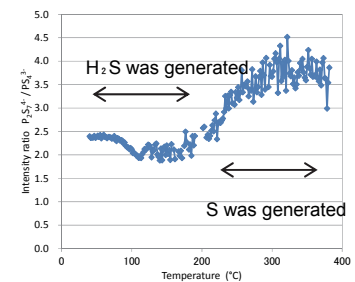
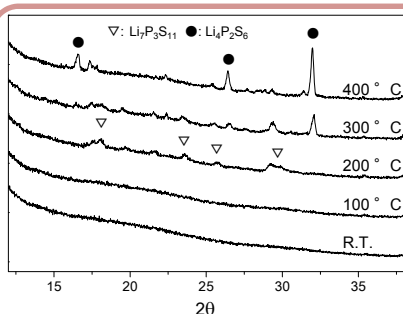


Fig.7 Relative intensity of $\text{P}_2\text{S}_7^{4-} / \text{PS}_4^{3-}$

- Change in Intensity ratio of $\text{P}_2\text{S}_7^{4-} / \text{PS}_4^{3-}$ => Content ratio of $\text{P}_2\text{S}_7^{4-}$ slightly tended to decrease under 200°C. Content ratio of PS_4^{3-} decreased above 200°C.



High temperature in situ XRD measurements

- $\text{Li}_7\text{P}_3\text{S}_{11}$ component started crystallization about 200°C.
 - $\text{Li}_4\text{P}_2\text{S}_6$ component started crystallization about 400°C.
- => Change in the structure of $\text{P}_2\text{S}_7^{4-}$, generation of structure of $\text{P}_2\text{S}_6^{4-}$ and its progress in crystallization with rising temperature were suggested.

- Structural analysis such as NMR, Raman and XRD
- Outgas analysis

- => reveal chemical structural changes and crystallization behavior induced by heat treatment,
- => useful for optimizing preparation conditions of solid electrolyte and examining possible correlation between those changes and ion conductivity.