

Local-structure Analysis of Li Oxy-sulfide Glass-Ceramic Solid Electrolytes

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In the global quest to tackle climate change and the promotion of sustainable energy sources, energy storage has become an important aspect and consequently has attracted great research attention. Solid state batteries promise increased energy density and safety in comparison to current commercial Li-ion batteries[1]. Fast ion conducting solid electrolyte materials are an essential part of solid-state batteries. Therefore, the study of suitable materials and the understanding of the conduction mechanisms is of high importance.

Sulfide and thiophosphate glasses have been identified as promising candidates as fast ion conducting materials and great progress has been made since the first studies in 1980[2]. One drawback of these materials is their sensitivity against humidity and stability on exposure to air. Recently, it was demonstrated that the doping of thiophosphate glasses with oxygen positively affects the ion conductivity[2]. Furthermore, an improvement of the chemical and physical stability of these doped glasses could be achieved. The combination of these two

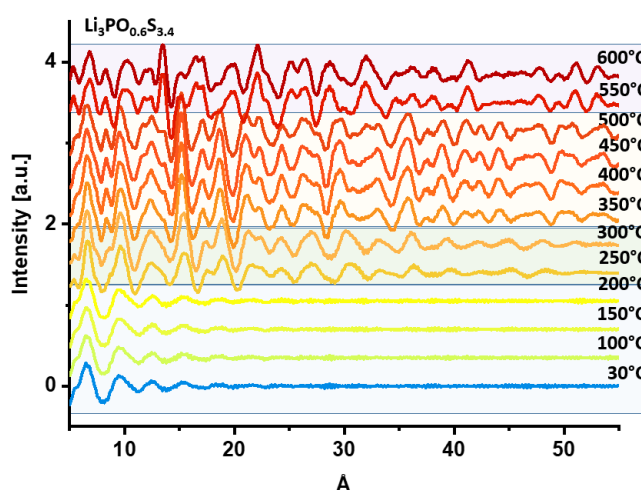


Fig. 1: PDF analysis of Oxy-sulfide glass ceramic

effects renders oxygen doping a promising strategy. However, very little is known so far about the local structure of the doped glasses and glass ceramics, yet this information is crucial to enable purposeful development and further improvement of these materials.

Hence, we have studied the local structure of oxy-sulfide glasses as well as their structural evolution and crystallization behavior with increasing temperature. Additionally, the influence of the starting materials was evaluated by comparing materials from two different set of starting materials using the same synthesis route. Oxy-sulfide glasses of the composition $\text{Li}_3\text{PO}_x\text{S}_{4-x}$ with $0 \leq x \leq 1.2$ were synthesized by ball milling appropriate amounts of either Li_2O , Li_2S and P_2S_5 , or Li_3PS_4 and Li_3PO_4 . Temperature dependent powder x-ray diffraction and pair distribution function (PDF) analysis, supported by Raman spectroscopy and other characterization techniques, was then used to identify crystal phases and structural moieties. Subsequently, impedance measurements were carried out to be able to link microstructure to ionic conductivity.

[1] Tan, D.H.S., Banerjee, A., Chen, Z. et al. From nanoscale interface characterization to sustainable energy storage using all-solid-state batteries. *Nat. Nanotechnol.* 15, 170–180 (2020). <https://doi.org/10.1038/s41565-020-0657-x>

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