Experimental report

19/09/2024

Proposal: 5-24-723 **Council:** 4/2023

Title: Understanding the influence of theanionic charge distribution on thelithium substructure in the Li6PSe5Br1-xIx substitution series

Research area: Materials

This proposal is a new proposal

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Samples: Li6PSe5Br
Li6PSe5Br0.6I0.4
Li6PSe5Br0.2I0.8
Li6PSe5Br0.8I0.2
Li6PSe5I
Li6PSe5Br0.4I0.6

Instrument	Requested days	Allocated days	From	To
D2B	3	3	22/09/2023	25/09/2023

Abstract:

Highly conducting solid electrolytes are needed to sufficiently replace liquid electrolytes in lithium-ion batteries. Sulfide argyrodites of the type Li6PCh5X (Ch = S, Se; X = Cl, Br, I) show promising conductivity values in the mScm¿1 range. The site disorder of the Ch2¿/X¿ lattice site has an influence on the conductivity and is tunable by the choice of the anion. The substitution from Br¿ to I¿ in the series Li6PSe5Br1¿xIx can further shed light on structure ¿ conductivity relations and help to understand the interplay of anion host framework and lithium diffusion.

Experimental Report on ILL Proposal 5-24-723

Understanding the influence of the anionic charge distribution on the lithium substructure in the $Li_{5.5}PSe_xS_{4.5-x}Cl_{1.5}$ substitution series

Due to problems with the initially planned samples, we measured the substitution series of $Li_{5.5}PSe_xS_{4.5-x}Cl_{1.5}$ ($0 \leq x \leq 2.5$, 0.5 steps) which perfectly fitted in the proposed time. This material is a lithium argyrodite, which belongs to a class of solid-state electrolytes that have the potential for the high ionic conductivities required for the use in solid state batteries. Previous powder neutron diffraction experiments of our group analysed the substitution series of $Li_6PSe_xS_{5-x}Cl$ and is the fundament of the new substitution series. The strong increase of ionic conductivity when going from Li_6PS_5Cl to $Li_{5.5}PS_{4.5}Cl_{1.5}$ is one of the reasons why these compounds are from great interest.[1] The goal of this study is to investigate the lithium substructure and the Ch^{2-}/X^- (*Ch* = S, Se; *X* = Cl) site disorder, since that is known to be one of the driving forces of fast lithium conduction.[1]

1. Experimental details

The substitution series was made by mixing the stoichiometric amount of LiCl, Li_2S, P_2S_5, Se and S and annealing them at 450 °C in a sealed quartz ampoules.[2] The hand ground samples were measured with powder neutron diffraction to determine the lithium substructure and the Ch^{2-}/X^- (*Ch* = S, Se; *X* = Cl) site disorder. The room temperature neutron powder diffraction data were collected on the D2B powder diffractometer with monochromatic neutron wavelength λ = 1.594 Å.

2. Results

Figure 1a shows the stacked neutron diffraction patterns of the $Li_{5.5}PSe_xS_{4.5-x}Cl_{1.5}$ substitution series. The TOPAS-software was used to perform Rietveld refinements to analyse the obtained neutron data and gain information about the Li^+ substructure in the substitution series that can be correlated to the transport. Caused by the increased anionic radius of selenium, the limit of selenium in the structure is around *x* = 2.5 (Figure 1a), and supports the X-ray diffraction results. Our preliminary results show a linear increase of the lattice parameter (Figure 1b) and indicates a successful infiltration.

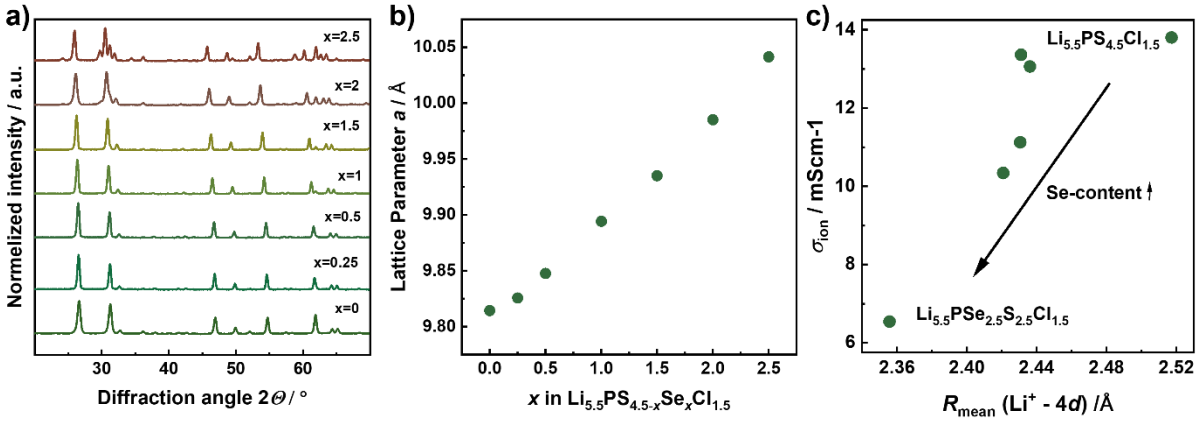

Figure 1: a) Neutron diffraction patterns of the investigated series $Li_{5.5}PSe_xS_{4.5-x}Cl_{1.5}$. Trends in b) lattice parameter and c) correlation between the room temperature ionic conductivity and the mean radius of lithium around the Wyckoff 4d position.

An overall trend in correlation between the room temperature ionic conductivity and the mean radius of the lithium Wyckoff 4*d* position (Li^+ "cages") was gained from the neutron refinement (Figure 1b) and also fits with previous results of our group.[3] It seems by adding selenium into the structure the

Li^+ "cages" are shrinking and therefore worsen the ionic conductivity. Further analyses of the lithium substructure and the anion Ch^{2-}/X^- (*Ch* = S, Se; *X* = Cl) site disorder is still work in progress.

3. Conclusion

Tuning the lithium substructure is one key to improve ion conduction in solid electrolytes as we show with our preliminary results for the substitution series XY. The decrease of R_{mean} within the Li^+ cages in the Li^+ substructure helps to understand the decreasing ionic conductivity along the substitution series. An in-depth analysis of the Ch^{2-}/X^- (*Ch* = S, Se; *X* = Cl) positions and occupancies may support the results and therefore allow us to improve solid state batteries.

4. References

[1] A. Gautam, M. Ghidiu, E. Suard, M. A. Kraft, W. G. Zeier, *ACS Appl. Energy Mater.* **2021**, *4*, 7309–7315.

[2] S. Ohno, T. Bernges, J. Buchheim, M. Duchardt, A.-K. Hatz, M. A. Kraft, H. Kwak, A. L. Santhosha, Z. Liu, N. Minafra, F. Tsuji, A. Sakuda, R. Schlem, S. Xiong, Z. Zhang, P. Adelhelm, H. Chen, A. Hayashi, Y. S. Jung, B. V. Lotsch, B. Roling, N. M. Vargas-Barbosa, W. G. Zeier, *ACS Energy Lett.* **2020**, *5*, 910–915.

[3] A. Gautam, M. Sadowski, M. Ghidiu, N. Minafra, A. Senyshyn, K. Albe, W. G. Zeier, *Adv. Energy Mater.* **2021**, *11*, DOI 10.1002/aenm.202003369.

5. Publications resulting from this work

P. Heuer *et al*. A comparative study of Cl-poor and Cl-rich argyrodite substitution series. Manuscript in preparation.