



Experiment title:
Structural investigations on the Na⁺ superionic conductor
Na₁₁Sn₂PS₁₂ and its derivatives

Experiment number:
CH-5582

Beamline:
BM31

Date of experiment:
from: 21.11.2018 to: 26.11.2018

Date of report:
04.04.2019

Shifts:
15

Local contact(s):
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Received at ESRF:

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Report:

Highly conductive solid electrolytes are a key component for the design of safe and high-power all-solid-state batteries. Until now, mainly lithium based solid electrolytes have been developed with impressive results: the ion conductivities of some of these systems^[1] reach those of liquid electrolytes used in commercial Li⁺ ion batteries. However, the future availability and the price of lithium are points of concern, so that Na⁺ ion conductors have come into the spotlight in recent years.

In this respect, we were able to synthesize and characterize the superionic conductor Na₁₁Sn₂PS₁₂ consisting exclusively of abundant elements and exhibiting a room temperature Na⁺ ion conductivity close to 4 mS/cm, the highest value known to date for sulfide-based solids.^[2] Its structure (**Figure 1**) is comprised of OD-tetrahedra of both [SnS₄]⁴⁻ and [PS₄]³⁻ complexly twisted against each other. This gives rise to a rather large pseudo-cubic unit cell with a ratio of lattice parameters of $c/a \approx 2$ leading to a strong overlap of reflections. Almost simultaneously, the same material was presented by two other groups independently, reflecting the high competition in this field of materials research.^[3,4]

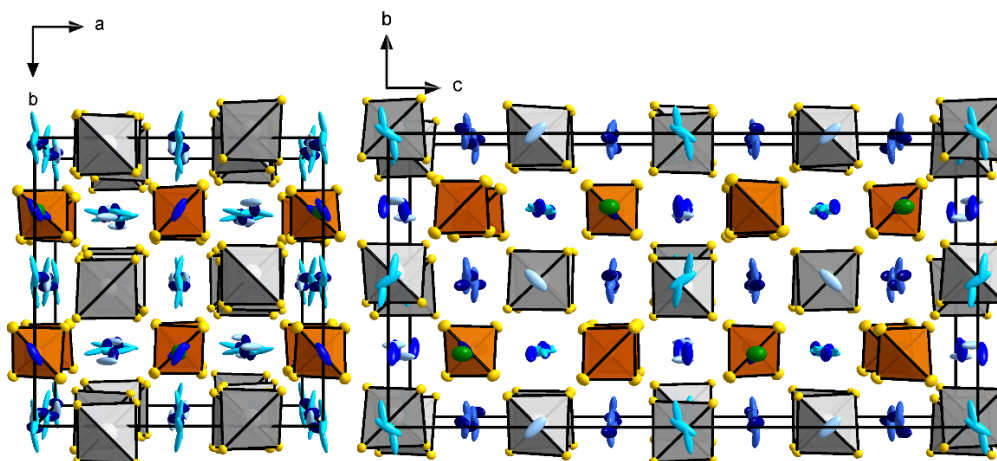


Figure 1: Projections of the crystal structure of Na₁₁Sn₂PS₁₂ (NaSnPS) along [001] (left) and [100] (right). Sn atoms and [SnS₄]⁴⁻ tetrahedra are drawn in gray, P atoms and [PS₄]³⁻ tetrahedra in orange, S atoms in yellow, and Na⁺ cations in different shades of blue and green to differentiate between six crystallographically distinct sites.

Results:

Following up on these initial reports, several substitutions proved possible: S by Se^[5] and P by As^[6] or Sb.^[7,8] Whereas the conductivity in all these compounds slightly decreased upon substitution, the structure was retained for all of them ($I4_1/acd$, $Z = 8$). It is furthermore possible to synthesize complete solid solution series $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ with $\text{Pn} = \text{P}, \text{As}, \text{Sb}$ and $\text{Na}_{11}\text{Sn}_2\text{PCh}_{12}$ with $\text{Ch} = \text{S}, \text{Se}$. The diffractograms of the solid solution of $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ with $\text{Pn} = \text{P}, \text{As}, \text{Sb}$ measured during our experiment CH-5582 are exemplarily shown in **Figure 2**. Investigations of the ionic conductivities of the depicted members are still ongoing. Together with the results of complementary single crystal diffraction experiments the data obtained at BM 31 is intended to be published in the near future.

Furthermore, we carried out temperature-dependent diffraction experiments on $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ and its As-analog $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$. For both compounds we observed (**Figure 3A,B**) a distinct phase transition starting at approx. 300 and 450 °C, respectively leading to a highly symmetric (and in both cases very similar) HT-phase. This phase was indexed by assuming $Fm\bar{3}m$ symmetry with a very small lattice parameter of $a = 3.56$ Å at 450 °C for $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$. Surprisingly, the arsenic-substituted counterpart led to virtually the same unit cell with $a = 3.56$ Å, however determined at the even higher temperature of 550 °C. The comparison with possible binary or ternary decomposition products like Na_2S or Na_3PS_4 proved unsuccessful. Due to time limitations the reversibility was only rudimentarily tested. But in case of $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ (**Figure 3B**) the reappearance of the initial tetragonal structure was confirmed. This is in line with expectations, since the tetragonal structure appeared to be highly reproducible in all our syntheses.

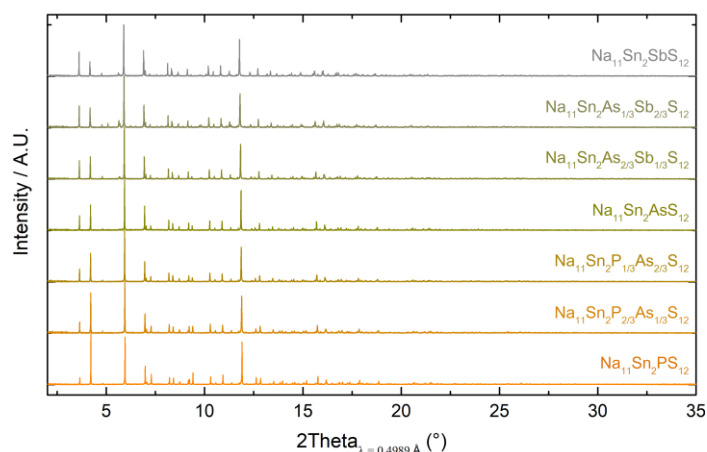


Figure 2: Stacked X-ray diffraction patterns of $\text{Na}_{11}\text{Sn}_2\text{PnS}_{12}$ with $\text{Pn} = \text{P}, \text{As}, \text{Sb}$ collected at beamline BM 31 (Swiss-Norwegian Beamline) at the ESRF in Grenoble/France ($\lambda = 0.49890$ Å).

The patterns of the new phase closely resemble the XRPD pattern of elemental Ni or alloys (for example with Fe) thereof. In order to verify these results, the experiment was repeated with our in-house X-ray diffractometer over the same temperature range. However, although the quality of the diffractograms was fairly modest, it could clearly be concluded that the initial phase surprisingly did not undergo any phase change. As a complementary technique we used DSC measurements of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ up to 550 °C (**Figure 4A**) to uncover this phase change. Unexpectedly, we detected only a very small signal at ca. 175 °C, which is in contrast to our observations depicted in **Figure 3A**. It is also in contradiction to an article^[9] reporting a DSC measurement of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ (**Figure 4B**) with a pronounced signal corresponding to a phase transition at essentially the same temperature (290 °C), at which we observed the phase change in our synchrotron powder diffraction experiments (SXRPD, **Figure 3B**). The reasons for these distinct differences and contradictions are not clear at the moment.

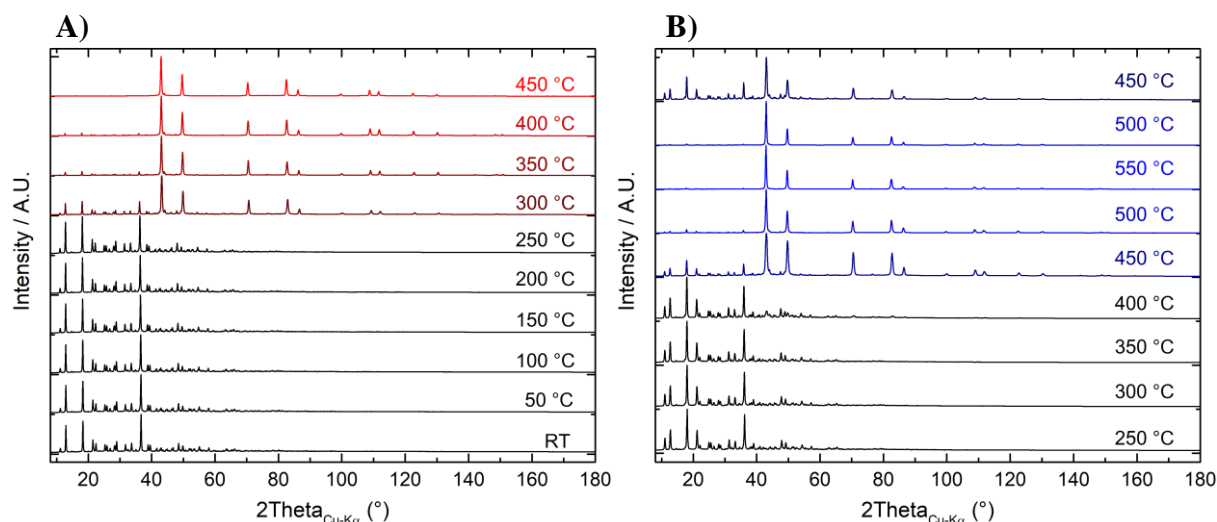


Figure 3: Stacked temperature-dependent X-ray diffraction patterns collected at beamline BM 31 (Swiss-Norwegian Beamline) at the ESRF in Grenoble/France. **A:** phase-evolution starting from tetragonal $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ (**black**) and subsequent formation of a new cubic phase (**red**) ($\lambda = 0.31670 \text{ \AA}$). **B:** phase-evolution starting from tetragonal $\text{Na}_{11}\text{Sn}_2\text{AsS}_{12}$ (**black**) and subsequent formation of a new cubic phase (**blue**) ($\lambda = 0.31694 \text{ \AA}$). All data were transformed to the $\text{Cu-K}\alpha$ wavelength.

These results are still mysterious, but an influence of the specific set-up of the synchrotron experiments on the observed effects can largely be excluded. Thus, based on our observations from SXRPD and complementary DSC experiments from literature^[9] we strongly believe that there is an interesting effect, which might depend upon the specific preparation of the samples under investigation. Further work to clarify the observed phenomena is under way.

References

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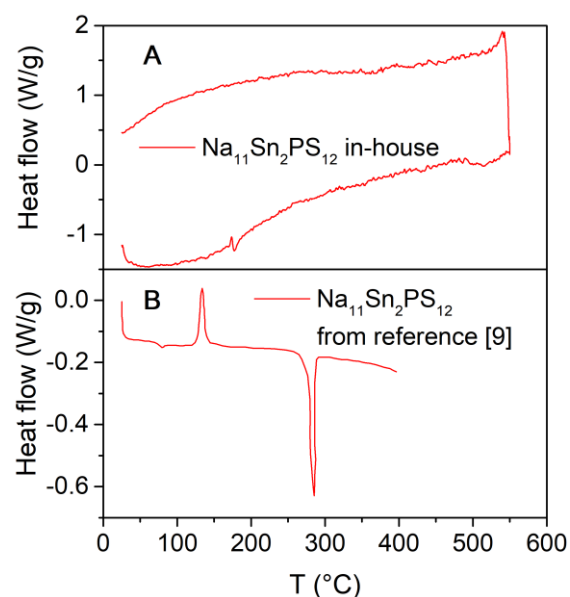


Figure 4: DSC curves; **A:** $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ measured in-house with only a minor feature around $175 \text{ }^\circ\text{C}$ and **B:** $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ adopted from reference [9] with pronounced signals at $140 \text{ }^\circ\text{C}$ and most importantly at $290 \text{ }^\circ\text{C}$.