



HAL
open science

Structure evolution of sodium thiophosphate electrolytes as function of the temperature

Sergio Mayer, Marta Mirolo, Alisson A. Iles Velez, Ove Korjus, Emmanuelle Suard, Lauréline Lecarme, Jean-Baptiste Ducros, Claire Villevieille

► To cite this version:

Sergio Mayer, Marta Mirolo, Alisson A. Iles Velez, Ove Korjus, Emmanuelle Suard, et al.. Structure evolution of sodium thiophosphate electrolytes as function of the temperature. 75th Annual Meeting of the International Society of Electrochemistry, Aug 2024, Montreal, Canada. , 2024. cea-04706851

HAL Id: cea-04706851

<https://cea.hal.science/cea-04706851v1>

Submitted on 23 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Structure Evolution of Sodium Thiophosphate Electrolytes as Function of the Temperature

S.F. Mayer^{1,2}, M. Miroló³, A.A. Iles Velez³, O. Korjus⁴, E. Suard⁴, L. Lecarme¹, J.B. Ducros², C. Villevieille¹

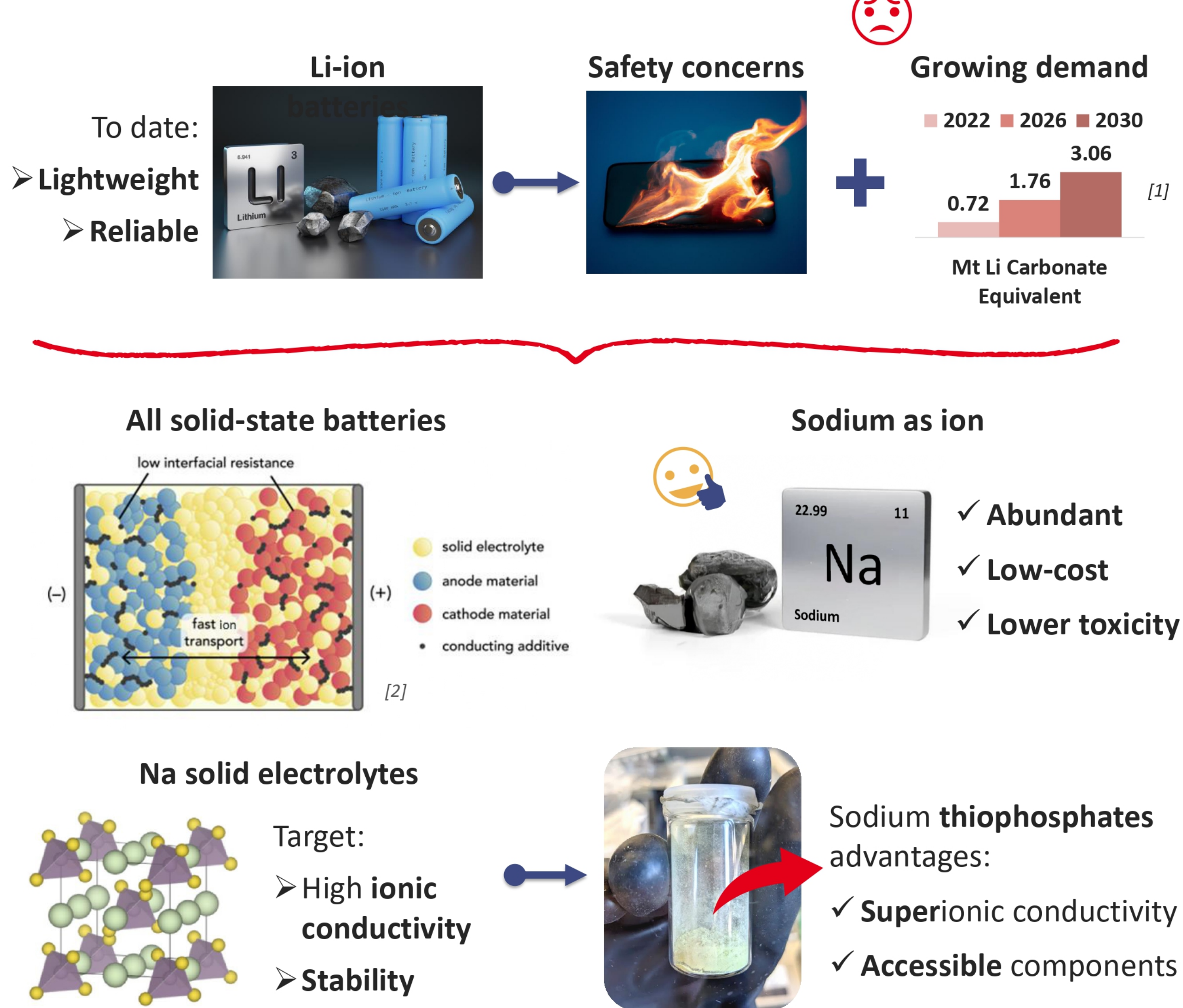
¹ Univ. Grenoble Alpes, LEPMI, Grenoble INP, CNRS, 38000 Grenoble France

³ European Synchrotron Radiation Facility, 38000 Grenoble, France

² Univ. Grenoble Alpes, CEA, Liten, DEHT, 38000 Grenoble, France

⁴ Inst. Laue Langevin, 38000 Grenoble, France

Introduction

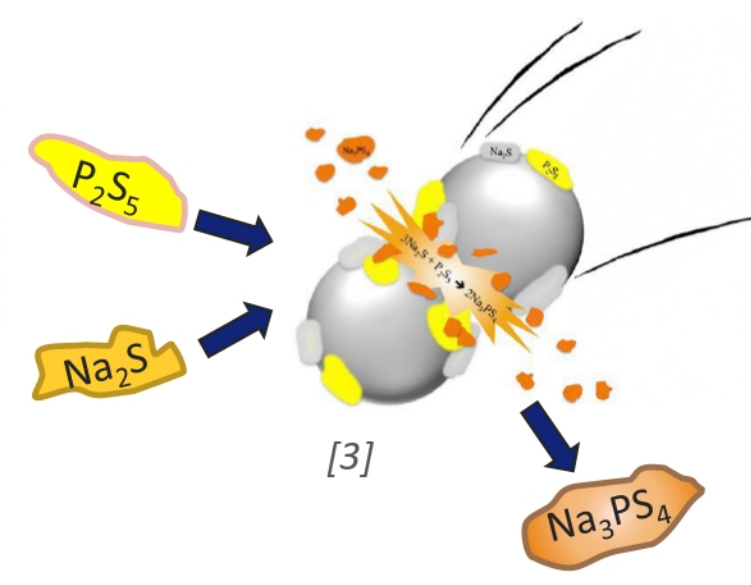


Methodology

Ball milling synthesis

Mechanochemical synthesis conditions:

- ZrO₂ jar + balls



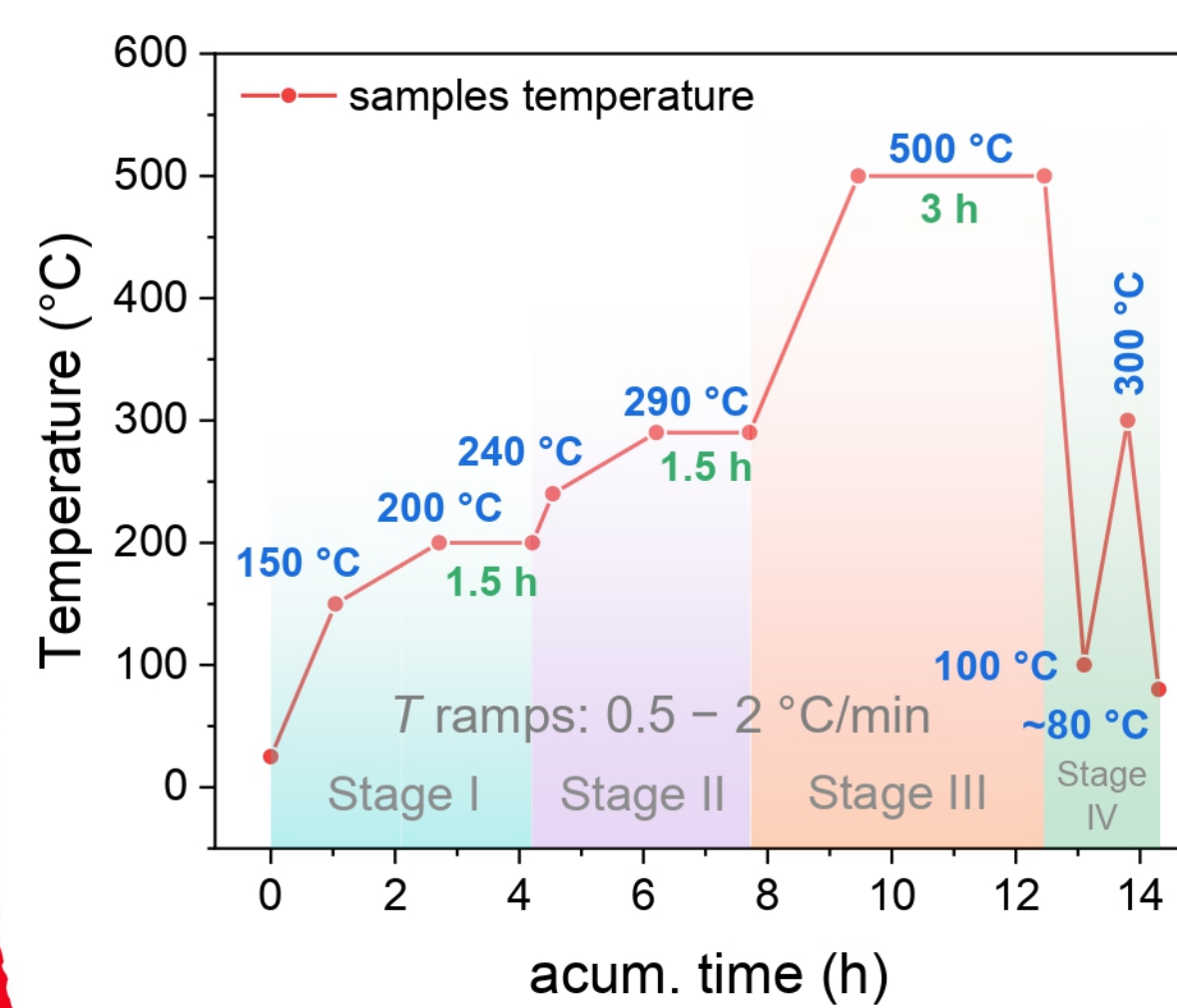
Amorphous Na₃PS₄ (am-NPS)

- Rotation speed: 510 rpm
- Balls: 35 g × Ø5 mm
- Milling time: 24 h

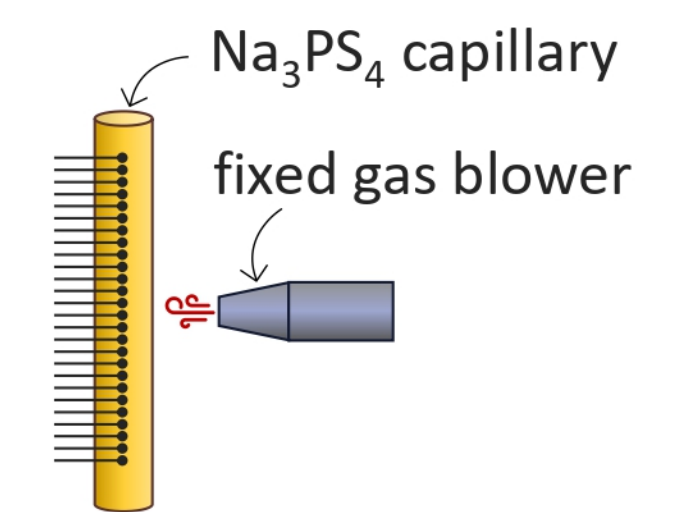
Semi-crystalline Na₃PS₄ (sc-NPS)

- Rotation speed: 600 rpm
- Balls: 35 g × Ø10 mm
- Milling time: 10 h

Heat treatment and X-ray diffraction



- Gas blower at fixed position
- 25 diffractograms near the heating region
- Optimal selection of the hot spot



- Data collection looped in time (hence in temperature)

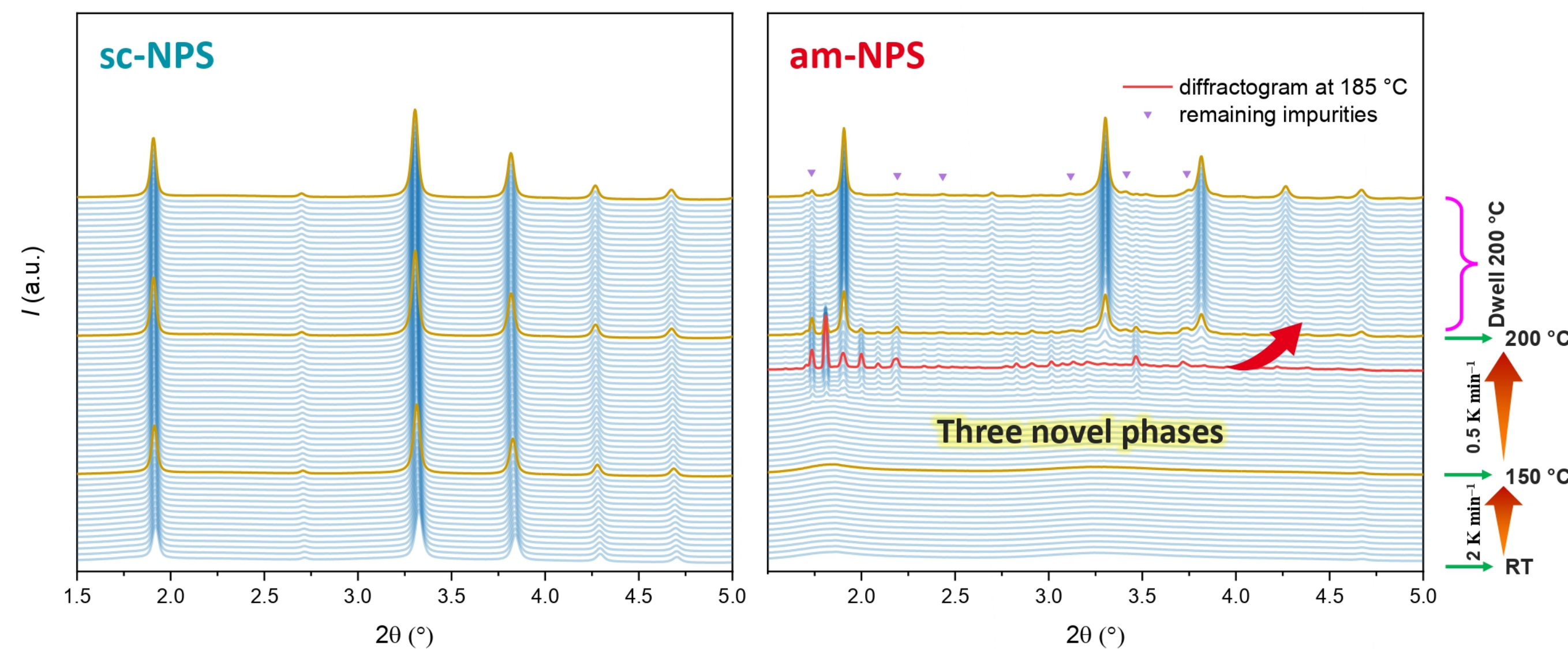
- Identification of crystallization temperatures and kinetics

Results and discussion

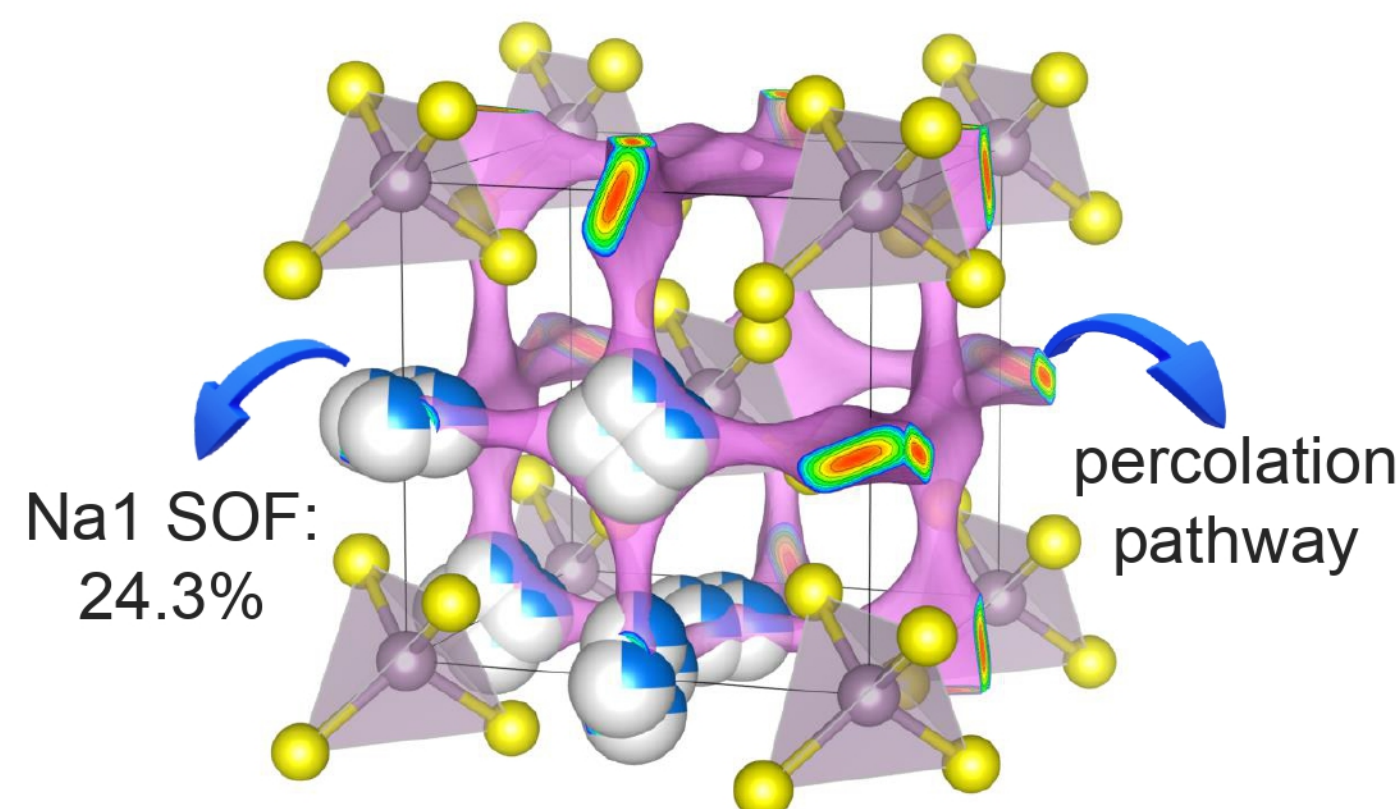
Crystallization process

RT → 200 °C

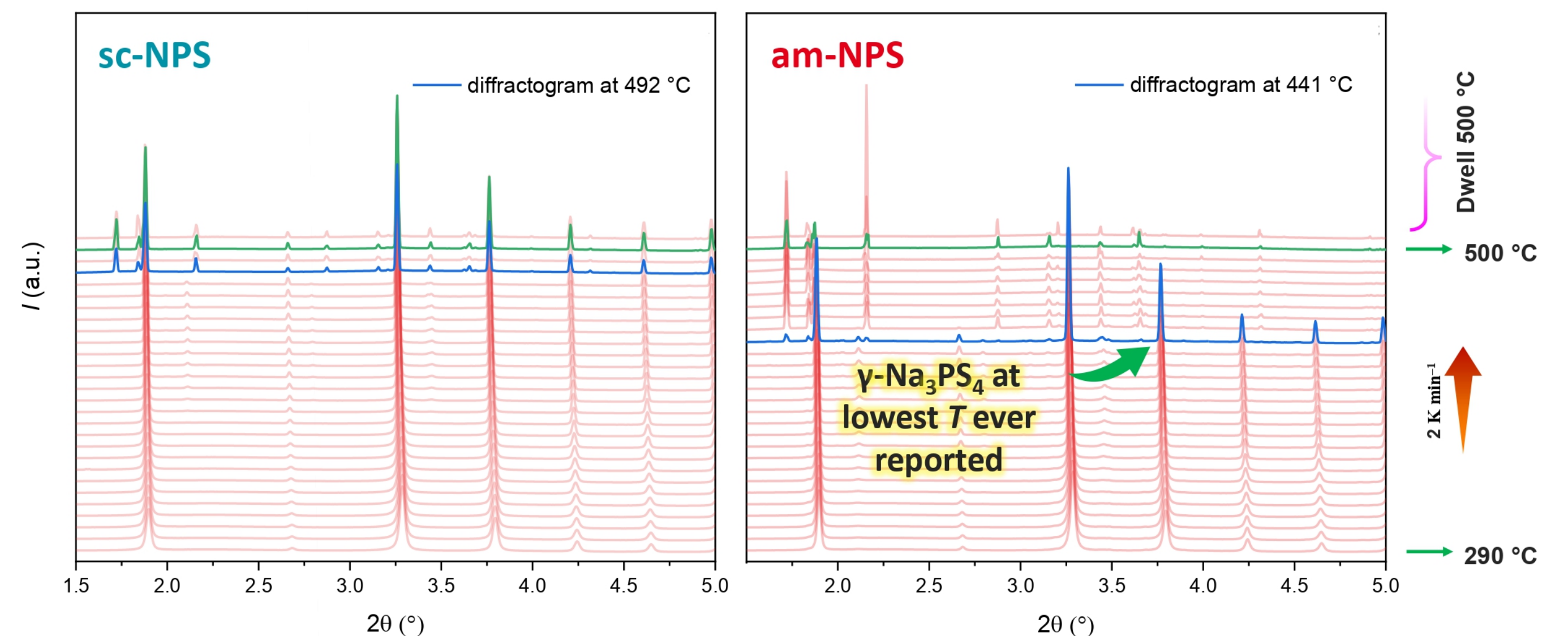
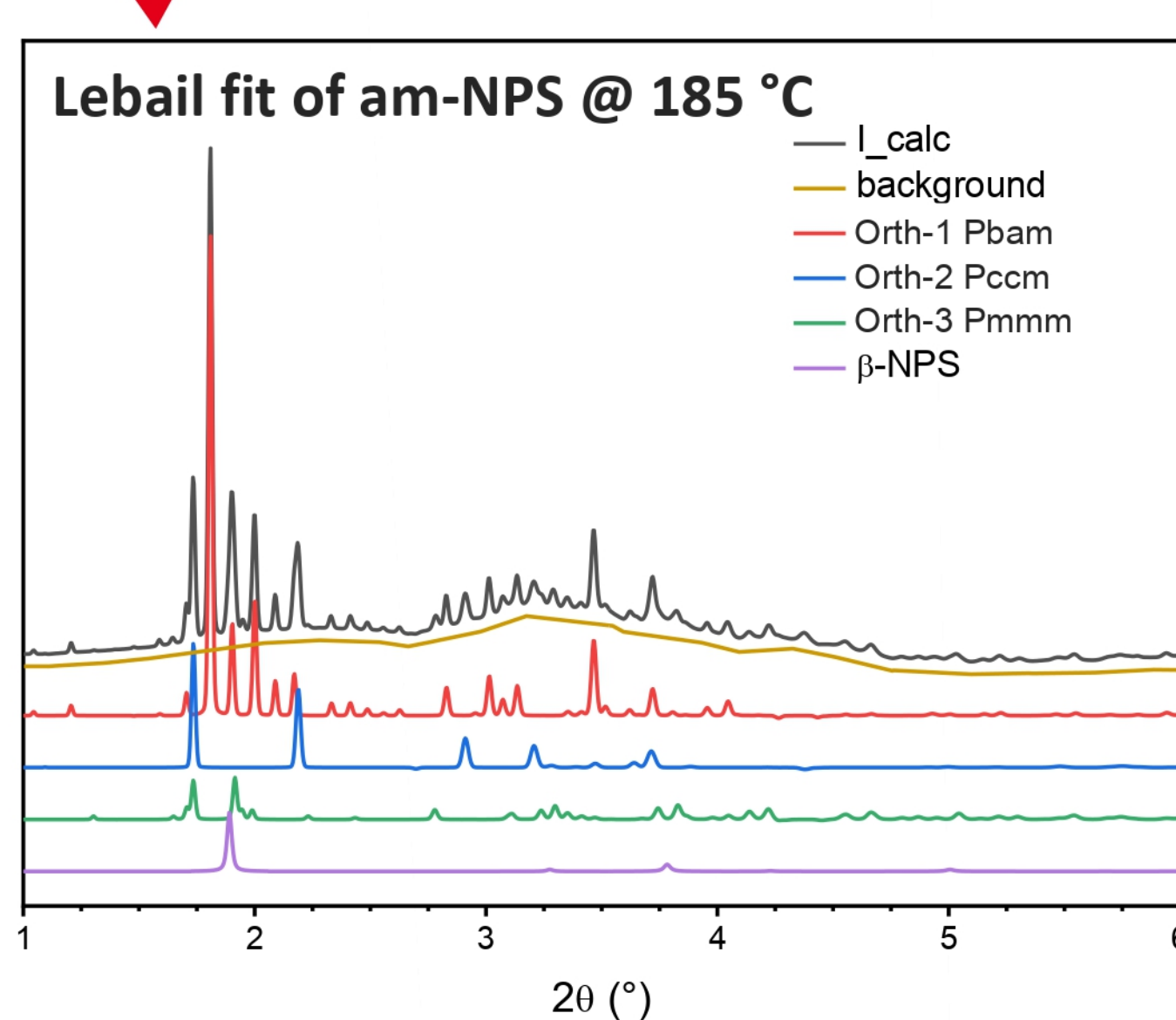
290 °C → 500 °C



The am-NPS presents the formation of the three novel orthorhombic phases at 185 °C

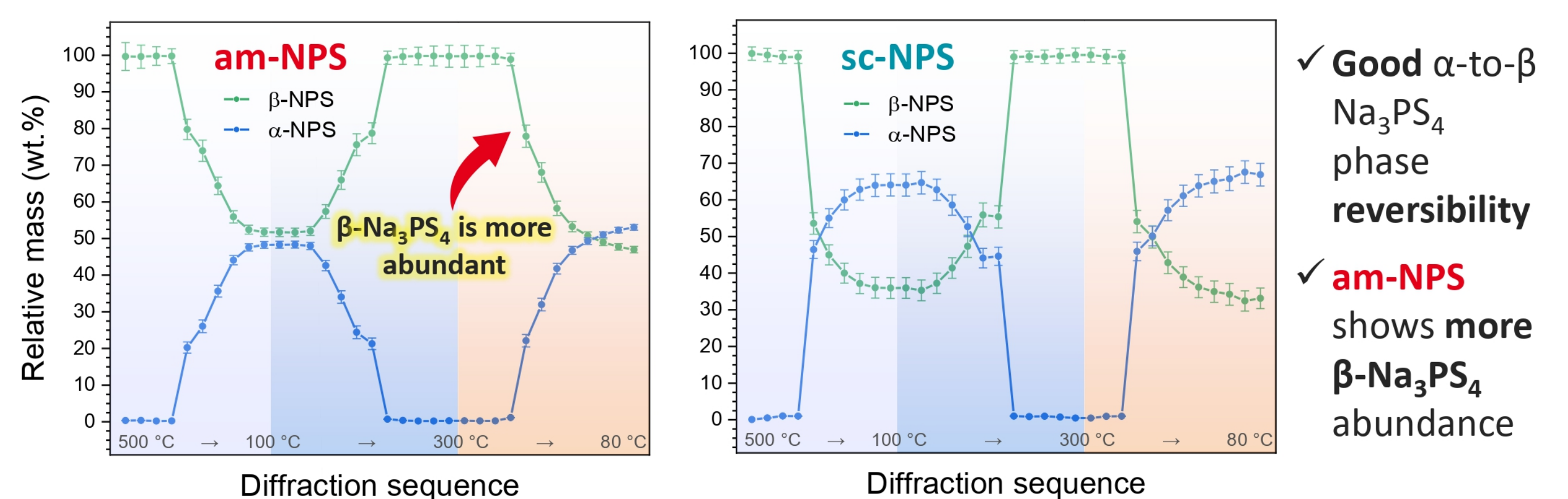


Structure of pristine sc-NPS from NPD and SXRD data refinement

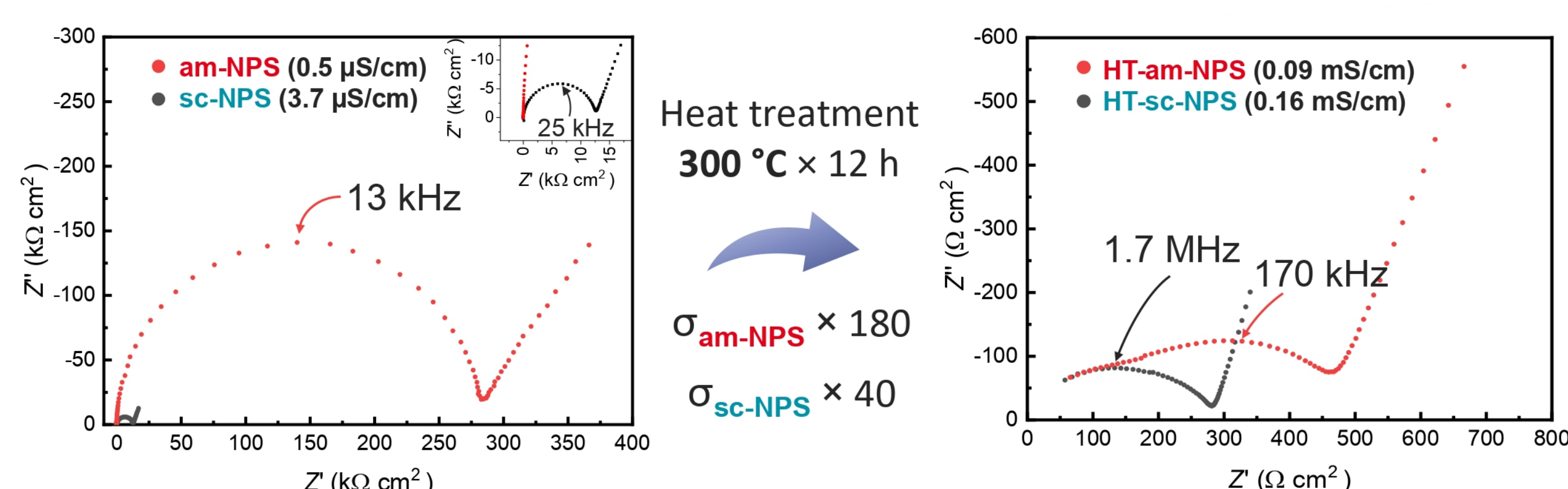


Blue curves → γ-Na₃PS₄ peaks appear. The β-to-γ phase transition is only complete for am-NPS, while sc-NPS exhibits β-Na₃PS₄ even after a 3 h plateau at 500 °C

Reversibility of α-to-β Na₃PS₄ phase transition



Evolution in ionic conductivity



Conclusions

- The ball milling conditions strongly affect the crystallinity of the pristine product
- The crystallinity of the samples impacts on the reaction pathway
- The heat treatment is essential to obtain high ionic conductivities

Perspectives

- Dope Na₃PS₄ with aliovalent elements (W, Mo, etc.) and compare with these results
- Try other ball milling conditions, e.g. in liquid

References

- 1 <https://www.mckinsey.com/featured-insights/sustainable-inclusive-growth/chart-of-the-day/plugging-in-to-the-lithium-market>
- 2 Nolan, A.M., Zhu, Y., He, X., Bai, Q., Mo, Y. Joule 2018, 2, 2016
- 3 Nguyen, H., Banerjee, A., Wang, X., Tan, D., Wu, E.A., Doux, J.M., Stephens, R., Verbit, G., Meng, Y.S. J. Power Sources 2019, 435, 126623