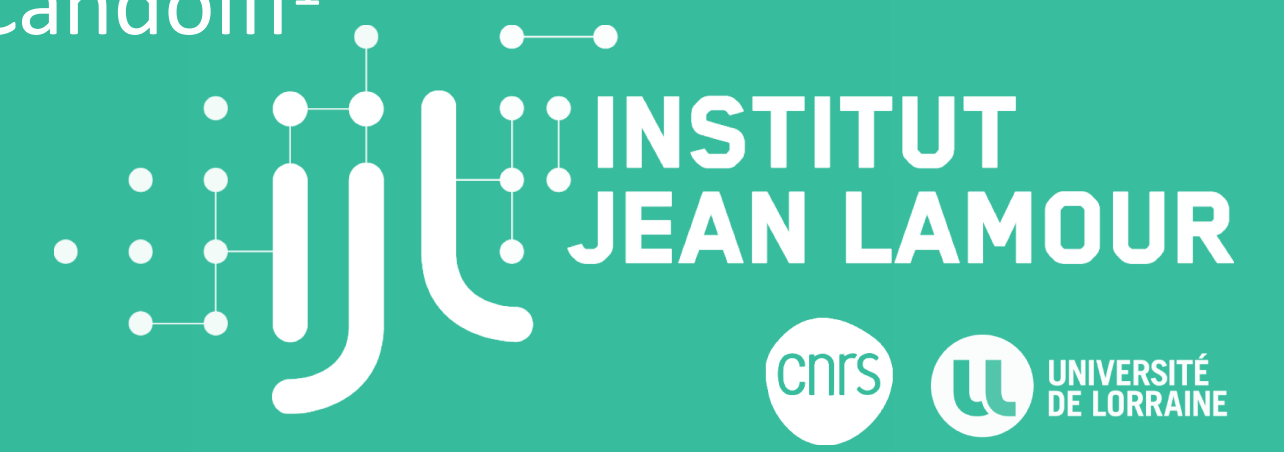


# Lattice Symmetry as a Key Factor Governing the Thermoelectric Properties of $\text{Cu}_2\text{SnSe}_3$ -based Compounds

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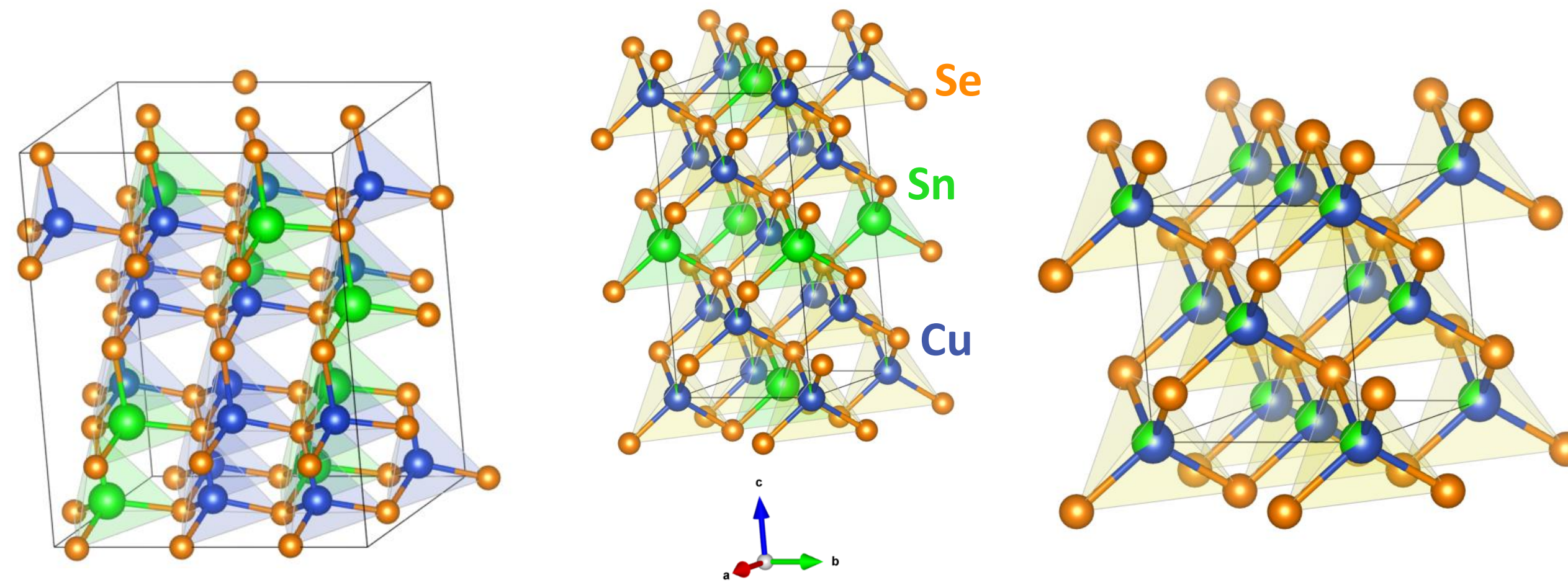
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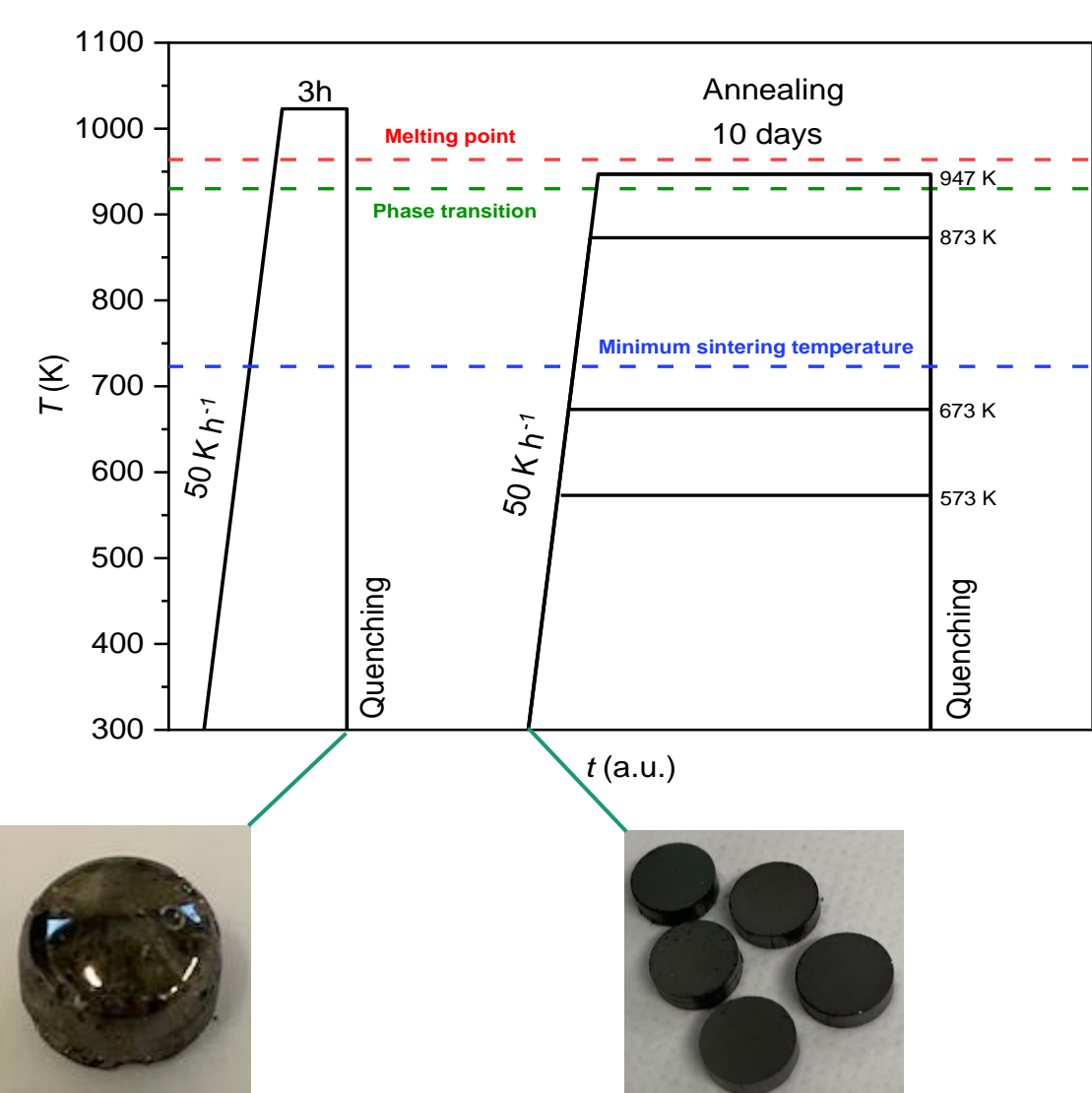
## Introduction

- Low  $\kappa_L$
- 3D hole-like conductive network
- Tunable transport properties
  - Polymorphic material
- Enhanced  $m_{\text{DOS}}^* = N_V^{2/3} m_b^*$  values for high symmetry structures



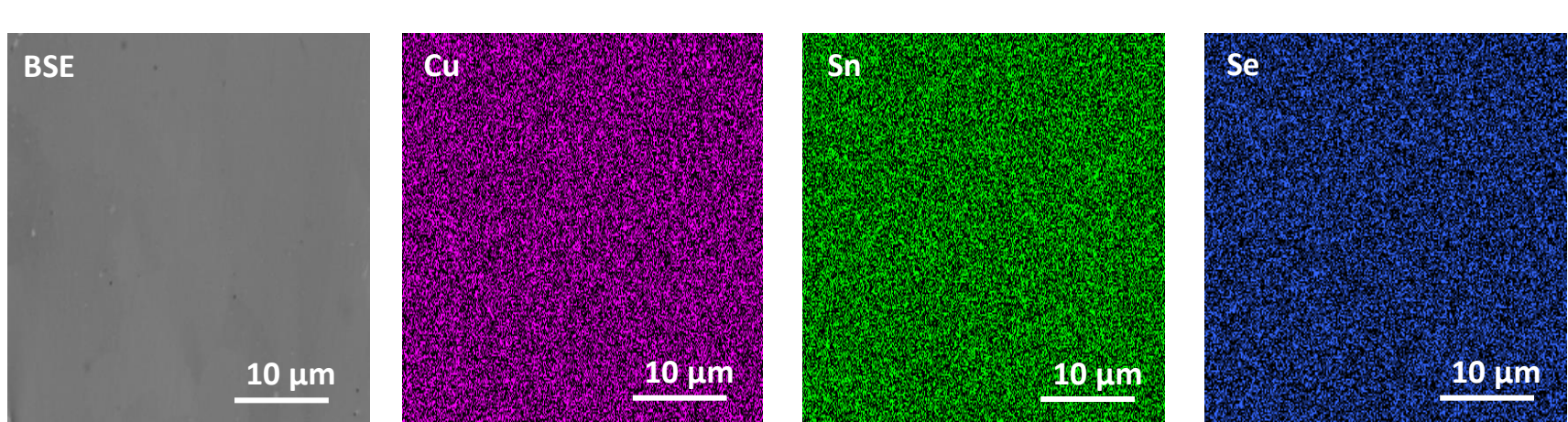
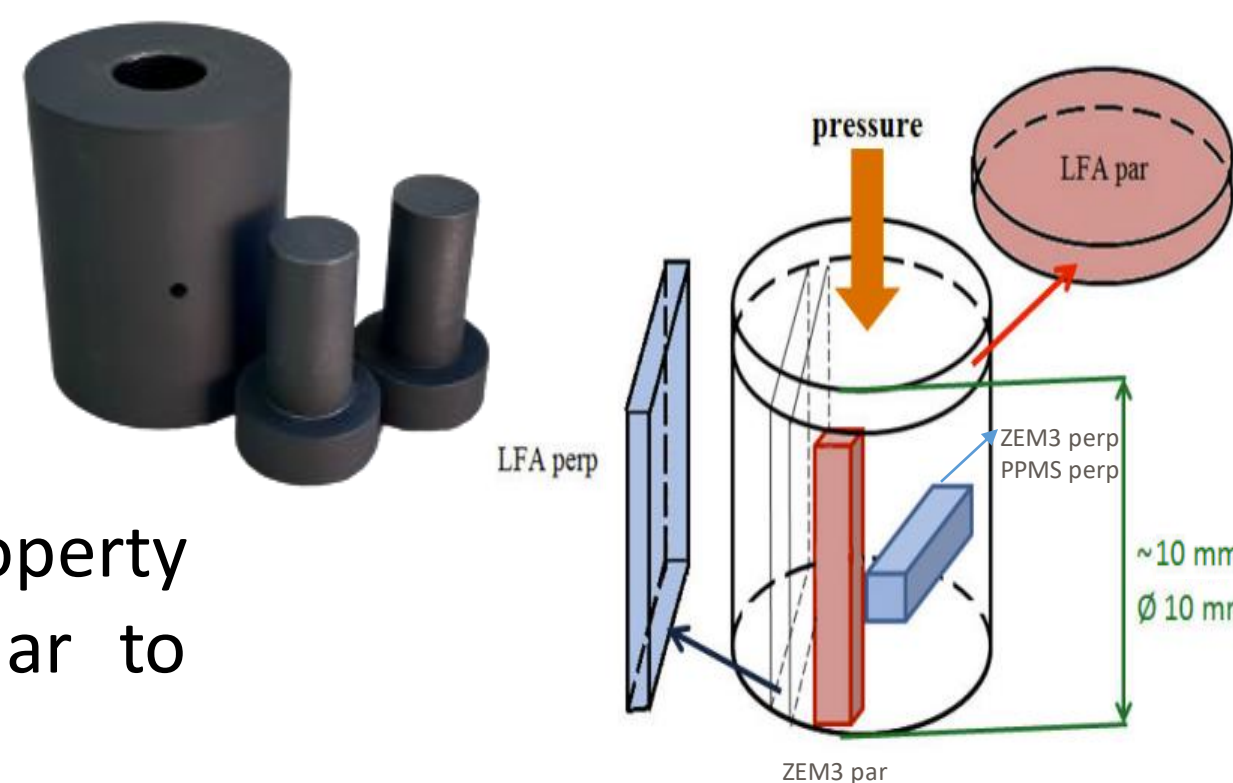
- Monoclinic/cubic phase transition achieved at 930 K
- Reducing  $G$  by maximizing  $S$  through Cu/Sn disorder
- Cation ordering lowers  $G$  by minimizing  $H$
- **Annealing temperature expected to tune monoclinic/cubic fractions**

## Synthesis



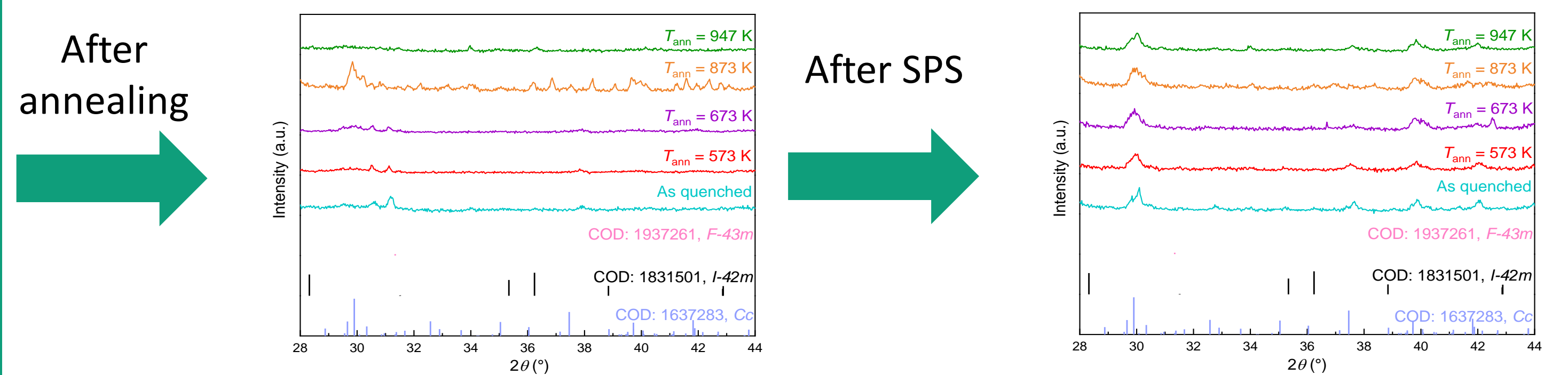
- Solid state synthesis in graphitized quartz tubes, evacuated, and sealed under inert environment of Ar/H<sub>2</sub> mixture
- Sealed ampoules heated up to 1023 K in a vertical rocking furnace for 3 hours directly followed by room-temperature water quenching
- Ingots crushed into powders and cold pressed into cylindrical pellets further annealed between 573 and 947 K for 10 days

- Densification by Spark Plasma Sintering
- Samples further cut for transport property measurements (parallel and perpendicular to the pressing direction)

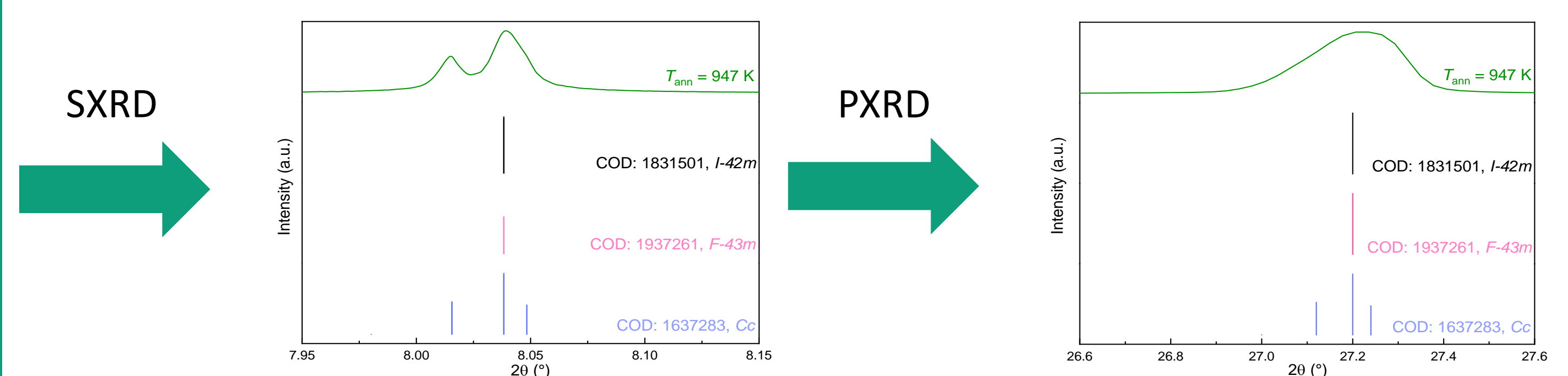


- Homogeneous distribution of the raw elements
- EPMA average compositions match the nominal values although Se losses are reported

## Powder and synchrotron X-ray diffraction



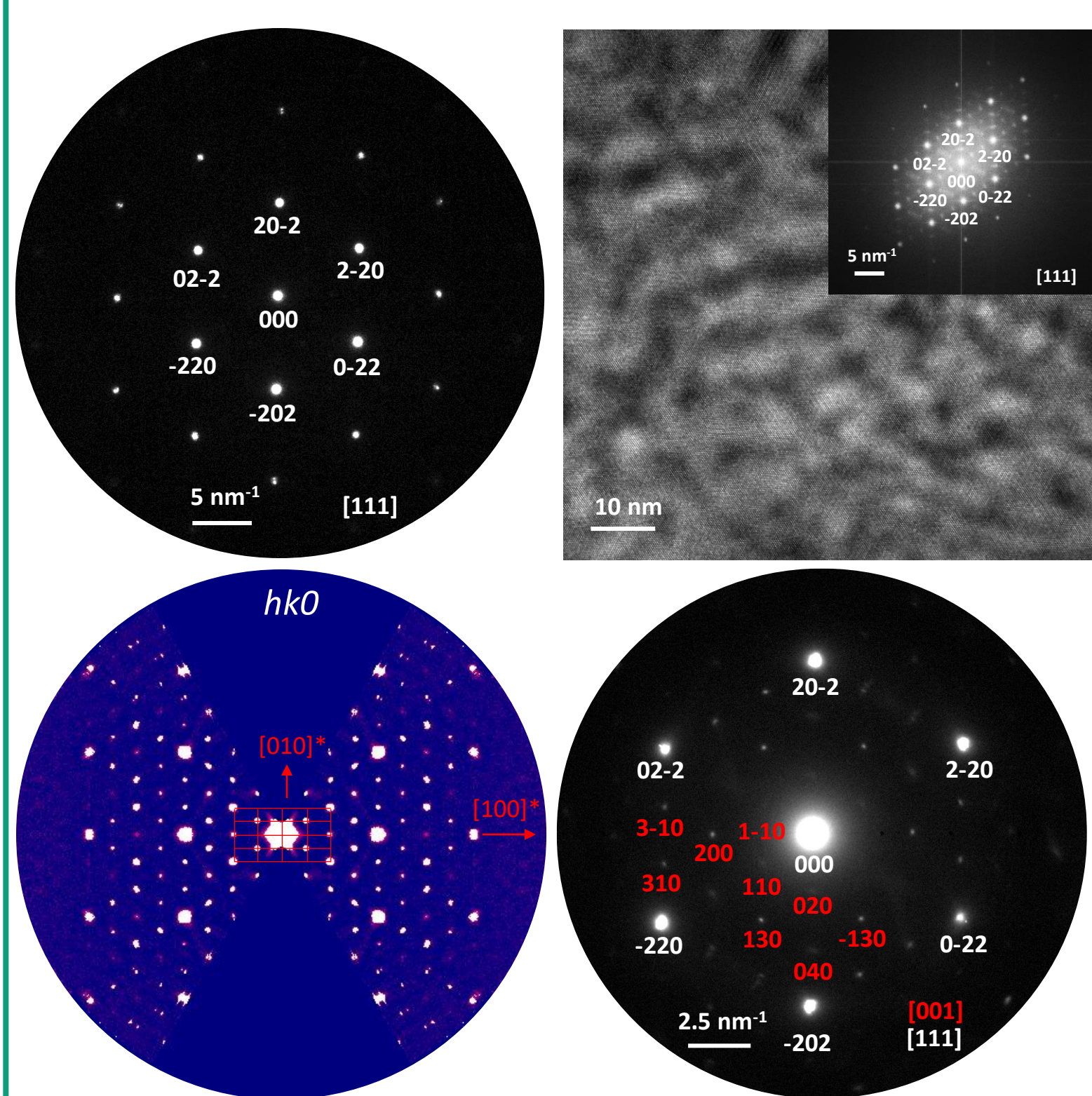
- PXRD patterns of the samples can be easily confused
- This challenge arises from the presence of three phases with closely overlapping peaks
- Distinguishing them requires attention to subtle details, such as the appearance of low-intensity peaks or the splitting of some high-intensity diffraction peaks



- $\lambda = 0.46113 \text{ \AA}$ ,  $0.002^\circ$  scan step for SXR against  $\lambda = 1.54056 \text{ \AA}$ ,  $0.028^\circ$  scan step for conventional PXRD

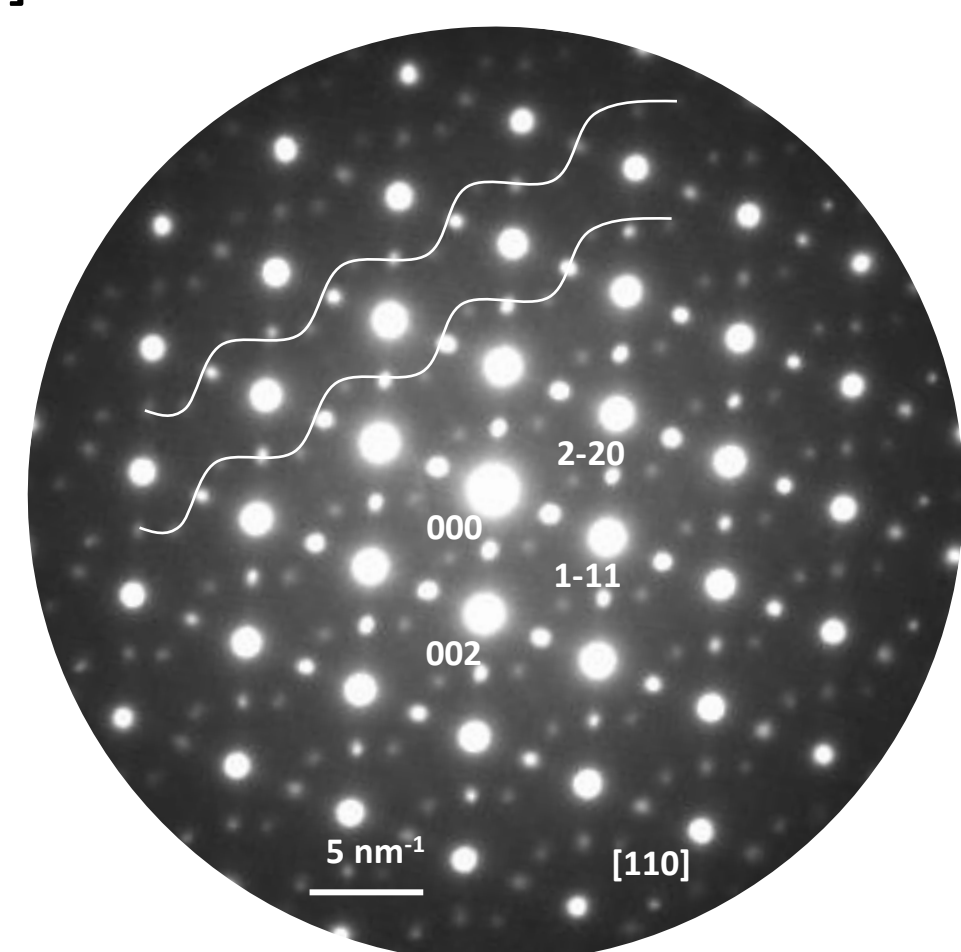
- Rietveld refinement reveals different monoclinic/cubic fractions

## Transmission electron microscopy

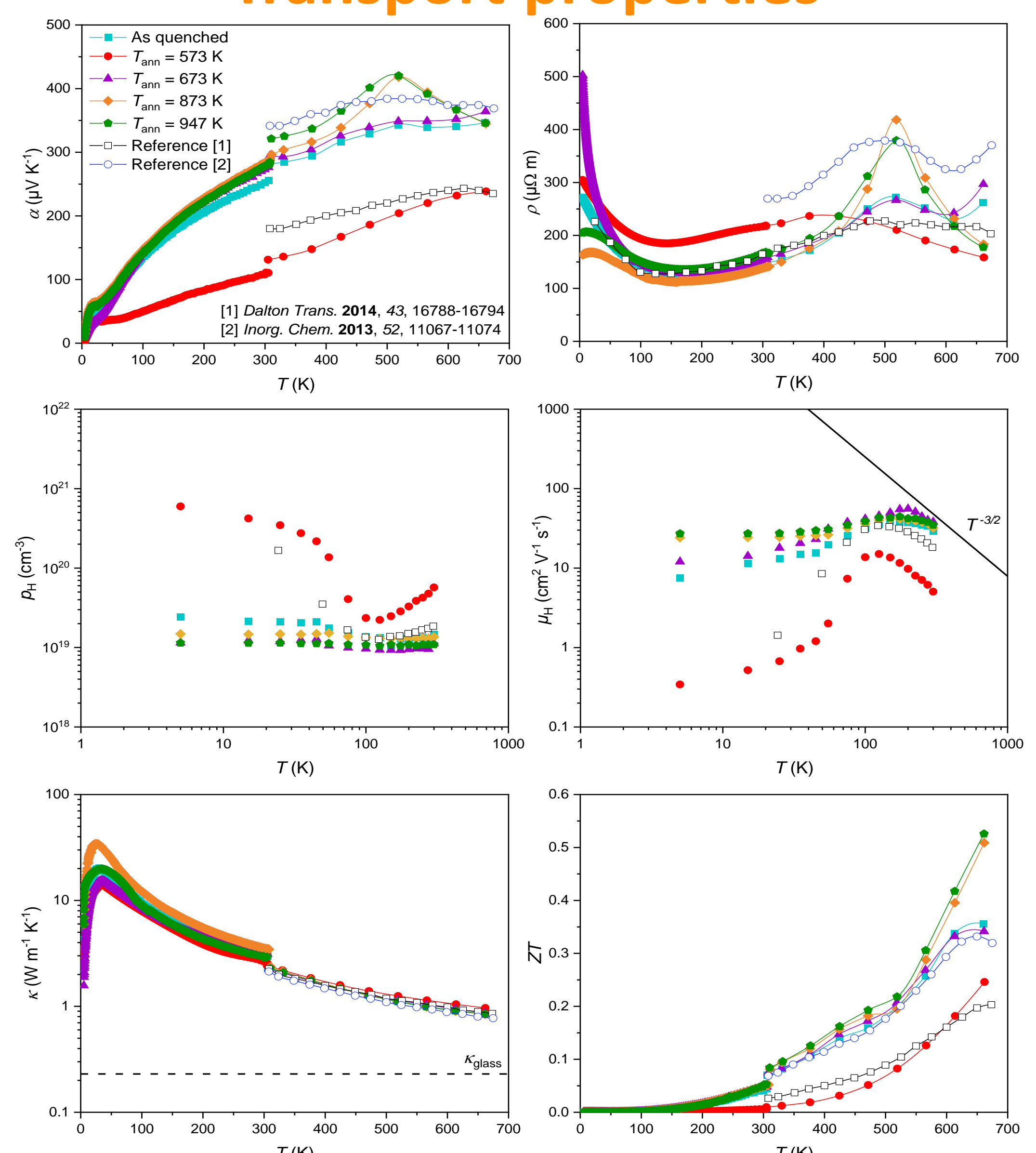


- SAED pattern suggests cubic symmetry along the [111] zone axis
- HRTEM and FFT reveal additional diffraction spots
- 3D reconstruction of reciprocal space confirms monoclinic symmetry
- Out-of-zone SAED reveals low-intensity reflections due to the coexistence of two distinct lattices
- Interplanar spacing measurements confirm the monoclinic unit cell along the [001] axis

- Non-continuous wave-like arrangement of sharp low-intensity spots, distinct from diffuse streaks usually associated to short-range order
- Attributed to long-range order
- It matches features reported along a similar zone axis in prior works



## Transport properties



- Annealing temperature has a weak influence on defect formation
- Peak  $ZT$  of 0.53 at 660 K for suitable monoclinic/cubic fractions

## Conclusion

This work highlights the strong influence of synthesis conditions on the thermoelectric properties of  $\text{Cu}_2\text{SnSe}_3$ -based compounds

While annealing temperature has limited effect on defects and charge carrier concentrations, it significantly alters the monoclinic-to-cubic phase ratio, influencing transport behavior. The 573 K sample shows variable-range hopping behavior with low mobility and thermopower values, leading to poor performance.

In contrast, 873 and 947 K annealed samples exhibit conventional transport, reaching a peak  $ZT$  of 0.53 at 660 K - the best value so far for undoped  $\text{Cu}_2\text{SnSe}_3$