Unravelling grain boundary influences on electronic and lattice thermal conductivity in Mn-doped SnTe thermoelectrics

MAX PLANCK INSTITUTE FOR SUSTAINABLE MATERIALS

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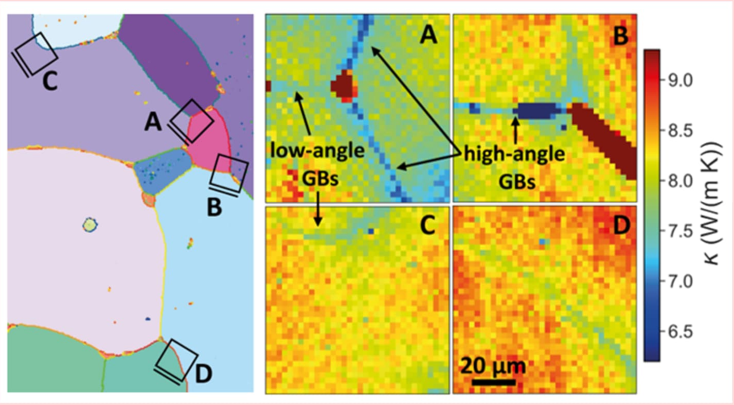
MOTIVATION

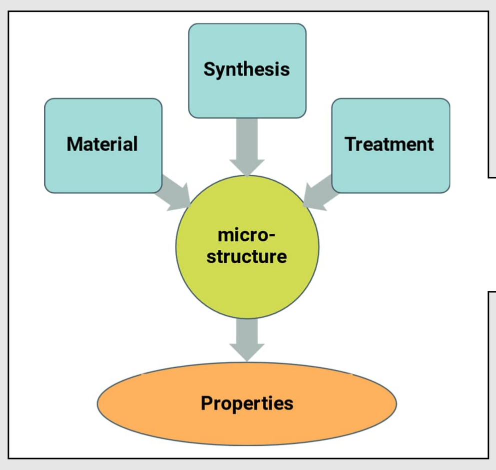


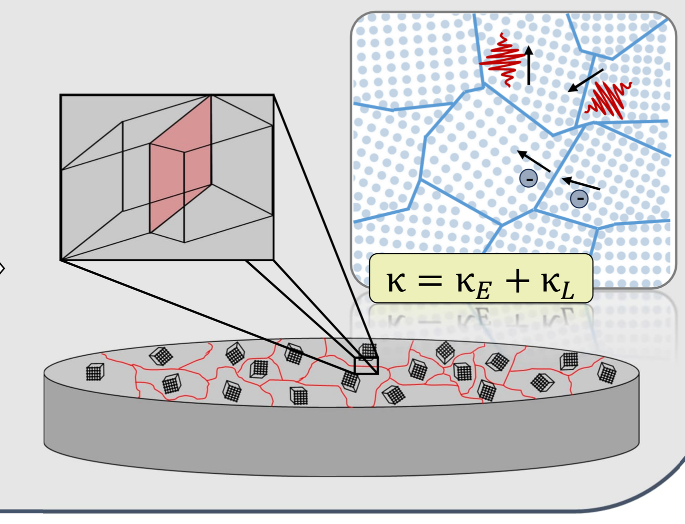
E. Isotta et al., 2023, Adv. Mater.

- Visualisation of **κ suppression at single grain boundaries (GBs)** possible
- Dependence on the **misorientation angle** found

How does the grain boundary type alter local κ suppression?

Does the κ suppression primarily originate in κ_E or κ_L?





KEY OBJECTIVES

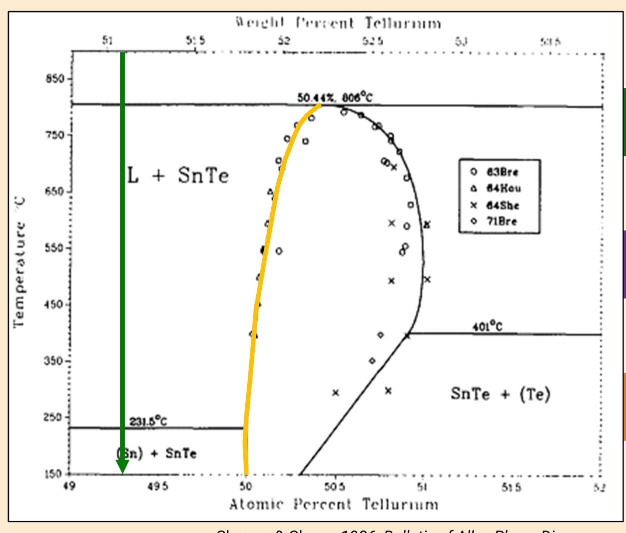
1. Understand correlation between atomic **arrangements**, **misorientation** angle and local **chemistry** and the **κ suppression** at grain boundaries in SnTe.
2. Determine whether the excess boundary resistance R_B originates from the **electronic or lattice thermal conductivity** in samples with systematically varied κ_E/κ_L ratio.

$R_B = f(\gamma_{GB}, \theta, \Sigma_{GB})$?

$R_B = f(\kappa_E, \kappa_L)$?

θ: Misorientation angle
Σ_{GB}: Symmetric grain boundary
γ_{GB}: Grain boundary energy

STRATEGY AND METHODS

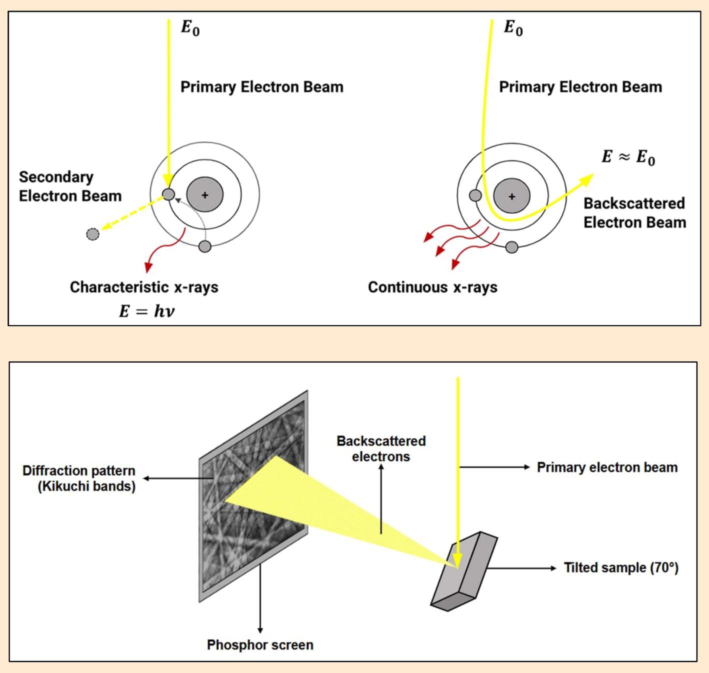

Sharma & Chang, 1986, Bulletin of Alloy Phase Diagrams.

$Sn_{1.03}Te$ — $\frac{\kappa_E}{\kappa_L} = 2.19^*$

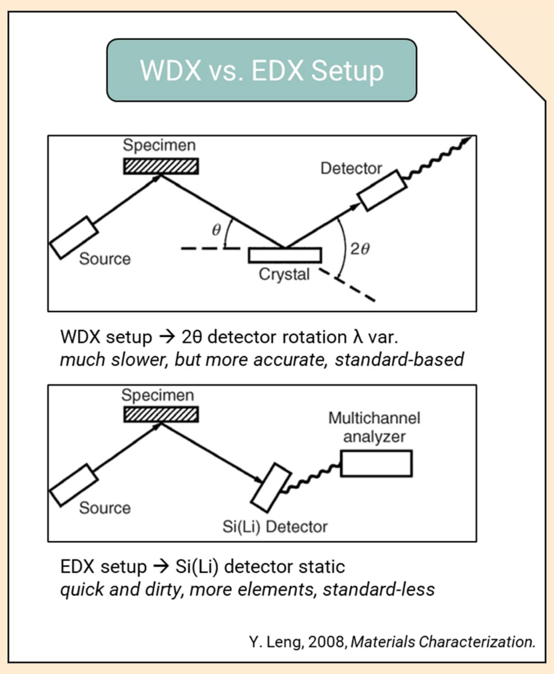
$Sn_{0.98}Mn_{0.05}Te$ — $\frac{\kappa_E}{\kappa_L} = 1.28^*$

$Sn_{0.92}Mn_{0.11}Te$ — $\frac{\kappa_E}{\kappa_L} = 0.62^*$

- Addition of **Mn to decrease κ_E** and κ_E/κ_L ratio
- Target $(Sn) + SnTe$ region to ensure **Sn-rich composition** of the SnTe phase
- Solid state synthesis and **slow cooling**

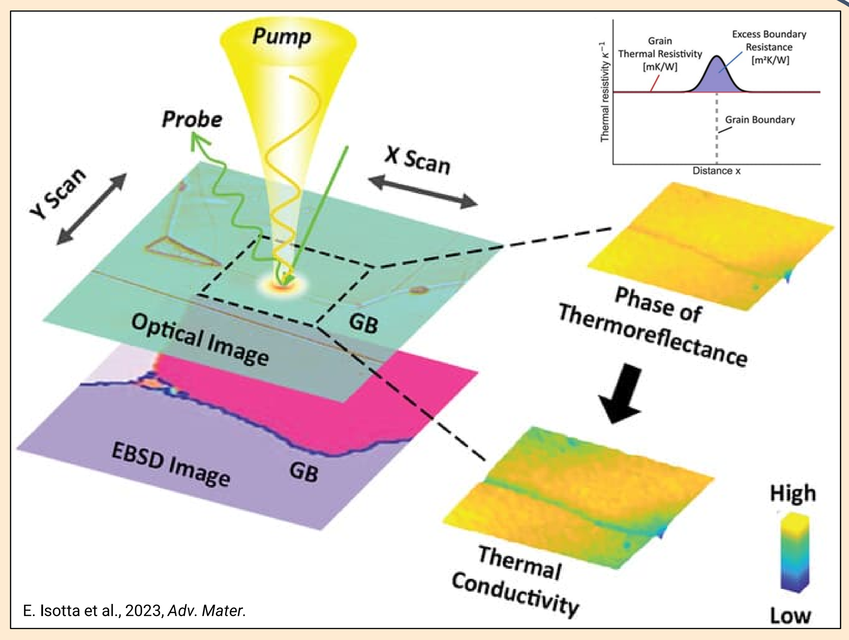


Electron Backscatter Diffraction
(i) Crystallographic space group (**crystal structure**)
(ii) The lattice **orientation**



Y. Leng, 2008, Materials Characterization.

Wavelength-/Energy-Dispersive X-ray Spectroscopy
Quantitative (WDX) and qualitative (EDX)chemical analysis

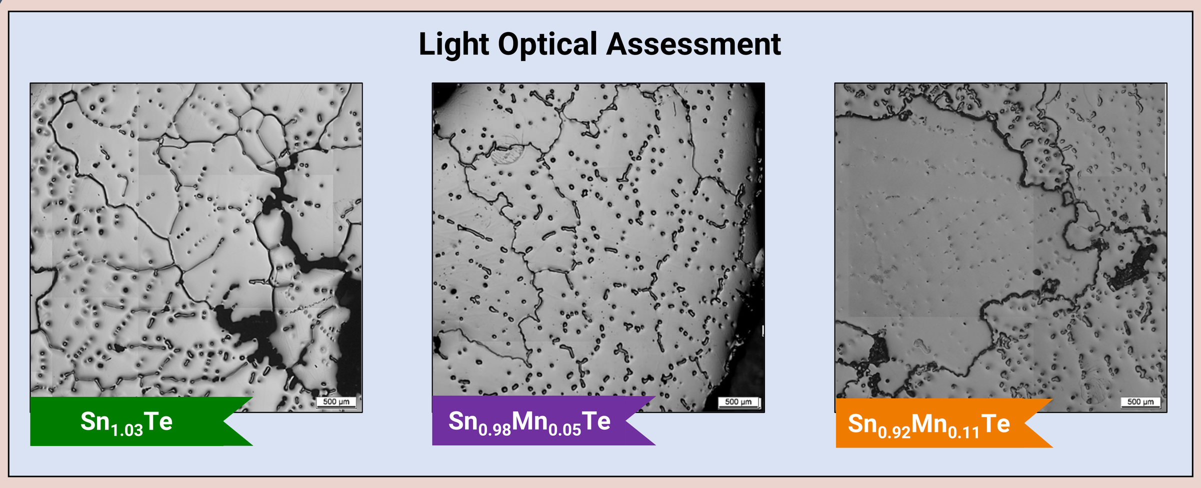


E. Isotta et al., 2023, Adv. Mater.

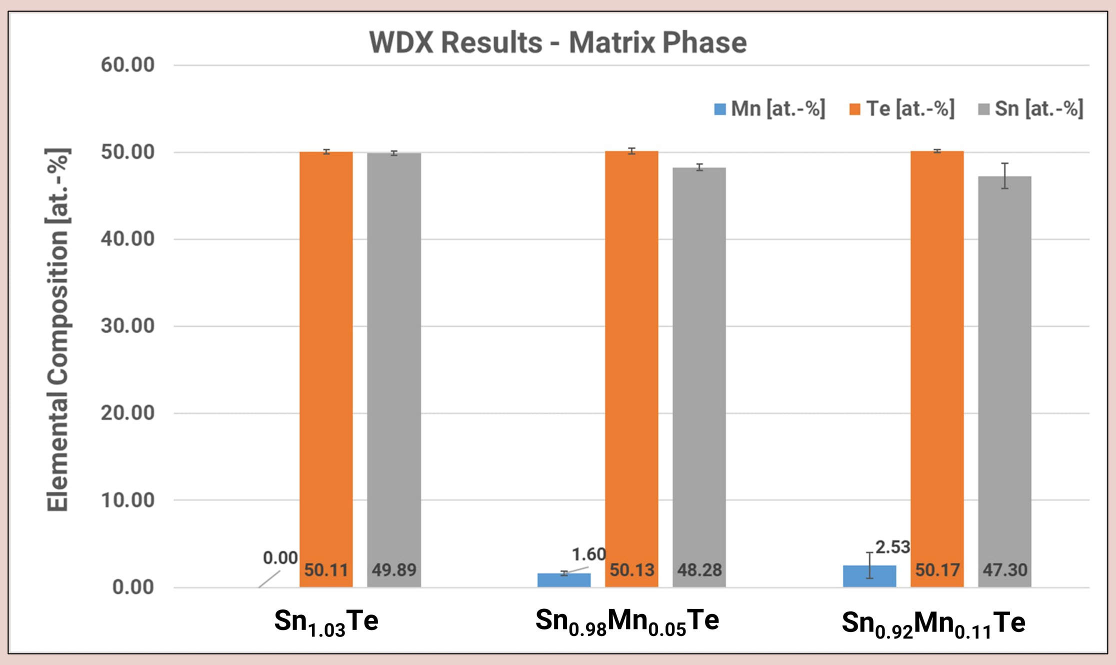
- **Two laser** beam setup
- Phase shift in probe is measured
- **Thermal conductivity** is calculated **from thermoreflectance phase**

3 SAMPLE COMPOSITIONS → **SCANNING ELECTRON MICROSCOPY** → **FREQUENCY DOMAIN THERMOREFLECTANCE**

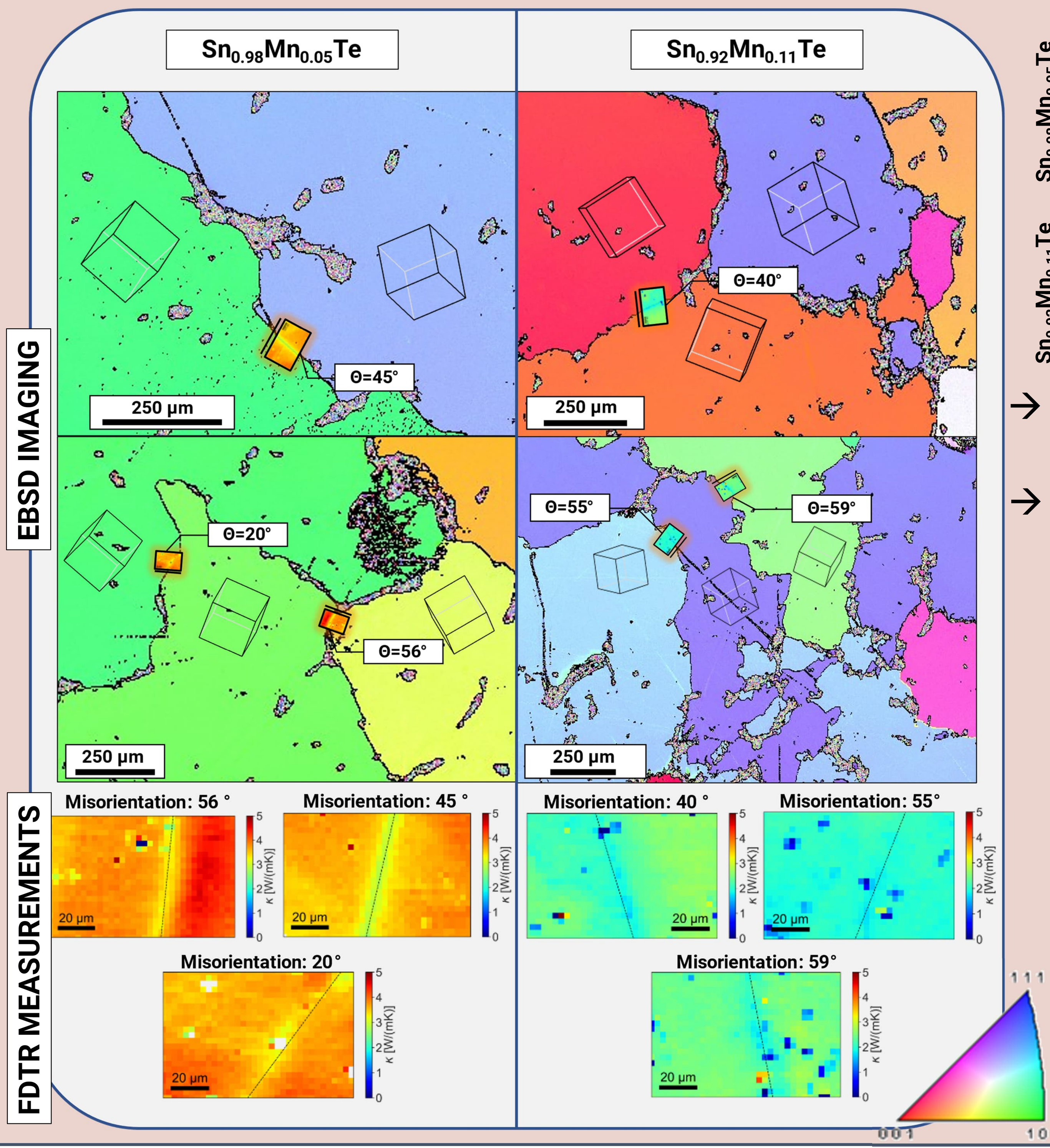
PRELIMINARY RESULTS

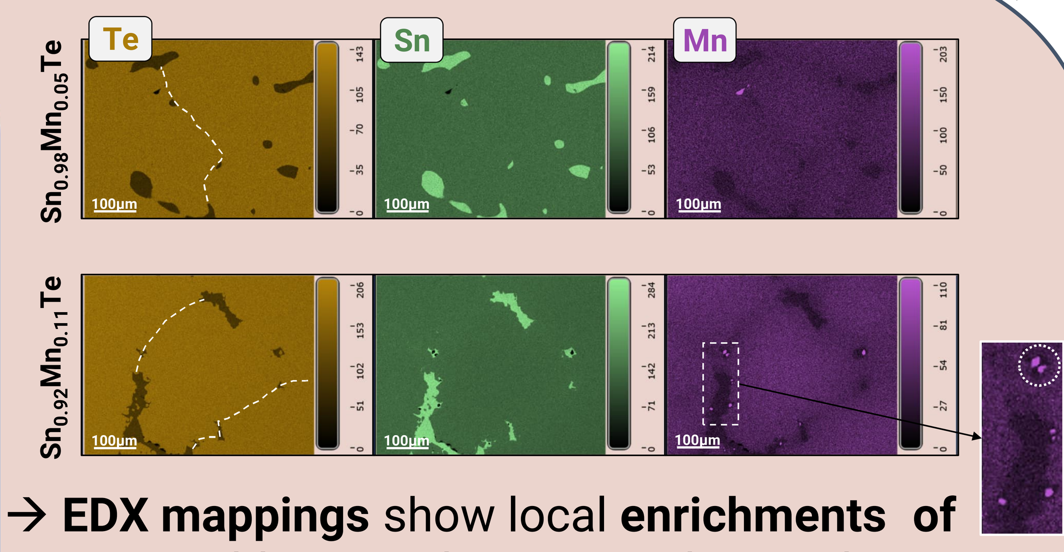


Very large grain sizes (diameters) of **up to 2 mm**
→ high ordering tendency

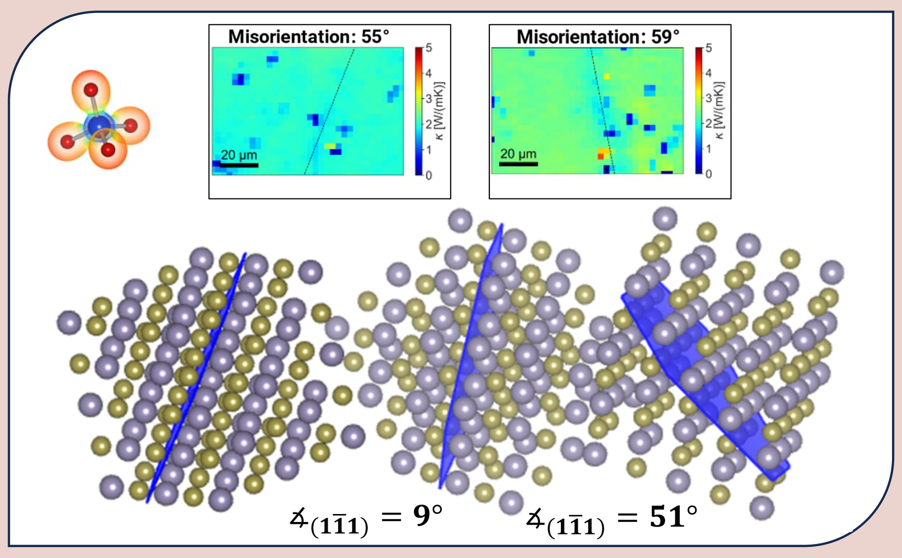


→ **Mn-content** systematically **lower than targeted**
→ Does Mn locally enrich?



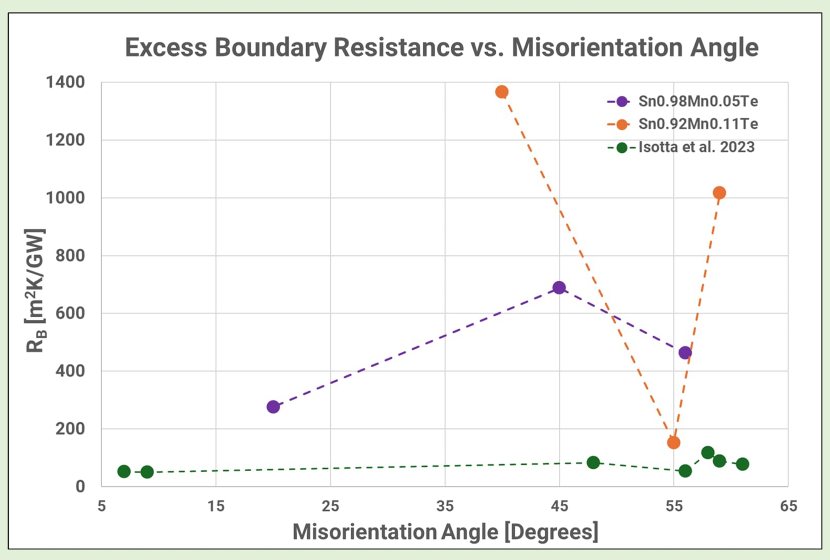


→ **EDX mappings** show local **enrichments of Mn** in addition to the expected Sn at the GBs
→ **GBs** appear to be **deficient in Mn**

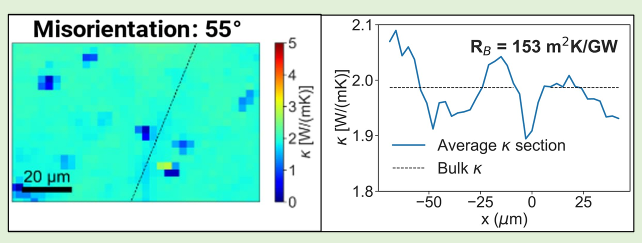


→ **Invisible boundaries** may correlate to the relative orientation of the $(1\bar{1}1)$ planes towards each other

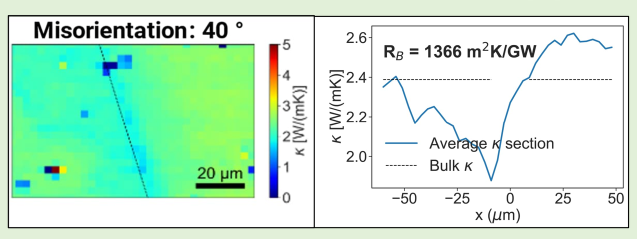
FIRST CONCLUSIONS



R_B can not be predicted by θ only!
→ **$\Delta\kappa$** takes on values between **0.1** and **0.7 W/mK**

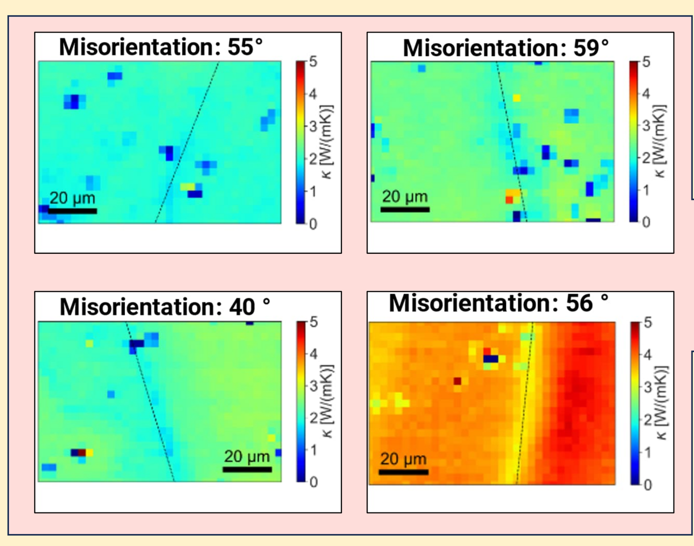


→ **Specific GBs** apparently do **not contribute** to the κ suppression



→ **Extended boundaries** are found to **stretch the κ suppression**

SELECTED OPEN QUESTIONS



- Why are certain GBs “invisible” to the FDTR measurements?
- How do “extended boundaries” depend on the GB plane and inclination to the surface?
- Why are there significant differences in κ across grains?

Transmission Electron Microscopy

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Northwestern University
MARIE CURIE ACTIONS
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