NSF/DOE Partnership on Thermoelectric Devices for Vehicle Applications

High-Performance Thermoelectric Devices Based on Abundant Silicide Materials for Vehicle Waste Heat Recovery

Investigators:

Li Shi, John Goodenough, Matt Hall, Jianshi Zhou

Department of Mechanical Engineering & Texas Materials Institute

University of Texas at Austin

&

Song Jin

Department of Chemistry

University of Wisconsin-Madison

Participating Students:

Xi Chen, Annie Weathers, Chad Baker, Libin Zhang, Daniel Salta (Texas)

Ankit Pokhrel, Steven Girard (Wisconsin)

Collaboration:

Hsin Wang, Olivier Delaire, Oak Ridge National Lab

Overview of Research

Objectives:

a) To increase the *ZT* of abundant silicides to a level competitive with the state of the art found in materials containing much more scarce and expensive elements

b) To enhance the thermal management system performance for silicide TE devices installed in a diesel engine

Tasks:

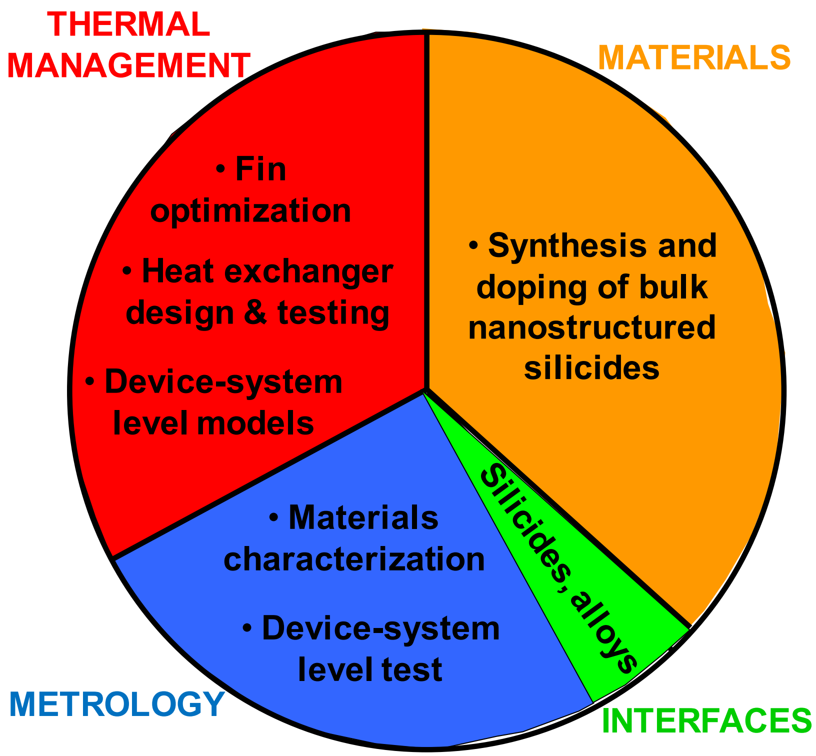
a) Investigate methods for scalable synthesis and position-dependent doping of bulk nanostructured silicides

b) Explore silicide and alloy interface materials with low contact resistance and improved thermomechanical compliance

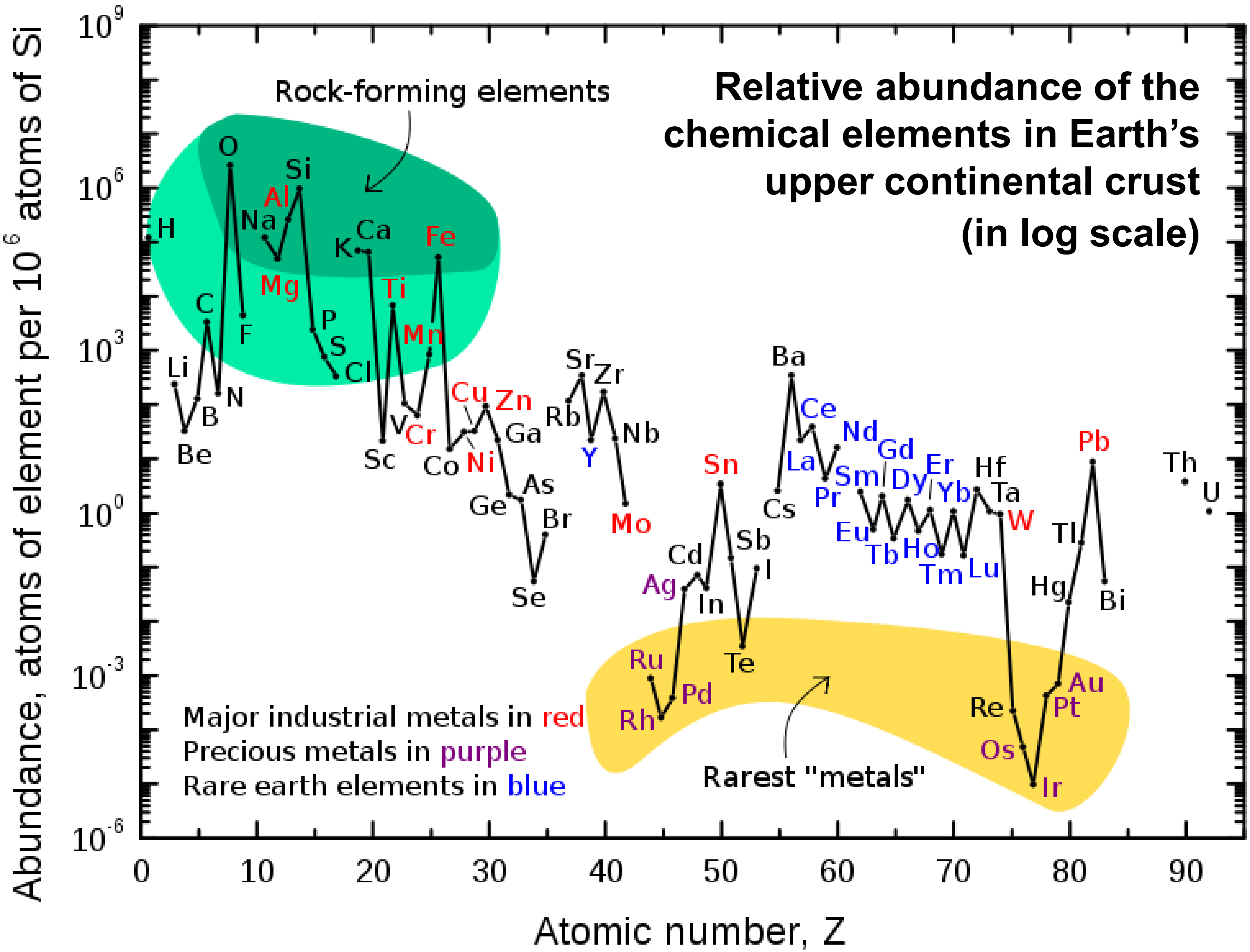
c) Characterize the TE properties of silicides at temperatures between 300 and 900 K

d) Develop computation models to guide the heat exchanger design and the placement of the TE elements of spatially varied TE properties

e) Test silicide TE waste heat recovery devices in a 6.7 liter Cummins diesel engine

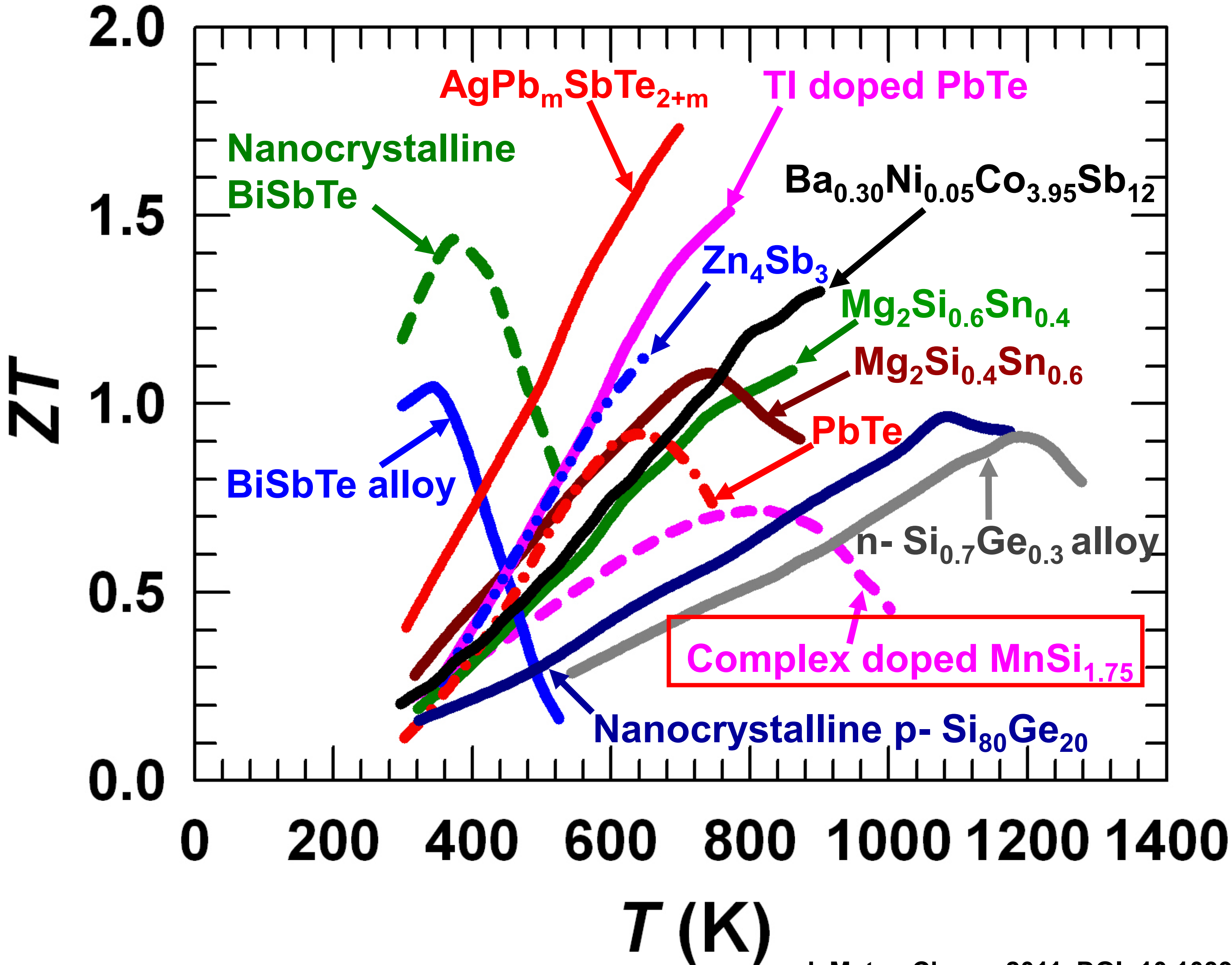


Index of Abundance of Elements



http://en.wikipedia.org/wiki/File:Elemental_abundances.svg

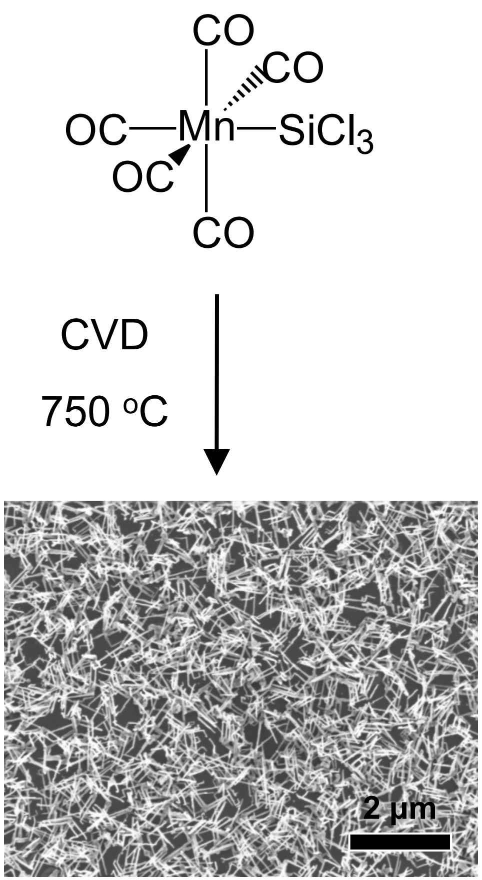
ZT of Bulk Thermoelectric Materials

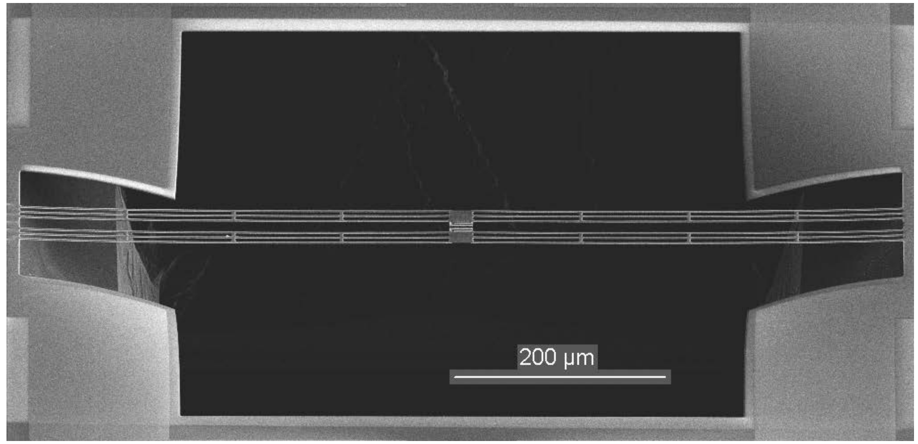


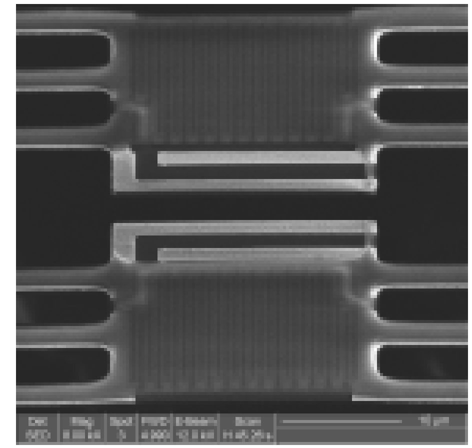
J. Mater. Chem., 2011, DOI: 10.1039/C0JM02755C

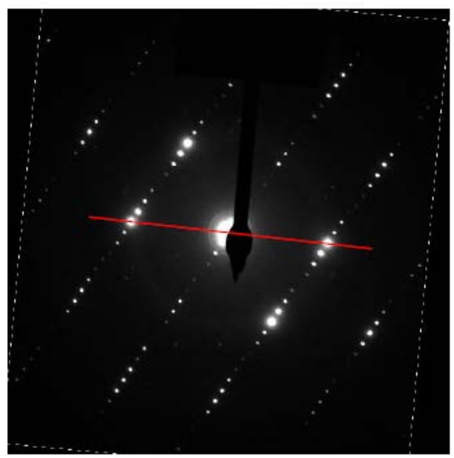
$MnSi_{1.75}$ Nanowire Synthesis and Characterization

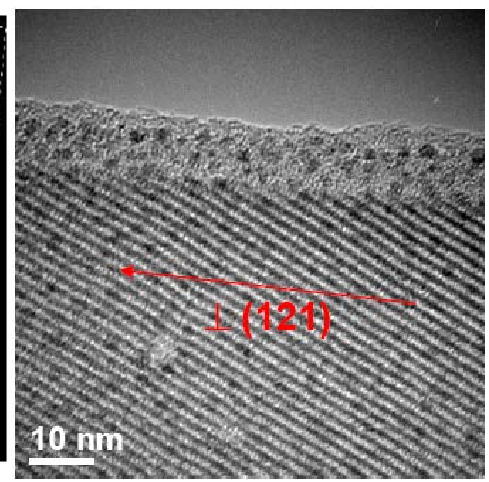
Zhou, Sczczech, Pettes, Moore, Jin, Shi, Nano Lett. **2007**, *7*, 1649.

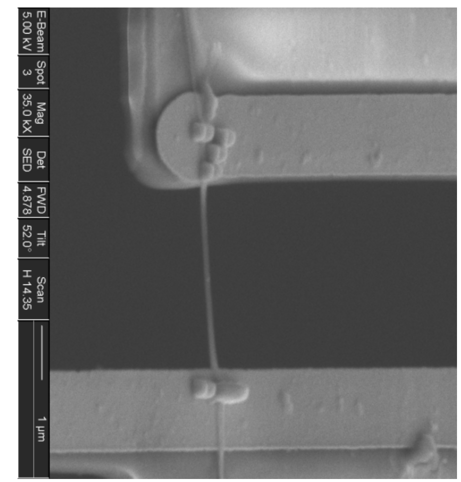








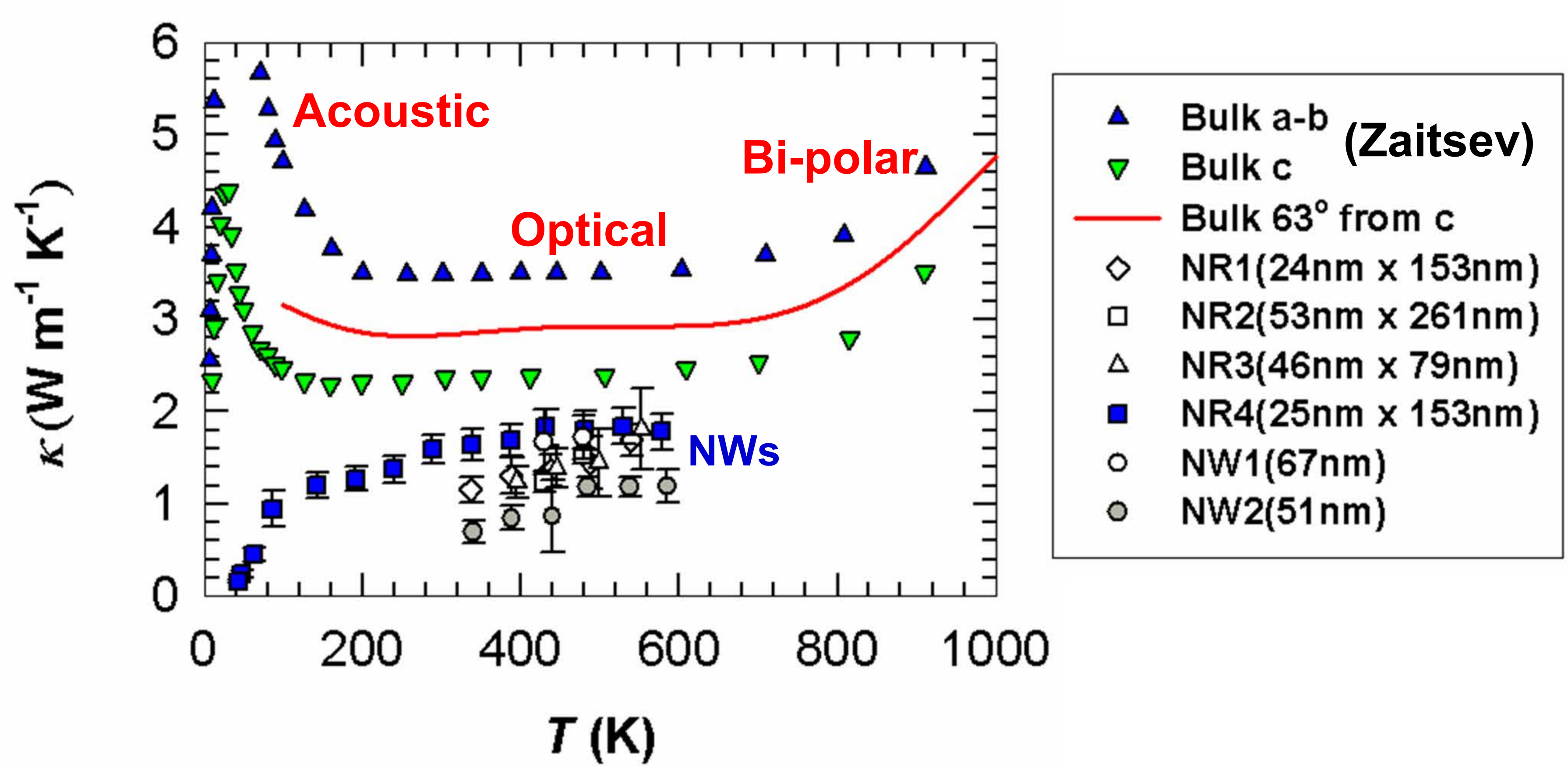




HMS NW synthesis: *Higgins & Jin JACS* **2008**, *130*, 16086.
Silicide NW review: *J. Mater. Chem.* **2010,** *20*, 223.

- Nanoribbon (NR) or NWs of $Mn_{39}Si_{68}$ or $Mn_{19}Si_{33}$
- c ≈ 17 nm
- Growth direction perpendicular to {121} planes, or 63° from the c axis

Glass-like Thermal Conductivity in HMS NRs and NWs

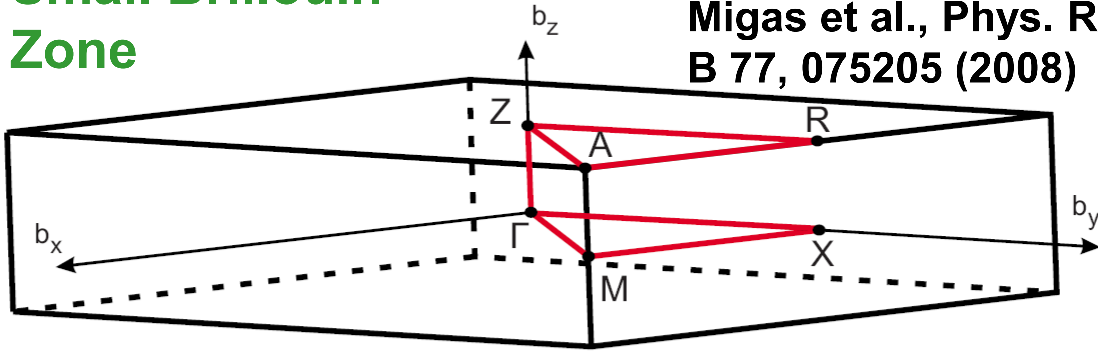


• Calculated amorphous thermal conductivity limit $\kappa_\alpha \approx$ 0.7 W/m-K.

• The transition from the phonon-crystal behavior in bulk to glass-like thermal conductivity in the $MnSi_{1.75}$ nanostructures reveals effects of surface scattering, especially for long-wavelength phonons.

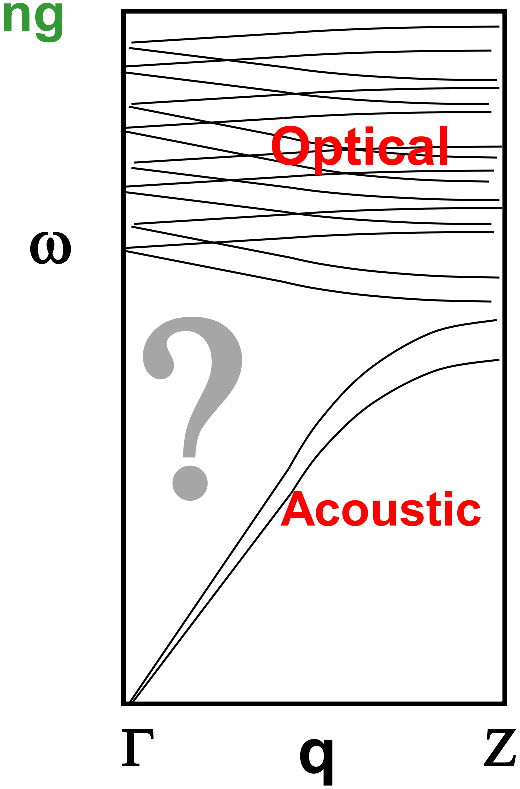
Higher Manganese Silicide ($MnSi_{1.75}$)

Small Brillouin Zone



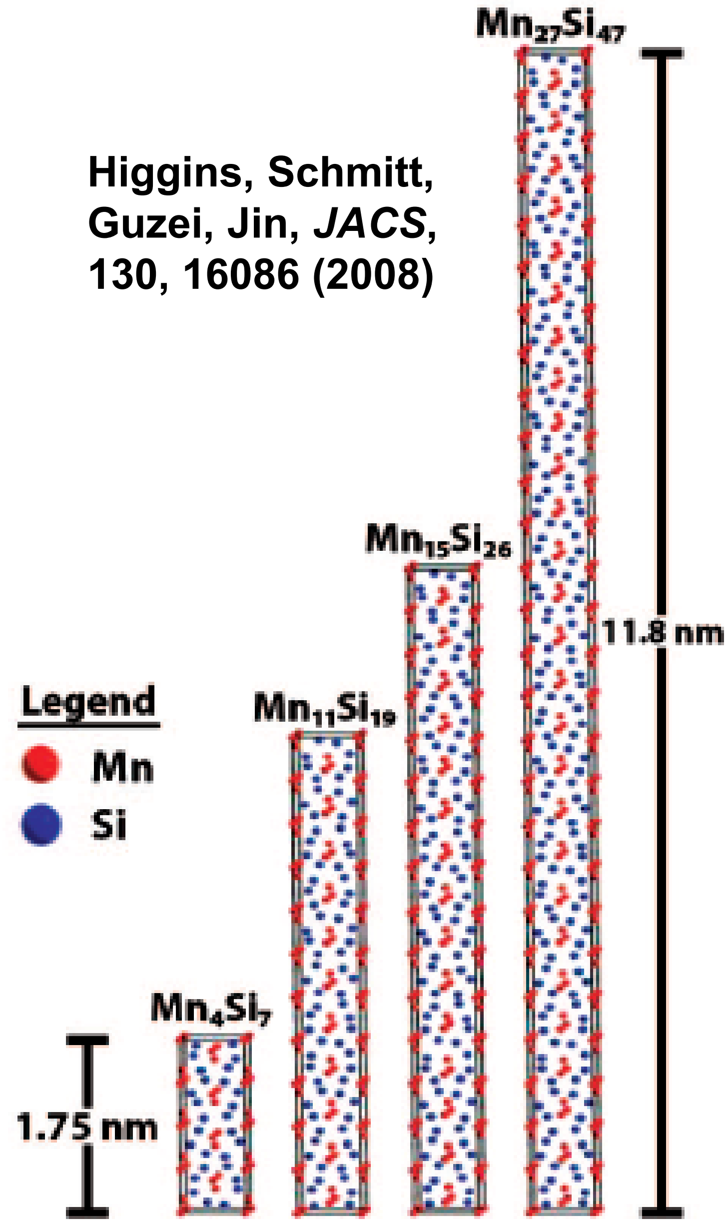
Migas et al., Phys. Rev. B 77, 075205 (2008)

Zone Folding

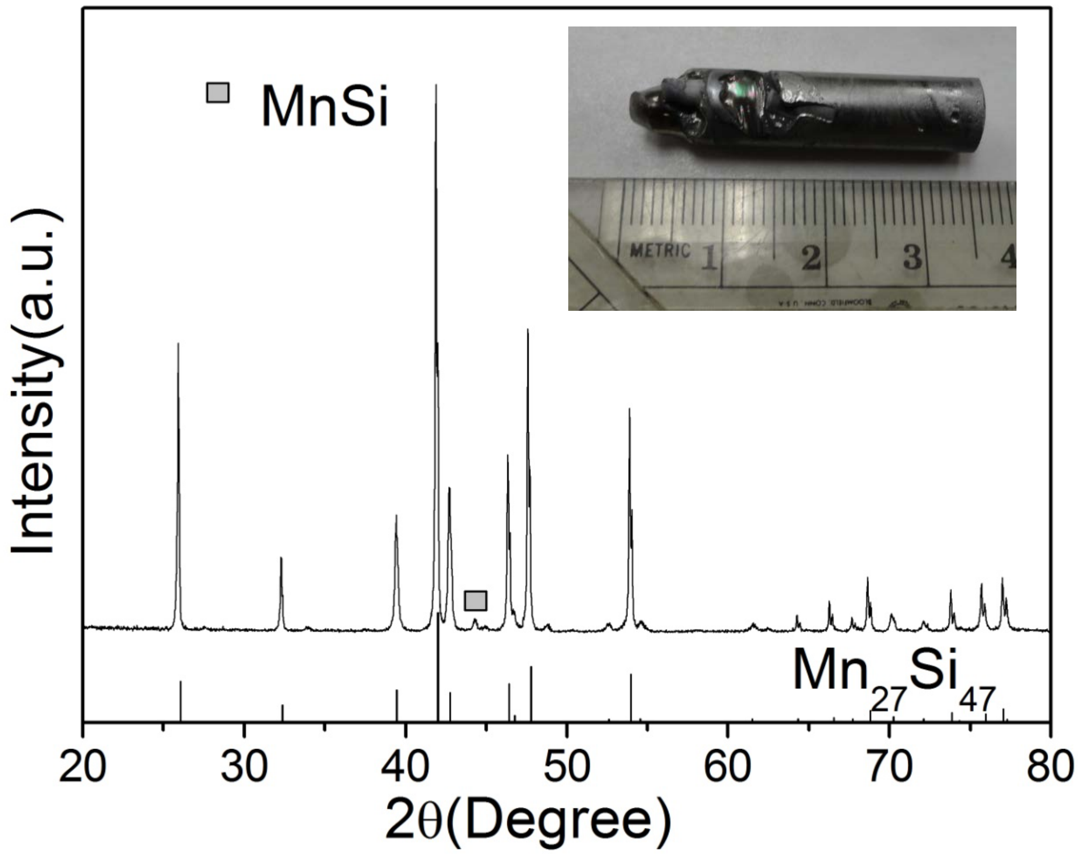


Large Primitive Cells

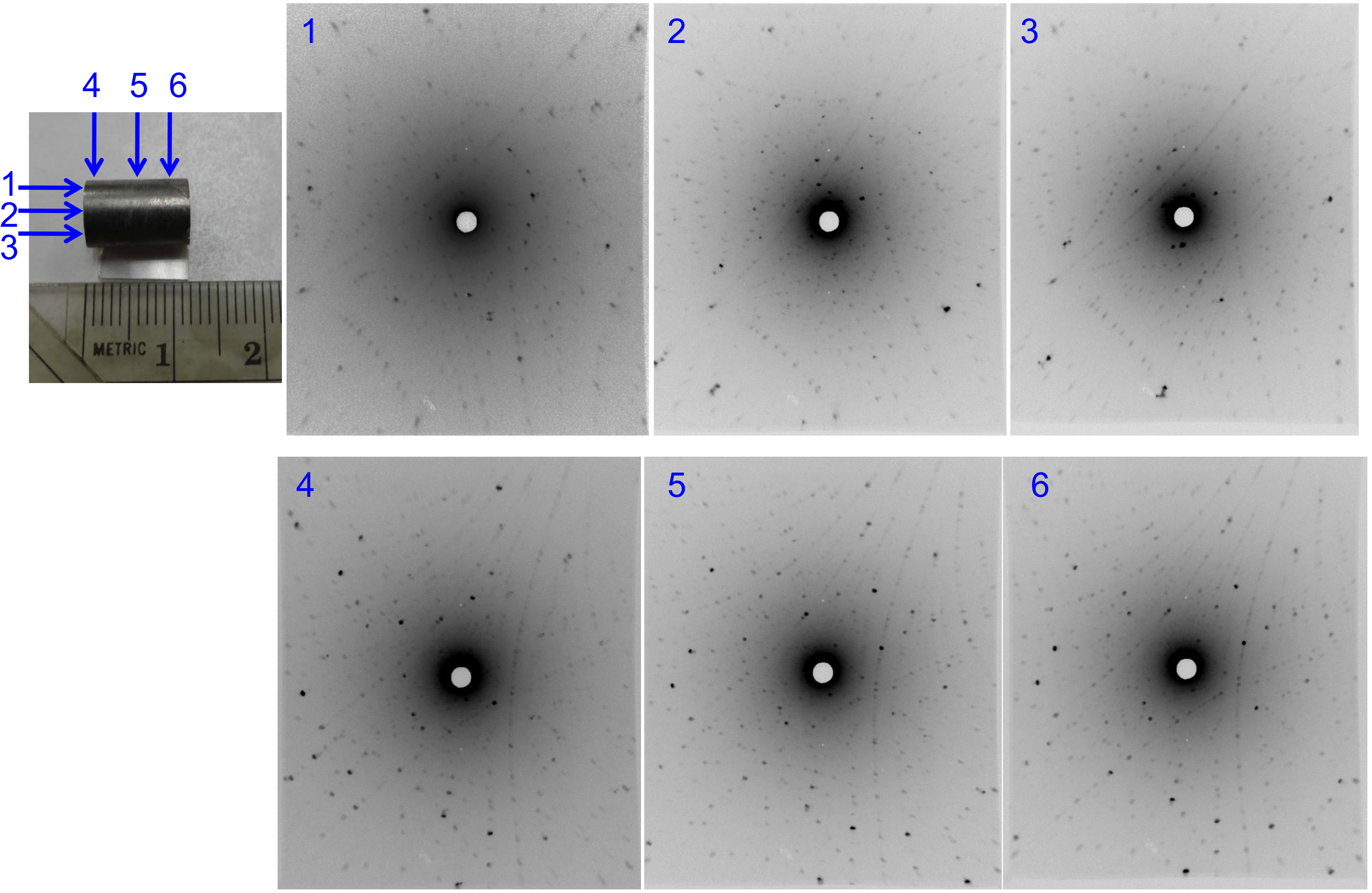
Higgins, Schmitt, Guzei, Jin, *JACS*, 130, 16086 (2008)



Floating Zone Synthesis of HMS Single Crystals

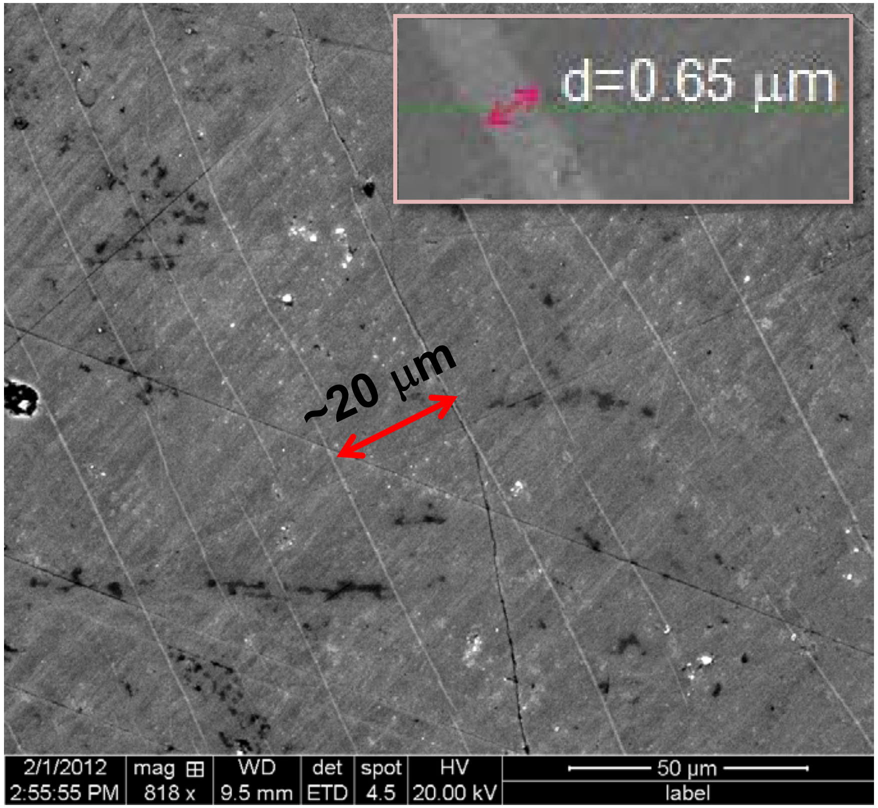


Laue Reflection Patterns of HMS Single Crystal

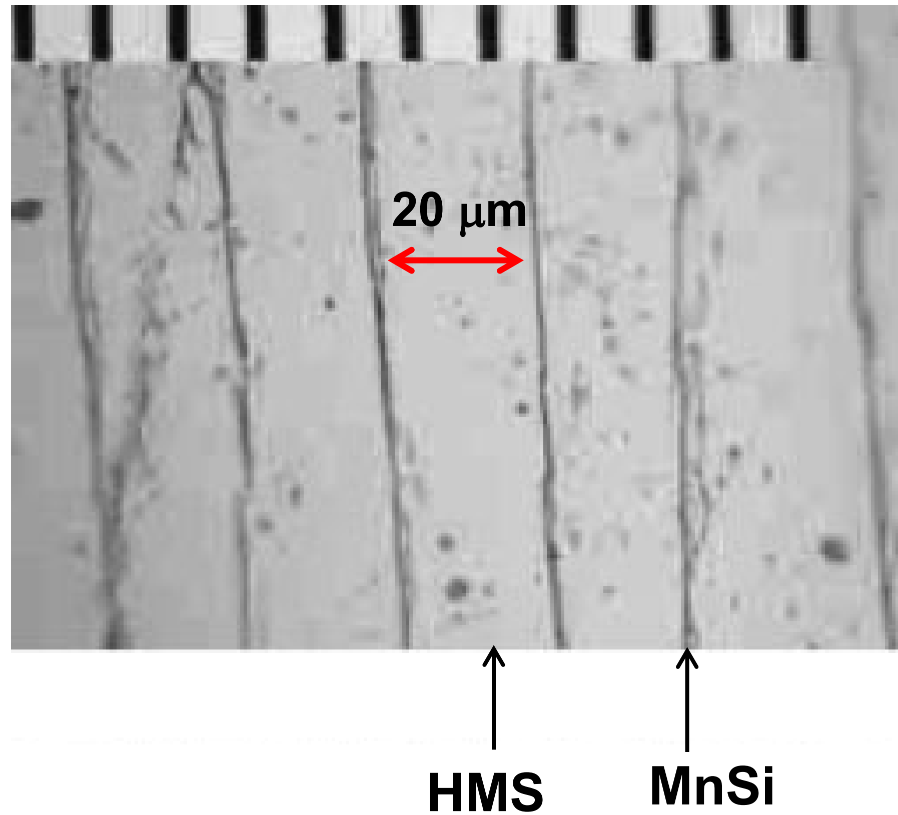


Microstructure of HMS Single Crystal

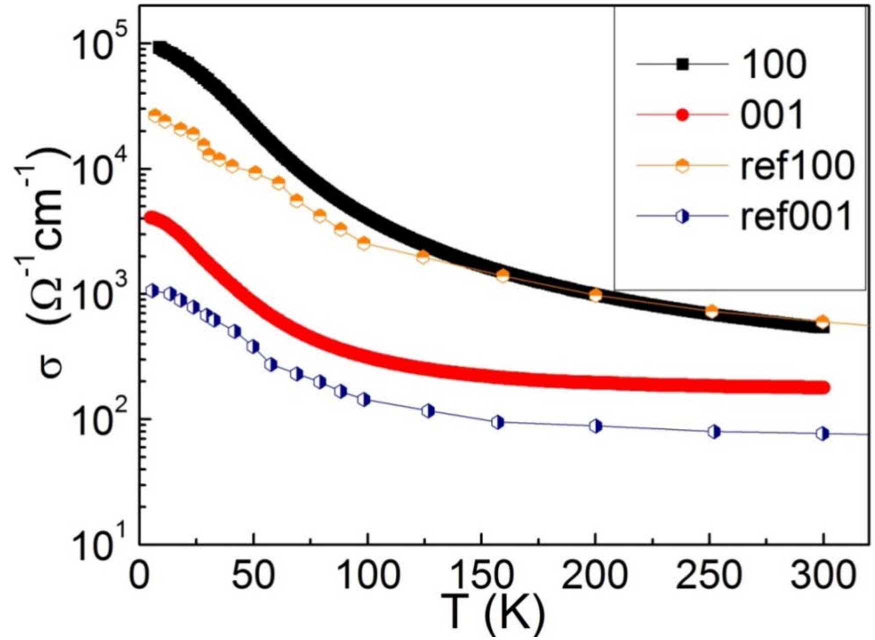
- **This work**

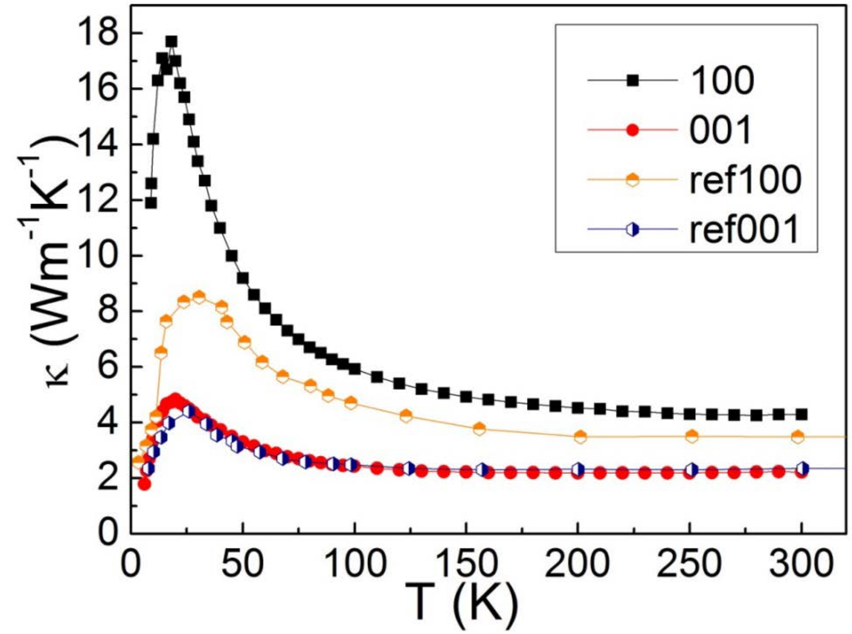


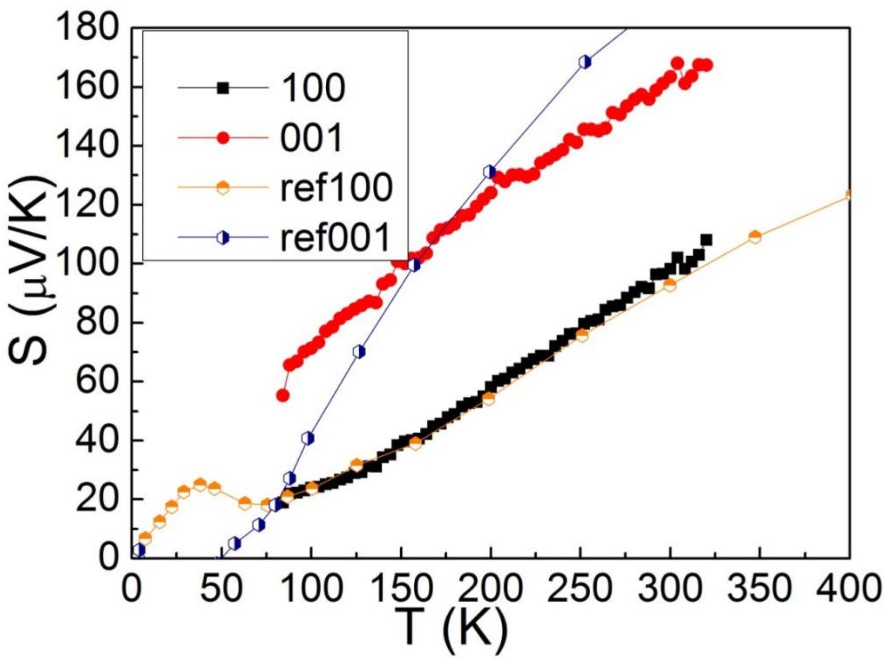
- Ref: I. Aoyama et al., Japanese Journal of Applied Physics 44, 8562 (2005) (Bridgman method)



Thermoelectric Properties of HMS Single Crystals







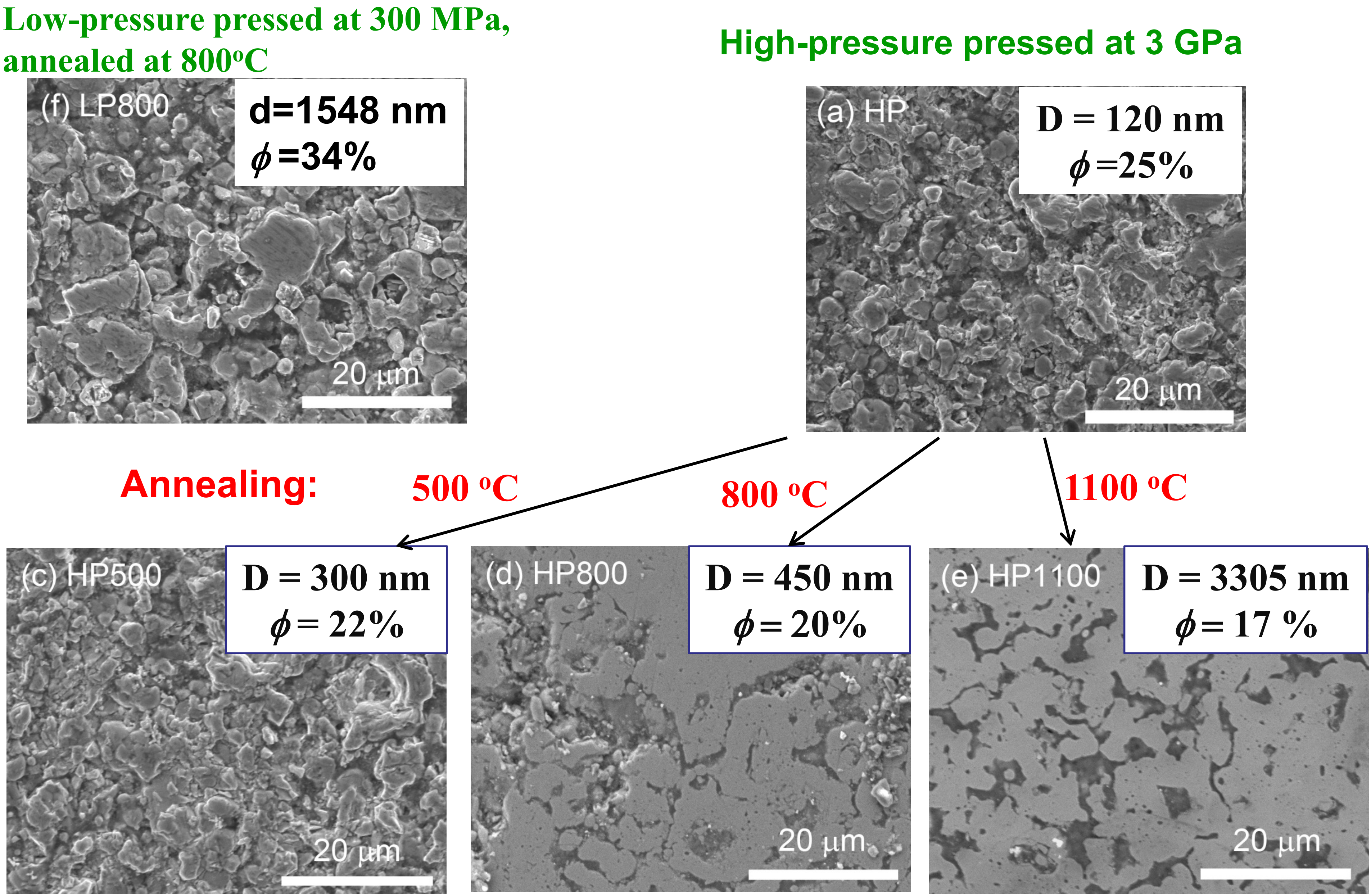
- Along the (100) direction, our sample shows similar *S*, but higher *σ* and *κ* at low *T* than literature values.

Ref: Fedorov and Zaitsev, in CRC Handbook of Thermoelectrics: macro to nano, Ed. D.M. Rowe,(*CRC press: Boca Raton*, FL, 2006). p. 31.

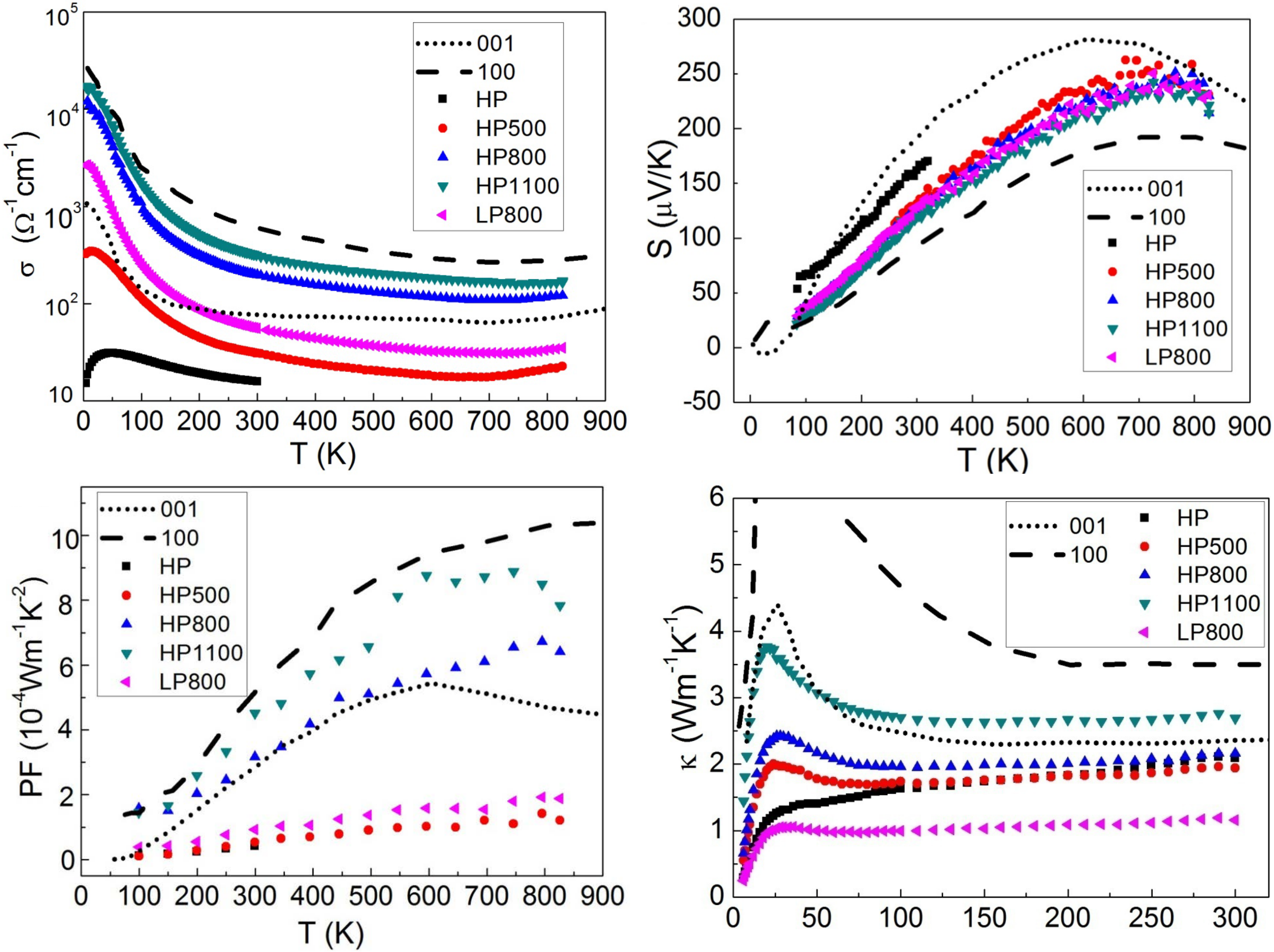
Neutron Scattering Measurements of Phonon Dispersion

- Neutron scattering data of our HMS single crystal have been obtained in collaboration with Olivier Delaire at ORNL, and are used to determine the phonon dispersion.

Synthesis of Porous HMS via Solid State Reaction and Cold Pressing



TE Properties of Cold-Pressed HMS

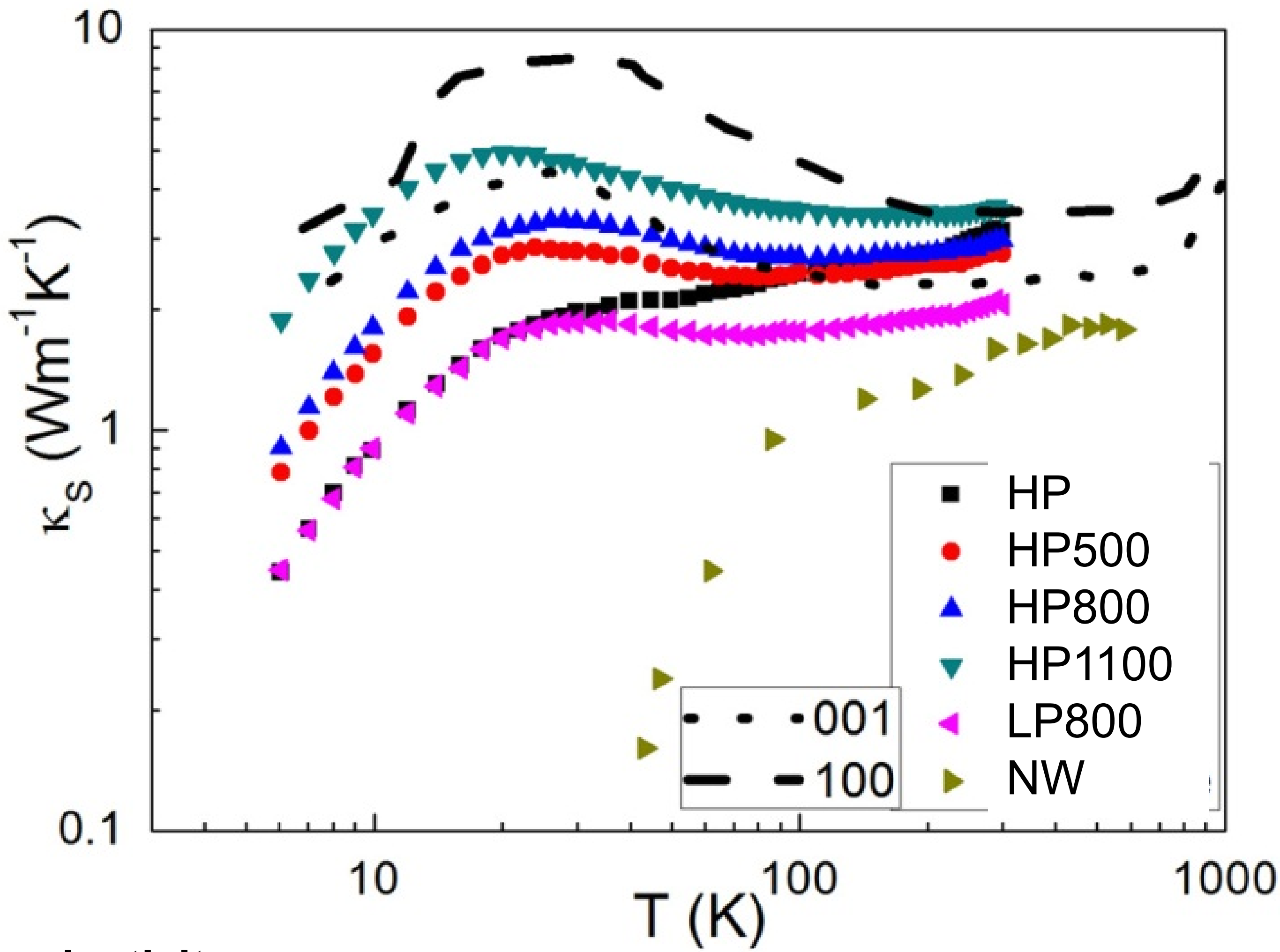


Literature [001] & [100] data from Zaitsev et al, in *CRC Handbook of Thermoelectrics*, 2006, Ed. Rowe

Solid Thermal Conductivity of Porous HMS

Effective medium approach → Solid thermal conductivity:

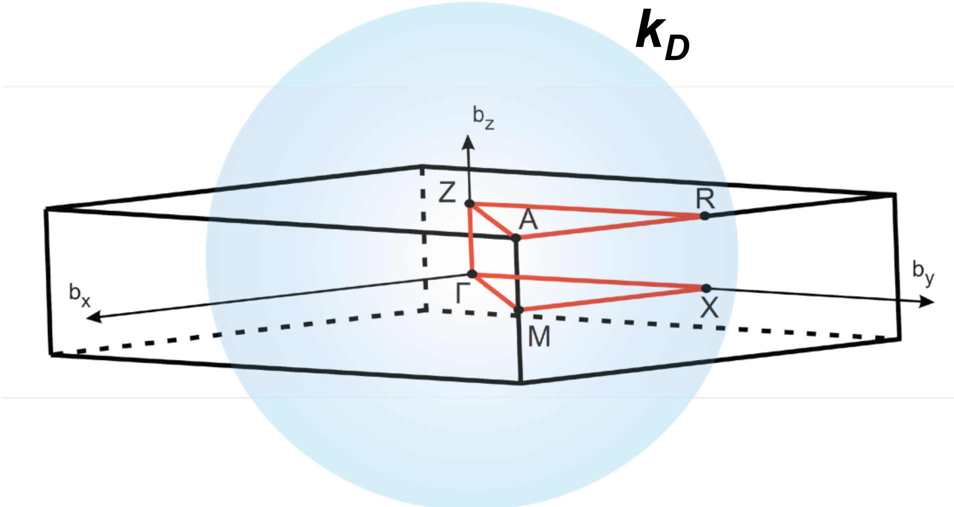
$$\kappa_s = \kappa \frac{2+\phi}{2-2\phi}$$



- **Lattice thermal conductivity $\kappa_l >> \kappa_e$**

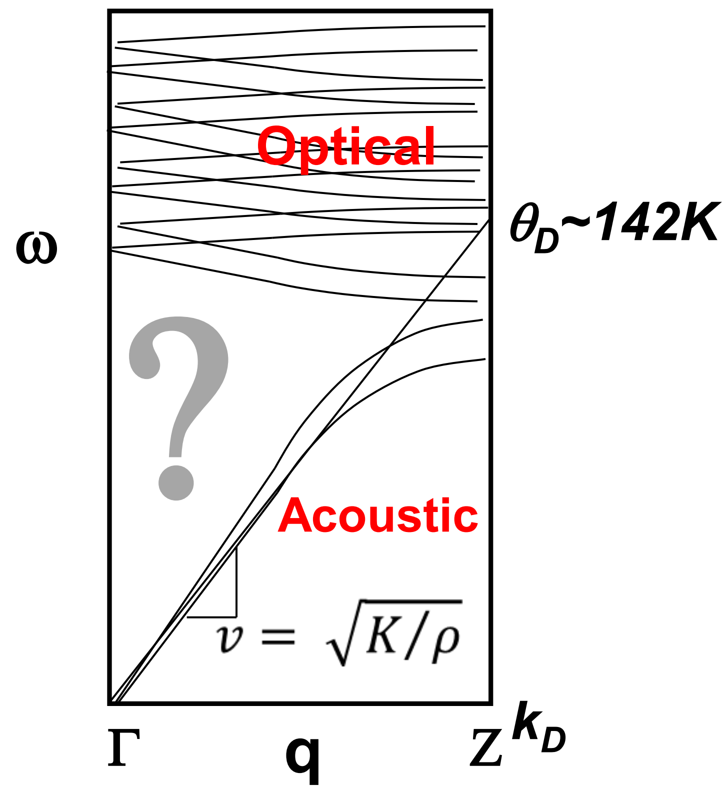
Debye Approximation

would be inaccurate, but *acceptable* for $T \ll \theta_D$

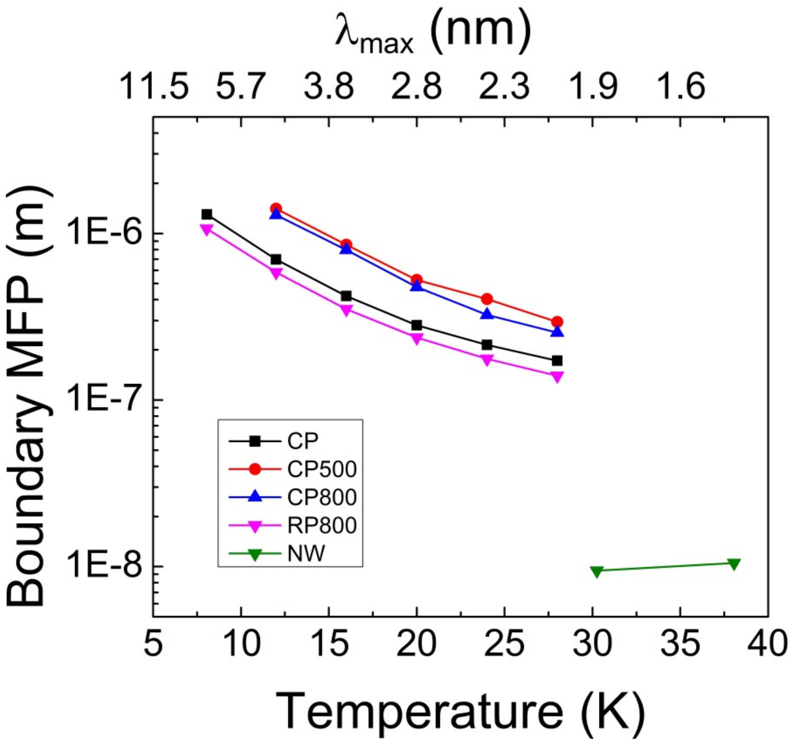


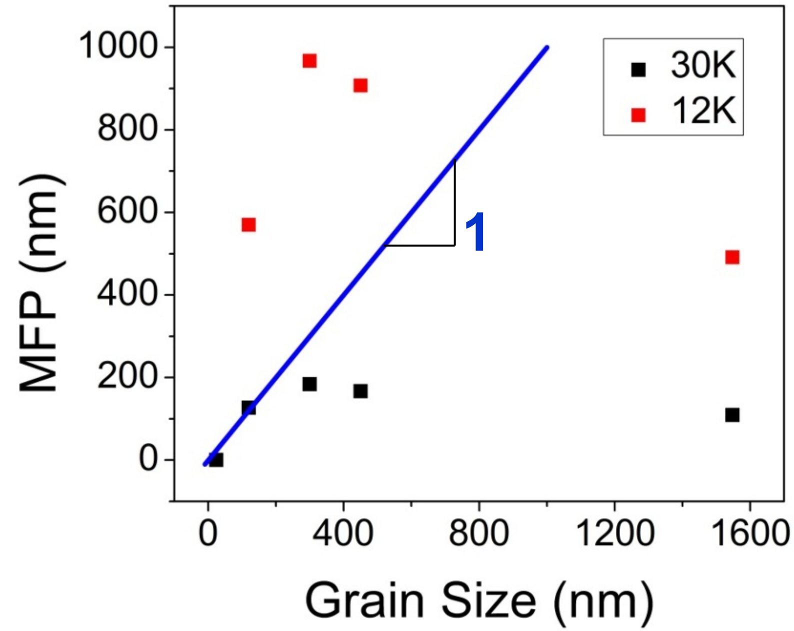
$$l = \frac{\kappa_l}{\int_0^{\omega_D} C(\omega)\, d\omega\, v / 3}$$

$$l_b^{-1} = l_{NW}^{-1} - l_{Single\ Crystal}^{-1}$$



Boundary Scattering Mean Free Path

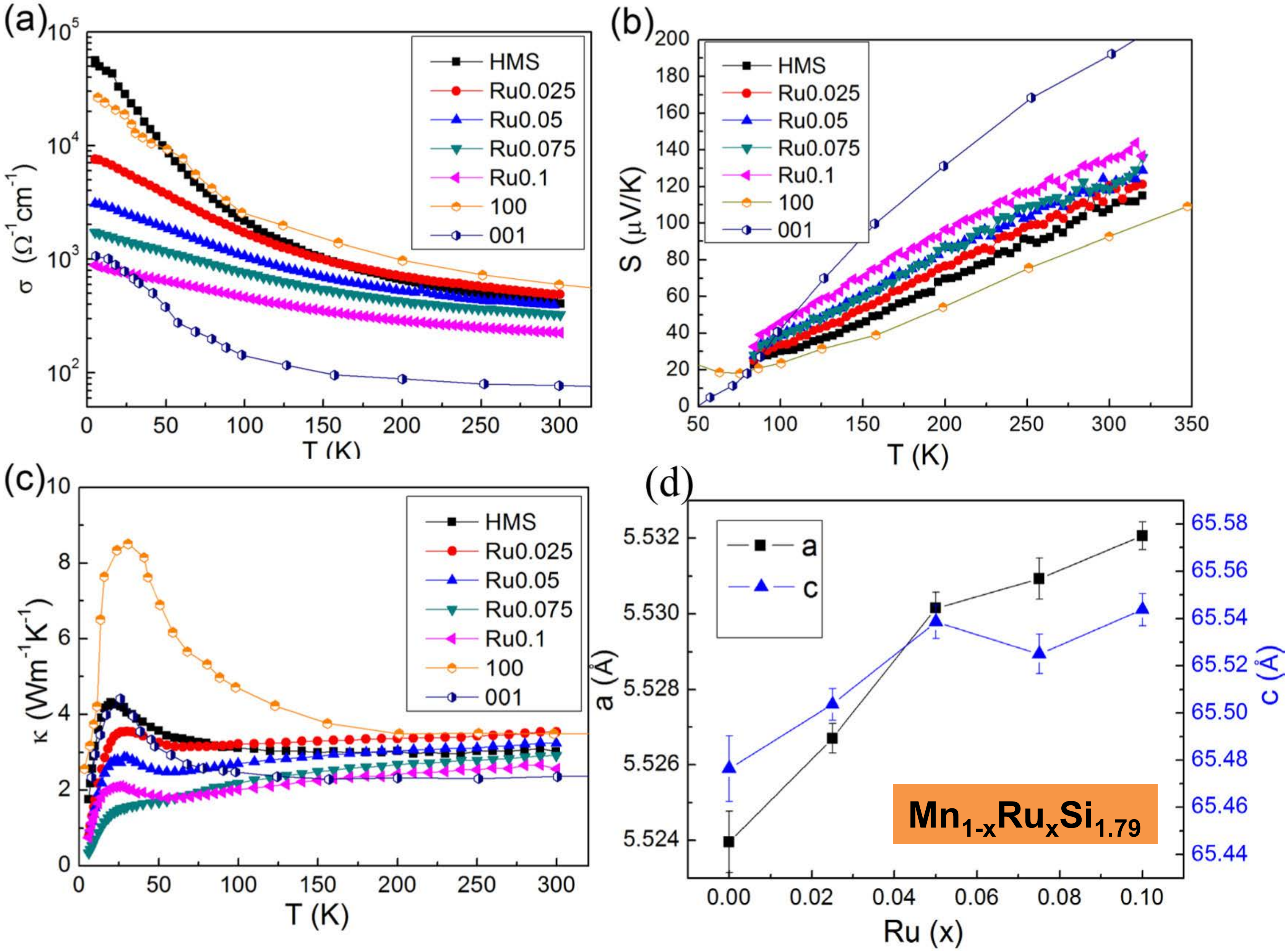




- The phonon-boundary scattering mean free path can be smaller than the grain size because of low phonon transmission across grain boundaries.

X. Chen, A. Weathers, A. L. Moore, J. S. Zhou, L. Shi, Journal of Electronic Materials (2012)

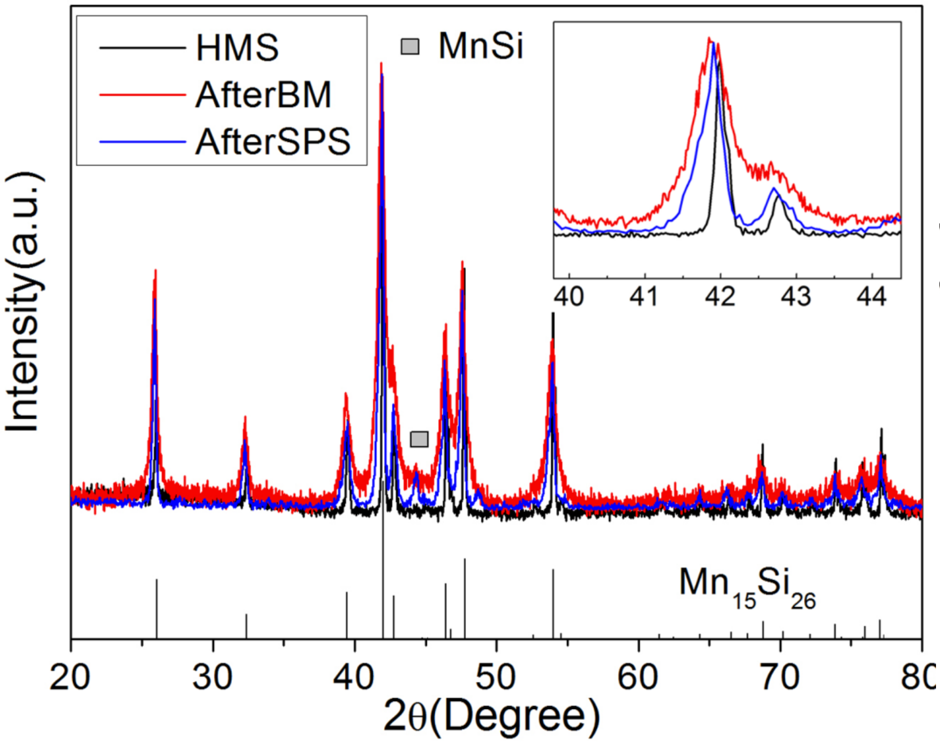
Solid-State- Reaction Synthesis of $Mn_{1-x}Ru_xSi_{1.79}$

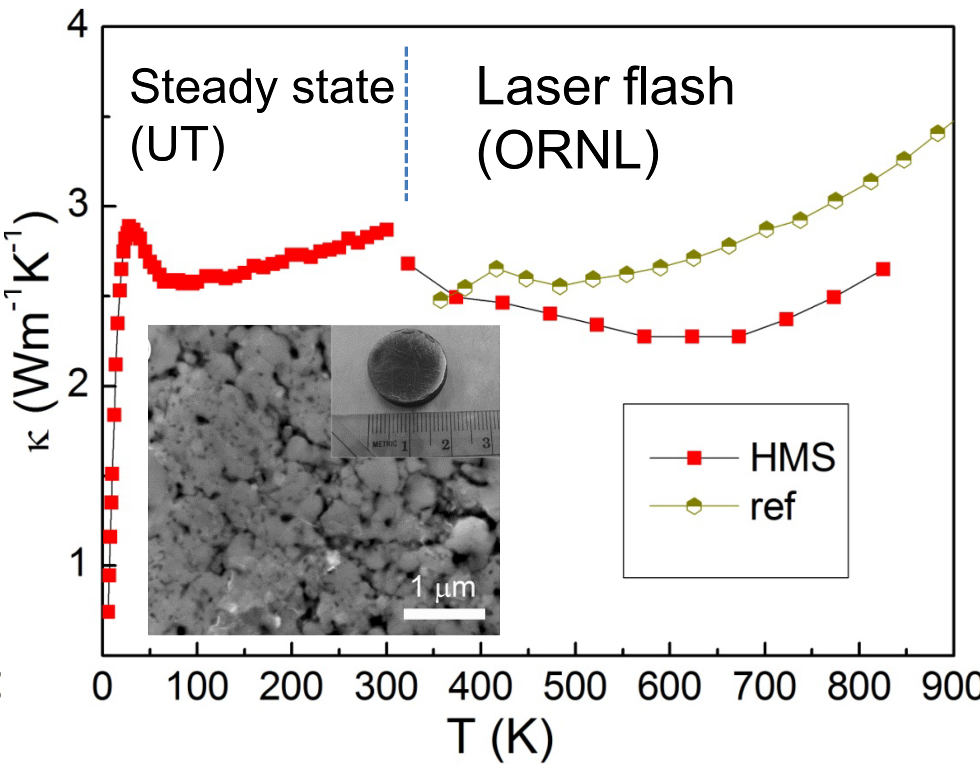


Literature [001] and [100] data from Zaitsev et al, in *CRC Handbook of Thermoelectrics*, 1994, Ed. Rowe

Synthesis of Nanostructured HMS by Ball milling (BM) and Spark Plasma Sintering (SPS).

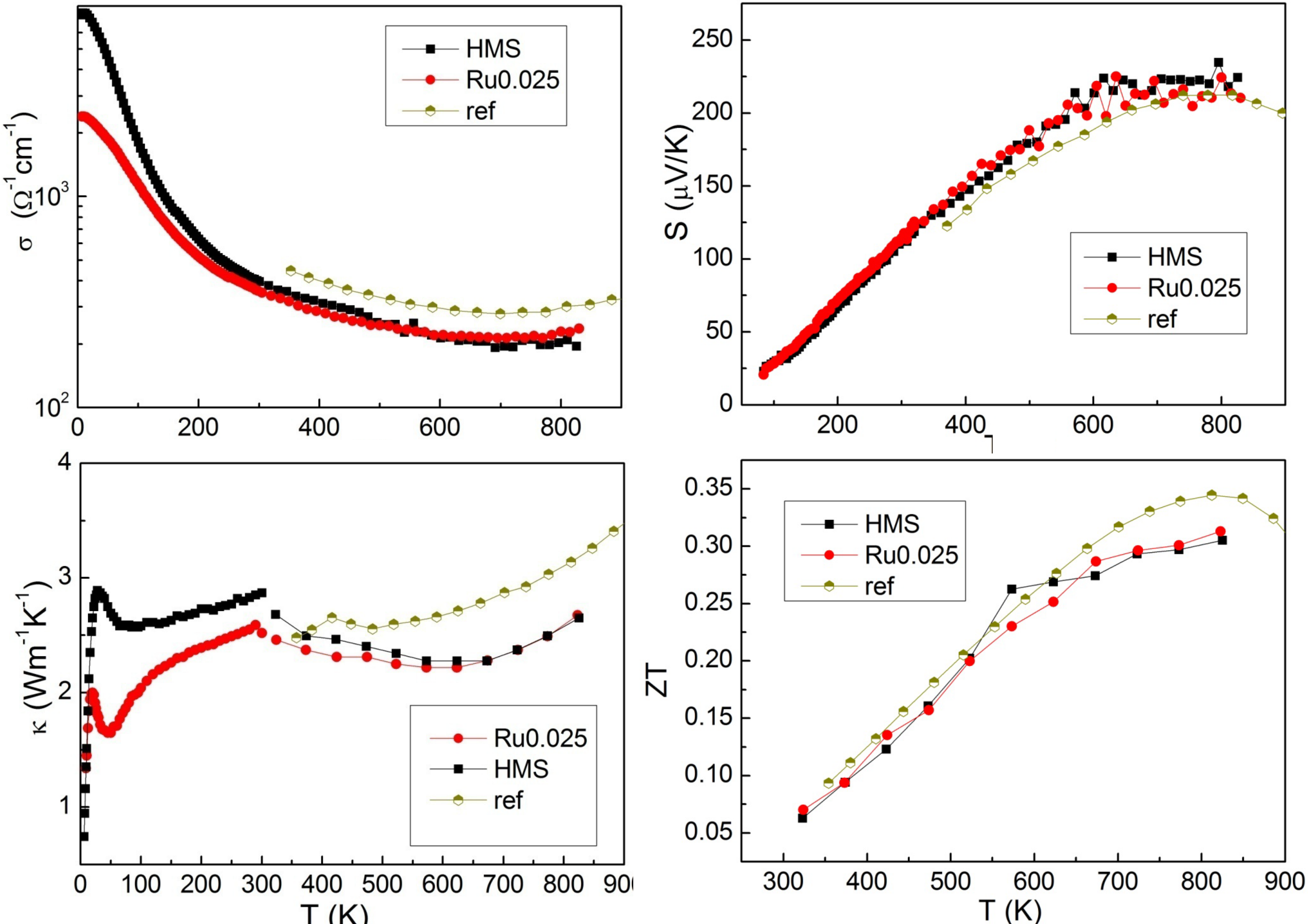
- Bulk HMS samples with the grain size of ~200 nm has been fabricated by BM and SPS. Small amount of MnSi phase can be found in the sample after SPS.





Ref: Erwin GroB et al., J. Mater. Res,10, 1995

SPS Synthesis and TE properties of $Mn_{1-x}Ru_xSi_{1.78}$

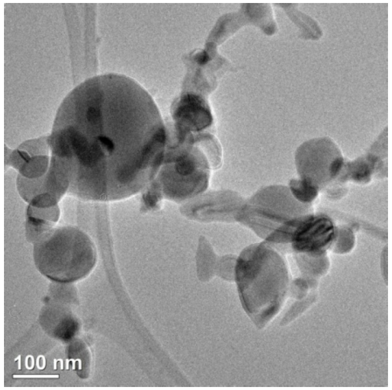


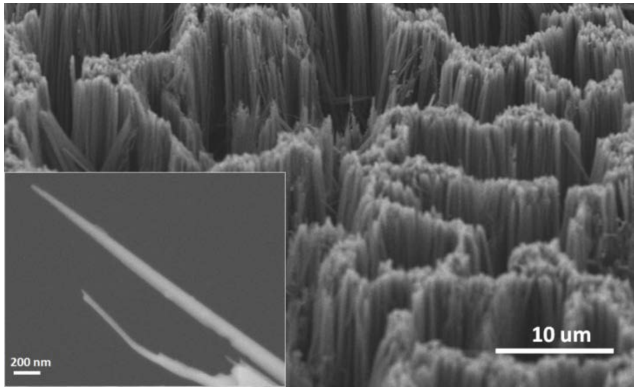
Ref: Erwin GroB et al., J. Mater. Res, 1995

Nanostructure Conversion Approach

Convert bulk Silicon(Si) nanostructures to nano-HMS

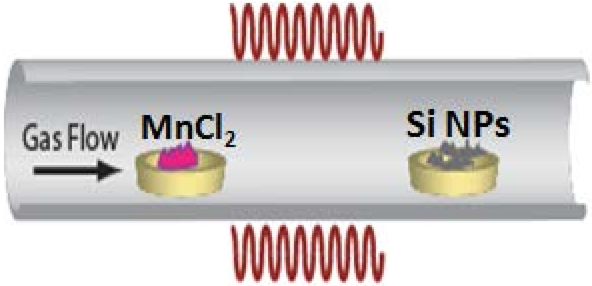
Si NPs

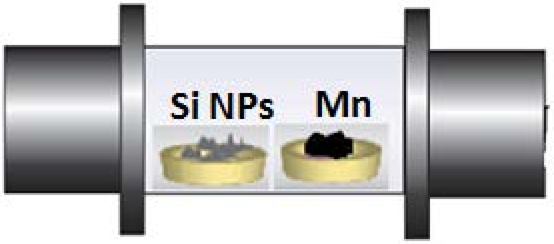




Si NWs

Mn and $MnCl_2$ precursor used in two different setup.

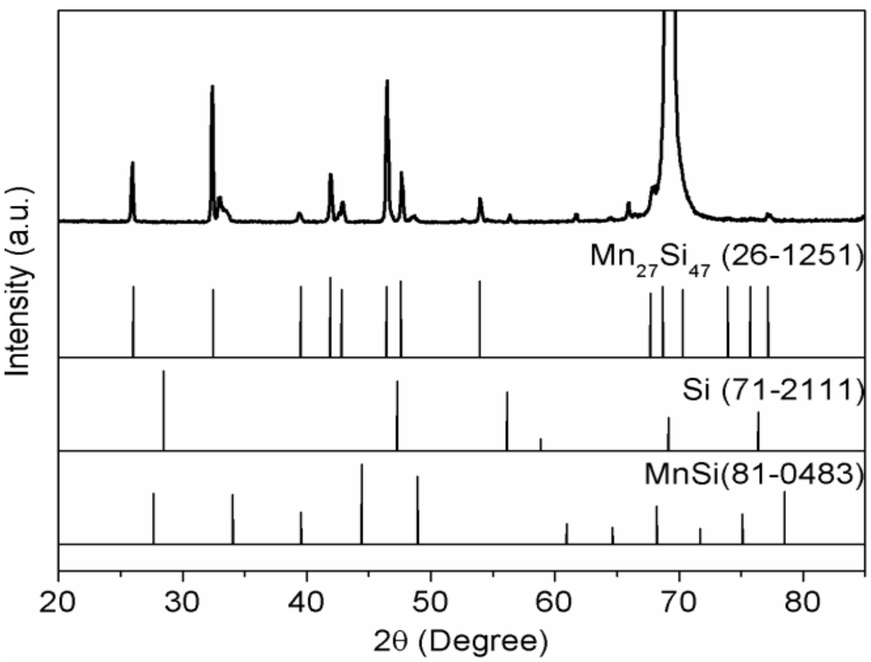




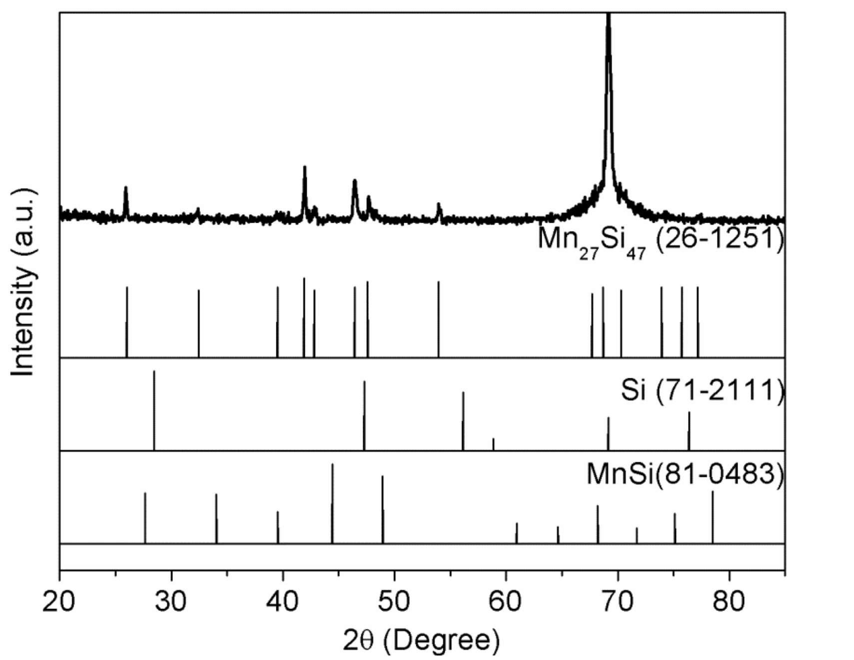
Conversion Results

- HMS is the major silicide phase formed at high temperatures for Si NPs conversion.
- HMS is the only phase formed at high temperatures for Si NWs conversion.

Si NPs conversion



Si NWs conversion



Summary

- $MnSi_{1.75}$ single crystals have been synthesized for characterization of its TE properties and phonon dispersion.

- Nanostructured $MnSi_{1.5}$ bulk samples have been synthesized with cold pressing and SPS with ~100 nm grain sizes. For some porous $MnSi_{1.5}$ prepared by cold pressing, the phonon mean free path is smaller than the grain size because of low phonon transmission coefficient across the grain boundary, resulting in reduced thermal conductivity compared to the bulk crystal value.

- A chemical conversion approach has been established to convert silicon nanostructures into HMS nanostructures of sub-100 nm grain sizes in order to further reduce the lattice thermal conductivity.

- Ru and other dopants are under investigation for increasing the power factor.