NSF/DOE Thermoelectric Partnership: High-Performance Thermoelectric Devices Based on Abundant Silicide Materials for Vehicle Waste Heat Recovery

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Overview

Timeline

- Project start date: October 1, 2010
- Project end date: September 30, 2013
- Percent complete: 15%

Budget

- Total project funding: $1,499,984
  - DOE share: $749,992
  - NSF share: $749,992
- Funding received in FY10: $499,991
- Funding for FY11: $499,993

Partners

- Collaboration:

  Hsin Wang,

  Oak Ridge National Lab

Barriers

- **Barriers**

  - Cost

  - Scale-up to a practical thermoelectric device

  - Thermoelectric device/system packaging

- **Targets**:
  - Earth-abundant silicide thermoelectric materials with performance competitive with the state of the art found in materials that contain rare elements
  - Single-body silicide TE legs with gradient doping instead of a segmented design to eliminate interfaces
  - Silicide interface and interconnect materials to further enhance thermomechanical durability

Objectives and Tasks

Objectives:

a) To increase the *ZT* of abundant, low cost, and bulk scale 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:

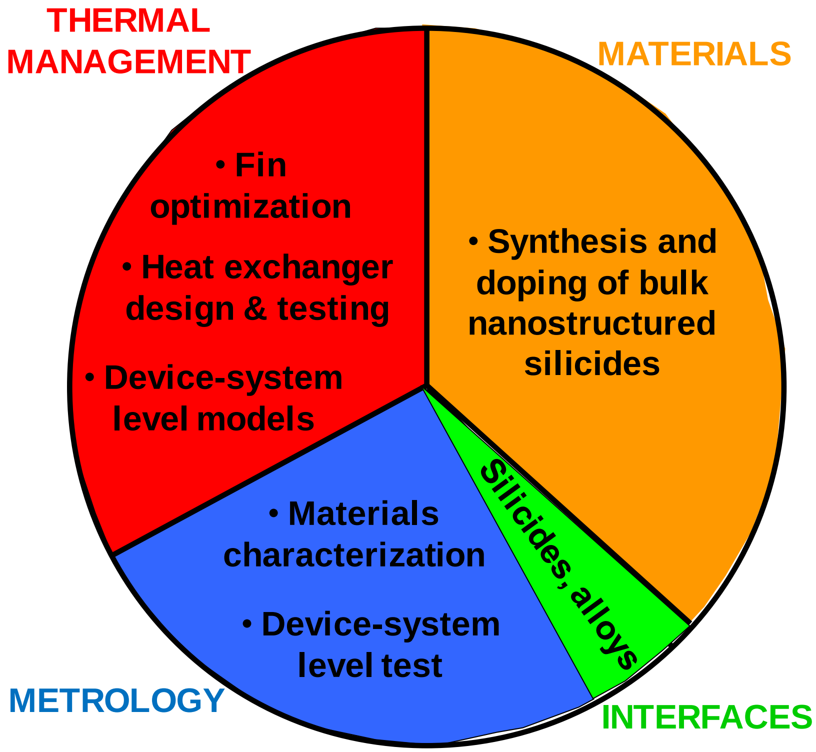
a) Investigate methods for scalable synthesis and position-dependant doping of bulk nanostructured silicides

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

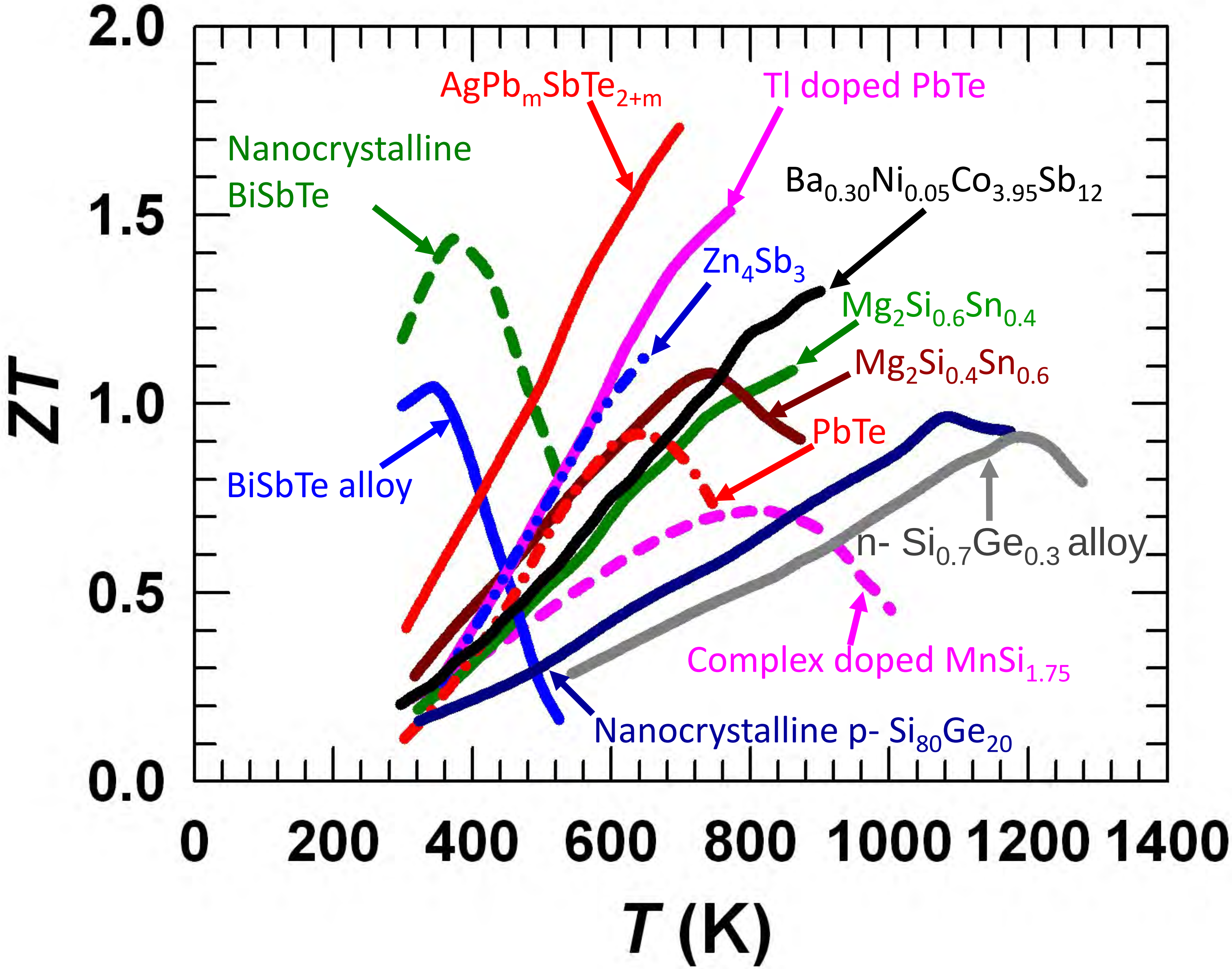
c) Characterize the TE properties of silicides at temperatures between 300 and 900 K

d) Develop computational 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

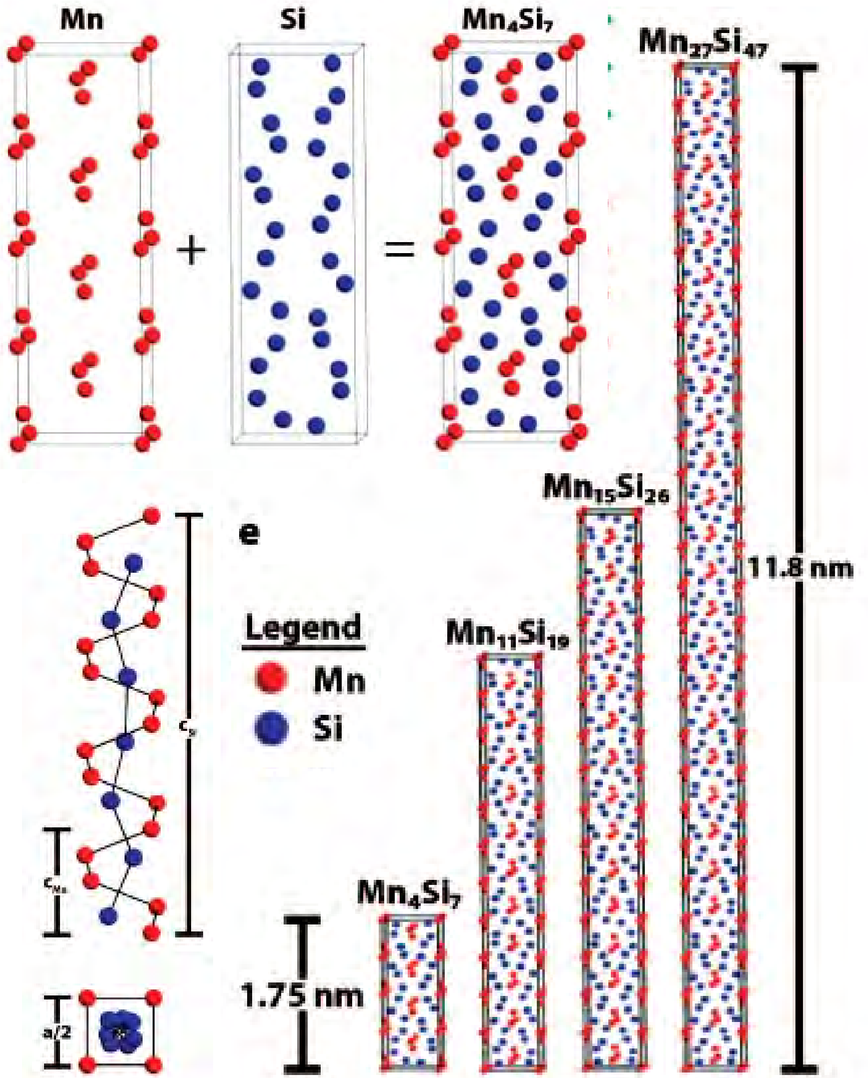


ZT of Bulk Thermoelectric Materials



Approach: Higher Manganese Silicides (HMS) or $MnSi_{1.75}$

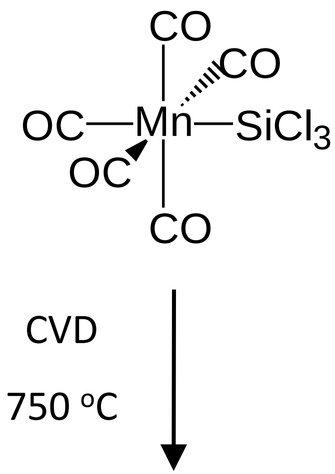
- Novotony Chimney Ladder Phase



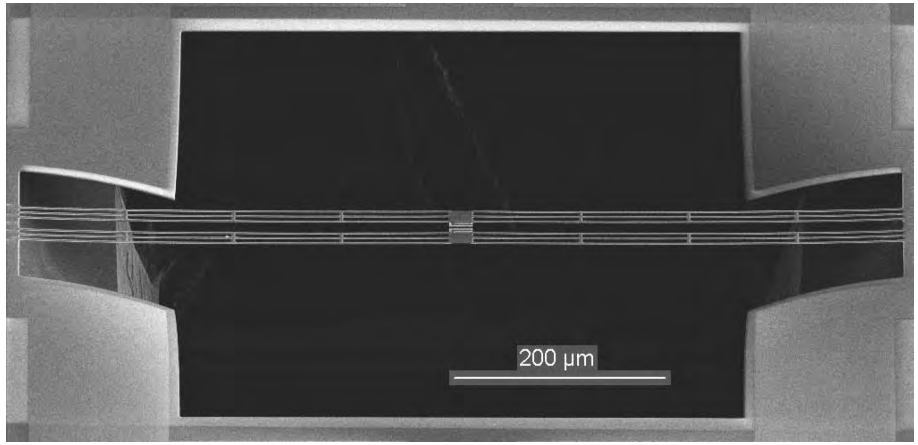
- Peak ZT close to ~0.7 at near 800 K reported in complex doped HMS by Zaitsev et al., in *CRC Handbook of Thermoelectrics*, 1994, Ed. Rowe

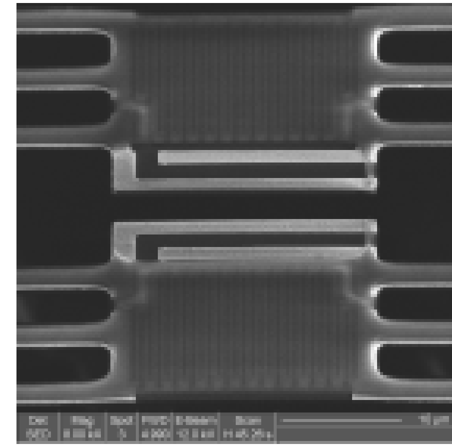
Higgins & Jin, *JACS*, 130, 16086 (2008)

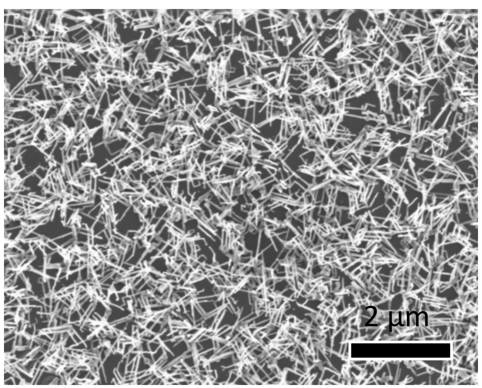
Accomplishments: Synthesis and Characterization of HMS Nanowires

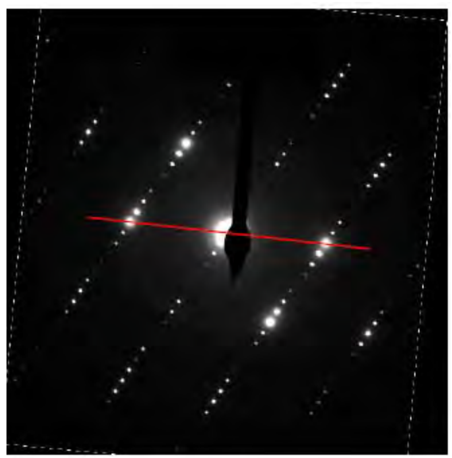


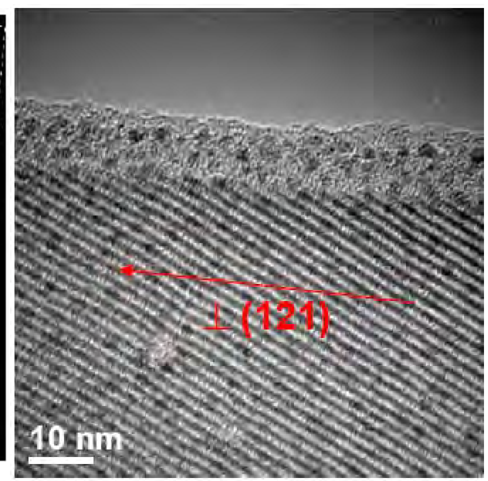
Zhou, Sczczech, Pettes, Moore, Jin, Shi, Nano Lett. 2007, *7*, 1649.

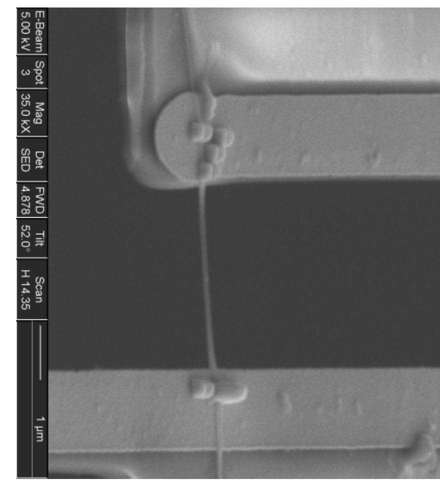








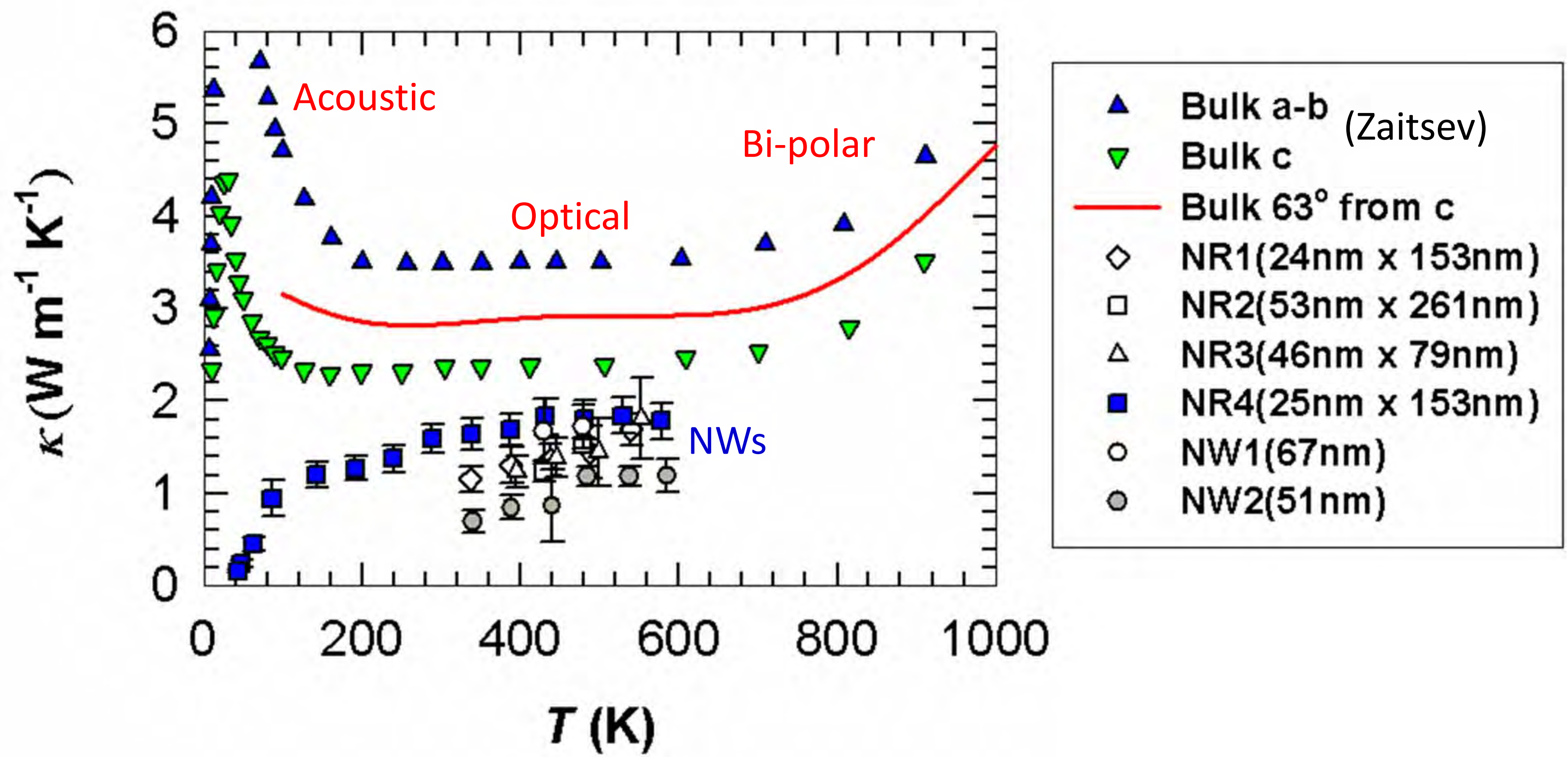




HMS NW synthesis: Higgins & Jin JACS 2008, *130*, 16086.
Silicide NW review: J. Mater. Chem. 2010, *20*, 223.

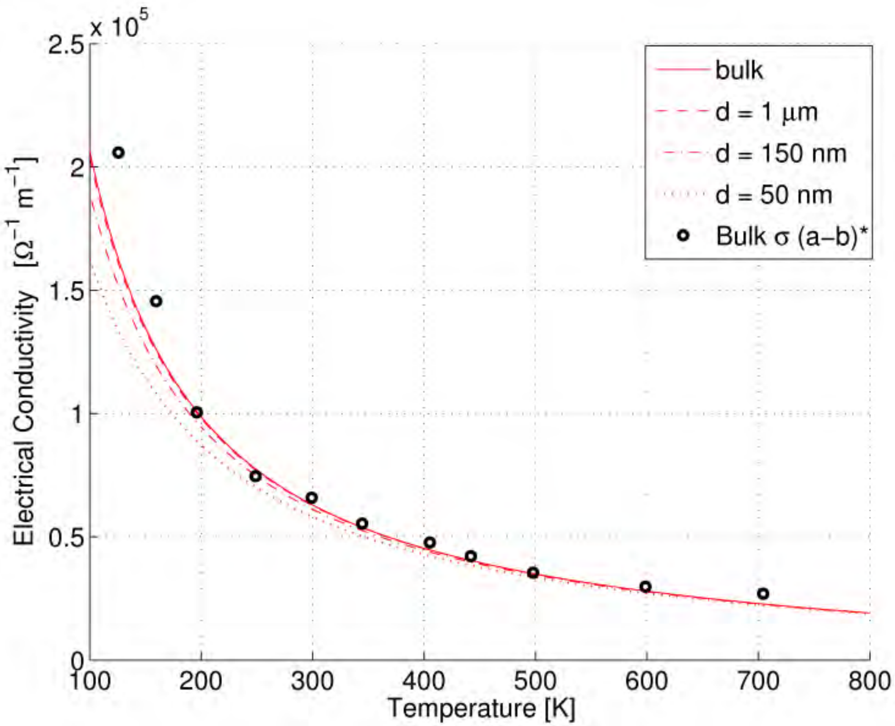
- Nanoribbon (NR) or NWs of $Mn_{39}Si_{68}$ or $Mn_{19}Si_{33}$
- c ≈ 17 nm
- Growth direction perpendicular to {121} planes, or 63° from the c axis

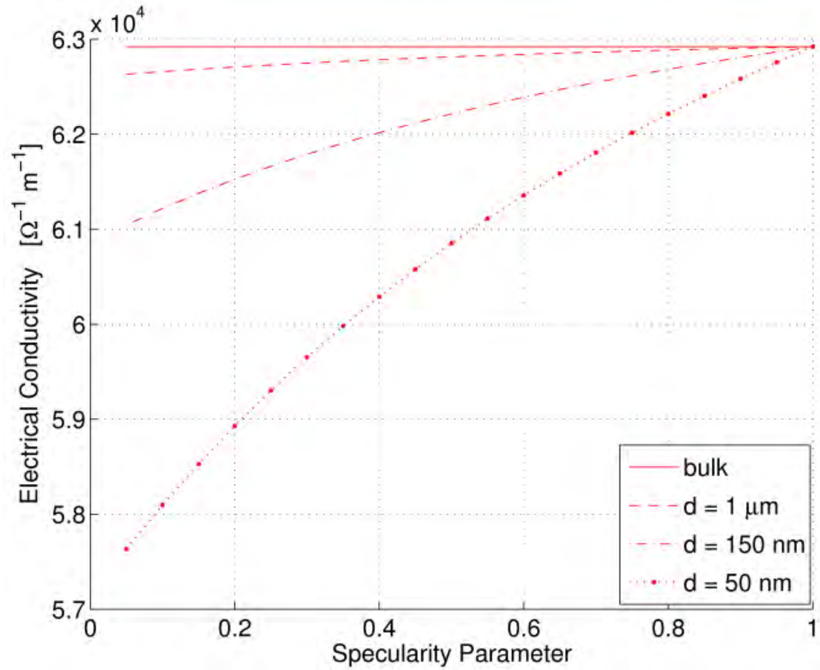
Accomplishments: Discovery of Amorphous Thermal Conductivity in HMS NRs and NWs



- Calculated amorphous thermal conductivity limit $\kappa_{\alpha} \approx$ 0.7 W/m-K.
- The transition from the phonon-crystal behavior in bulk to amorphous thermal conductivity in the $MnSi_{1.75}$ nanostructures reveals effects of surface scattering, especially for long-wavelength phonons.

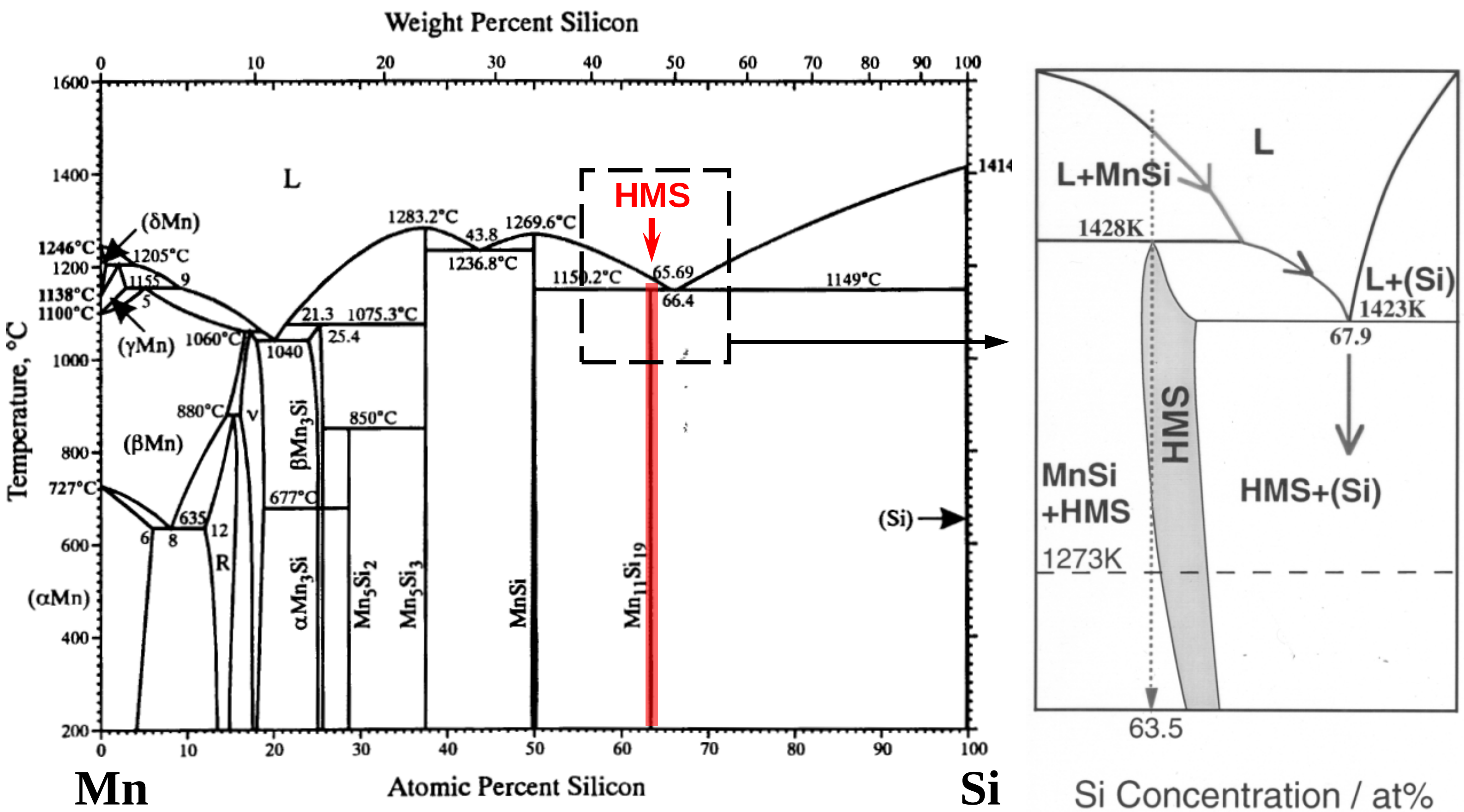
Accomplishments: Modeling Size Effect on Electron Transport in $MnSi_{1.75}$ Nanowires





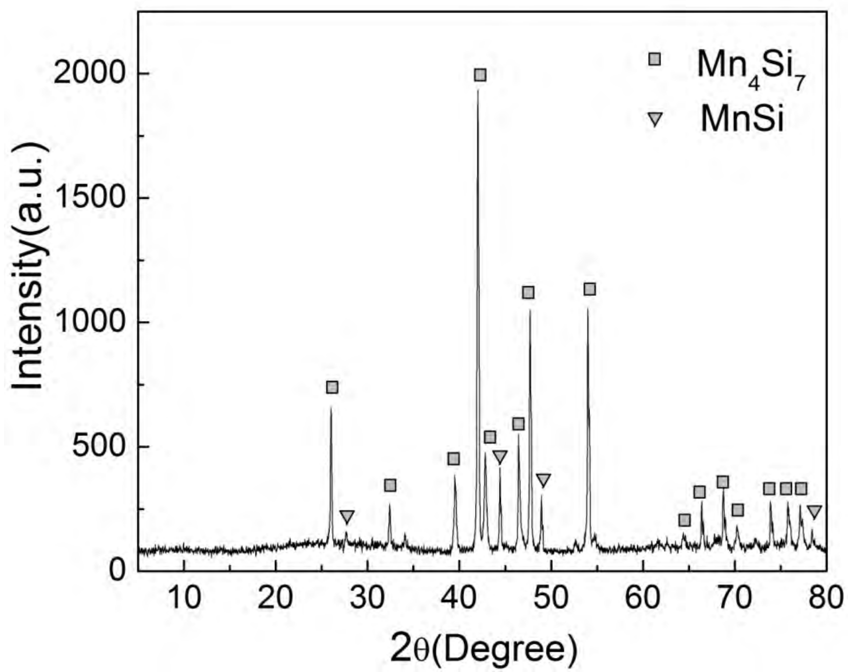
Bulk data used for comparison are from V.K. Zaitsev, "Thermoelectric Properties of Anisotropic MnSi_1.75" in *CRC Handbook of Thermoelectrics*, D.M. Rowe, Ed. Boca Raton, FL: CRC Press, 1995, 299-309.

Approach: Bulk HMS Synthesis via Two-step Solid-State Reaction

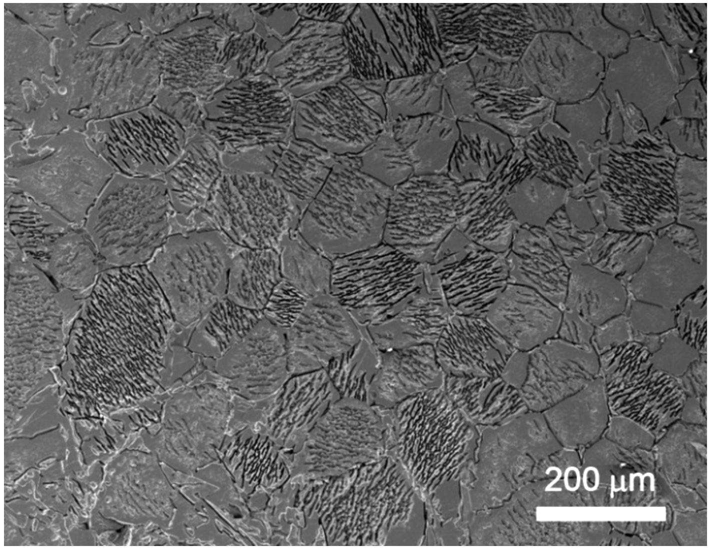


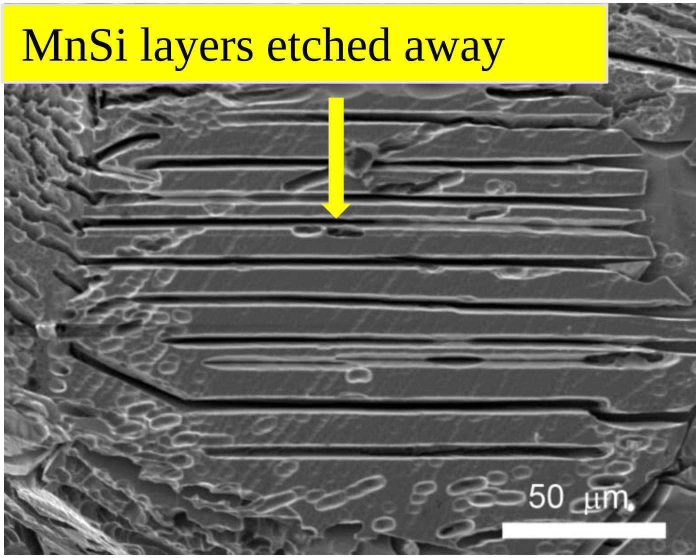
Mn + Si $\xrightarrow[\text{1 h}]{\text{Ball milling}}$ Mn, Si mixture $\xrightarrow[\text{973 k,48 h}]{\text{Sealed in a tube}}$ ingot $\xrightarrow{\text{Grinding}}$ powder $\xrightarrow[\text{1 h}]{\text{Ball milling}}$ mixture $\xrightarrow[\text{1473 k,48 h}]{\text{Sealed in a tube}}$ HMS

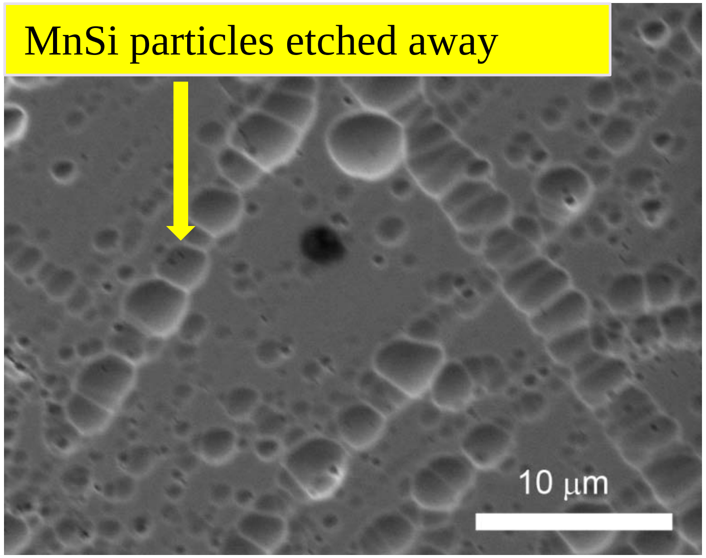
Accomplishments: Synthesis of Bulk HMS With MnSi Phases



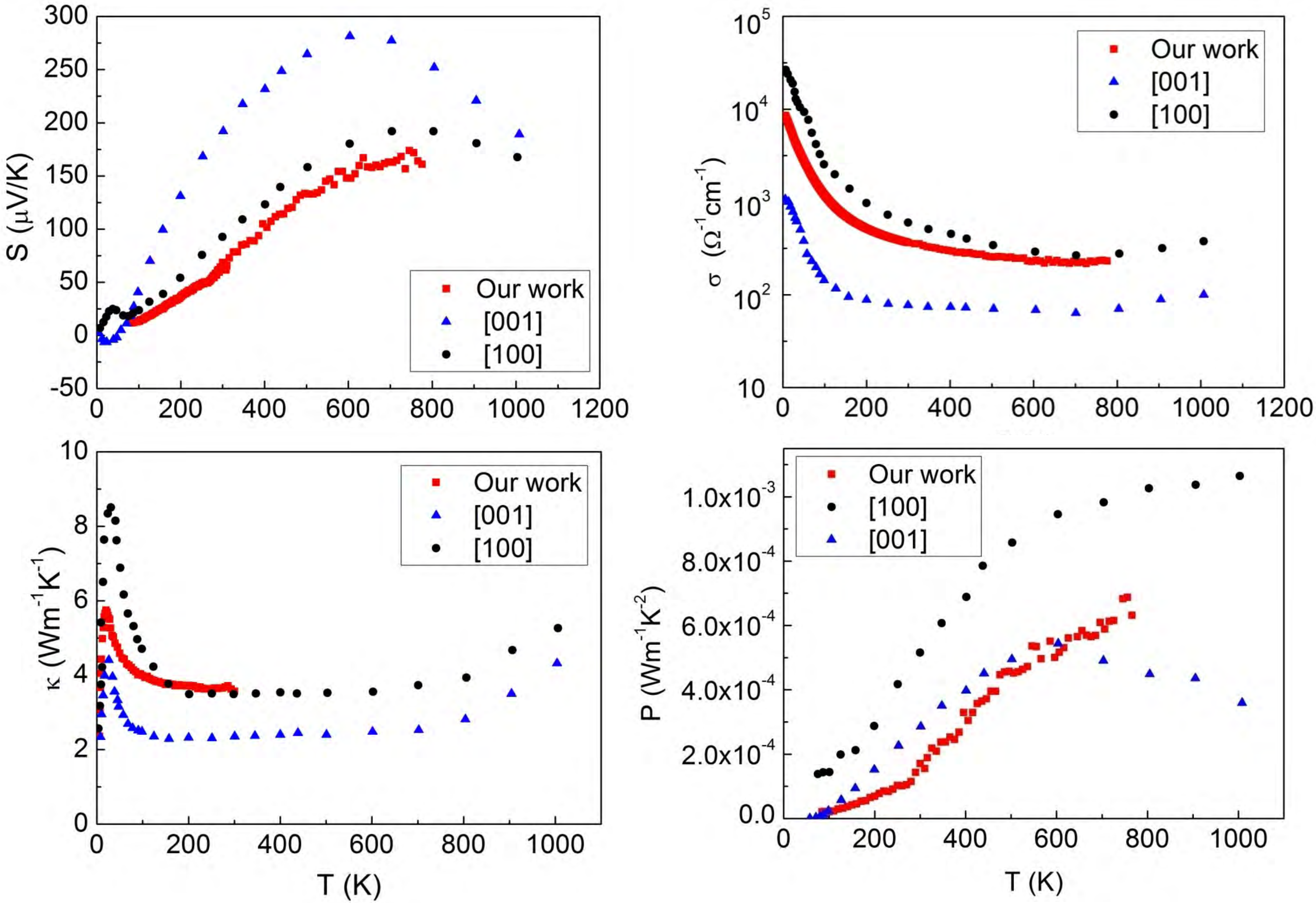
SEMs of HMS sample surface after polishing and 60-s selective etching of MnSi in $HF:HNO_3:H_2O$=1:6:13







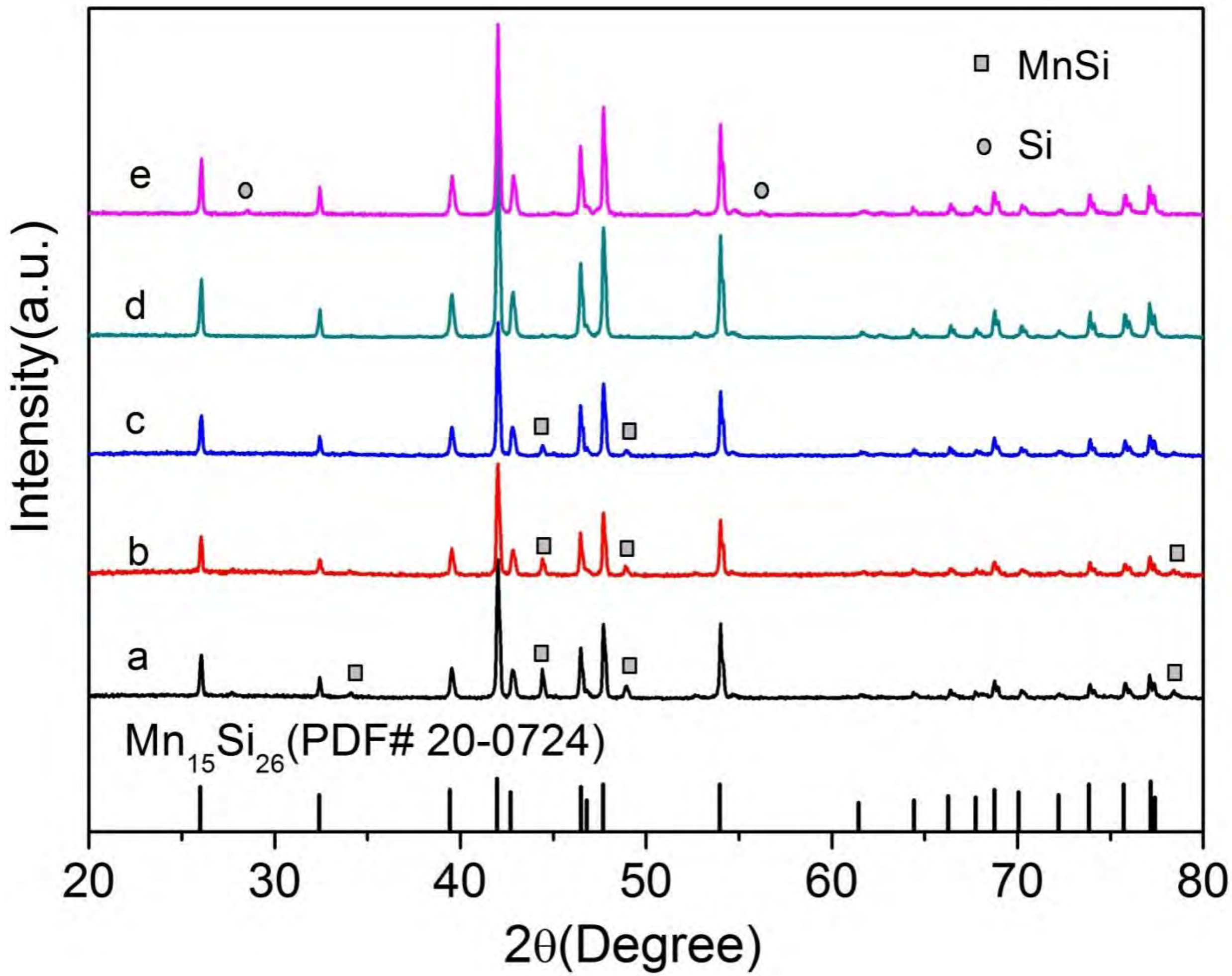
Accomplishments: TE Properties of Bulk Un-doped HMS with MnSi phases



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

Accomplishments: Synthesis of Pure HMS without MnSi and Si Phases

- $MnSi_x$ was synthesized by solid state reaction in a vacuumed quartz tube (700°C, 48 h).
- The amount of MnSi decreased with increase of Si, and pure HMS was obtained at x=1.83.



e:MnSi1.89

d:MnSi1.83

c:MnSi1.80

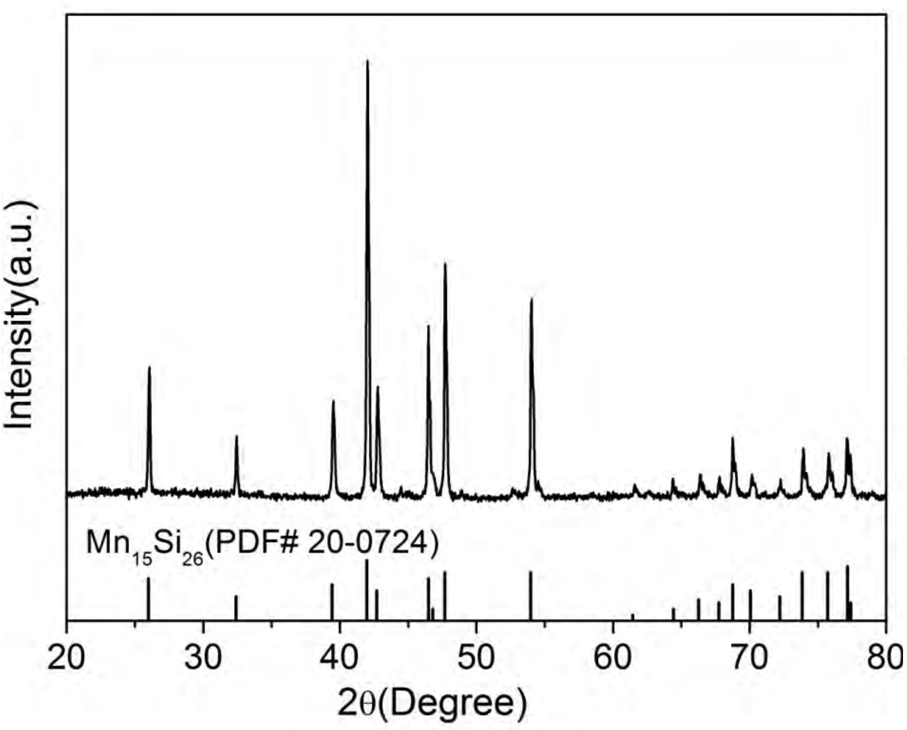
b:MnSi1.77

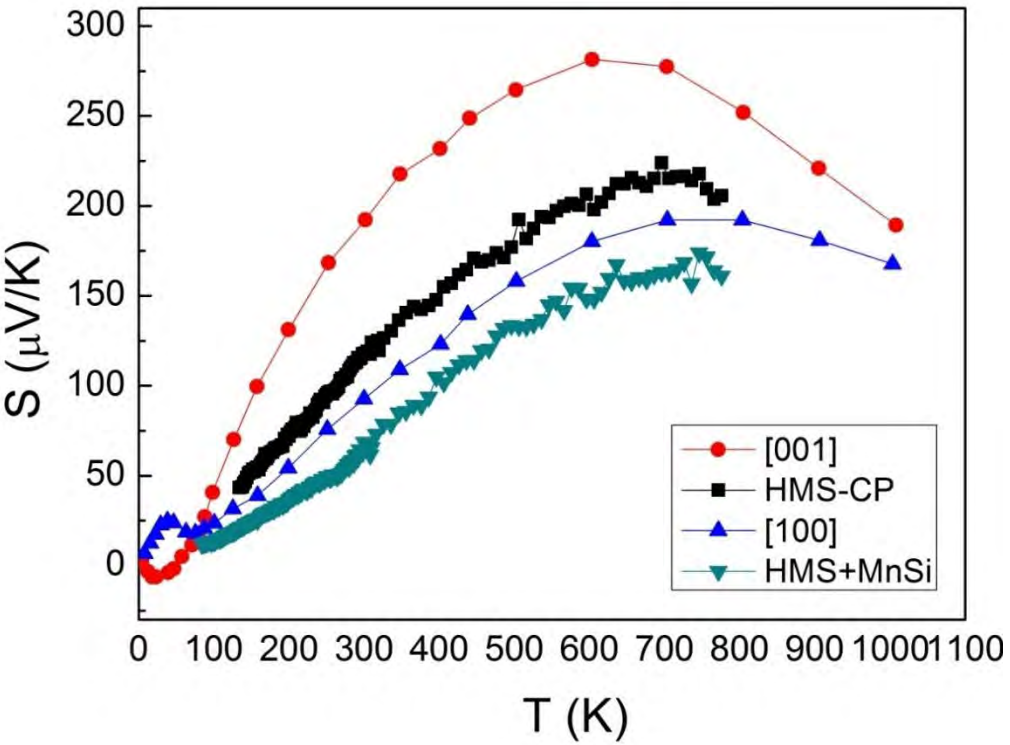
a:MnSi1.74

Accomplishments: Synthesis and TE Property of Pure HMS

Synthesis method:

HMS obtained at 700 ºC for 48h → cold press → **Pellets** → annealed in vacuum, 700 ºC, 10 h → **Sample for TE measurement**





XRD after annealing

Seebeck coefficient of cold-pressed HMS

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

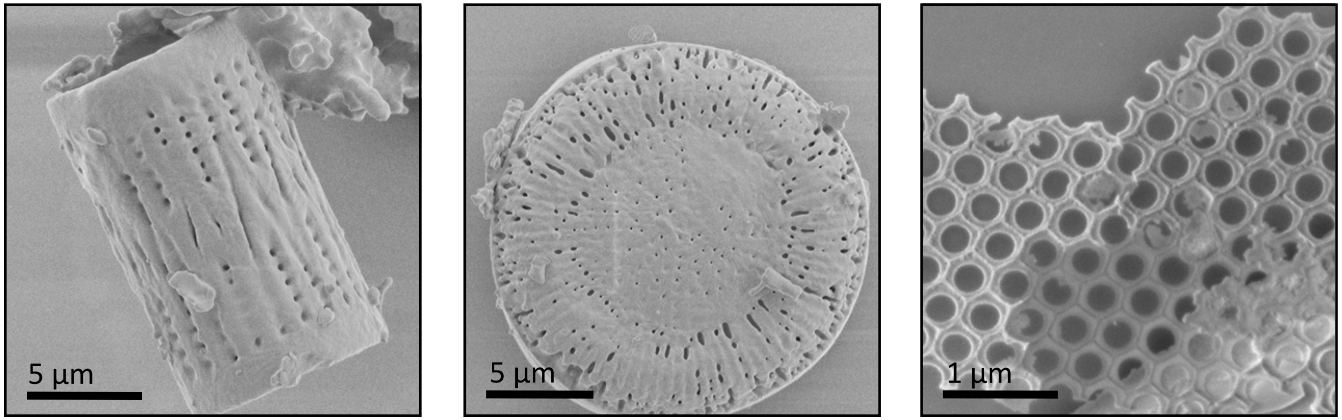
Future Work in HMS Materials Research

- Converting MnSi microlayers and microparticles in HMS into nanoparticles to scatter long wavelength phonons
- Ball milling / solution synthesis of HMS nanoparticles for making bulk nanocomposites
- Tuning the *ZT* peak position via position-dependant doping
- Converting diatomaceous earth into bulk nanostructured silicides

Future Work:
Converting Diatomaceous Earth into Bulk Nanostructured Silicides

Szczech & Jin *J. Solid State Chem.* 2008, *181*, 1565.

Silica



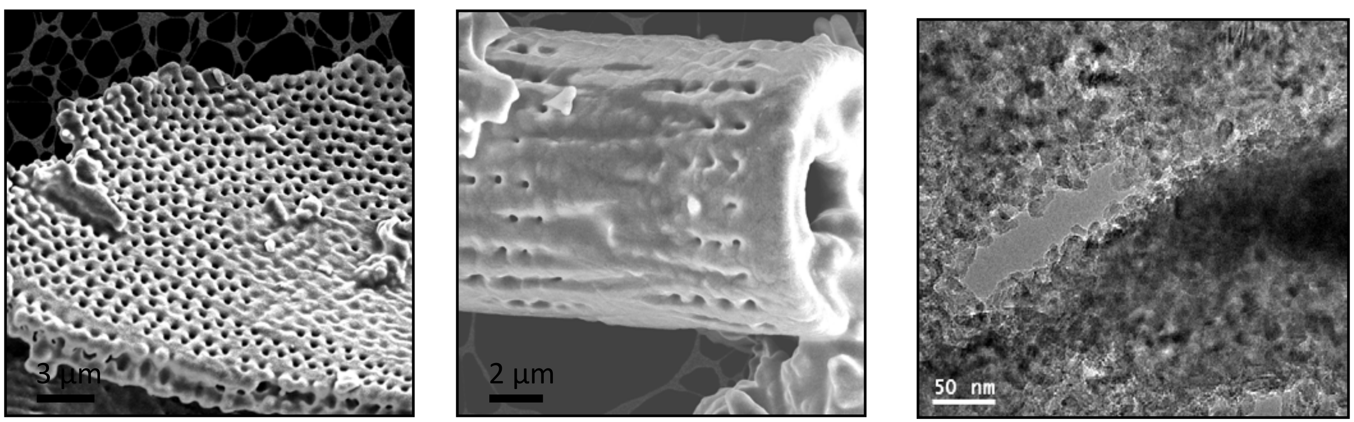
SiO_2 *(s)* + 2 Mg *(g)* → Si *(s)* + 2 MgO *(s)*

Si *(s)* + 2 Mg *(g)* → Mg_2Si *(s)*

Mg_2Si/MgO composite with nanoscale grains

Mg_2Si

(silicon)

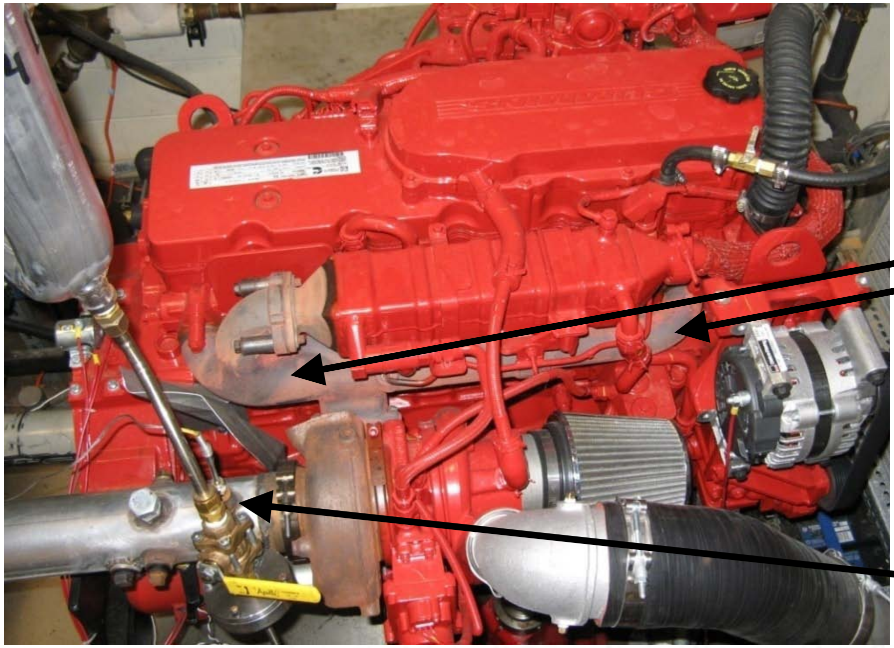


Expand to doped $MnSi_{1.75}$ and $Mg_2Si_{1-x}Sn_x$

Approach: Integration of TE Devices in a 6.7 liter Cummins Diesel Engine

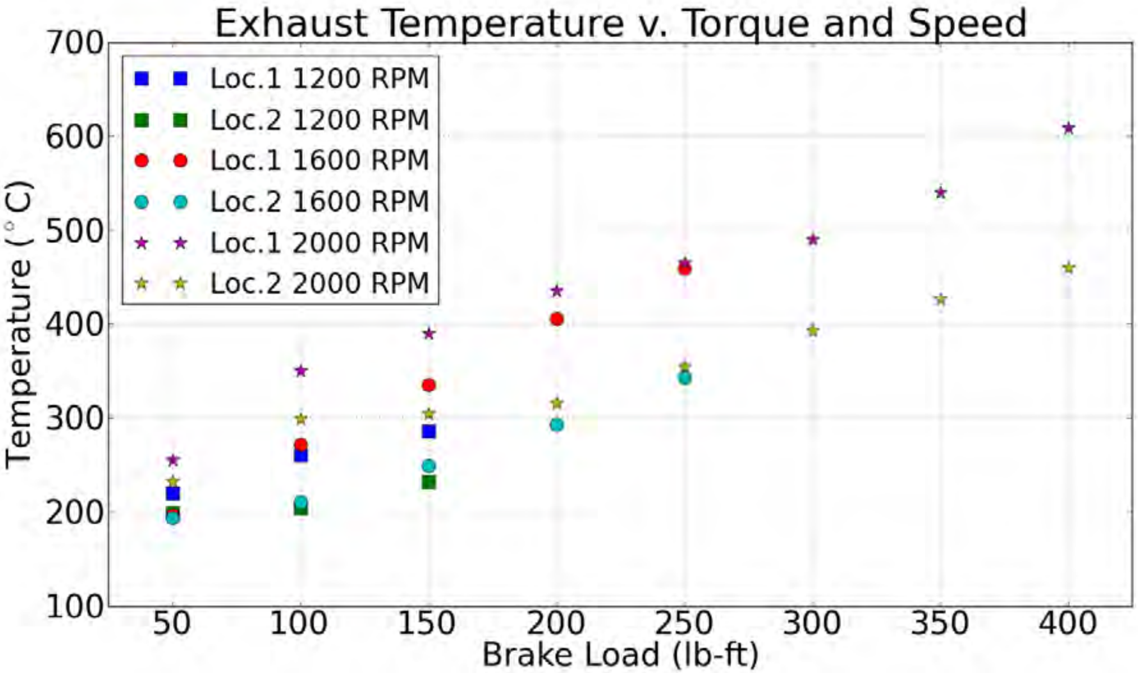
Exhaust after-treatment (DOC/DPF)

Engine



Location 1: Manifold

Location 2: Post Turbo



Approach:
Thermodynamic Systems Model

- Primary constraints: maintain temperature of 250°C into exhaust after-treatment system, maintain acceptable pressure drops throughout exhaust system.
- **Assumptions**: TE heat exchanger is able to extract all available heat subject to temperature constraints and with cold side temperature of 25°C.
- Model has yet to account for spatial variation of TE properties along TE module

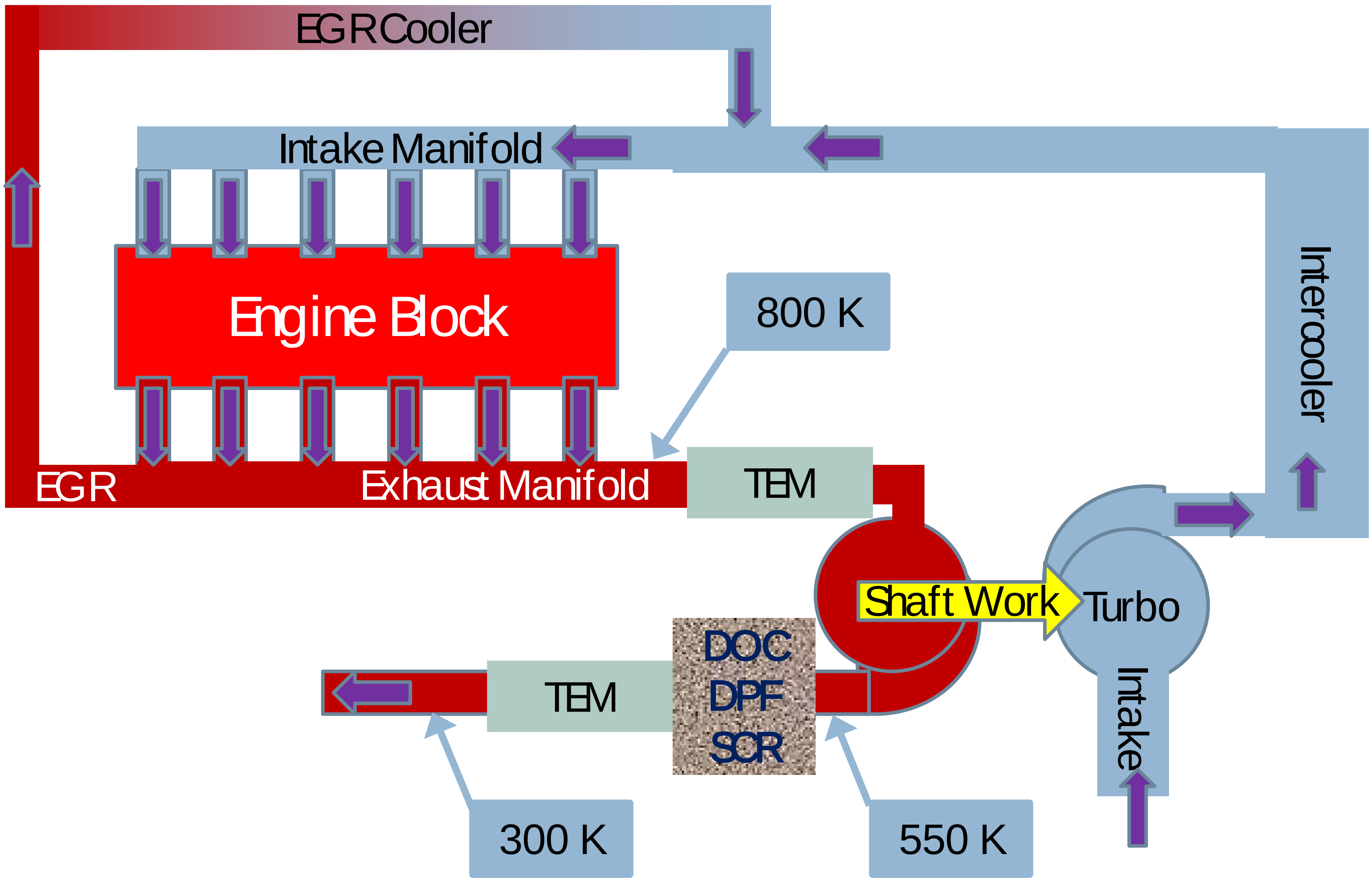
$$\eta_{TE,max} = \frac{\Delta T}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h}$$

$$\eta_{sys} = \frac{\eta_{TE}\dot{Q}_h - \dot{W}_{pumping}}{\dot{m}\psi}$$

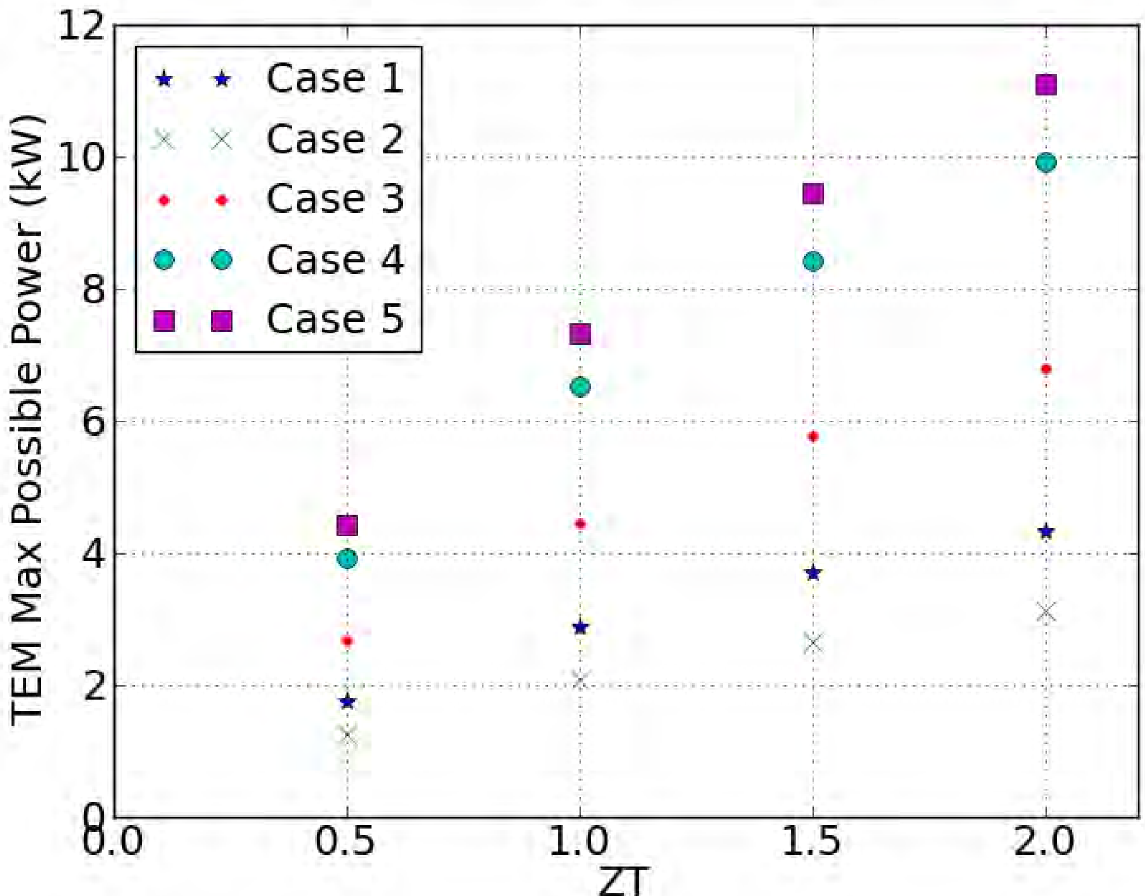
Future Work: Systems Modeling

- Two computer models currently being developed
  - **Thermodynamic systems model** to optimize thermoelectric device locations in engine exhaust
  - **Heat Transfer model** for improving TE module performance
  - Both to be integrated as one model and to account for transient exhaust conditions
- Components include:
  - TE Module(s)
  - Turbocharger
  - Exhaust aftertreatment system
  - EGR cooler

Possible TE Module Locations



Accomplishments:
Preliminary System Level Analysis Results



- RPM = 2000
- Brake Torque = 300 lb-ft
- Charge flow rate = 7.8 kg/min
- Exhaust port temperature = 800 K
- Engine exhaust availability = 81.1 kW

Case 1: single TEM > turbo > after-treatment

Case 2: turbo > single TEM > after-treatment

Case 3: turbo > after-treatment > single TEM

Case 4: turbo > TEM > after-treatment > TEM

Case 5: TEM > turbo > after-treatment > TEM

Collaborations

- Partners

  We plan to collaborate with Dr. Hsin Wang of Oak Ridge National Lab to employ their high-temperature TE characterization facility to validate our in-house measurement results.

Summary

- **Relevance:** The cost, scale-up, and packaging barriers for thermoelectric vehicle waste heat recovery devices are being addressed by fabricating abundant silicide materials-based thermoelectric devices with enhanced device efficiency and heat exchanger system performance.
- **Approaches:** Bulk $MnSi_{1.75}$ and $Mg_2Si_{1-x}Sn_x$ with nano-grains or nanoparticle inclusion are being synthesized via both solid state reaction and chemical conversion from diatomaceous earth to fabricate single-body silicide TE legs with gradient doping instead of a segmented design to eliminate interfaces. Silicide interface and interconnect materials are investigated to enhance thermomechanical durability. New heat exchanger designs are investigated to enhance thermal management performance.
- **Accomplishments:** In nanostructured complex $MnSi_{1.75}$, the contributions to κ from high-frequency phonons and low-frequency phonons have been found to be suppressed by the complex structure and interface scattering, respectively, to obtain glass-like thermal conductivity. Pure $MnSi_{1.75}$ bulk samples have been synthesized and the properties have been measured. Preliminary exhaust temperature measurements and thermodynamic modeling results have been obtained.
- **Collaboration:** We will collaborate with Dr. Hsin Wang of Oak Ridge National Lab to employ their high-temperature TE characterization facility to validate our in-house measurement results.
- **Future Work:** We will conduct theoretical modeling and experiments to investigate various heat exchanger configurations for enhancing heat transfer to the TE devices, and continue our investigation of synthesis techniques to produce single-body TE legs based on nanostructured bulk silicides with gradient doping.