NSF/DOE Thermoelectrics Partnership: Thermoelectrics for Automotive Waste Heat Recovery

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Presenter: Xianfan Xu

Purdue University

In Partnership with General Motors Global R&D and Oak Ridge National Laboratory

Project ID # ACE074

Overview

Timeline

- Project state date: January 2011
- Project end date: December 2013
- Percent complete: 6.5%

Budget

- Total project funding
  - DOE: $695,913
  - NSF: $695,912
- Funding received in FY10: $0
- Funding for FY11: $446,785

Barriers

- Barriers addressed
  - Advanced TE materials
  - Efficient heat exchanger
  - Thermal interface materials
  - Metrology tool development

Partners

- General Motor R&D Center, Dr. G. P. Meisner
- Oak Ridge National Laboratory, Dr. H. Wang

Relevance - Objective

- This project is in collaboration with the General Motors Global R&D (GM) to develop thermoelectric (TE) waste heat recovery systems, or TE generators (TEG), at a scale commensurate with the global vehicle manufacturing enterprise.
- Research/development at Purdue is to develop the fundamental understanding and technology improvements needed to make viable the efficient conversion of waste heat to electricity and to assist deployment/commercialization of TEG at GM
- We carry out research the following four areas:
  - development of TE materials,
  - development of thermal interface materials,
  - design and development of efficient heat exchangers,
  - development of advanced metrology tools.

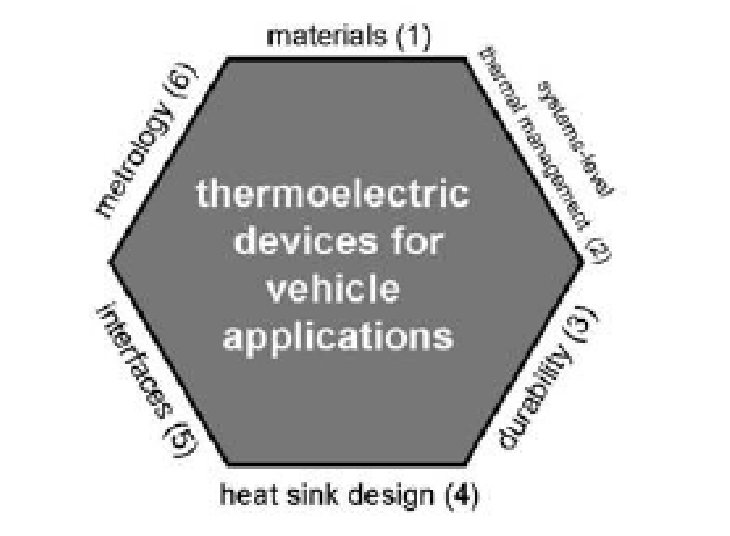
Milestone – Project Timeline

	Timeline (in months)					
Thrust	6	12	18	24	30	36
1. TE materials a. filled-skutterudites b. nanowire low-T materials c. Nanoscale oxides d. metal/semiconductor laminates	mat. 1 develop-ment develop-ment develop-ment	mat. 2 develop-ment develop-ment develop-ment	mat. 3 TE module TE module TE module	mat. 4 TE module TE module TE module	mat. 5 testing testing testing	mat. 6 testing testing testing
2. Thermal design a. heat exchanger b. thermal interface materials	design CNT for low-T applica-tions	design CNT for low-T applica-tions	design/ fabrication/testing* Other nanoma-terials for high-T	design/ fabrication/testing* Other nanoma-terials for high-T	design/ fabrication/testing* Other nanoma-terials for high-T iteration	design/ fabrication/testing* Other nanoma-terials for high-T iteration
3. Metrology	x	x	x	x	x	x

* GM

Approach - Overview

NSF/DOE targeted areas:



Focused areas of this project:

- TE Materials
  - Filled-skutterudites
  - Nanowire TE materials
  - Nanoscale oxides
  - Metal-semiconductor laminate TE materials
- Heat sink - high temperature side heat exchanger
- CNT thermal interface materials
- Metrology

Approach – TE Material Development

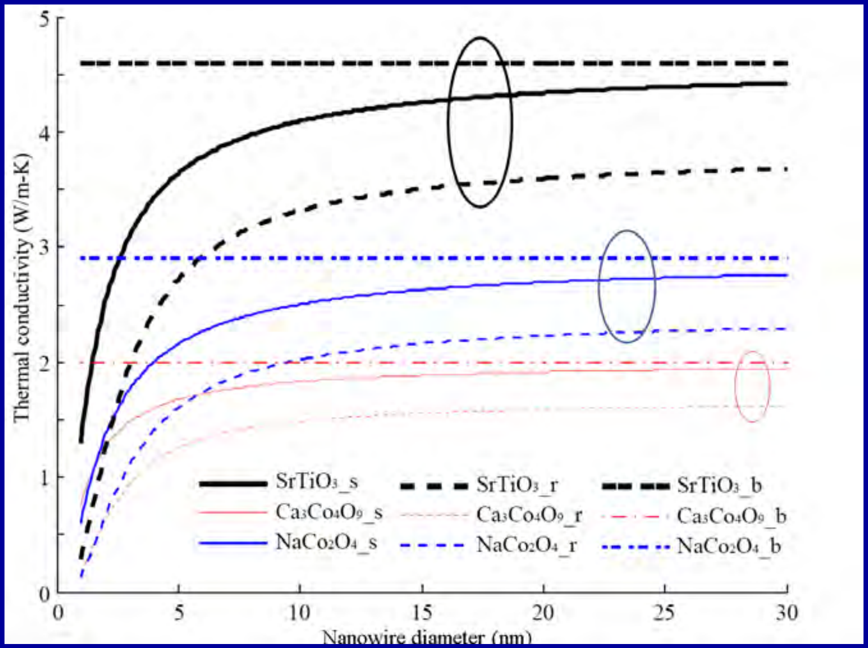
1 - Thermal conductivity reduction in filled-skutterudites

- An ultrafast laser system is used to investigate phonon dynamics – phonon scattering in TE materials
- Phonon dynamics is related to thermal conductivity and the figure of merit of TE materials

Experimental facility

Approach – TE Materials Development

2 – Nanowire TE materials



Concept: Reduction of thermal conductivity of complex metal oxides through nanostructuring can significantly improve the ZT.

Complex metal oxides could be an non-toxic and abundant material-based alternatives to replace skutterudite and Si-Ge for high-temperature application due to their extremely high stability in oxidative atmosphere. But their ZT was historically low due to large thermal conductivity (~5 W/m-K for NaxCoO2, ~3W/m-K for Ca3Co4O9).

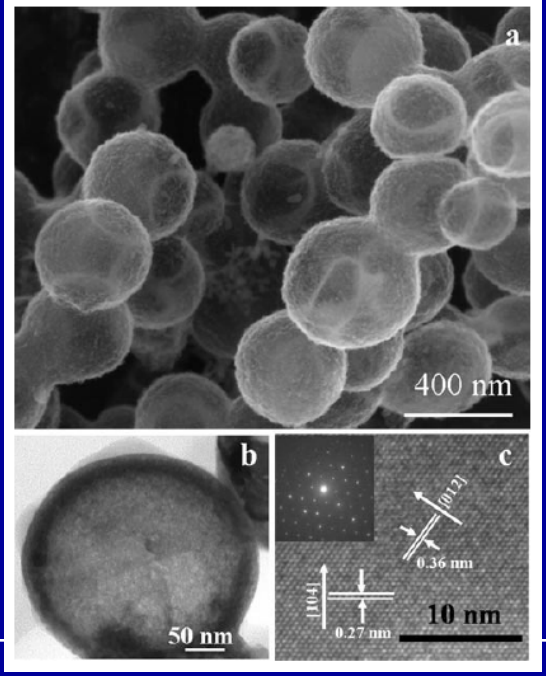
MRS Bulletin 31, 199-205 (2006)
Journal of Alloys and Compounds 387, 56–59 (2005)

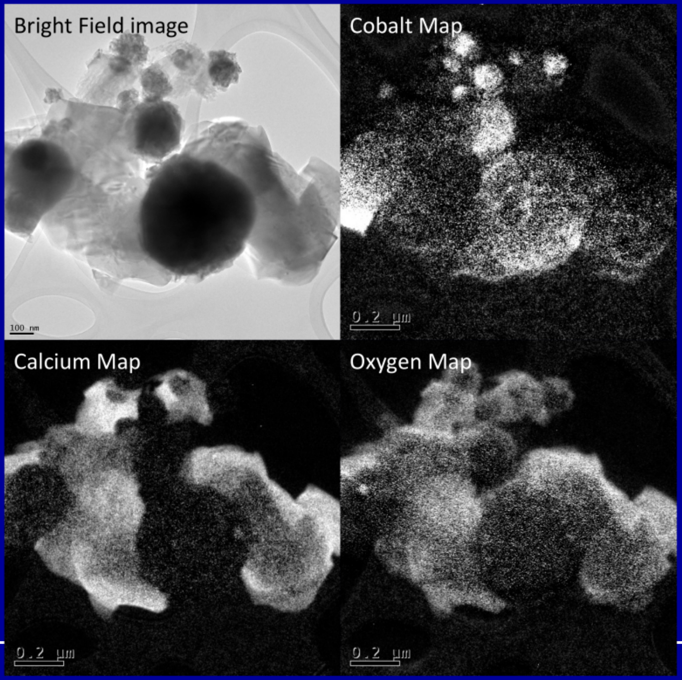
Approach – TE Materials Development

3 – Nanoscale oxide TE materials

Concept: Use simple chemical routes (e.g., solution synthesis, calcination) to create mechanically self-supporting, nanoporous networks of oxide thermoelectrics

Single-crystal α-Fe_2O_3 shells from carbon nanosphere templates, Eswaramoorthy group (JNCASR) Jagadeesan et al. Angew. Chem. Int. Ed. 2008, 47, 7685 –7688

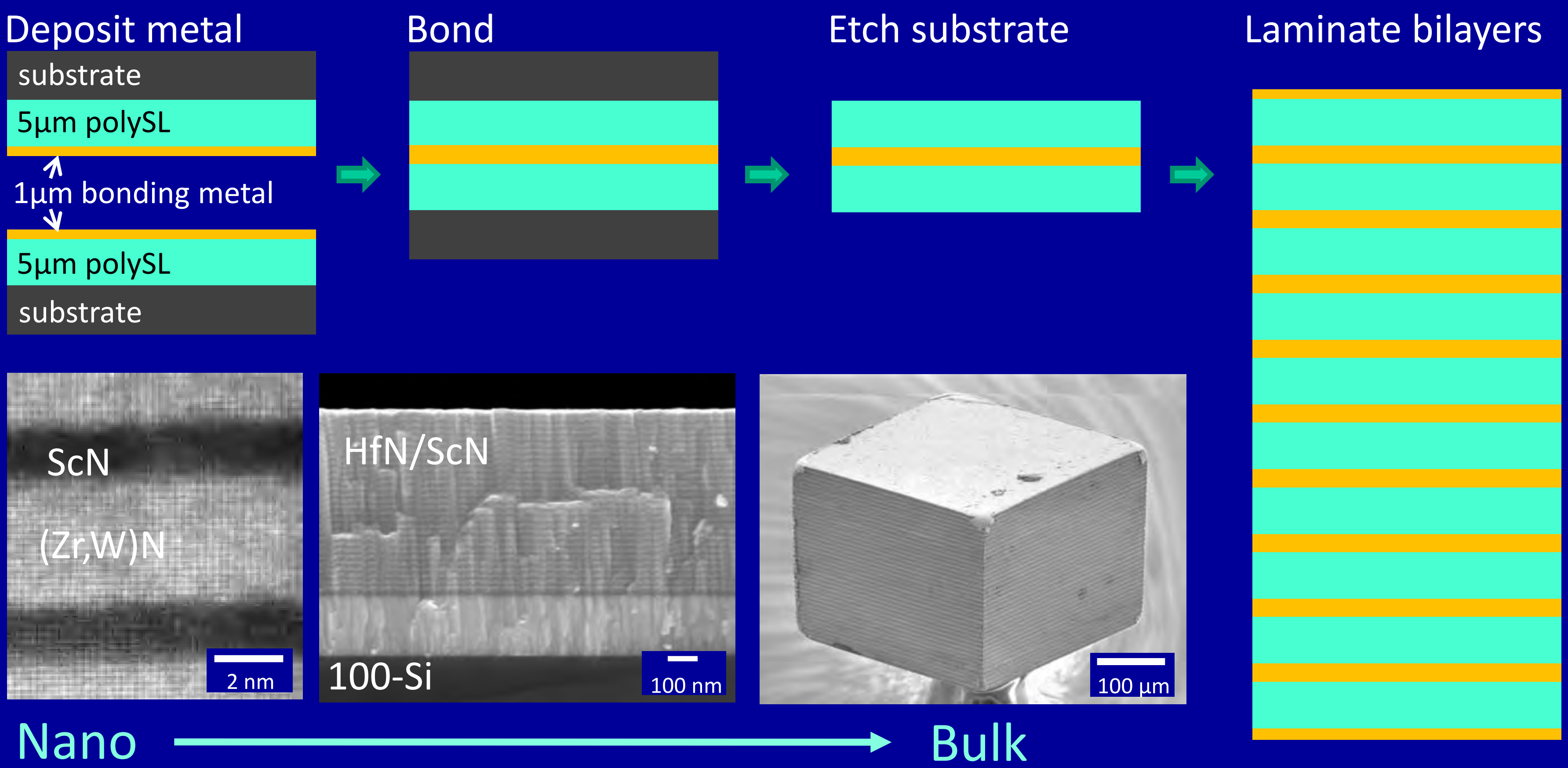




Approach – TE Materials Development

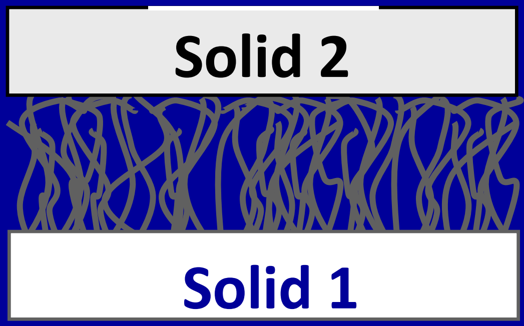
4 – Metal/semiconductor laminate TE materials

Concept: <u>Nano-to-Bulk:</u> utilize lamination process to create bulk-like elements from nanostructured metal-semiconductor thin-film superlattices.

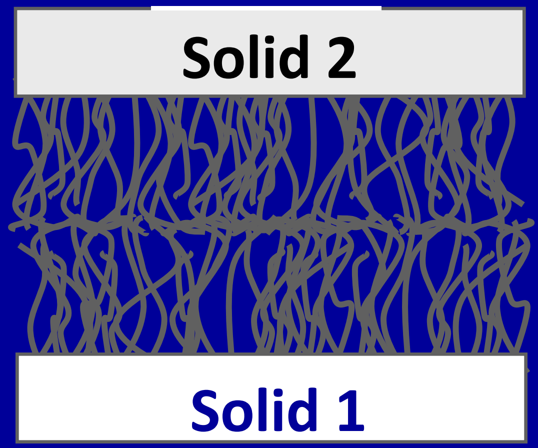


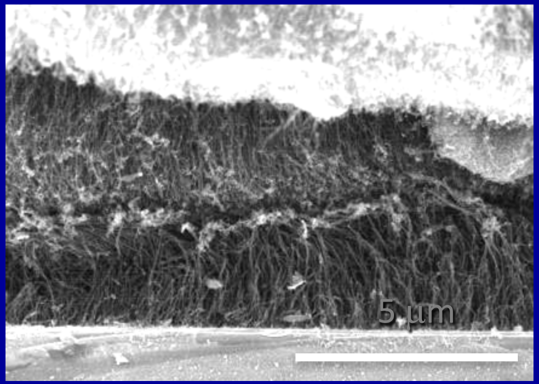
Approach – Thermal Interface Materials

One-sided interface

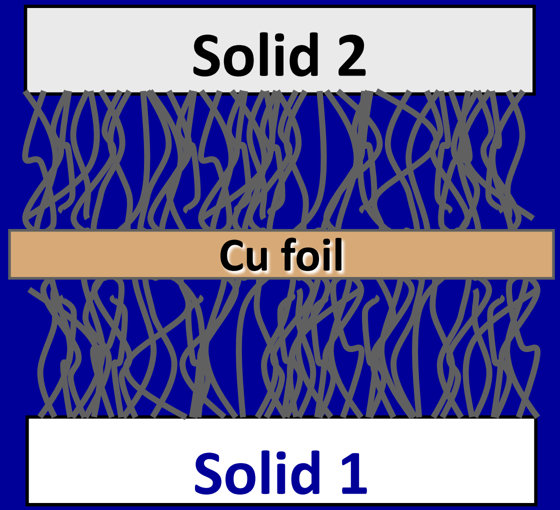


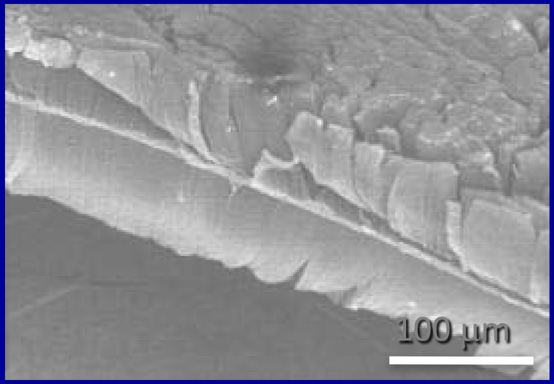
Two-sided interface





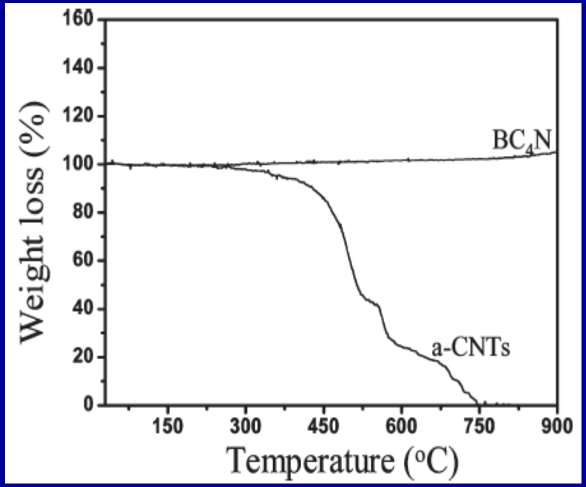
CNT/foil interface



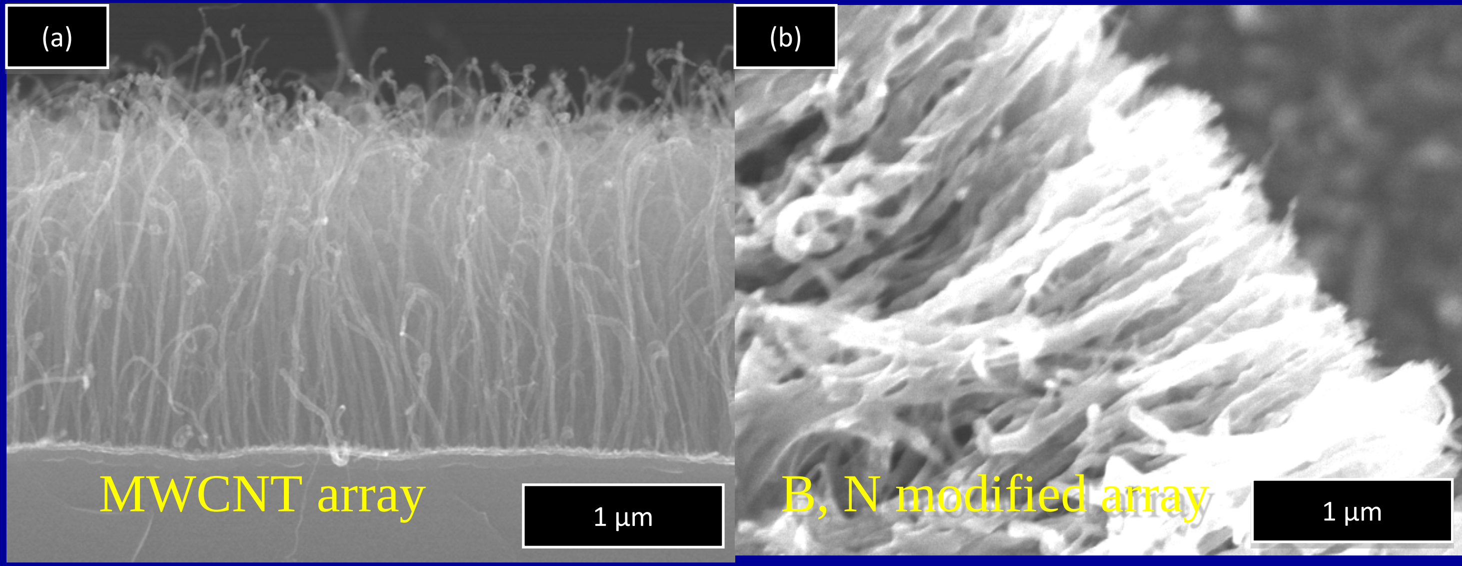


Approach – Thermal Interface Materials

Raidongia et al. (J. Mater. Chem. 2008, 18, 83-90) demonstrated large improvements in thermal stability of nanotubes by conversion to BC_4N



Our work:



Approach – Heat Exchanger

- Use existing GM prototype as a baseline and point of departure for heat exchanger design

- Investigate alternate heat exchanger topologies to assess overall energy delivery to TEG
    - Flowpath length/diameter
    - Diffuser optimization to remove flow separation
    - Investigation of the use of fins to augment heat transfer
    - Investigation of integrated fin assemblies that incorporate TEGs within the fins themselves

Approach – Metrology

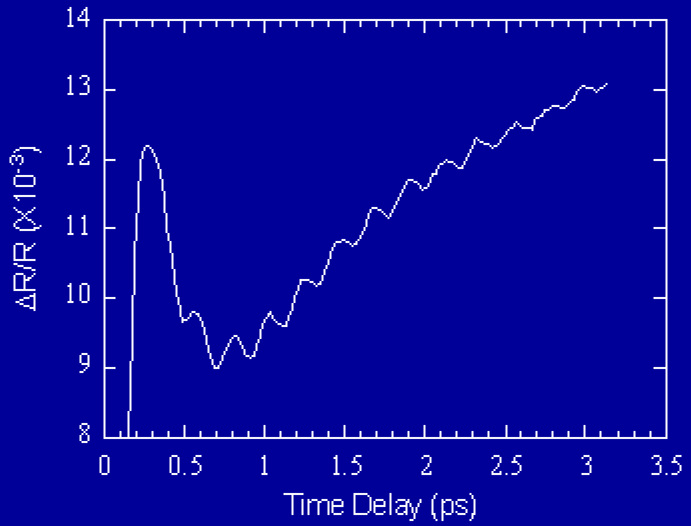
- Measure thermal transport properties and thermal contact resistance using
  - laser thermal reflectance method
  - photoacoustic method

- Measure electrical properties, Seebeck coefficient, etc. at the Oak Ridge National Laboratory

Technical Accomplishments – TE Materials Development

1. Thermal conductivity reduction in filled-skutterudites

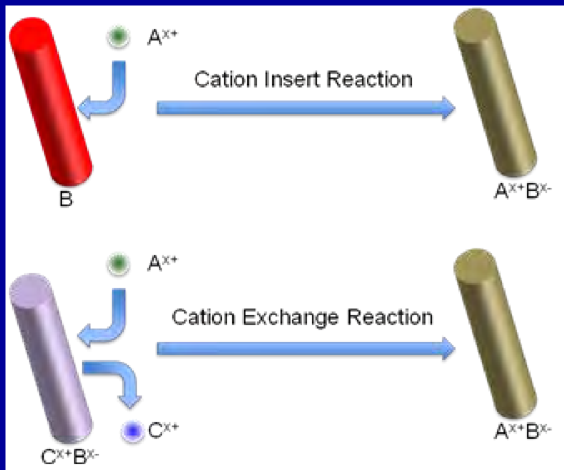
- Studied phonon scattering in filled-skutterudites (provided by GM) and its correlation with thermal conductivity reduction



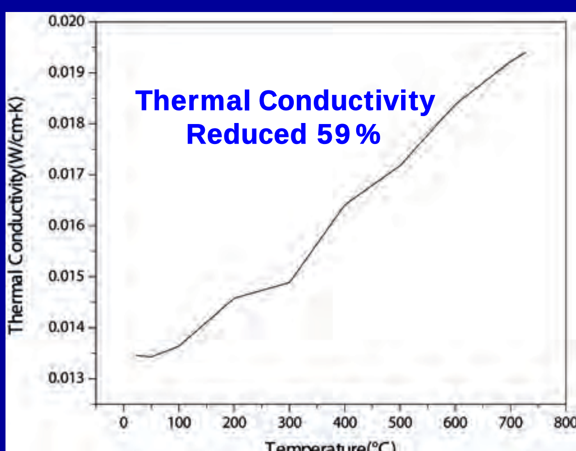
Oscillation is due to filled elements, which scatters phonons and reduces thermal conductivity

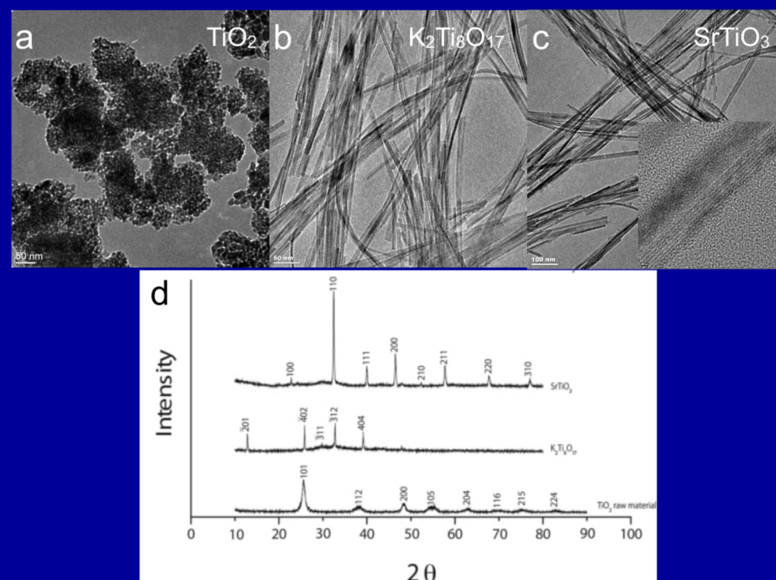
Technical Accomplishments – TE Materials Development

2 – Nanowire TE materials



Using the self-templated growth mechanism, we have been able to mass produce the molecular scale complex metal oxide nanostructures. We have observed ~ 60% reduction in thermal conductivity in the pellet containing 6 nm $SrTiO_3$ nanowires compressed by spark plasma sintering.





Yadav, G. G., Zhang, G., Qiu, B., Susoreny, J. A., Ruan, X., Wu, Y.*, "General Synthesis of Molecular Scale Perovskite Oxide Nanowires and Their Potential Applications in High Temperature Thermoelectric Conversion", submitted to *Journal of American Chemical Society.*

Technical Accomplishments – TE Materials Development

3 – Nanoscale oxide TE materials

Calcium Nitrate (0.884 g) + Cobalt Nitrate (1.09g) (1:1 molar)

↓

Dissolve in 75 ml ethanol + add carbon spheres (1.0 g) + Sonication in water bath for 1h

↓

Stirred at 70 C in 500 rpm for 18h

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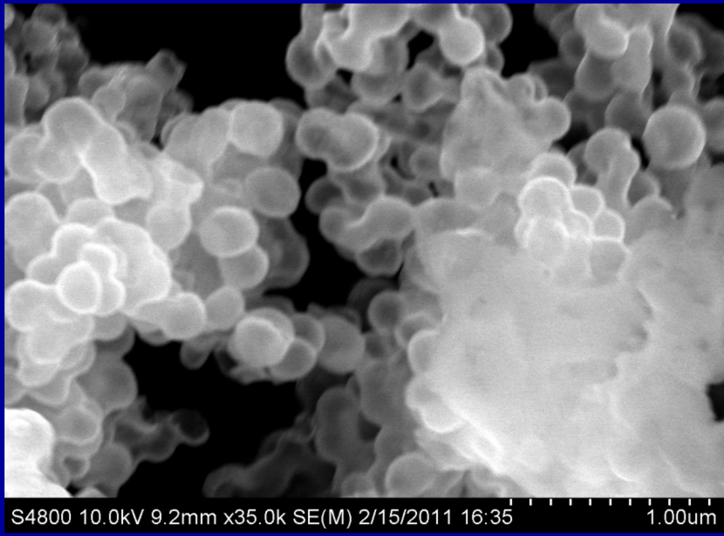
Wash thoroughly with water, and the same process is repeated once more with stirring 18 H

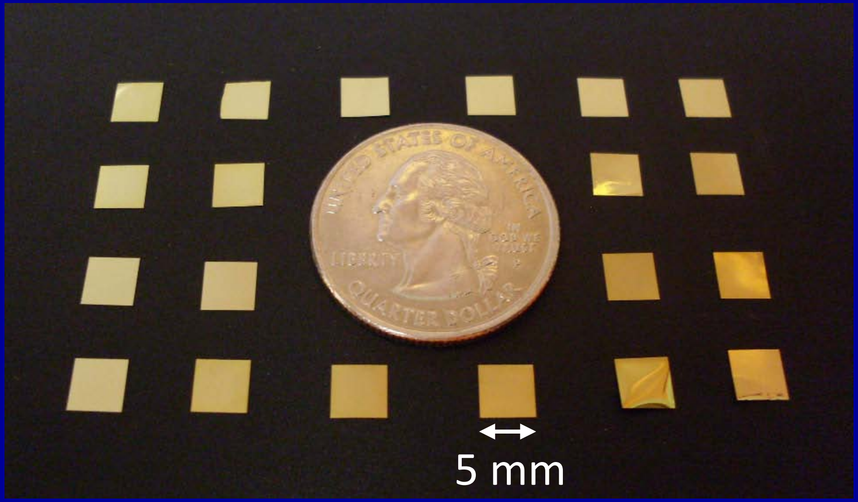
↓

Heated at 125C to dry; Calcination at 500 C for 3h at 3deg/min

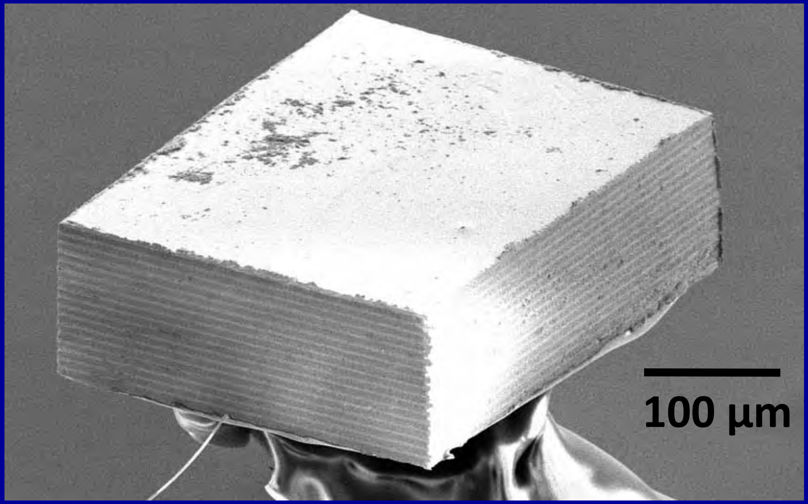


Technical Accomplishments – TE Materials Development

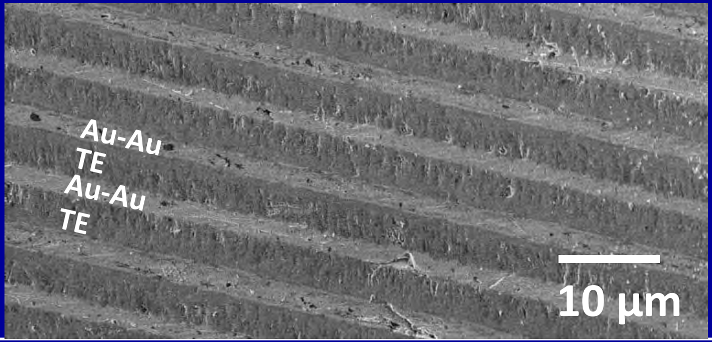
4 – Metal/semiconductor laminate TE materials



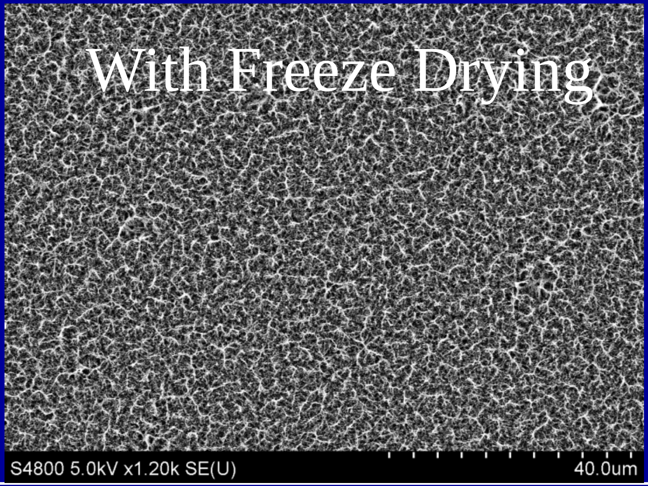
Twenty freestanding 14 µm bilayer foils
6 nm HfN/ 6nm ScN superlattice

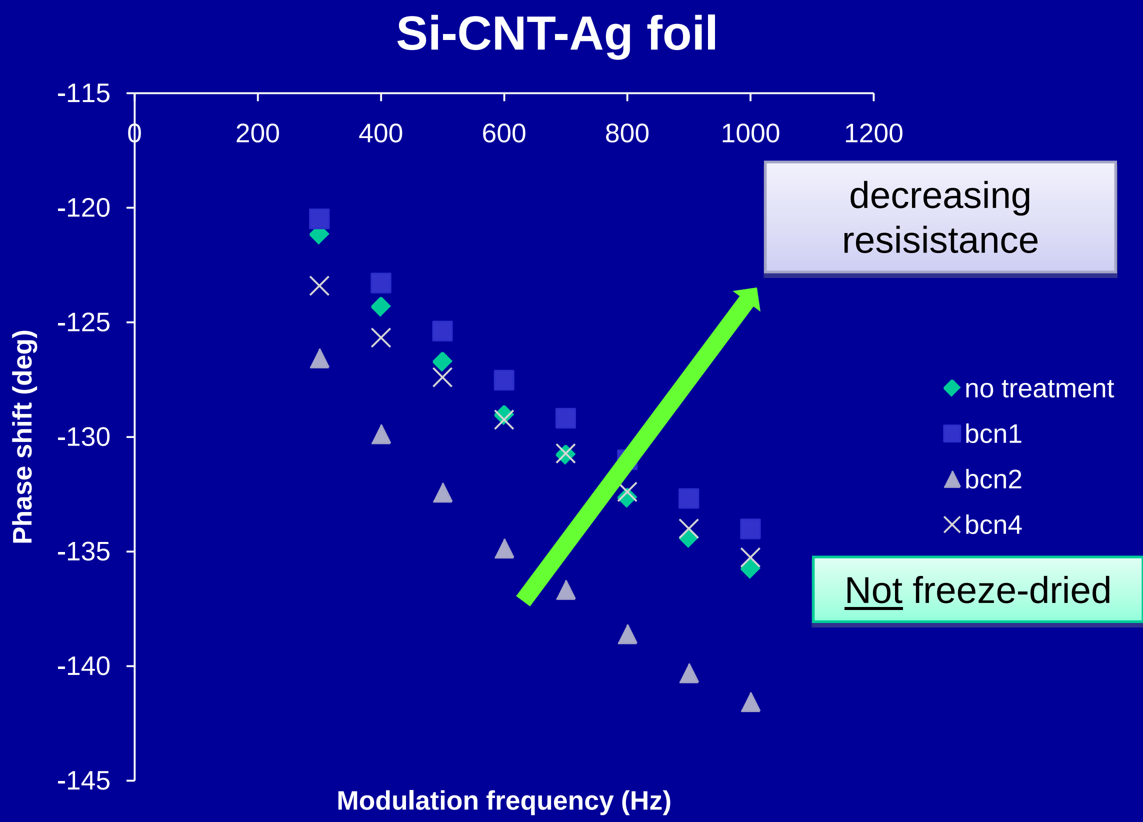


110 µm x 300 µm x 377 µm laminate



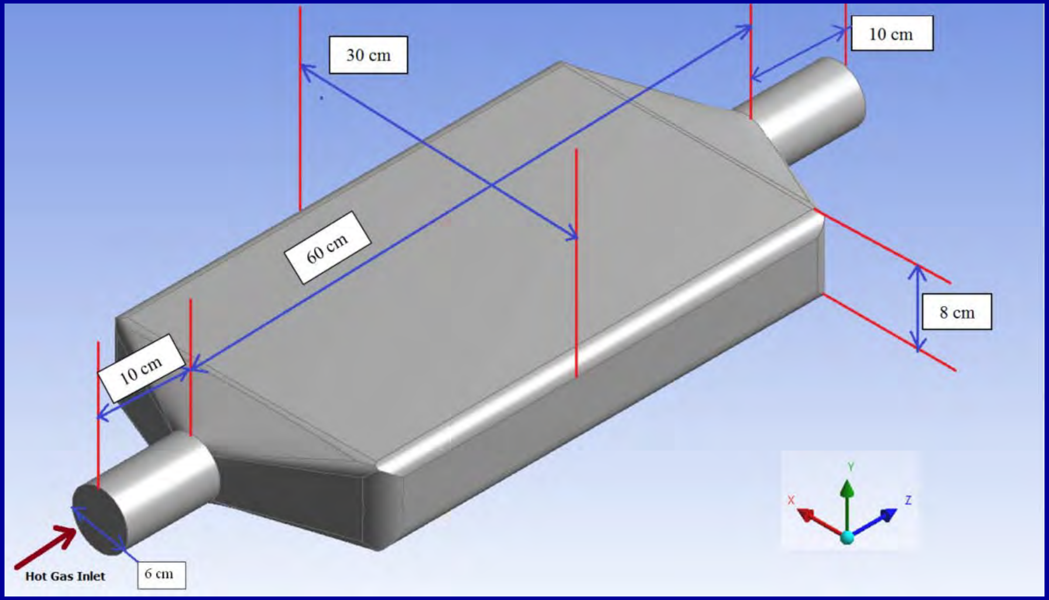
Technical Accomplishments – Thermal Interface Materials





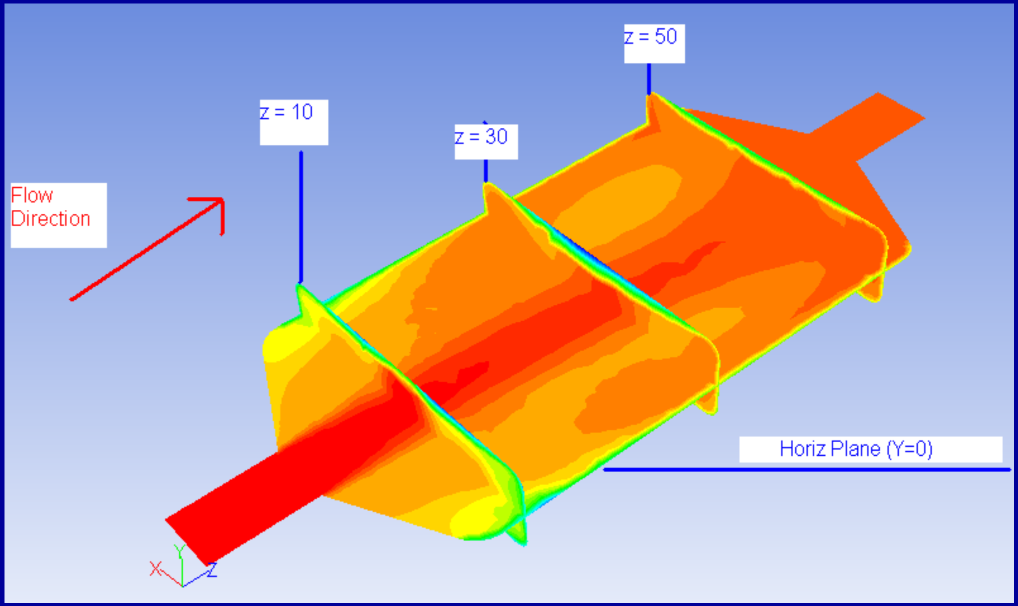
Technical Accomplishments – Heat Exchanger Design

- Baseline geometry transitions from circular pipe to rectangular box that contains TEGs
- Created and analyzed baseline geometry in Fluent



Technical Accomplishments – Heat Exchanger Design

- Analysis of baseline geometry shows substantial flow separation in conical diffuser section
- Limited heat transfer in separated flow region at side walls of rectangular duct



Future Work

- Investigate skutterudites with different filling strategies
- Complex Metal Oxide Molecular Wires - Optimize electrical conductivity of $SrTiO_3$ and find cheaper dopant to replace Nb^{5+} and Develop similar approach to synthesize $Ca_3Co_4O_9$ nanowires and $NaCo_2O_4$ nanowires
- CCO nanoshell - Identify and optimize CCO composition/phase and measure TE transport properties
- Metal-semiconductor laminates - Switch from Au-Au bonding to Cu-Cu bonding; address contact resistance issues
- Thermal interfaces - Optimize B-C-N structures for thermal stability and interface conductance
- Characterize thermal contact resistances of CNT interface materials and the figure of merit of TE materials
- Explore alternate diffuser designs to remove flow separation and improve heat transfer in baseline heat exchanger configuration, and explore alternate heat exchanger configurations to increase heat exchange to the TEGs

Collaborations

- GM: collaborations on
  - filled-skutterudite studies
  - heat exchanger design and development
  - testing on TEGs
- Oak Ridge National Laboratory: providing access to metrology facilities for thermal and electrical property measurements

Summary

- Studies on filled-skutterudites is underway to provide an understanding on thermal conductivity of skutterudites with different filling strategies
- Complex Metal Oxide Molecular Wire: investigated the suitable materials for large scale thermoelectric applications, successfully synthesized the molecular wires of complex metal oxides, demonstrated the theory and experimental proof of thermal conductivity reduction in $SrTiO_3$
- CCO Nanoshells - Nanoshell morphology demonstrated; TE testing underway
- Metal-semiconductor laminates - Laminate approach demonstrated; TE testing underway
- Thermal interface - B-C-N modification to CNT arrays demonstrated; optimization underway for TIM operation at elevated temperatures
- Heat exchanger analyses initiated and on pace to provide advanced concepts in next 6-9 months

Acknowledgement:
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NSF, PM: Dr. Ted Bergman