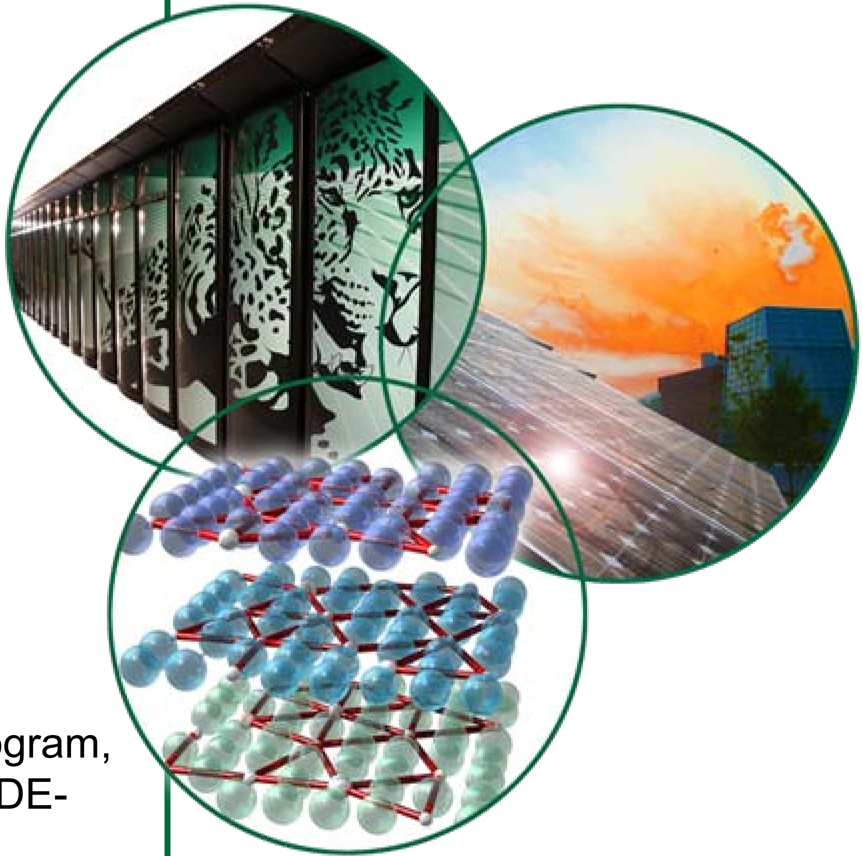
Thermoelectric Material Development and Characterization at ORNL

D Ray Johnson, David Singh, Hsin Wang, Andy Wereszczak, Chaitanya Narula, Larry Allard



Research sponsored by the Propulsion Materials Program, DOE Office of Vehicle Technologies, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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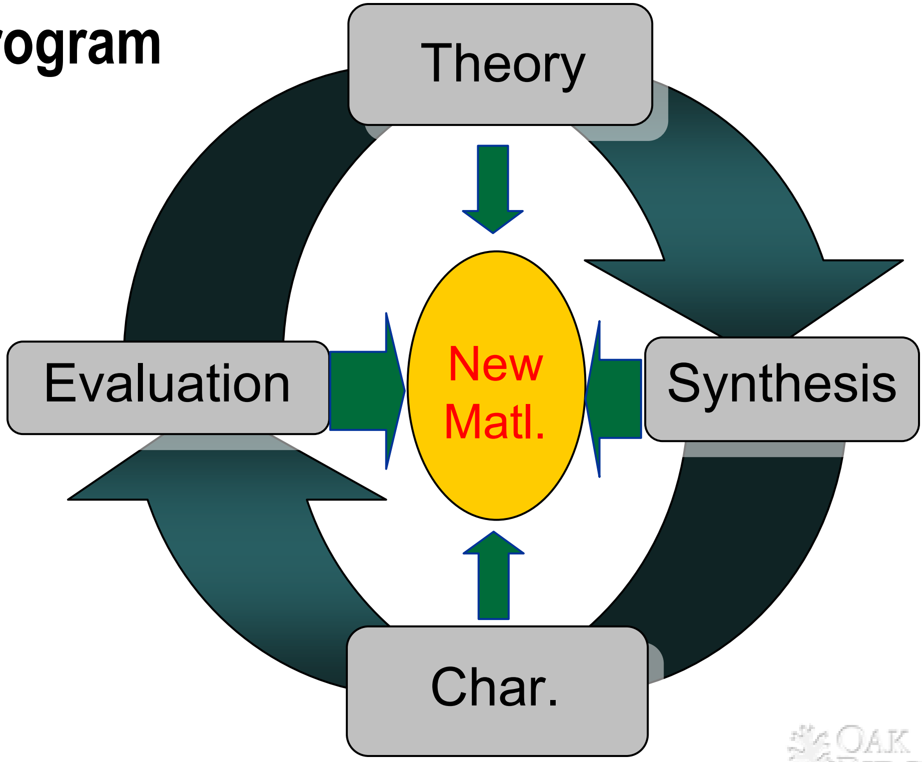
The present effort began with a workshop at ORNL in November 2006

- A Program Plan for a comprehensive R&D program involving industry, universities and government labs was developed for DOE
- The program has not yet been funded
- ORNL has developed a modest program to demonstrate the concept



ORNL Has Proven Track Record in Discovery of New Thermoelectric Materials

- First to demonstrate that the "electron-crystal phonon-glass" concept worked ; results published in *Science* [B.C. Sales, D. Mandrus, R. K. Williams, 272, (1996) 1325].

- Conducted seminal work in solid state physics of thermoelectrics; see, for example: The best Thermoelectric, G. D. Mahan and J. O. Sofo, PNAS,Vol. 93,pp 78436-7439,July 1996.

Filled Skutterudite Antimonides: A New Class of Thermoelectric Materials

B. C. Sales,* D. Mandrus, R. K. Williams

A class of thermoelectric materials has been synthesized with a thermoelectric figure of merit *ZT* (where *T* is temperature and *Z* is a function of thermopower, electrical resistivity, and thermal conductivity) near 1 at 800 kelvin. Although these materials have not been optimized, this value is comparable to the best *ZT* values obtained for any previously studied thermoelectric material. Calculations indicate that the optimized material should have *ZT* values of 1.4. These ternary semiconductors have the general formula RM_4X_{12} (where R is lanthanum, cerium, praseodymium, neodymium, or europium; M is iron, ruthenium, or osmium; and X is phosphorus, arsenic, or antimony) and represent a new approach to creating improved thermoelectric materials. Several alloys in the composition range $CeFe_{4-x}Co_xSb_{12}$ or $LaFe_{4-x}Co_xSb_{12}$ ($0 < x < 4$) have large values of *ZT*.

The coupling between heat and electrical currents in a solid has fascinated scientists since the early experiments of Lenz in 1838. He placed a drop of water on the junction of Bi and Sb metal wires. Passing an electric current through the junction in one direction caused the water to freeze, and reversing the current caused the ice to melt rapidly; a thermoelectric refrigerator was thus created. This phenomenon remained little more than a curiosity until the early 1950s, when it was found that doped semiconductors could increase the efficiency of thermoelectric devices to values that allowed their practical use in specialized applications in which reliability was more important than economy (*1*). Today, portable thermoelectric coolers can be powered from a car battery for food storage or can be energized from a computer power supply to provide active cooling for high-density integrated electronic chips. A closely related thermoelectric effect produces electricity if a temperature gradient is established across the device. These thermoelectric generators are used as power sources for many of NASA's deep space probes (*2*) and are currently of interest in the automobile industry for power generation from exhaust and engine heat.

Materials used today in thermoelectric devices—Bi_2Te_3-Sb_2Te_3 alloys for refrigeration and Si-Ge alloys for power generation at elevated temperatures—were developed in the early 1960s. The main drawback of thermoelectric devices is their efficiency, which depends on materials properties through the dimensionless parameter ZT, where T is the temperature and $Z = S^2/\kappa\rho$ (where S is the thermopower or Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity). Although many materials have been investigated in the intervening 35 years, the efficiency of thermoelectric devices has not improved significantly. However, theory shows that there is no fundamental maximum limit to ZT (*1*, *2*). Moreover, several plausible extrapolations, based on the use of optimum values for known materials, indicate that ZT values of 2 to 4 are possible (*1*, *3*). A value of $ZT = 3$ would make thermoelectric home refrigerators economically competitive with traditional compressor-based refrigerators. We present initial experimental data on a new class of thermoelectric materials, filled skutterudites. Although these materials are clearly unoptimized, they ex-

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R. K. Williams, Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

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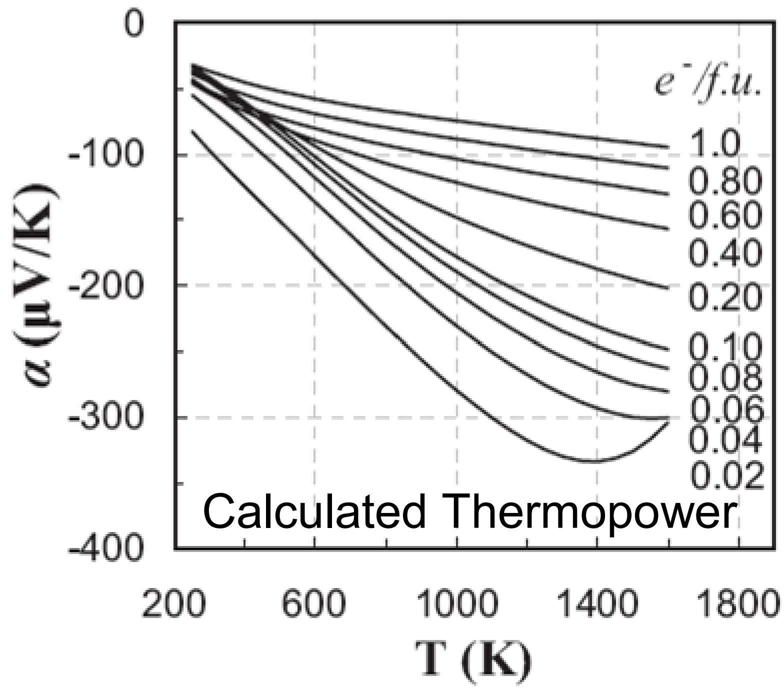
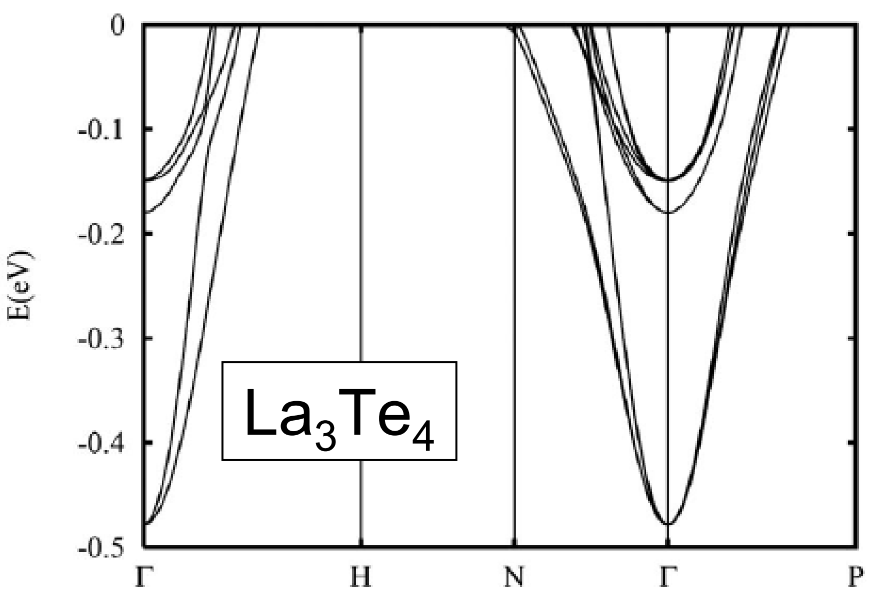
Computational Theory

David Singh

- First Principles calculations of electronic structure & TE properties
- Calculation vibrational properties & identify methods to minimize thermal conductivity
- Calculate electrical transport properties via Boltzmann transport equations
- Extensive validation was done for both conventional and oxide thermoelectrics





Comparison of ORNL calculations with experimental data (CalTech) led to explanation for high *ZT* of La_3Te_4 and doping dependence in terms of a combination of heavy and light bands

➔A new route to high *ZT* at high *T* that can be applied to other materials.

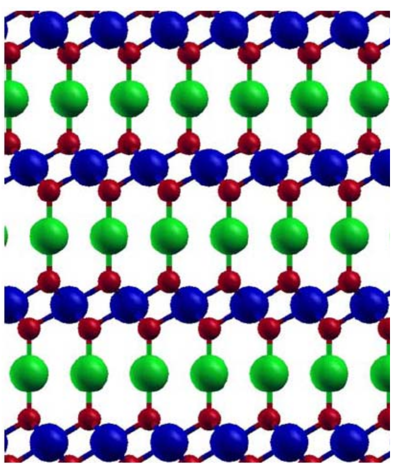
A.F. May, D.J. Singh and G.J. Snyder, Phys. Rev. B **79**, 153101 (2009)

Search for New Oxide Thermoelectrics

David Singh

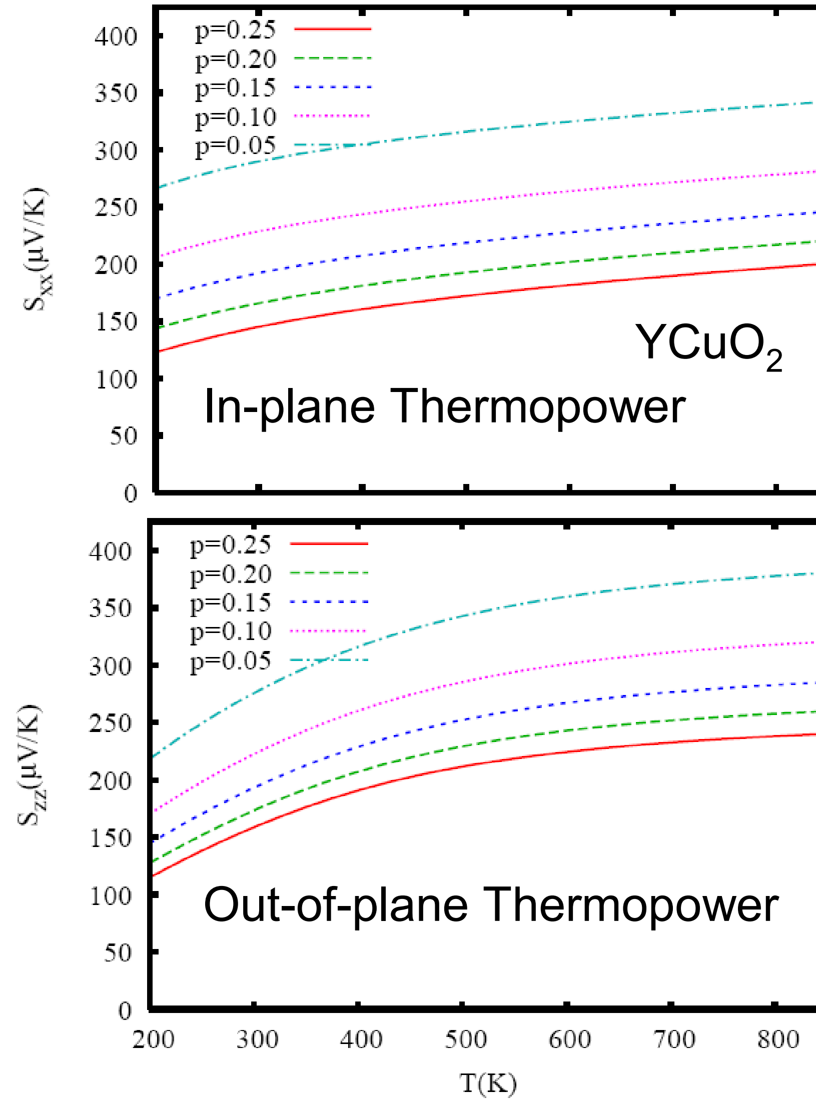
Use design rules and exploration with first principles calculations to find promising oxide compositions for experimental investigation.

Goals are high *ZT*, reduced anisotropy and affordable compositions.



$YCuO_2$ found to have thermopower superior to Na_xCoO_2 at appropriate doping levels combined with much more isotropic properties.

Need experimental investigation of conductivity and doping.

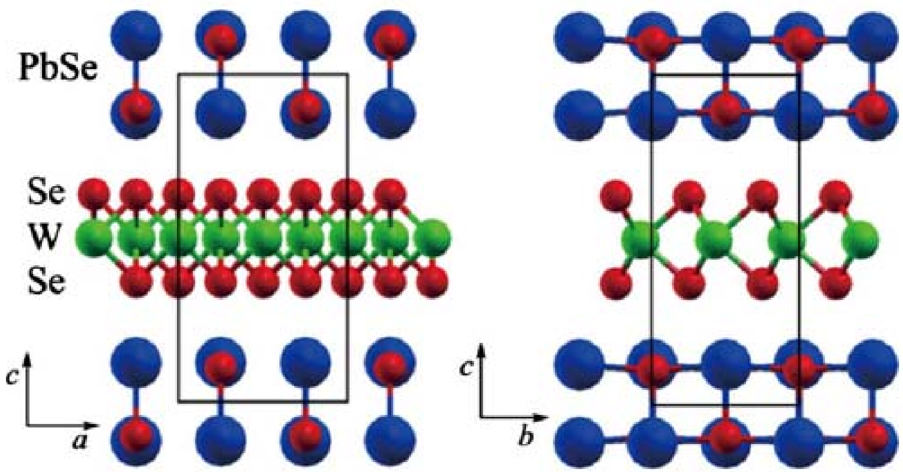


D.J. Singh, Phys. Rev. B **77**, 205126 (2008)

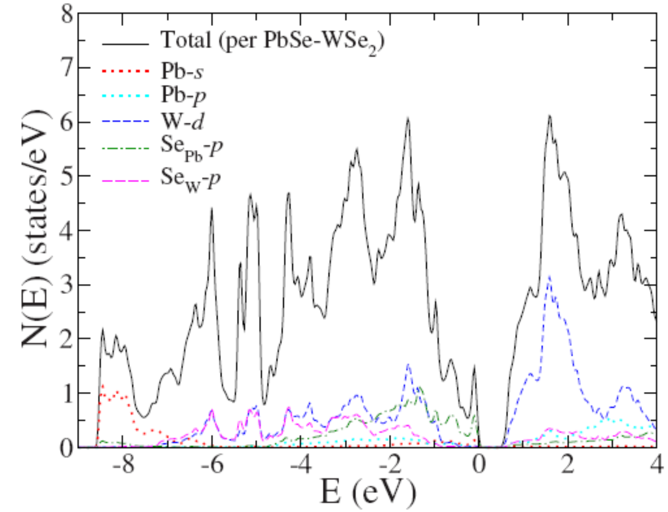
Nanostructured Thermoelectrics

David Singh

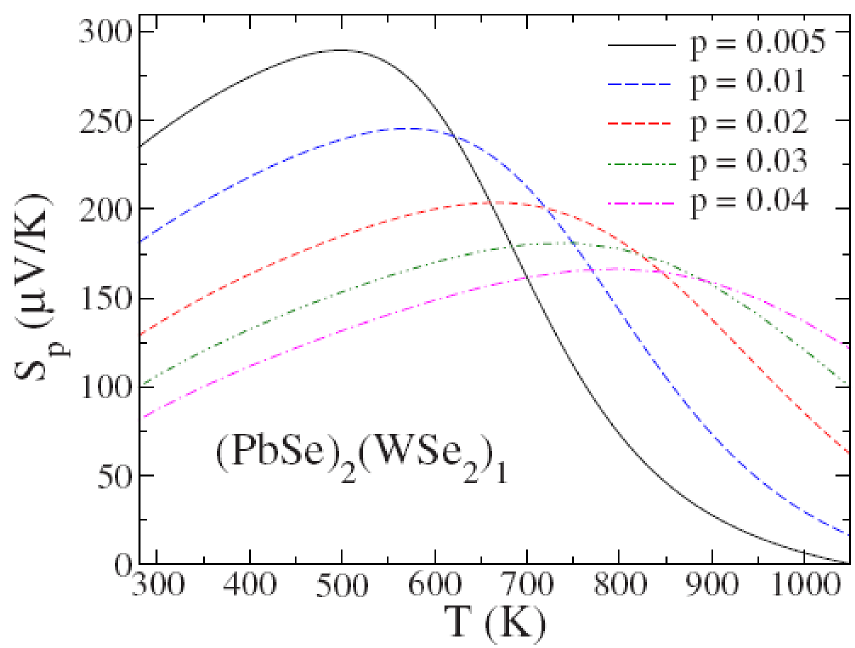
Identify key length scales and doping level dependence of thermoelectric properties.



Low thermal conductivity PbSe – WSe_2 Intergrowth Compounds synthesized at Oregon State (Johnson)



Electronic structure, transport properties (ORNL)

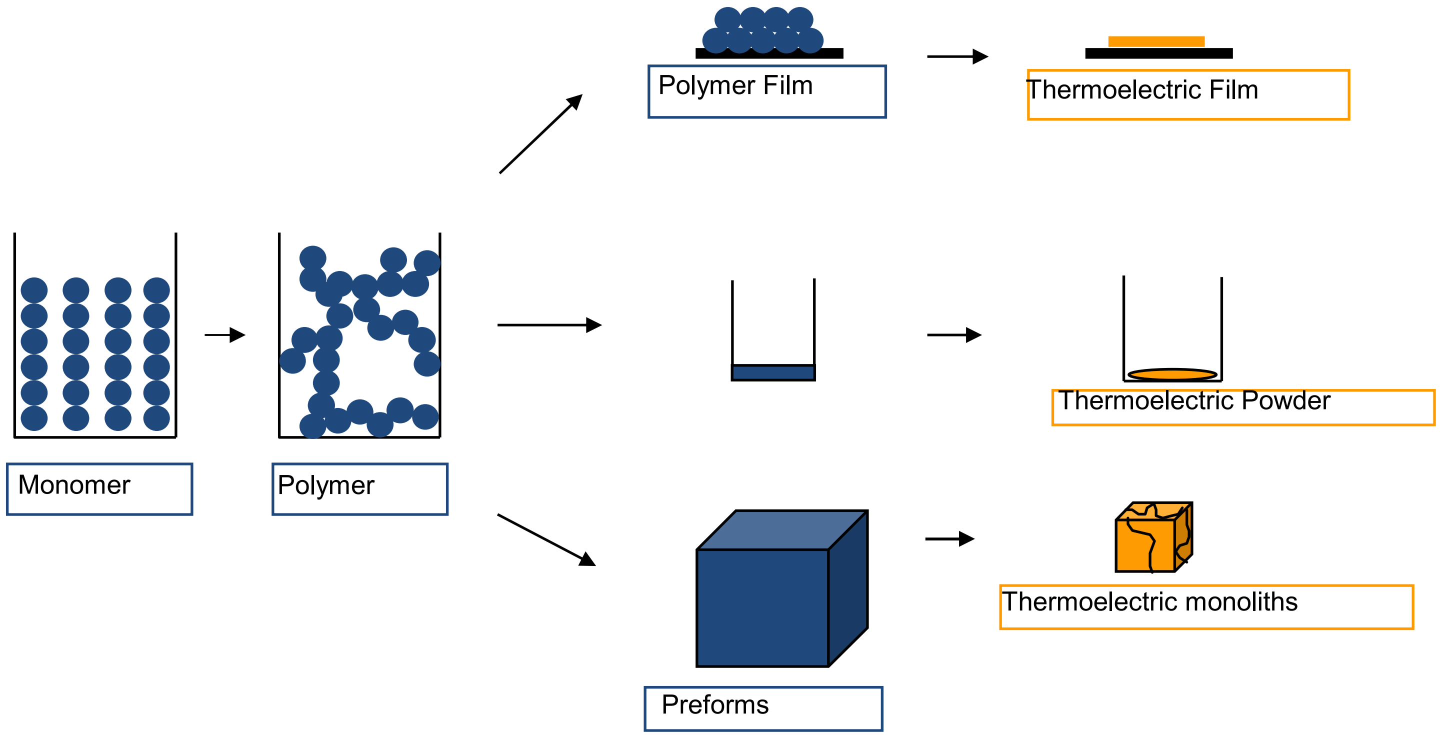


- Found that PbSe nanostructured with WSe_2 (e.g. mechanical alloying) can be a high *ZT* material if heavily doped
- Desirable length scale for nanostructuring was identified (few nm depending on *T*)

L. Zhang and D.J. Singh, Phys. Rev. B **80**, 075117 (2009)

Ceramic Precursor Approach to Thermoelectric Materials

Chaitanya Narula



- Demonstrated for $SrTi(Nb)O_x$ and $Ca_3Co_4O_9$ and suitable for Chalcogenides as well
- **Nanosizing** depends on precursor selection and processing condition
- Opportunities for synthesis of new thermoelectric materials
- Advantages:
  - **Low-cost** synthesis
  - Suitable for **mass manufacturing** of components on assembly line

* Partially supported by US Army RDECOM/TARDEC

Example – nanosized n-type Niobium doped $SrTiO_3$

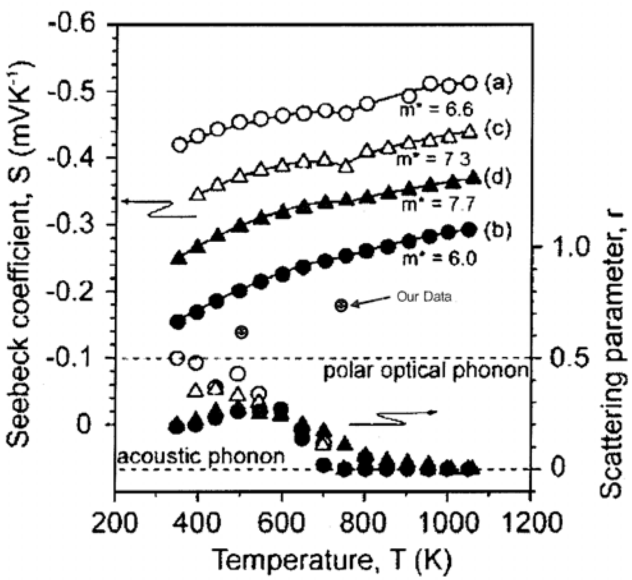
Chaitanya Narula

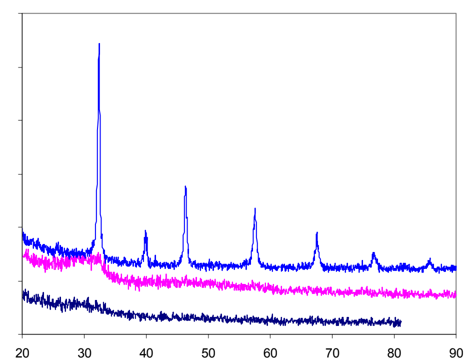
a mixture of $0.1\ Sr[Nb(OPr^i)_6]_2$, $0.45 Ti(OPr^i)_4$ and $0.45 Sr_2Ti(OPr^i)_8(^iPrOH)_5$

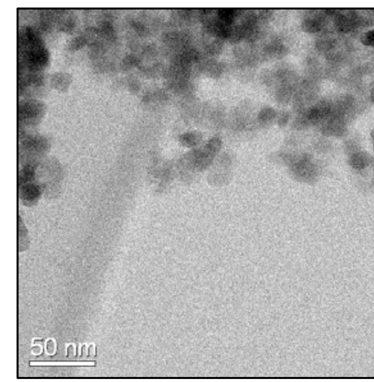
→

a mixture of $0.1\ Sr[Nb(OPr^i)_6]_2$, $0.45 Ti(OPr^i)_4$ and $0.45 Sr_2Ti(OPr^i)_8(^iPrOH)_5$ + H_2O

→







nanoparticles

Seebeck coefficient as compared with single crystals

Thin Films have also been fabricated

**Ohta and Nomura, J Appl Physics 97, 034106 (2005)*

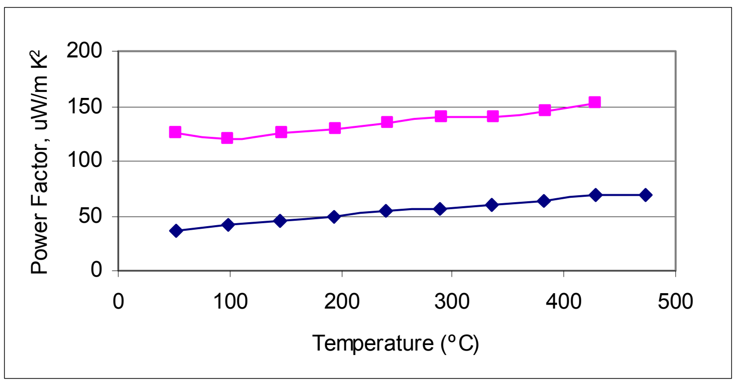
Example –p-type $Ca_3Co_4O_9$

Chaitanya Narula

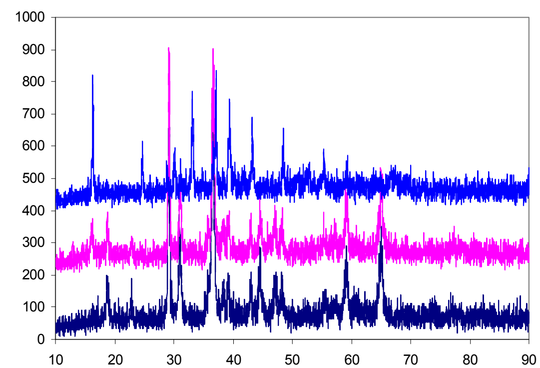
A mixture of a new precursor, $[Ca(OCH_2CH_2OCH_3)_2Co(OOCCH_3)_2]$ and $Ca(OCH_2CH_2)OCH_3)_2$

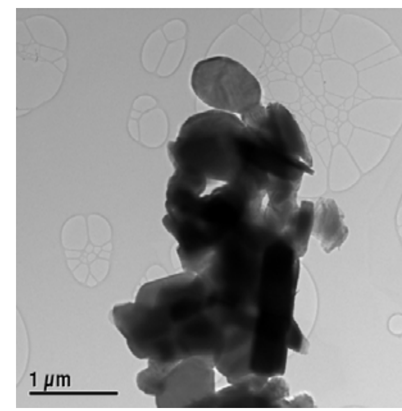
→

A mixture of a new precursor, $[Ca(OCH_2CH_2OCH_3)_2Co(OOCCH_3)_2]$ and $Ca(OCH_2CH_2)OCH_3)_2$ + H_2O



Power factor after hot-pressing and re-oxidizing comparable to literature value





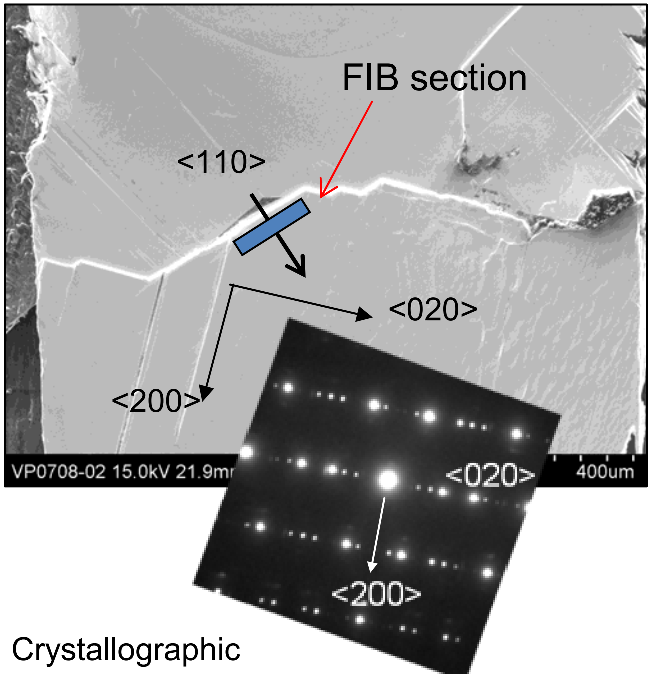
Powder Characterization

Thin Films have also been fabricated

Aberration-corrected STEM imaging of calcium cobaltite ($Ca_3Co_4O_9$) thermoelectric material

Larry Allard

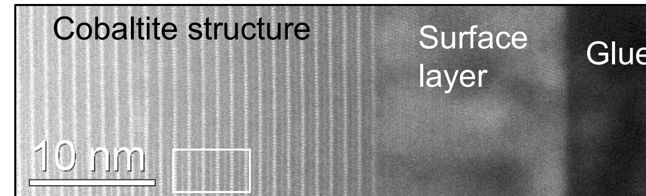
SEM image of cobaltite crystal surface

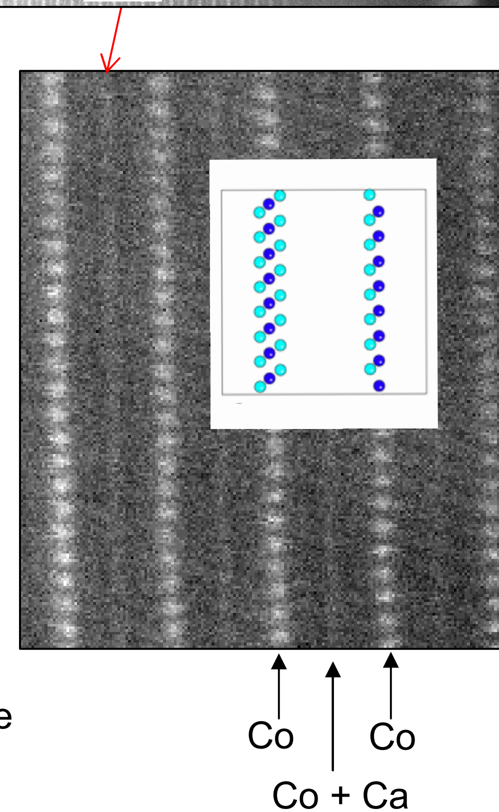


Crystallographic directions determined from electron diffraction.

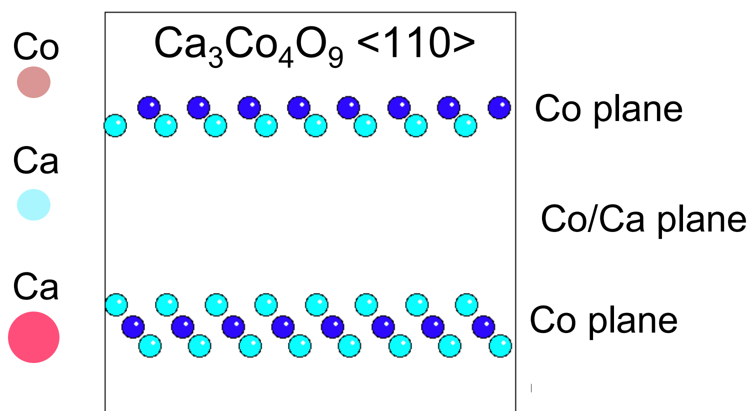
HTML's JEOL 2200FS STEM/TEM with aberration corrector for 0.7Å resolution in dark-field imaging

Focused Ion Beam thin section





The Ca cobaltite ($Ca_3Co_4O_9$) structure has been described as comprising CoO_2 layers intercalated within the known Ca_2CoO_3 lattice.

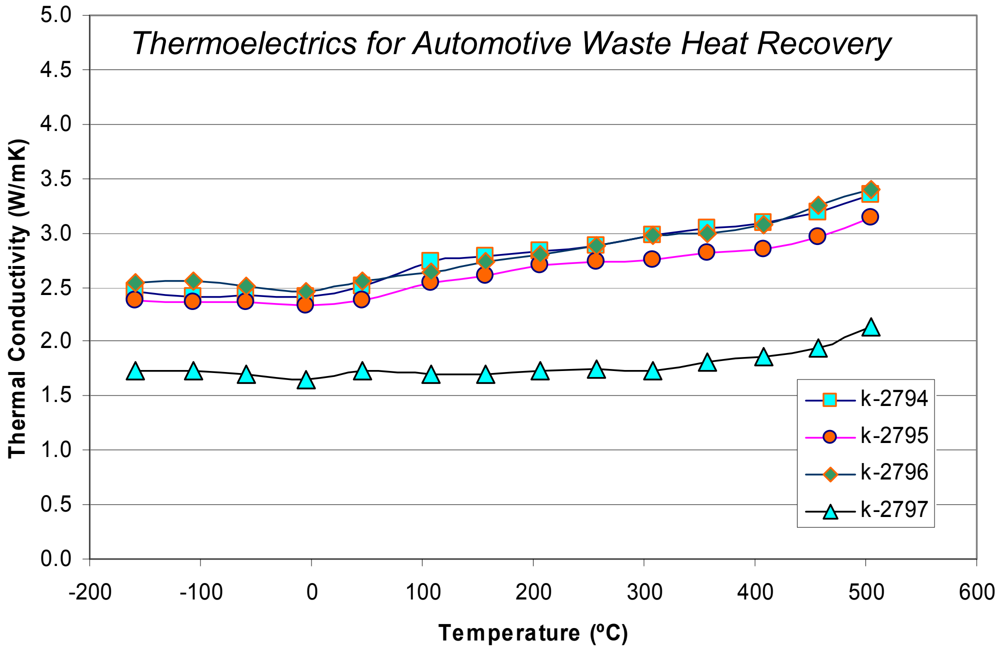


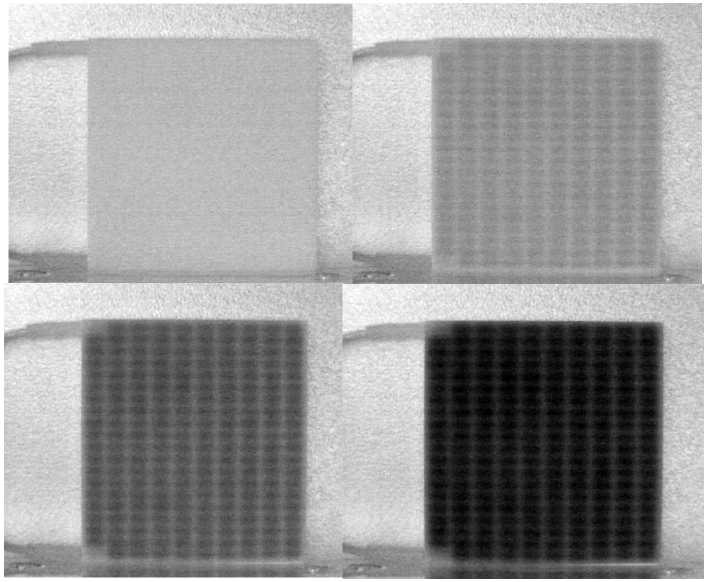
Thermoelectric Characterization at HTML

Hsin Wang

Thermal Conductivity:
<u>*Anter FL5000*</u>
Thermal diffusivity:
Laser/xenon flash
<u>*Netzsch DSC 404 C*</u>
Specific heat: DSC
-150 to 1500ºC

Infrared Imaging:
Temperature mapping
Module performance
Non-contact temperature measurement

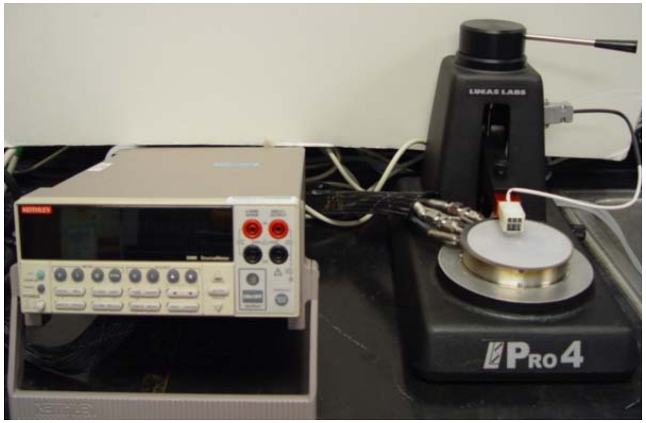




IR Images of Thermoelectric Module Cooling (Gray scale: Black = Cold and White = Hot)

Thermoelectric Characterization at HTML

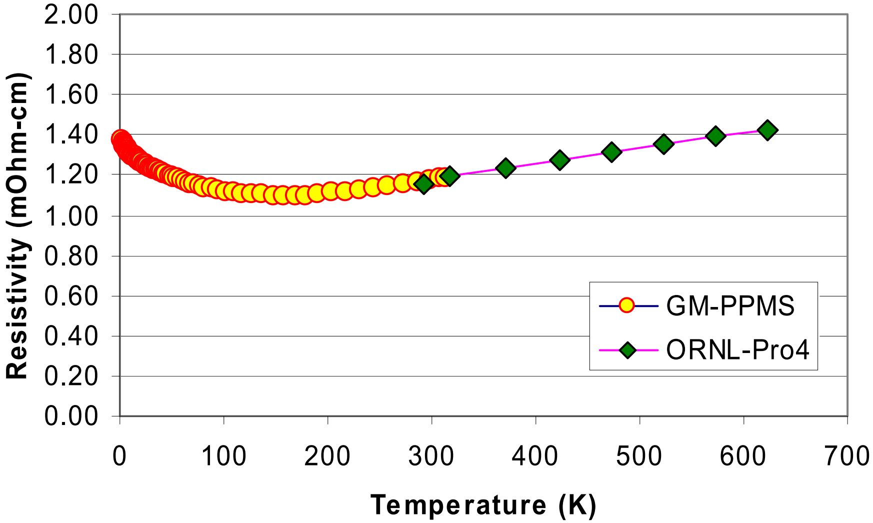
Hsin Wang



Electrical Resistivity:
Signatone Pro4
4-point in-line resistivity probe
RT- 500ºC (air)

Seebeck Coefficient:
ULVAC ZEM2 (M8)
Resistivity and Seebeck
Low pressure helium gas
13-22 mm long prism and cylindrical samples
RT – 800ºC

Electrical Resistivity of GM Bulk Thermoelectrics

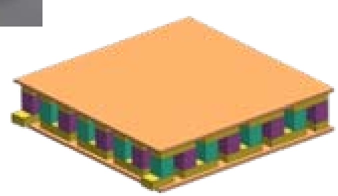


2006-2009: Bulk Thermoelectrics Characterization at ORNL

Hsin Wang

Thermoelectric Materials:

- Skutterudites:
  - N-type: Double and Triple filled
    - Yb-filled
    - Ba-Yb filled
    - Ba-Yb-La filled
  - P-type:
    - Misch metal-filled
    - Ce-filled
- PbTe (n-type and p-type)
- TAGS
- Clathrates (Type I &II)
- Antifluorite: Mg_2Si (Sn)
- LAST-m
- Oxides



Collaboration:

Industries:

- General Motor R&D
- General Electric CR&D
- Marlow Industries
- RTI

Universities:

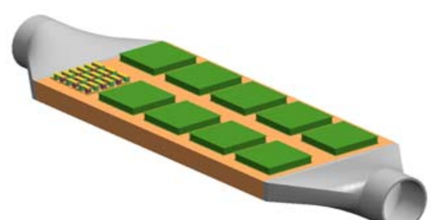
- University of Michigan
- Michigan State University
- University of South Florida

DOE Labs:

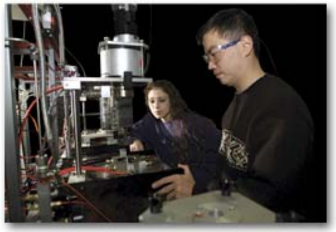
- Argonne National Laboratory
- Pacific Northwest National Laboratory
- Brookhaven National Laboratory

International:

- Shanghai Institute of Ceramics, Chinese Academy of Sciences
- University of Waterloo, Canada



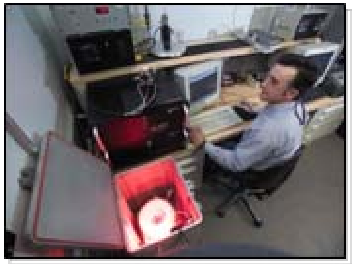
The High Temperature Materials Lab User Program is Available to the Domestic Thermoelectrics Community



Thermophysical Properties

X-Ray and Neutron Diffraction

Microstructural Analysis

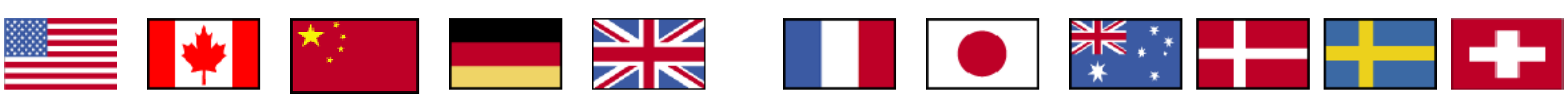


Mechanical Properties

New International Energy Agency Annex on Thermoelectrics

Hsin Wang

- **Main Tasks:**
  - Assess the state-of-the-art for thermoelectric materials and identify critical issues
  - **Develop standard testing methods and procedures**
  - Conduct international round-robin tests
  - Exchange Technical information
  - Characterize key properties
- **Participating Countries:**
  - US and Canada (initial members)
  - Japan, China, Germany, UK, France, Denmark, Sweden, Switzerland, Australia



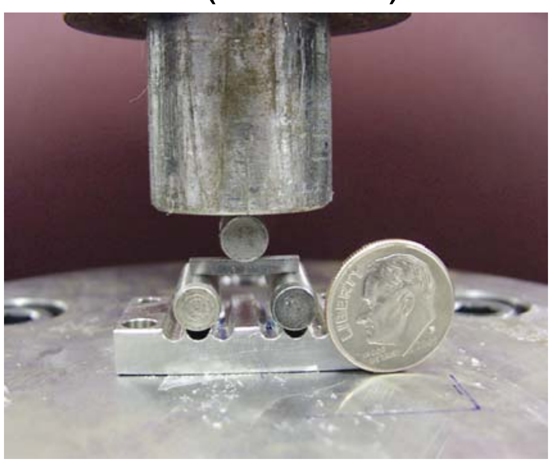
ORNL is modeling the mechanical behavior of thermoelectric materials and modules

Andrew Wereszczak

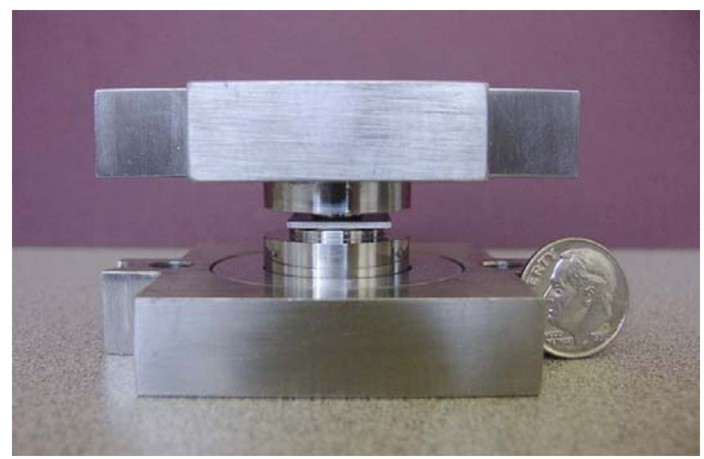
- **Measure needed thermomechanical and thermophysical properties of candidate TE materials**

- **Combine measured data with established probabilistic reliability and design models to achieve durable design**

3-Pt Flexure (Uniaxial)



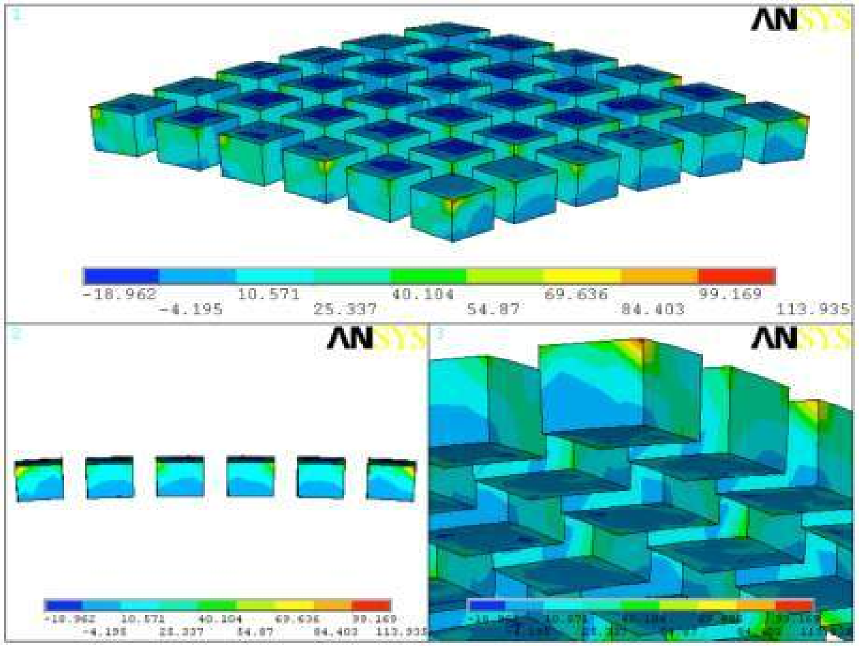
Ring-on-Ring (Biaxial Flexure)



Mechanical characterization and modeling results used to optimize strength and durability

Andrew Wereszczak

- **High 1st principal tensile stresses exist in the bulk and on surfaces and edges**
- **Apply (censored) strength data to estimate and reduce risk of fracture**
- **Improve reliability by:**
  - **Improving strength**
  - **Lowering tensile stresses in legs via geometry changes**



Finite Element Analysis

Must manage the competition and concurrent activities of Edge- vs. Surface- vs. Volume-based strength limitation

Thank You!

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