

Non-Equilibrium Synthesis and Characterization of Bulk High Performance Thermoelectric Materials for Power Generational and Cooling

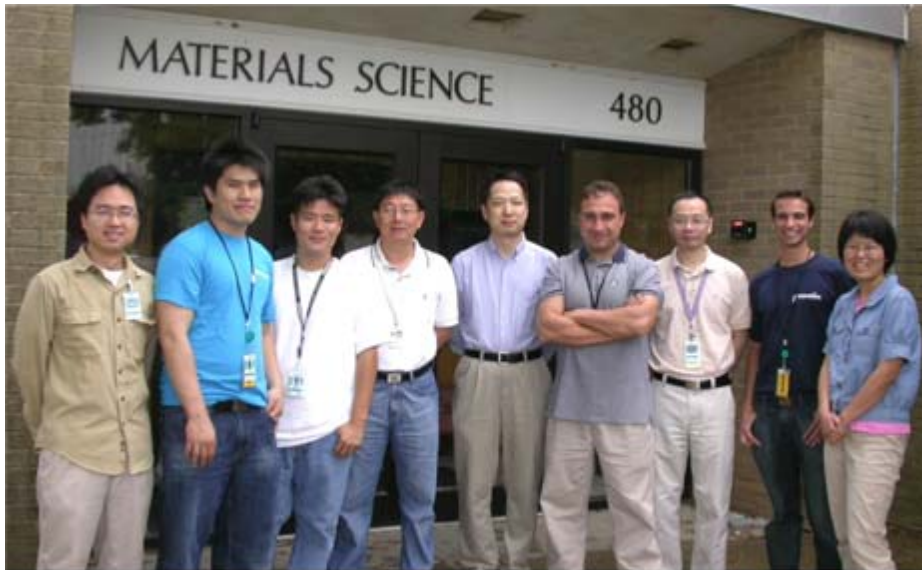
Qiang Li

Advanced Energy Materials Group
Brookhaven National Laboratory



BNL Thermoelectric Materials Program Overview

Advanced Energy Materials Group on TE



Thermoelectricians at Brookhaven National Laboratory - August 6, 2009

Collaborations

- Electron & optical spectroscopy
- T. Valla, C. Homes, and P. Johnson
- Neutron and X-ray scattering
- S. Shapiro and S. Bilenge
- Electron Microscopy Institute
- L. Wu, E. Sutter, Y. Zhu
- Theoretical Institute
- M. Rice, W. Ku, and P. Allen (SBU)

➤ BNL-NCLS

➤ BNL-CFN

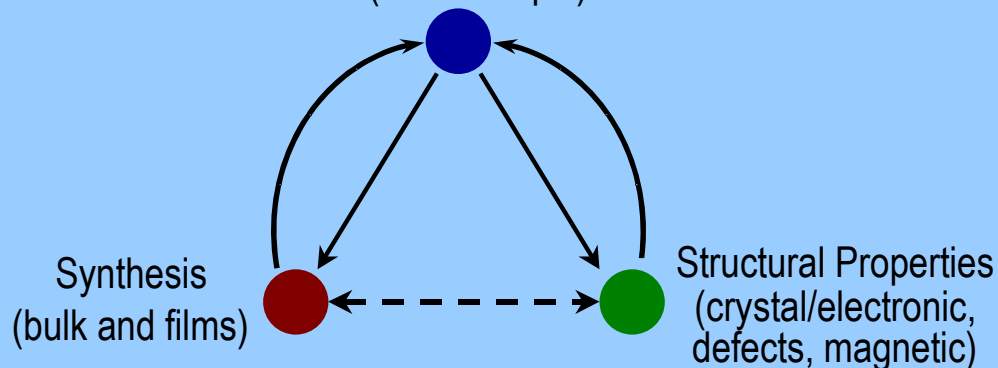
➤ SBU-MPI

➤ External:

- J. Yang and X. Shi (GM/BNL CRADA)
- C. Li and C. Ulher (U. of M/DOE-WH)
- H. Wang –HTML (ORNL) –SNS, NIST
- R. Funahashi (AIST, Japan)



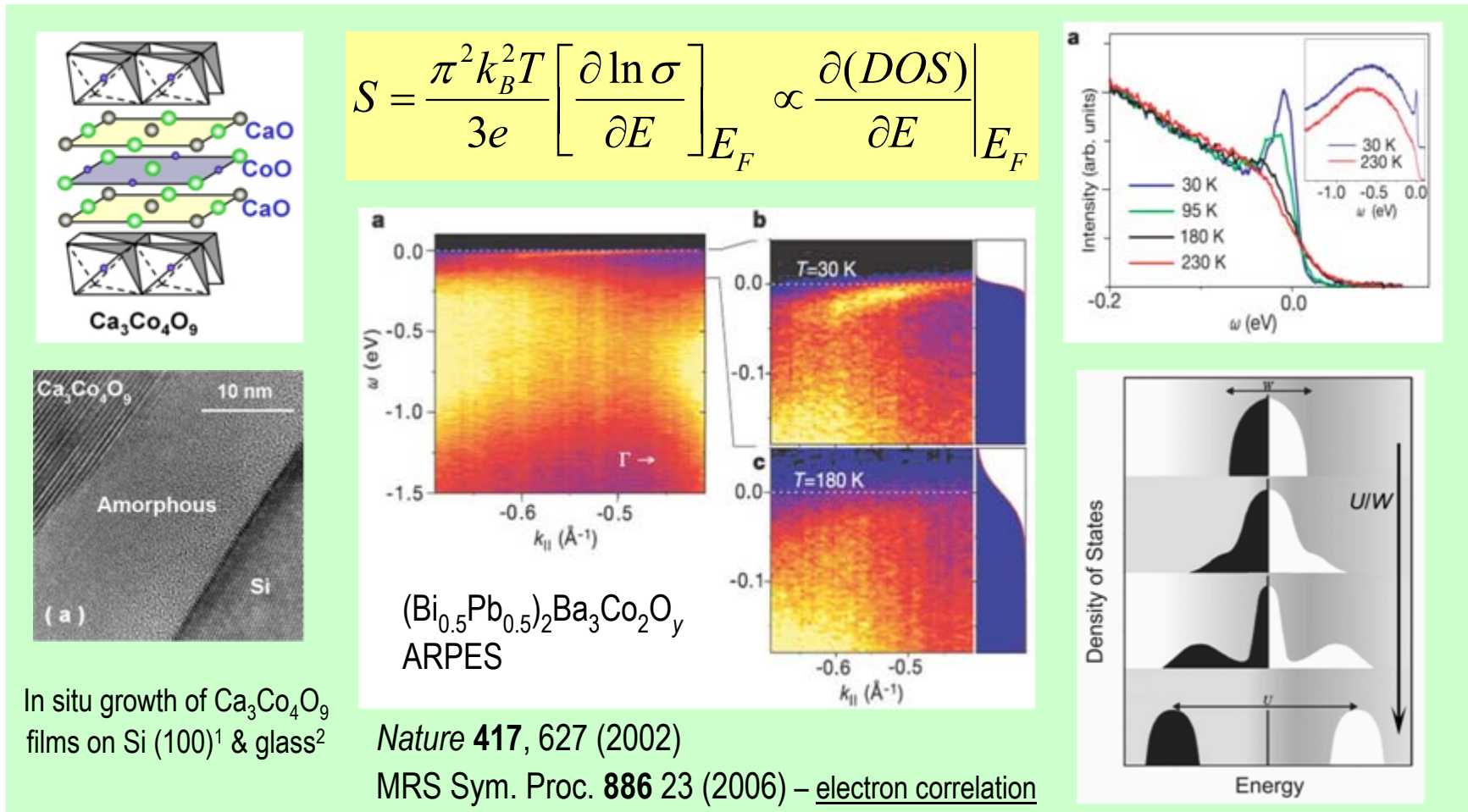
Thermoelectric Properties and Modules
(Macroscopic)



BNL Thermoelectric (TE) Materials Program Overview

Our research focuses:

- 1) Exploring new avenues to TE materials research: e.g. oxides
 Searching for resonant structure in e-DOS near Fermi-level: Cobaltates



1) *Appl. Phys. Lett.* **86**, 082103 (2005); 2) *Appl. Phys. Lett.* **87**, 171912 (2005)

BNL Thermoelectric (TE) Materials Program Overview

2) Developing cost-effective and industrially-scalable TE Materials and technology for power generation and refrigeration

– Bulk high performance TE materials

(2006 – present, DOE-WHR, BNL/GM CRADA, BNL-TM-Fund)

Non-equilibrium (Melt-spin + Hot press or SPS)*



+



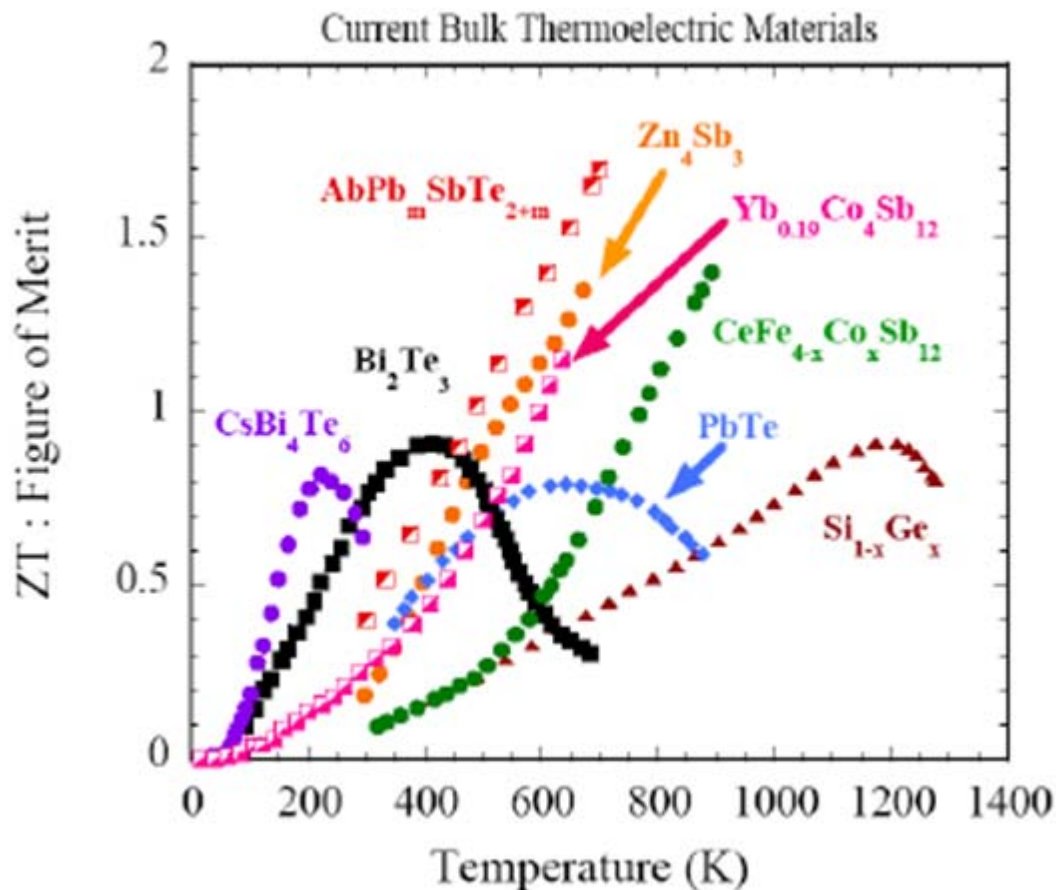
- TE Modules

*WUT, SIC (China), Fraunhofer (Germany), and others

Bulk Thermoelectric Materials

Terry M. Tritt & Mas Subramanian
MRS Bulletin TE Theme, March 2006

$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_L} = \frac{S^2}{L_0} \bullet \frac{1}{1 + \frac{\kappa_L}{L_0 \sigma T}}, \quad \kappa_e = L_0 \sigma T$$

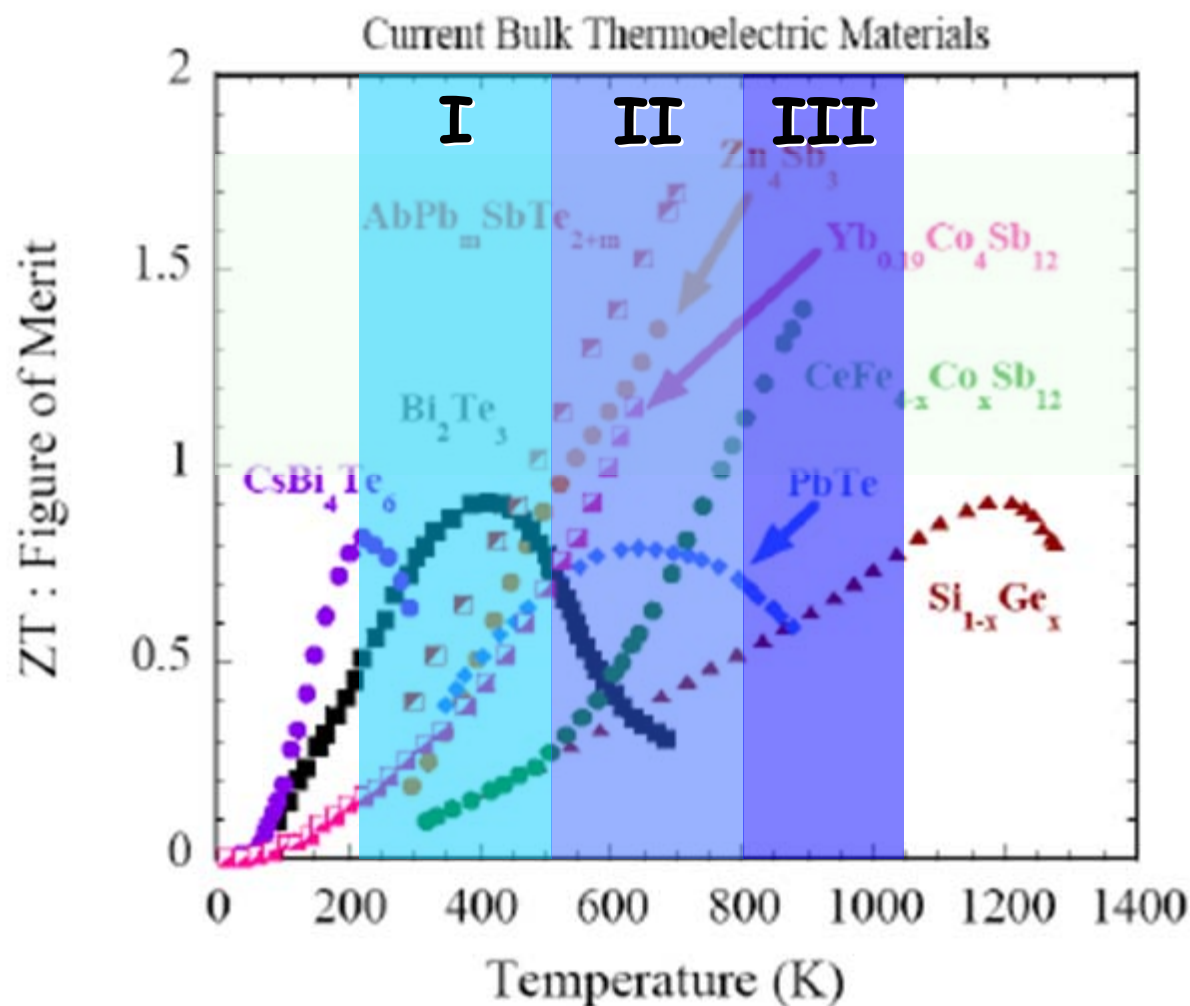


Objectives:

- ZT ~ 1.0 - 1.5 by increasing power factor and reducing lattice thermal conductivity simultaneously
- Good thermal and mechanical Properties
- Cost effective and industrial scalable

BNL's Interests in Bulk High Performance TE Materials

Terry M. Tritt & Mas Subramanian
MRS Bulletin TE Theme, March 2006



Materials of interests:

Region I (250K – 500K)

Tellurides

Region II (500K – 800K)

Filled skutterudites

Magnesium silicides

Region III (800K – 1050K)

Oxides - cobaltates

Conventional solid state synthesis of filled Skutterudites

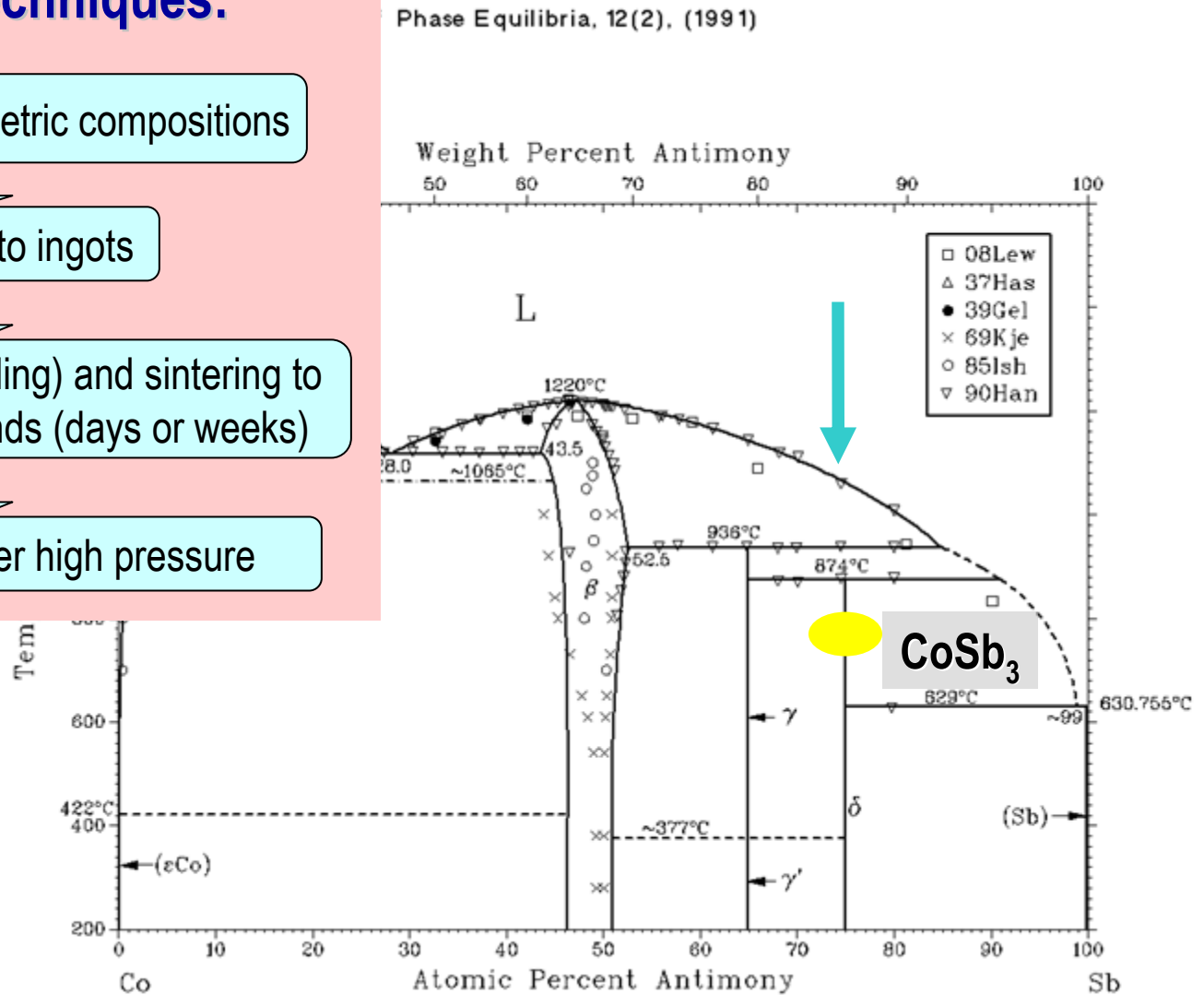
Conventional solid state synthesis techniques:

Melting the stoichiometric compositions

Quench into ingots

Powdering (e.g. ball milling) and sintering to single phase compounds (days or weeks)

Densification under high pressure



Non-equilibrium Synthesis

Conventional solid state synthesis techniques:

Melting the stoichiometric compositions

Quench into ingots

Powdering (e.g. ball milling) and sintering to single phase compounds (days or weeks)

Densification under high pressure

BNL's non-equilibrium synthesis techniques*

Rapid solidification (Fig. 1) starting materials into near amorphous ribbons in ~ seconds

Direct conversion and densification under high pressure (Fig. 2) in minutes

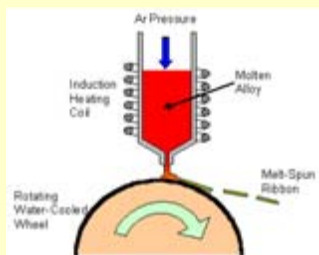
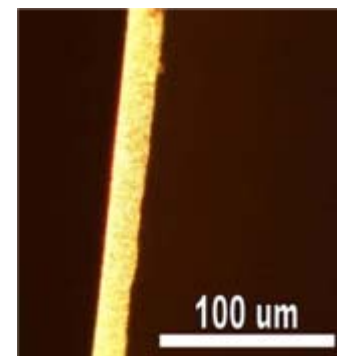
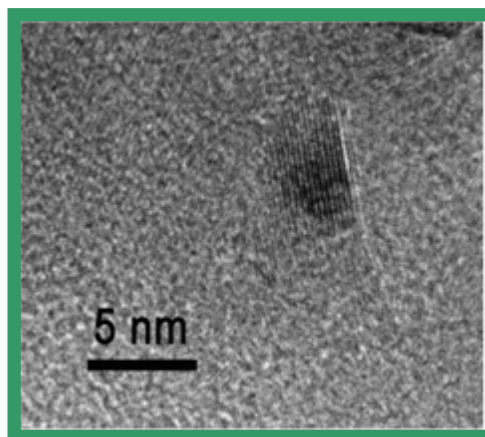
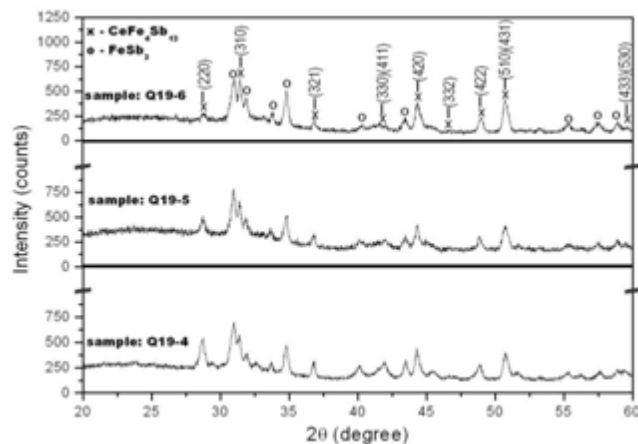
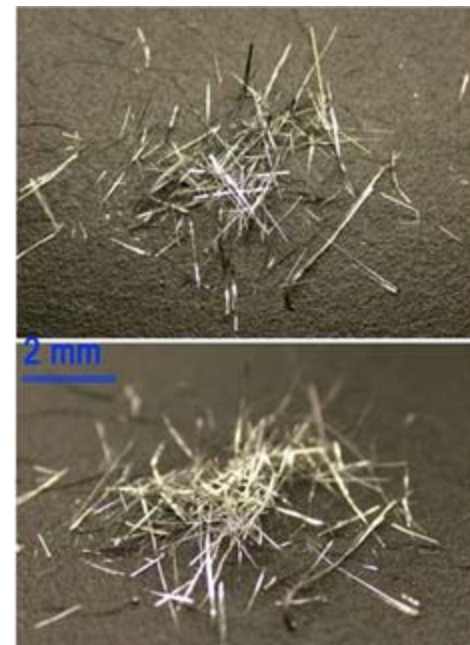
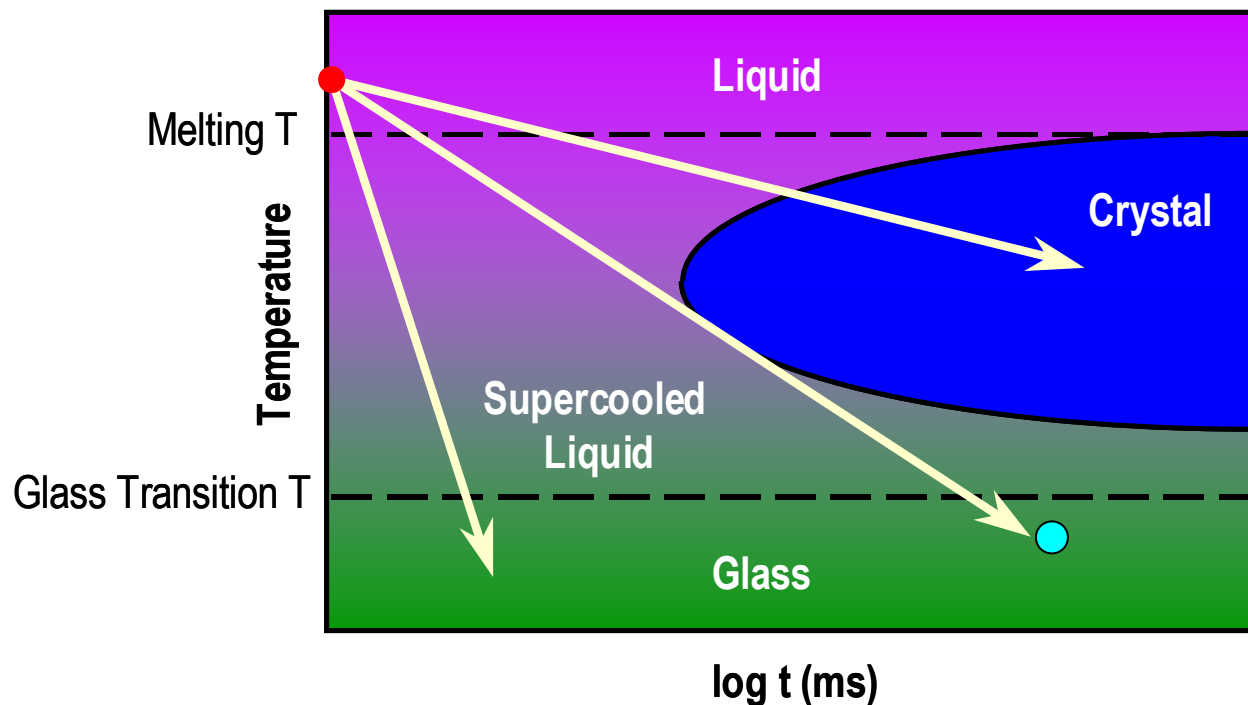


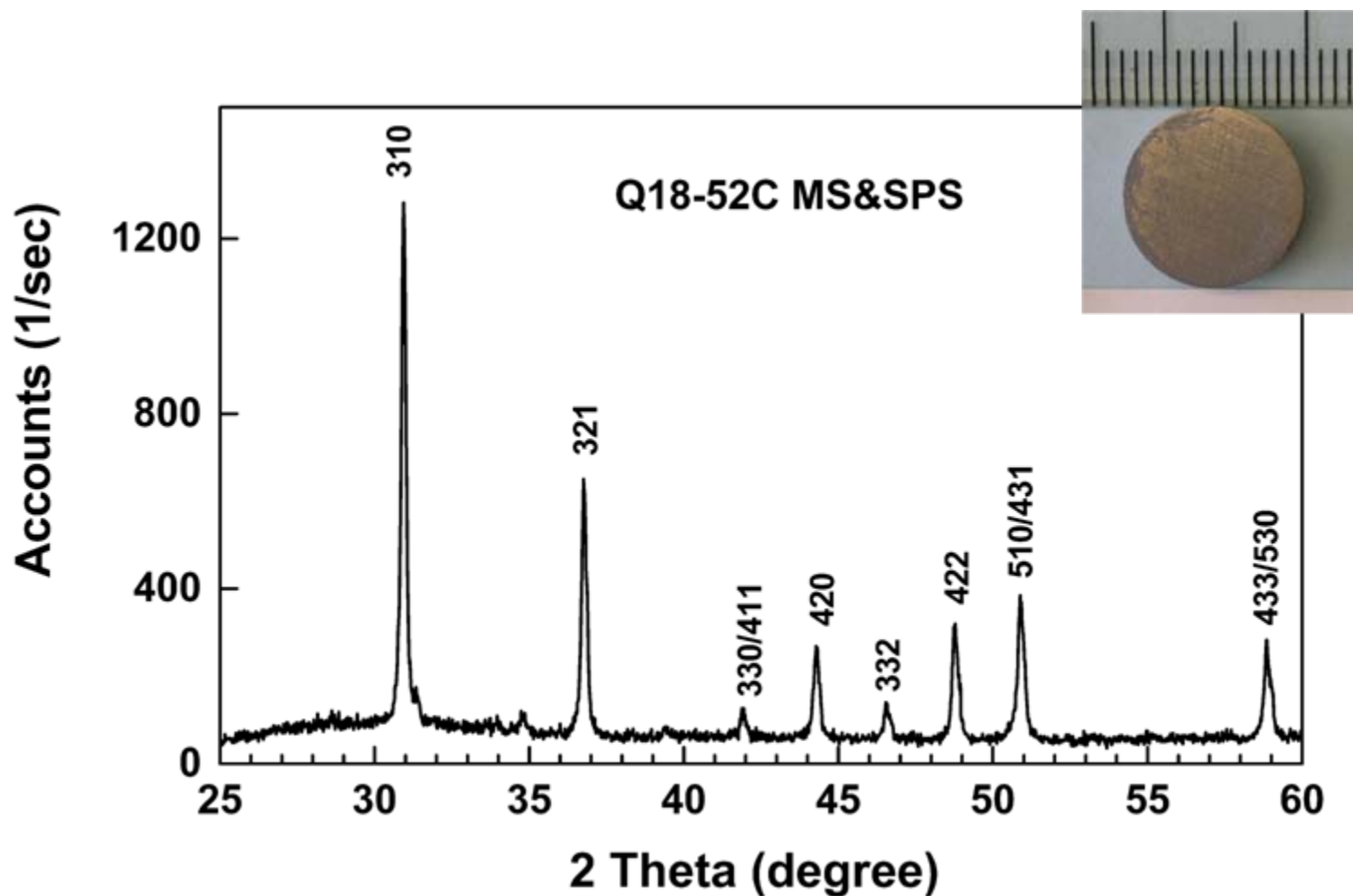
Fig. 2 SPS (GM, not shown) and Hot Press
Max. rate 300°C/s, Max. P = 4000 Kbar, Max. T = 2500°C at BNL and SBU

X-ray Diffraction and TEM of Melt-Spun $CeFe_4Sb_{12}$ *



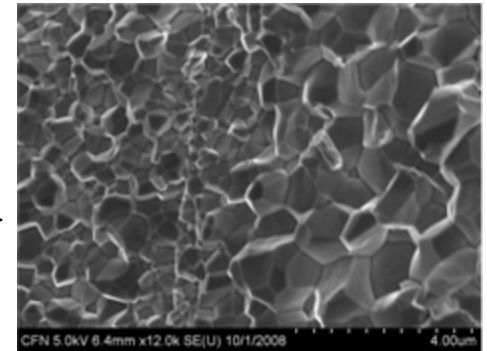
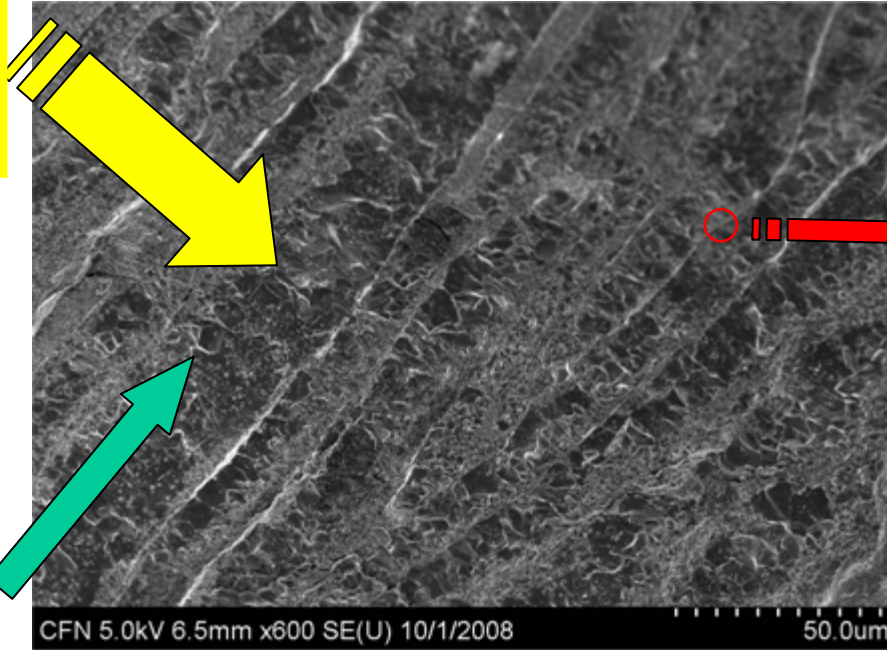
*BNL - MS+SPS processed p-type filled skutterudites - ICT2008

Structures of Melt-Spun+HP Samples (2 min conversion)



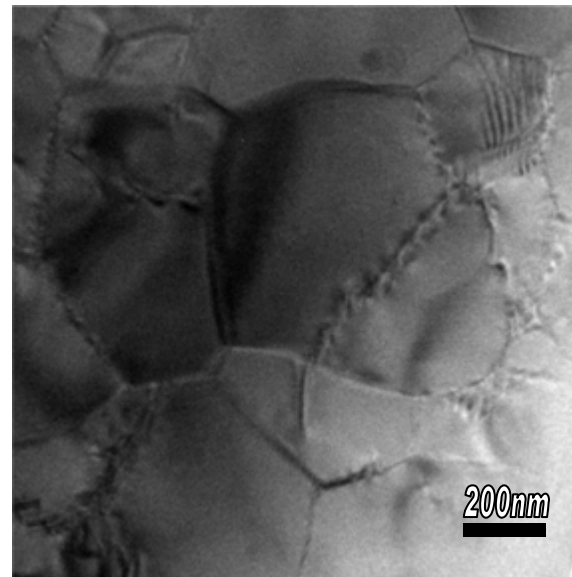
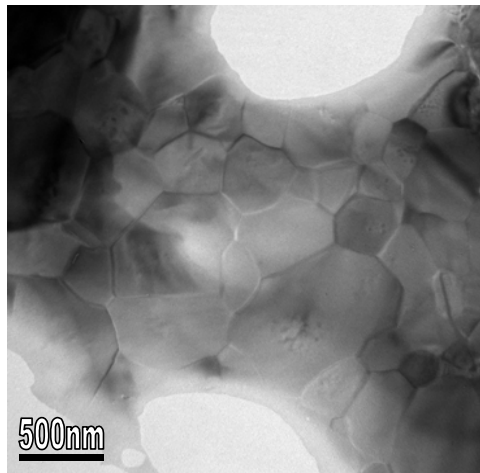
Structures of Melt-Spun+HP Samples (2 min conversion)

Pressure
direction

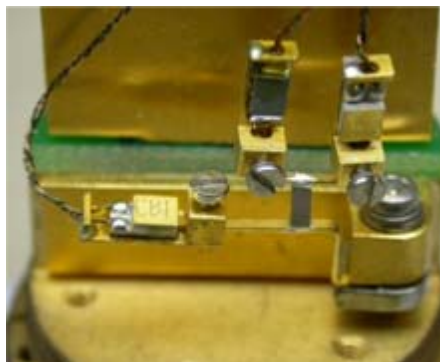
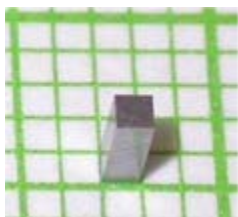


Ribbon
length
direction

- Very dense (~100%)
- Variable grain sizes
~ 50nm – 1μm

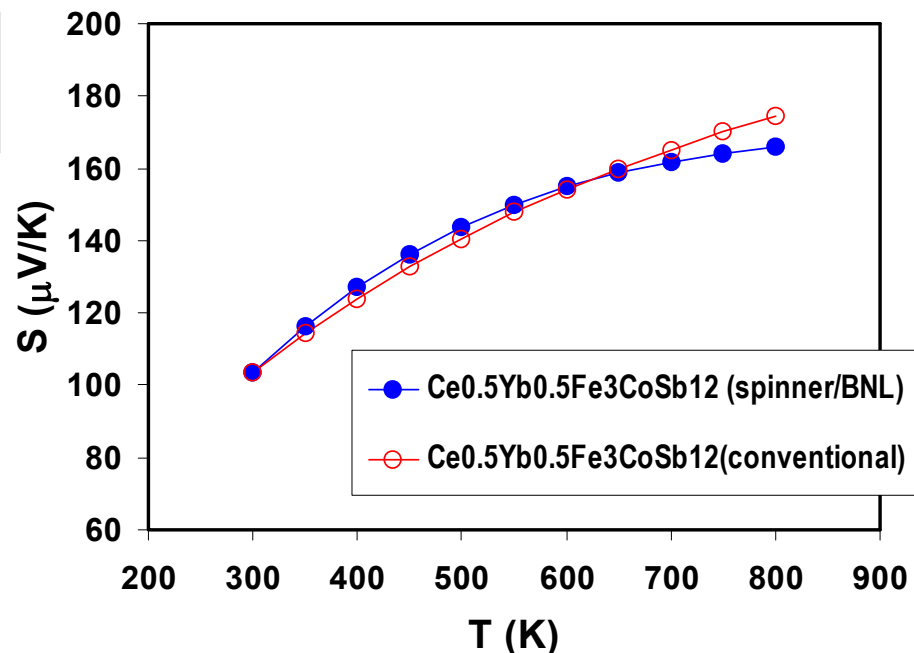
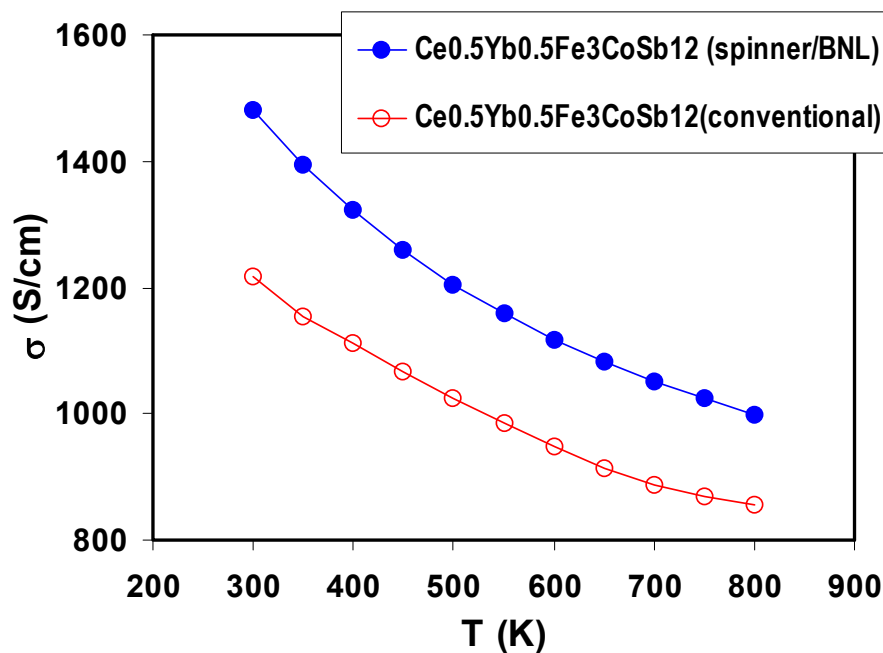


Thermoelectric Properties Characterization*



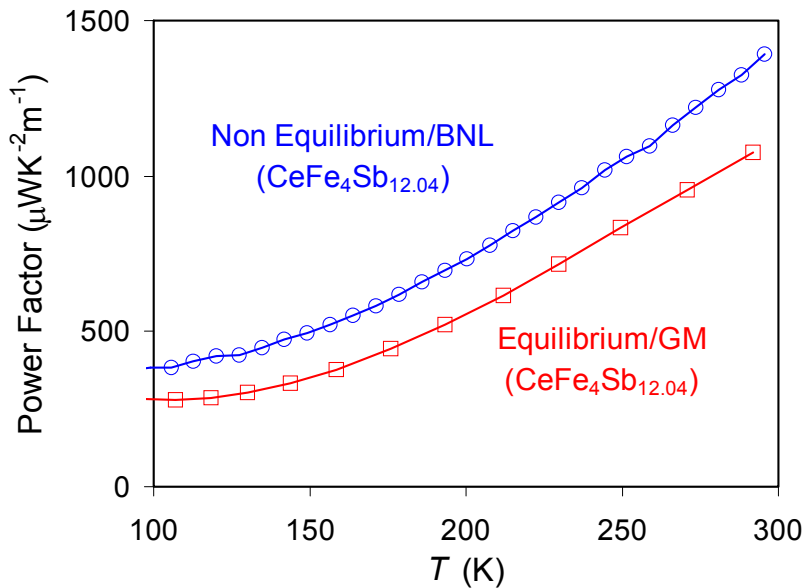
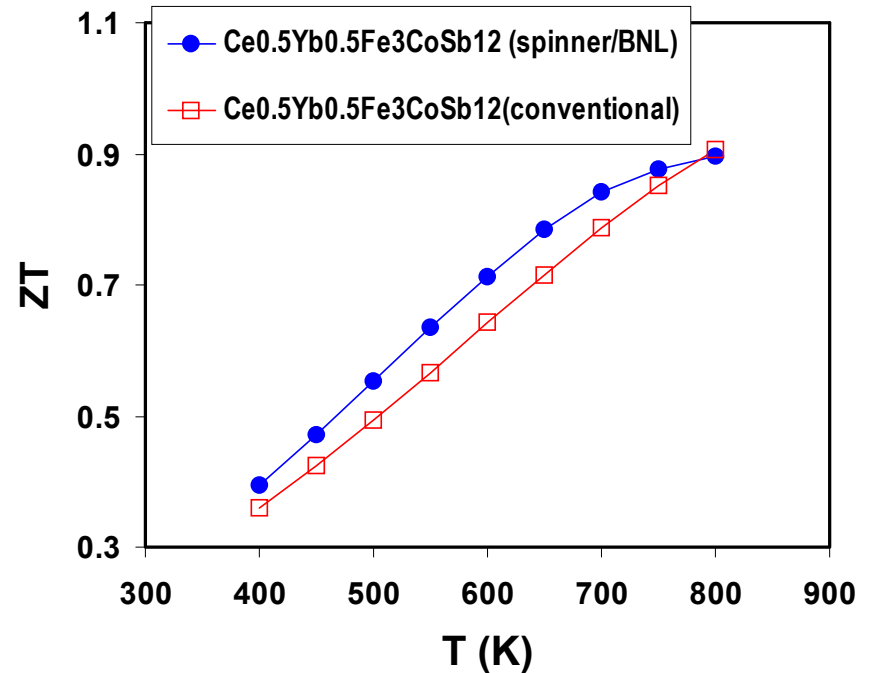
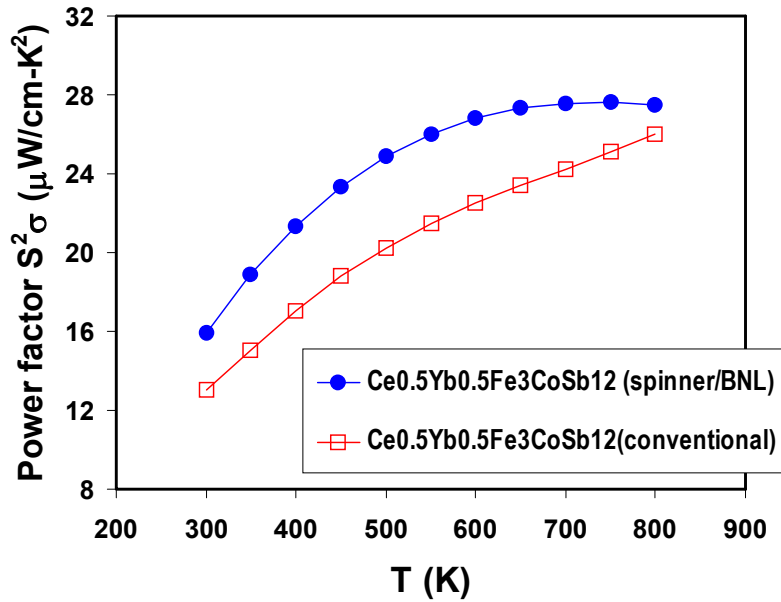
Q18-52D
DSCN1840

$$ZT = \frac{S^2 \sigma}{\kappa_T} T = \frac{S^2 \sigma}{(\kappa_L + \kappa_e)} T$$



*High temperature thermoelectric properties measured by C. Uher's group

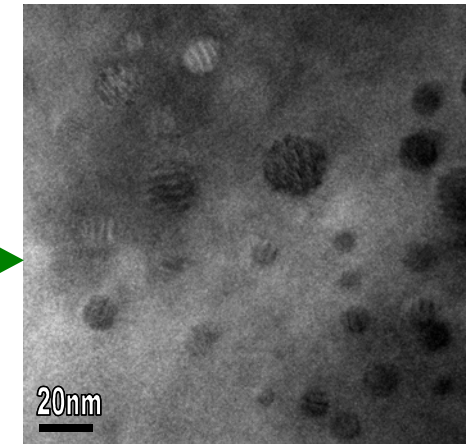
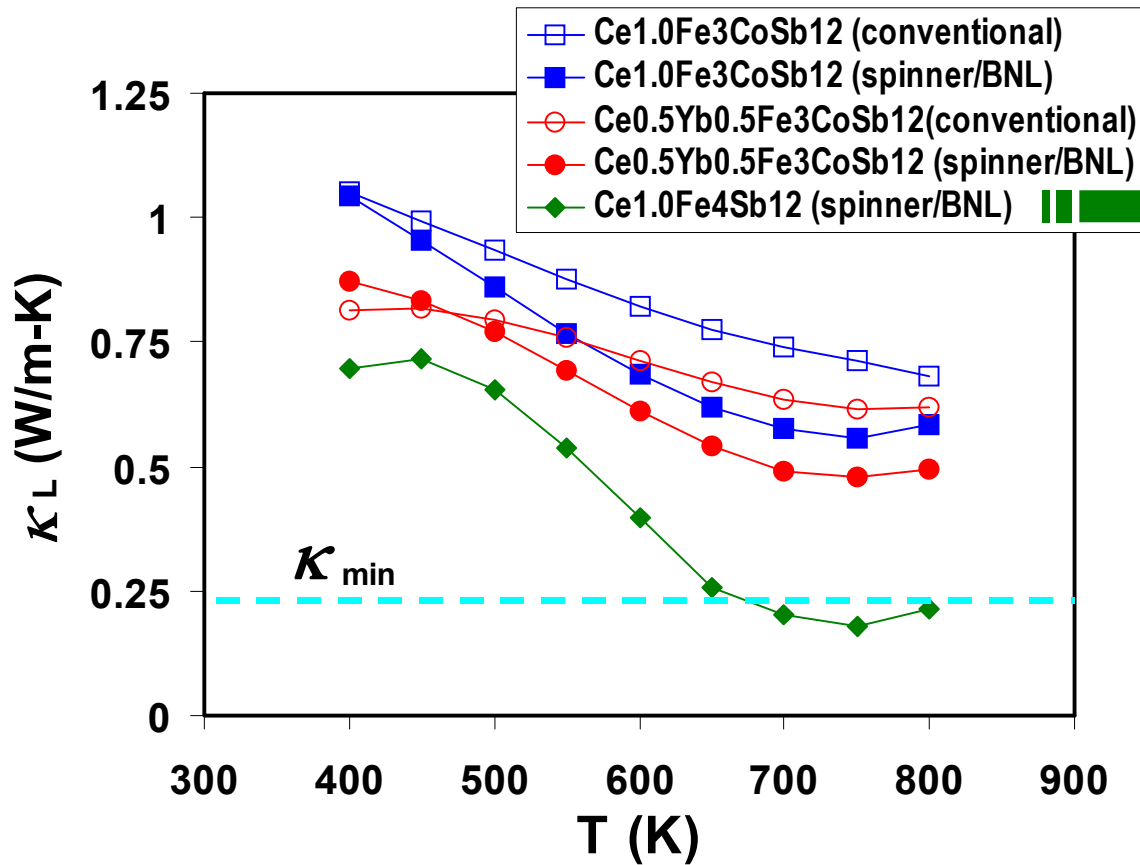
Power Factor and Figure of Merit ZT



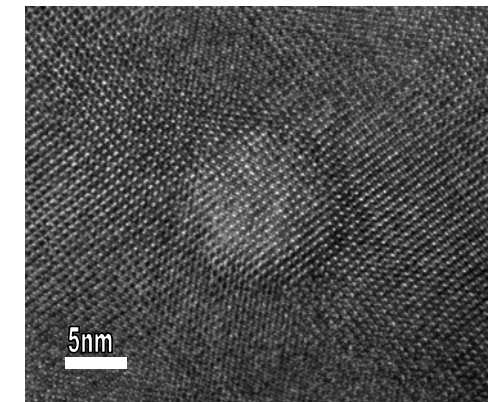
20%-30% enhancement in Power Factor for BNL's samples over the entire temperature region

$$ZT = \frac{S^2\sigma}{\kappa_T} T = \frac{S^2\sigma}{(\kappa_L + \kappa_e)} T$$

Low Lattice Thermal Conductivity!



TEM - nanostructures

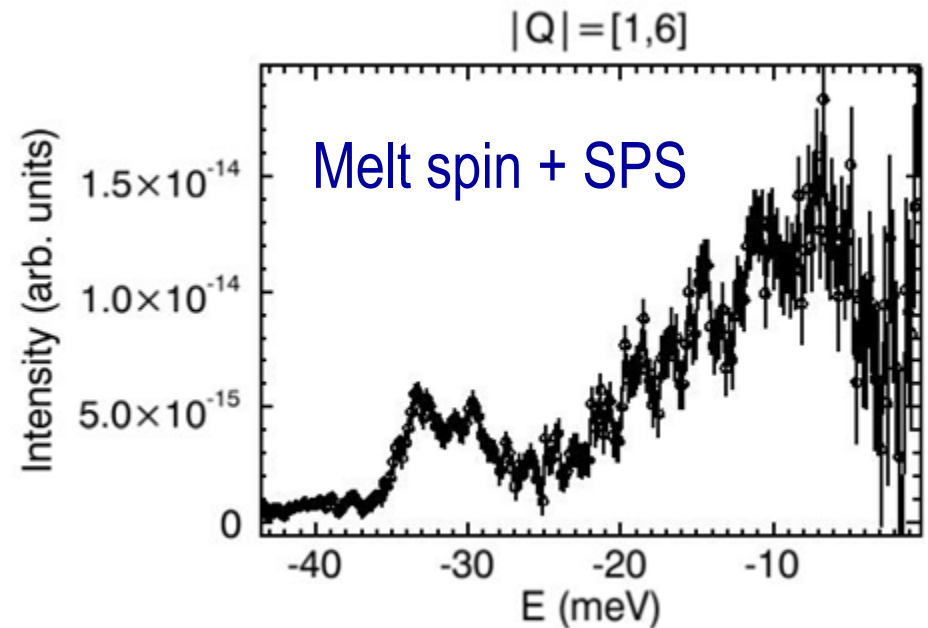
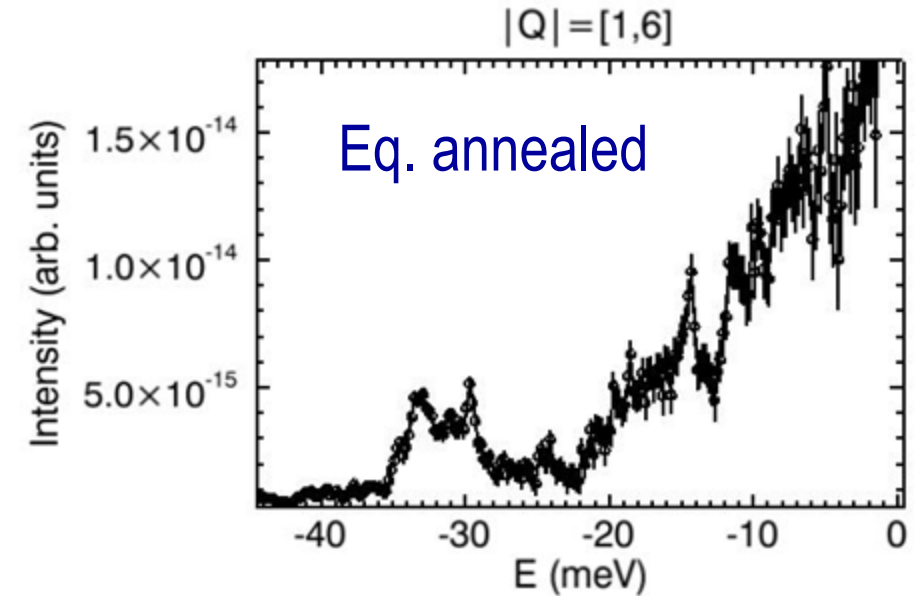
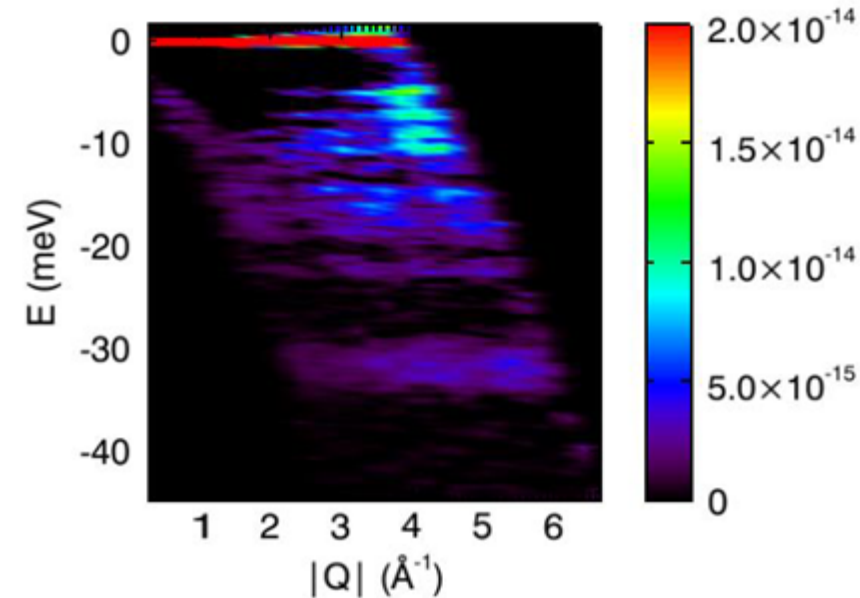


HRTEM - Coherent lattice match between the nano-particle and the matrix

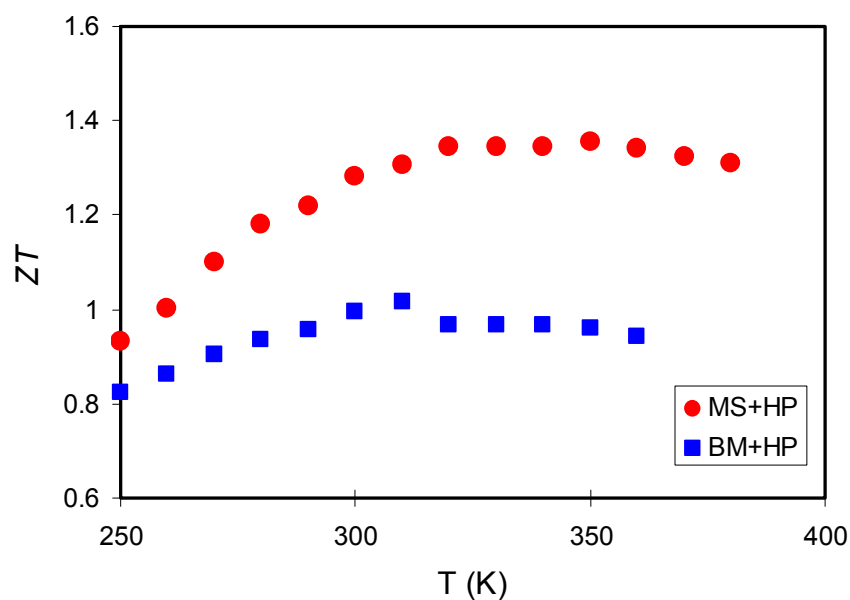
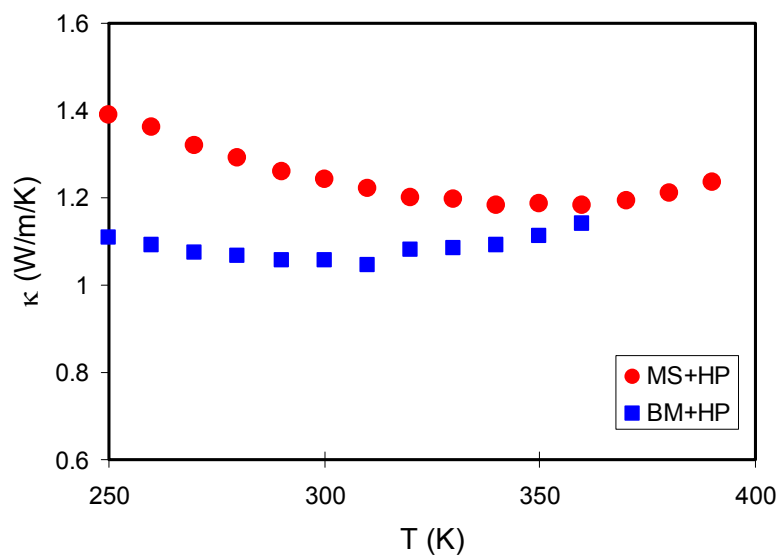
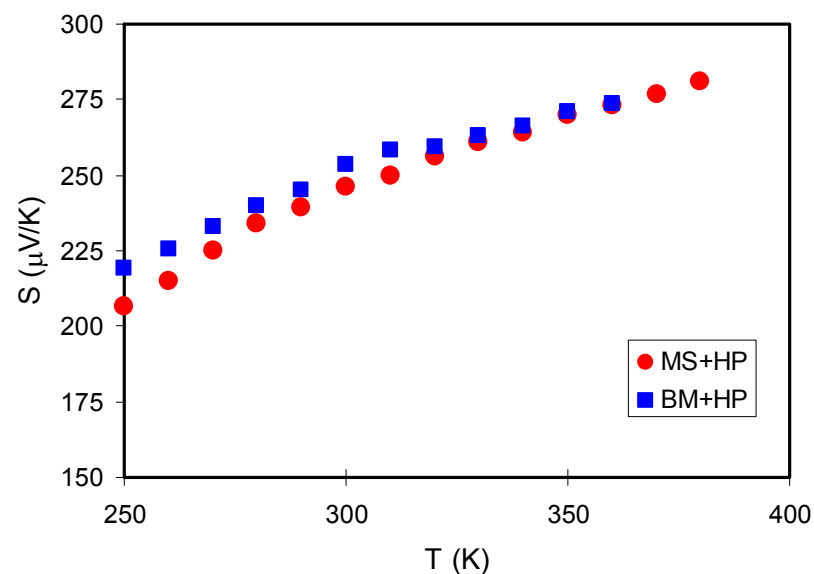
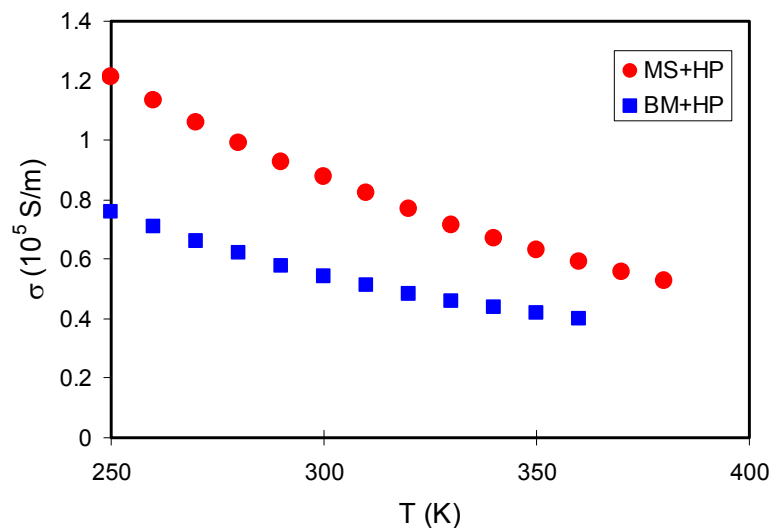
κ_L obtained by using Wiedmann-Franz law
 κ_{min} is the alloy limit

Inelastic neutron scattering of Ce-filled skutterudites

*I. Domitrov, S. Shapiro, Q. Li, and
M. Manley (LLNL) ORNL-SNS

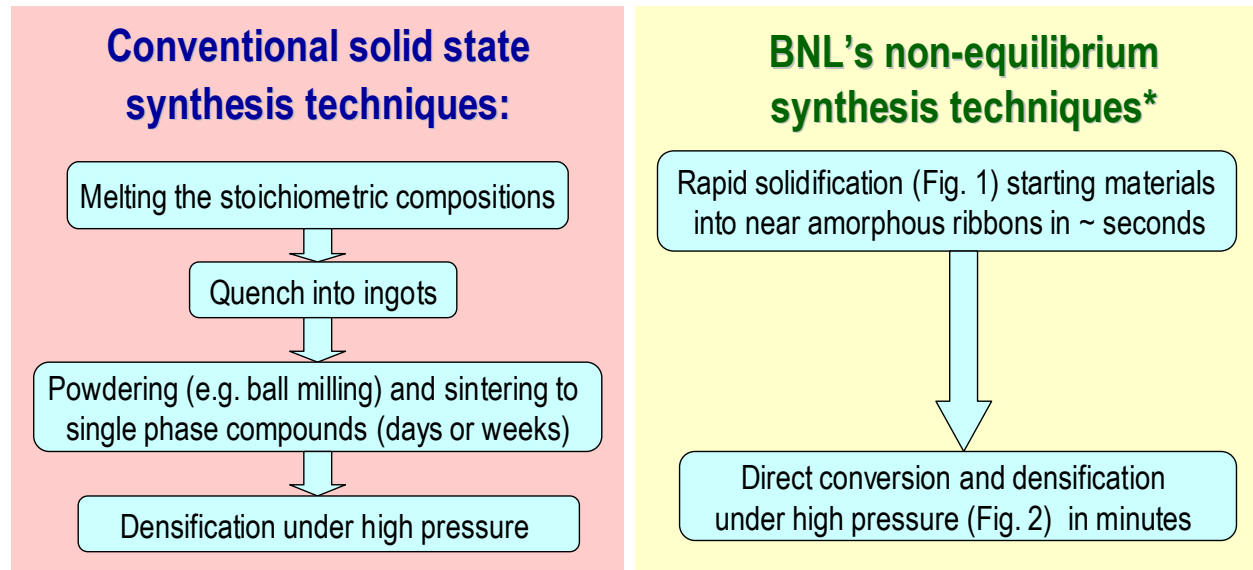


TE Properties of MS+HP processed $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3^*$



*Measured along the same direction: $I//\Delta T$

Advantages of non-equilibrium process



- ❖ Higher filling fraction, higher density, and higher mechanical strength
- ❖ More control of micro- to nano-structures to increase the power factor, while simultaneously reducing the lattice thermal conductivity
- ❖ Reduced processing time by orders of magnitude and industrially scalable
- ❖ Applicable to a wide range of TE and other energy-related materials
(High ZT values in several PG and RG thermoelectric materials)

Conclusions

Non-equilibrium synthesis can increase power factor by enhancing electrical conductivity, and reduce lattice thermal conductivity simultaneously in several filled skutterudites and telluride based compounds and alloys.

The cost-effective, industrial scalable non-equilibrium processed materials appear to have better and reproducible thermoelectric and mechanical properties that are ready for practical applications.

This work supported in part by DOE-BES, DOE-EERE (WHR), GM (GM/BNL-CRADA), and AUI (BNL)-Tech Maturation Fund