Correlation Between Structure and Thermoelectric Properties of Bulk High Performance Materials for Energy Conversion

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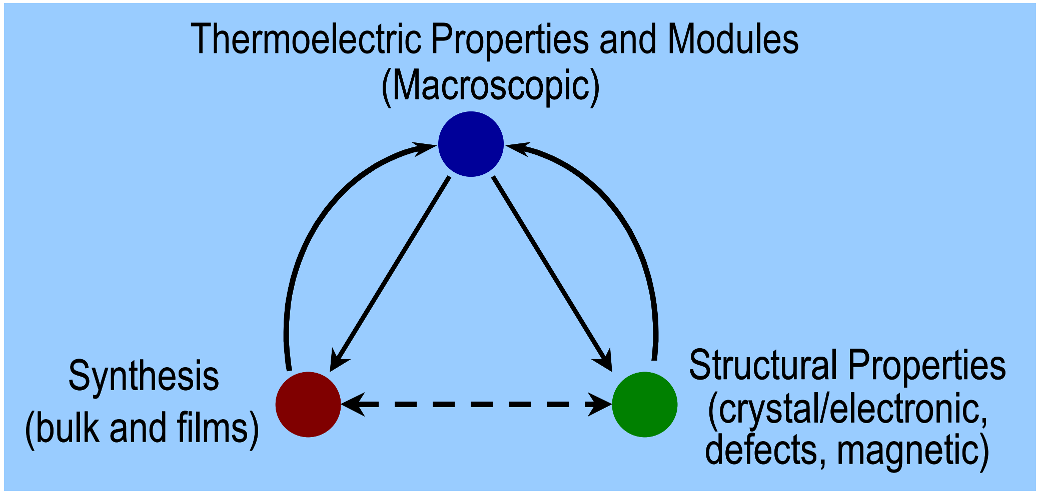
DOE TE-Workshop, San Diego, Jan 5, 2011

Thermoelectrics Research at BNL and Collaborations

Advanced Energy Materials Group



BNL Collaborations

- Electron & optical spectroscopy
  - T. Valla, C. Homes, P. Johnson
- Neutron and X-ray scattering
  - S. Shapiro, E. Bozin
  - S. Billinge (BNL/Columbia U.)

External Collaborations

- GM: J. Yang and X. Shi (now in SICCAS);
- SICCAS: X. Shi, W. Zhang, J. Yang, & L. Chen
- U of Michigan: C. Ulher
- ORNL: H. Wang (HTML) G. Ehlers (SNS)
- Boston College: Z. Ren and Q. Jie (formal student)

- <u>NSF/DOE TE Partnership:</u>

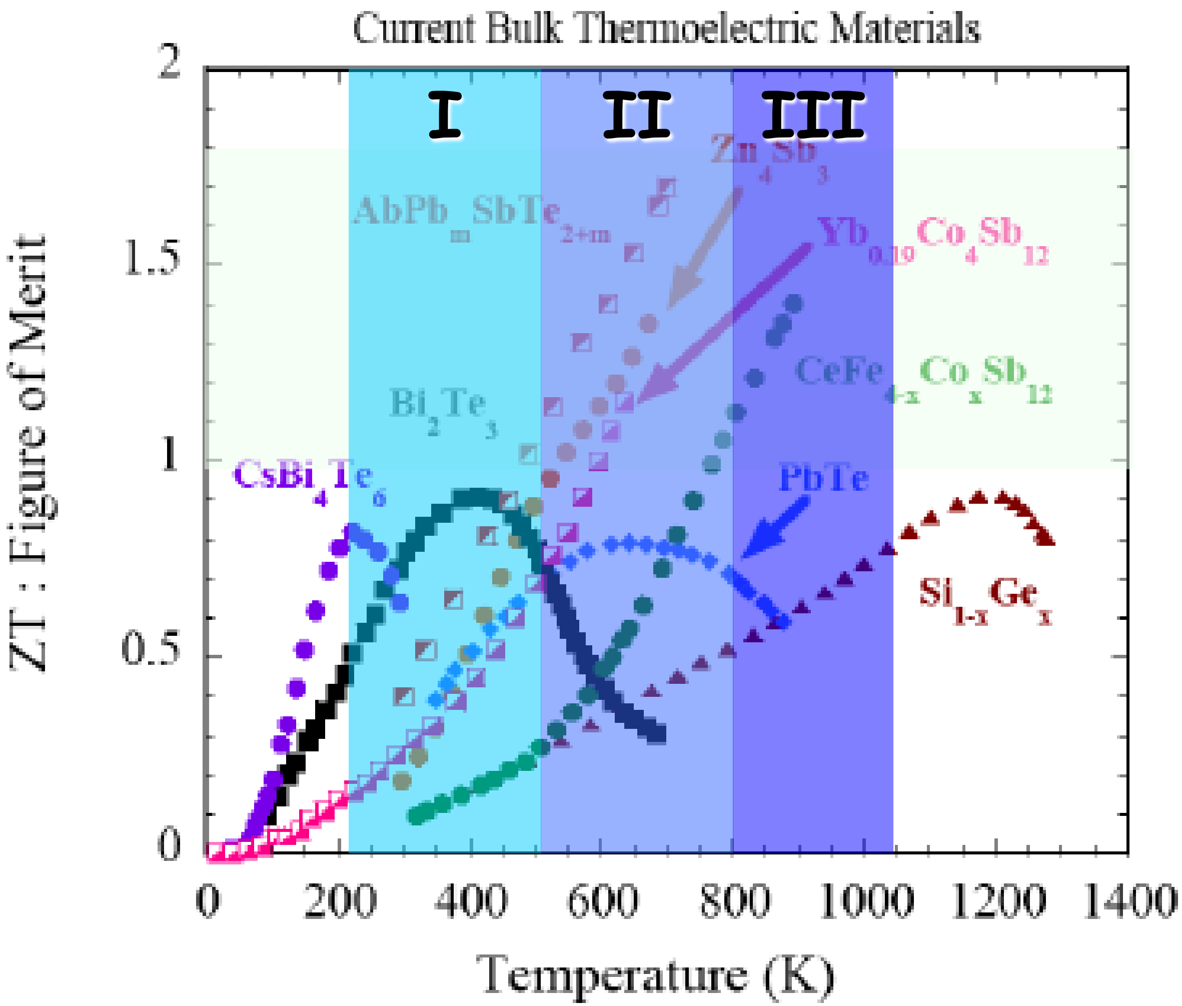
- BNL/Stony Brook Univ. (Zuo,et al)
- BNL's role:

1) Non-equilibrium synthesis and applying to thermal spray

2) TE property characterization

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

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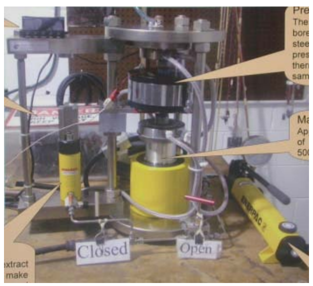
BNL Thermoelectric (TE) Materials Program Overview

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

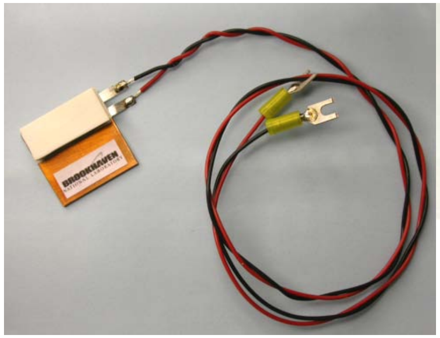
- ***Bulk high performance TE materials***

Non-equilibrium (Melt-spin, several high energy milling)

+ Hot press or SPS (GM and SICASC)*

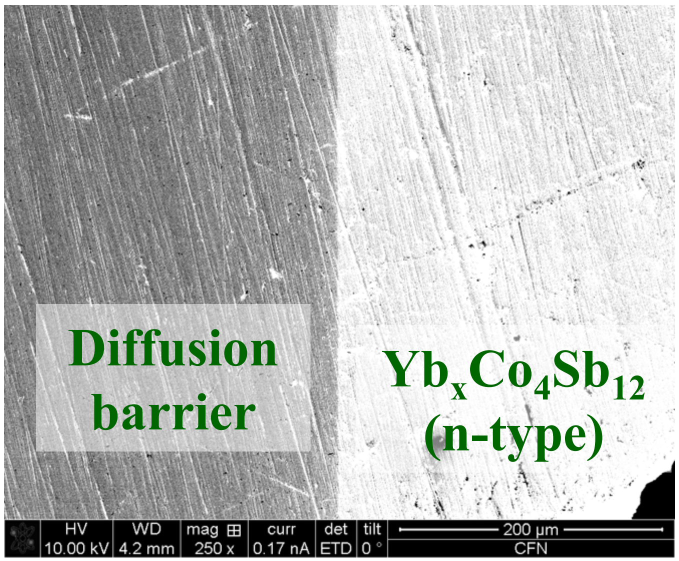


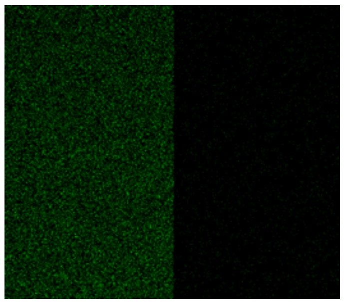
Thermoelectric (TEP) module development at BNL



TEP module

2x4 n- and p-type legs





EDX mode of interface

Power out-put testing platform for TEP module

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

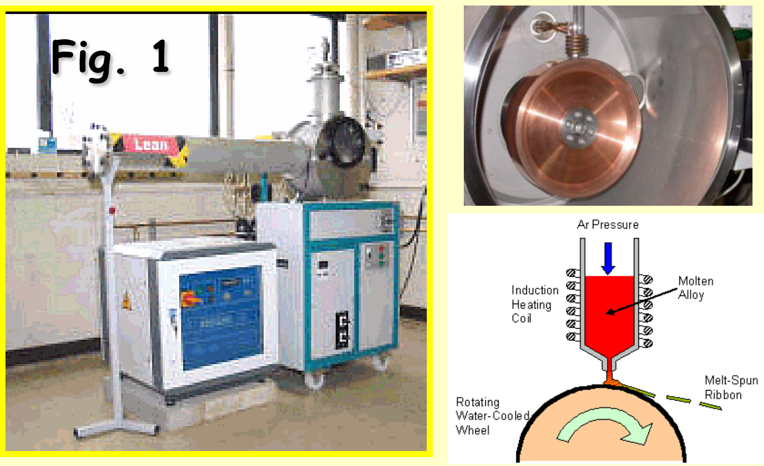
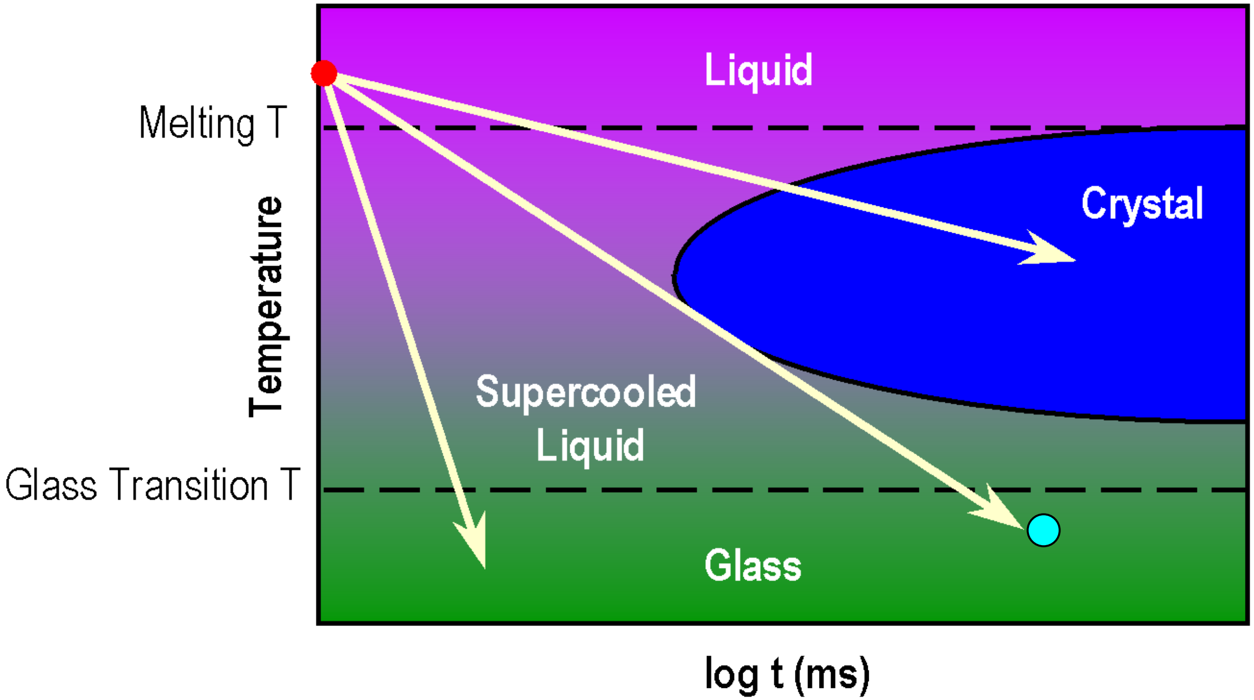
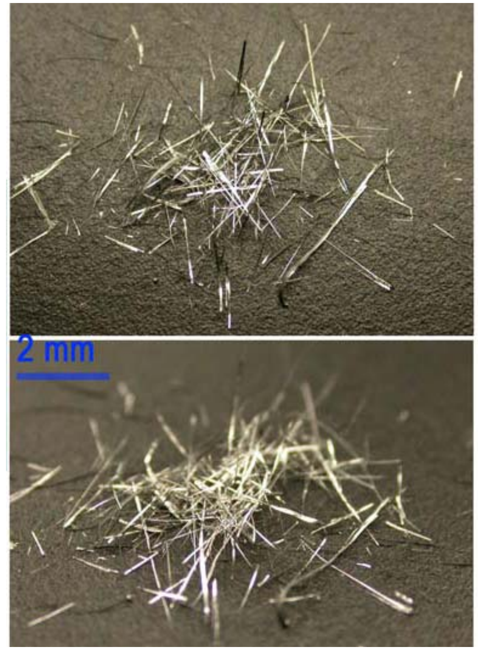
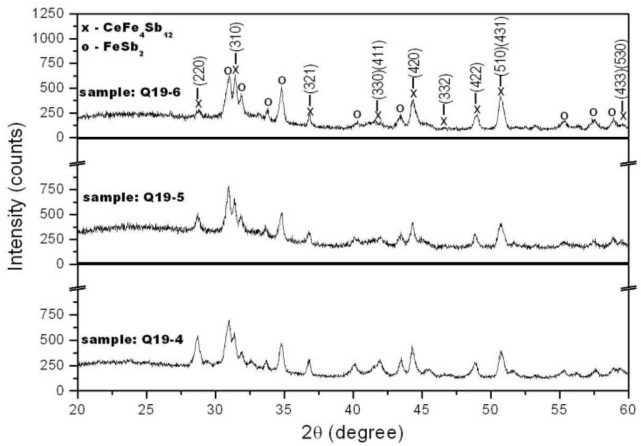


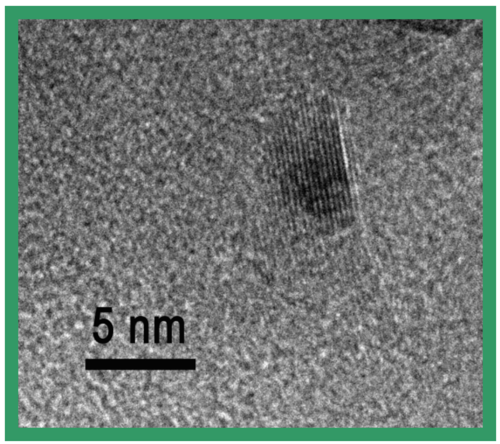
Fig. 2 Hot Press Max. rate 300^0C/s, Max. P = 4000 Kbar, Max. T = 2500^0C at BNL and SBU

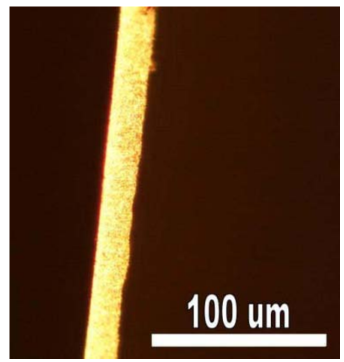
*X-ray Diffraction and TEM of Melt-Spun $CeFe_4Sb_{12}$**





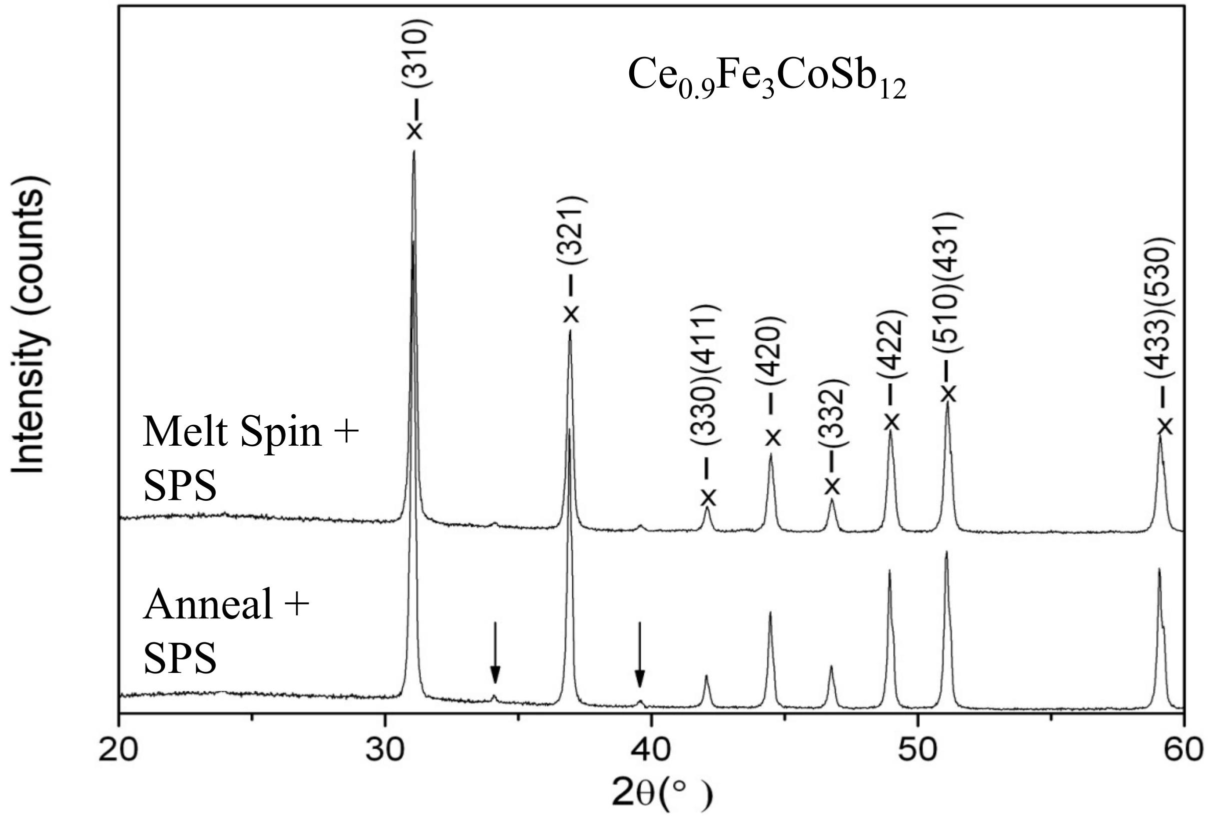


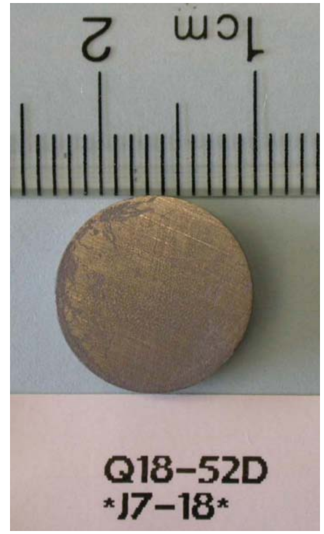




*Li, et al - MS+SPS processed p-type filled skutterudites - ICT2008 Proceedings

XRD of Melt-Spun+SPS (5 min) and Long Term Annealed+SPS $Ce_{0.9}Fe_3CoSb_{12}$ Samples

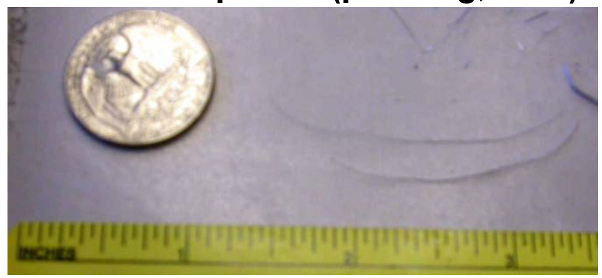


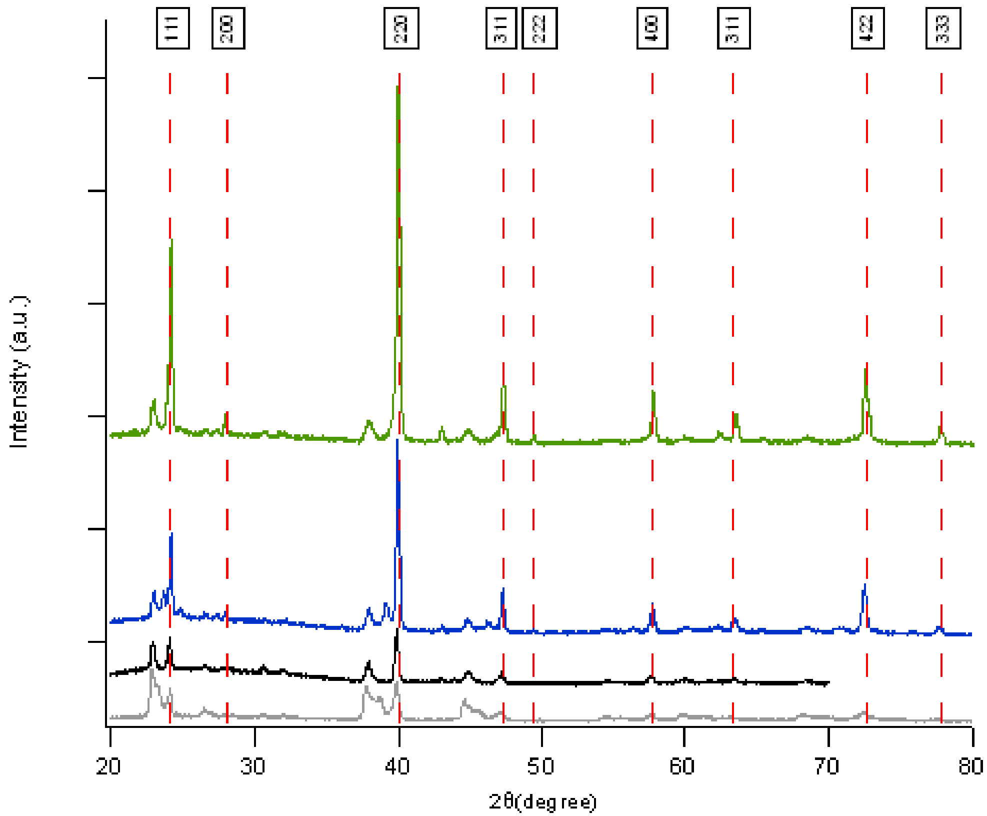


- Ribbons have been fully sintered within 5 min

$Mg_2Si_{0.4}Sn_{0.6}$

US-patent (pending, BNL)





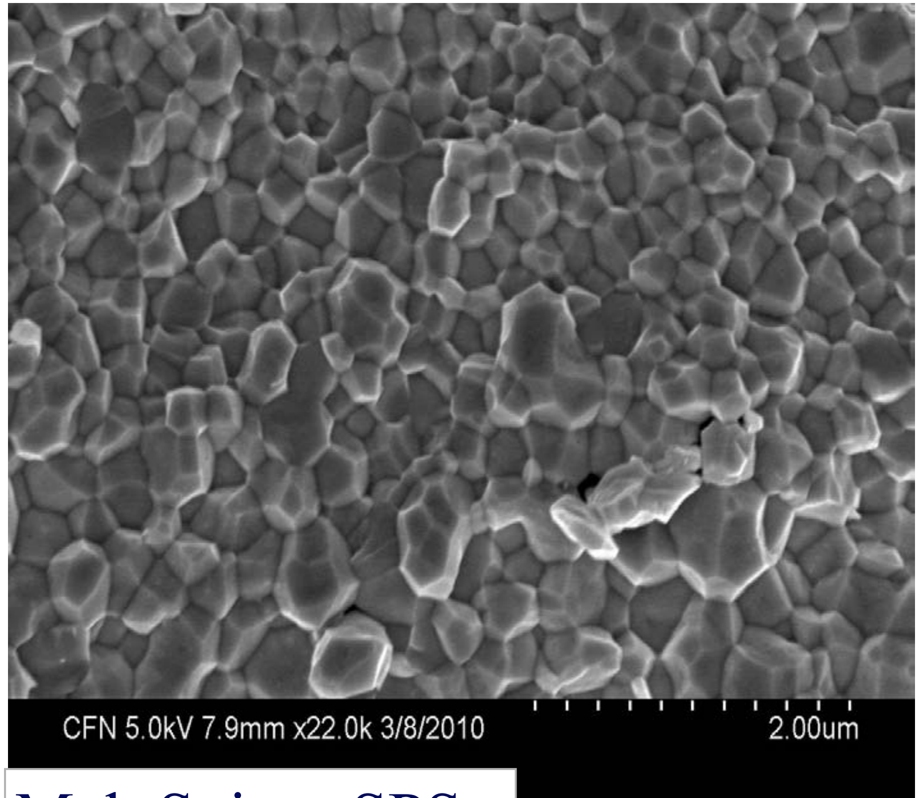
Hot Press, 800˚C 2 hr, 50 MPa

Hot Press, 800˚C 1 hr, 50 MPa

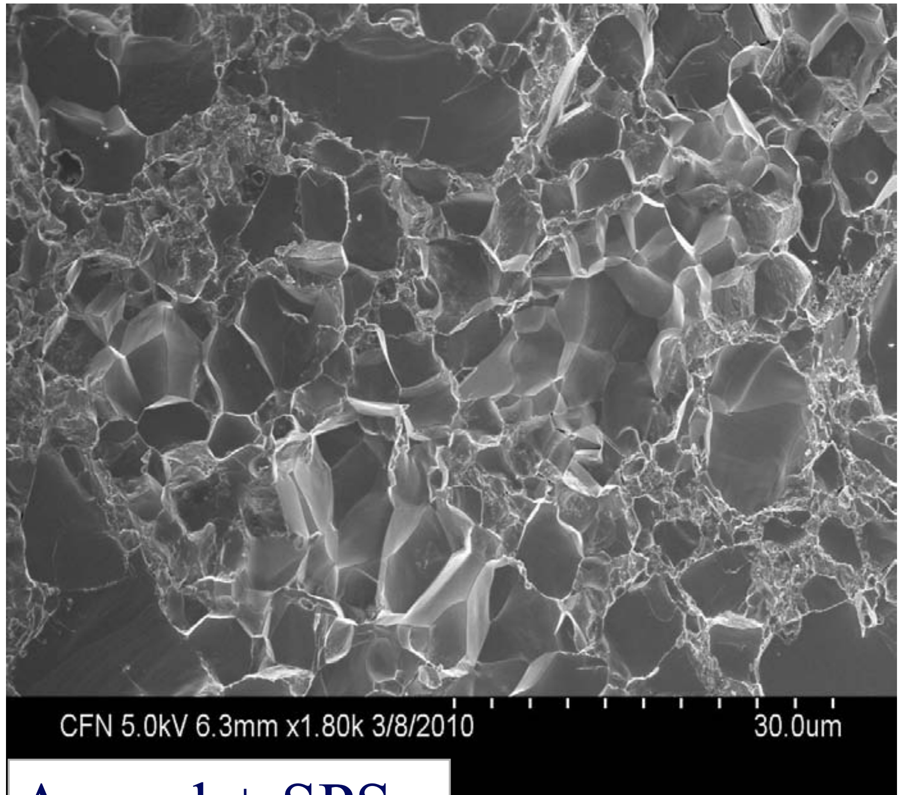
Hot Press, 800˚C 10 min, 50 MPa

Annealing at 760˚C, for 24 hr

SEM Images of Melt-Spun+SPS and LT Annealed +SPS Fractured $Ce_{0.9}Fe_3CoSb_{12}$ Samples



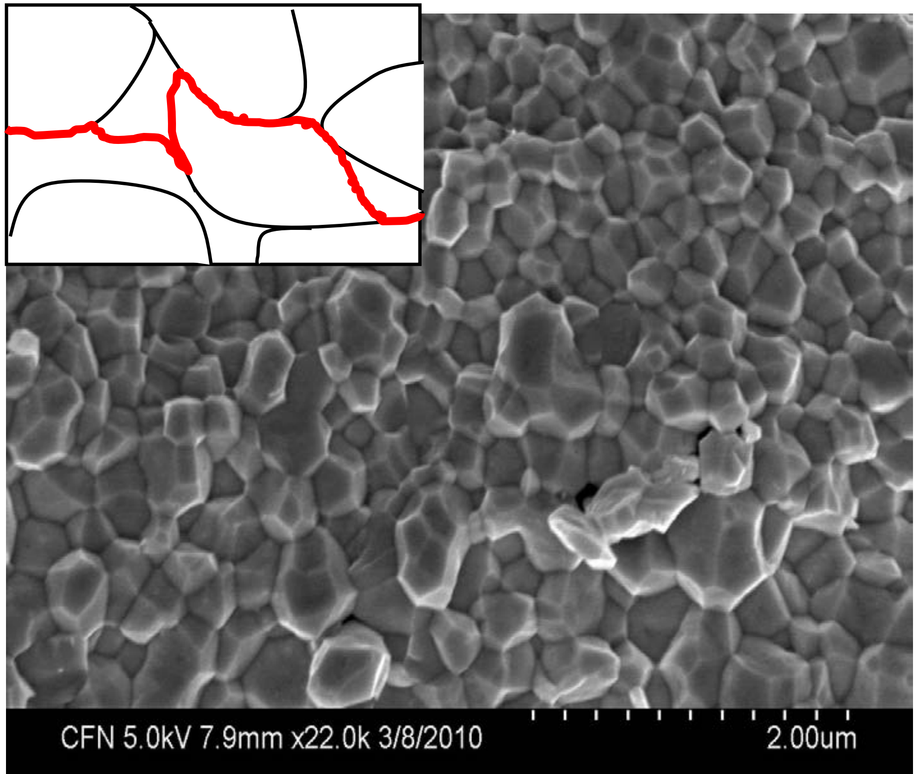
Melt Spin + SPS



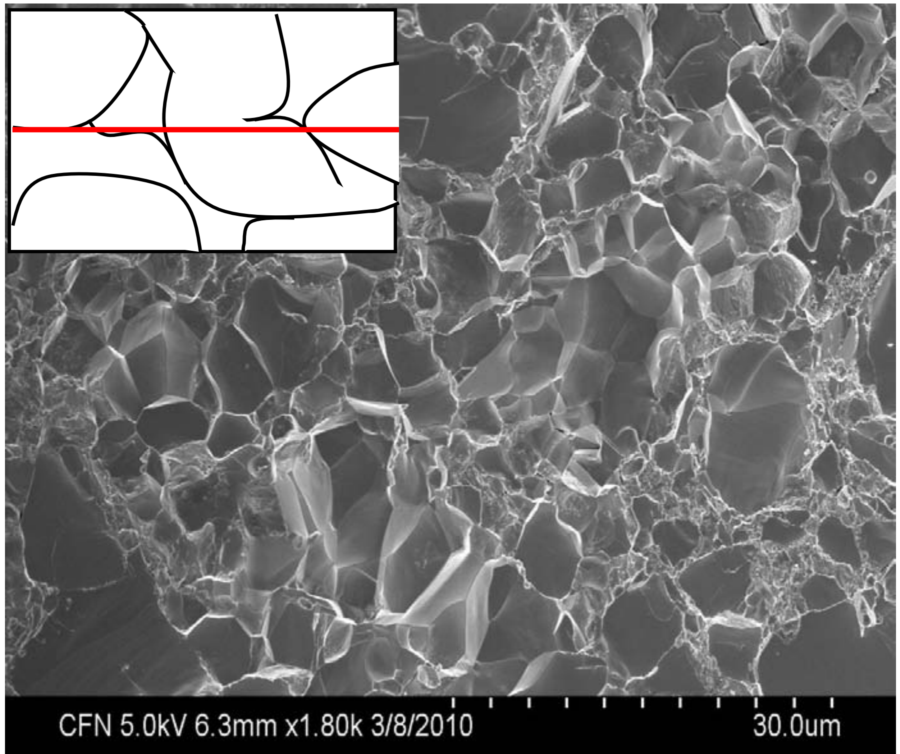
Anneal + SPS

- Grain size ~ 150-500nm
- Better fracture toughness could be expected

SEM Images of Melt-Spun+SPS and LT Annealed +SPS Fractured $Ce_{0.9}Fe_3CoSb_{12}$ Samples



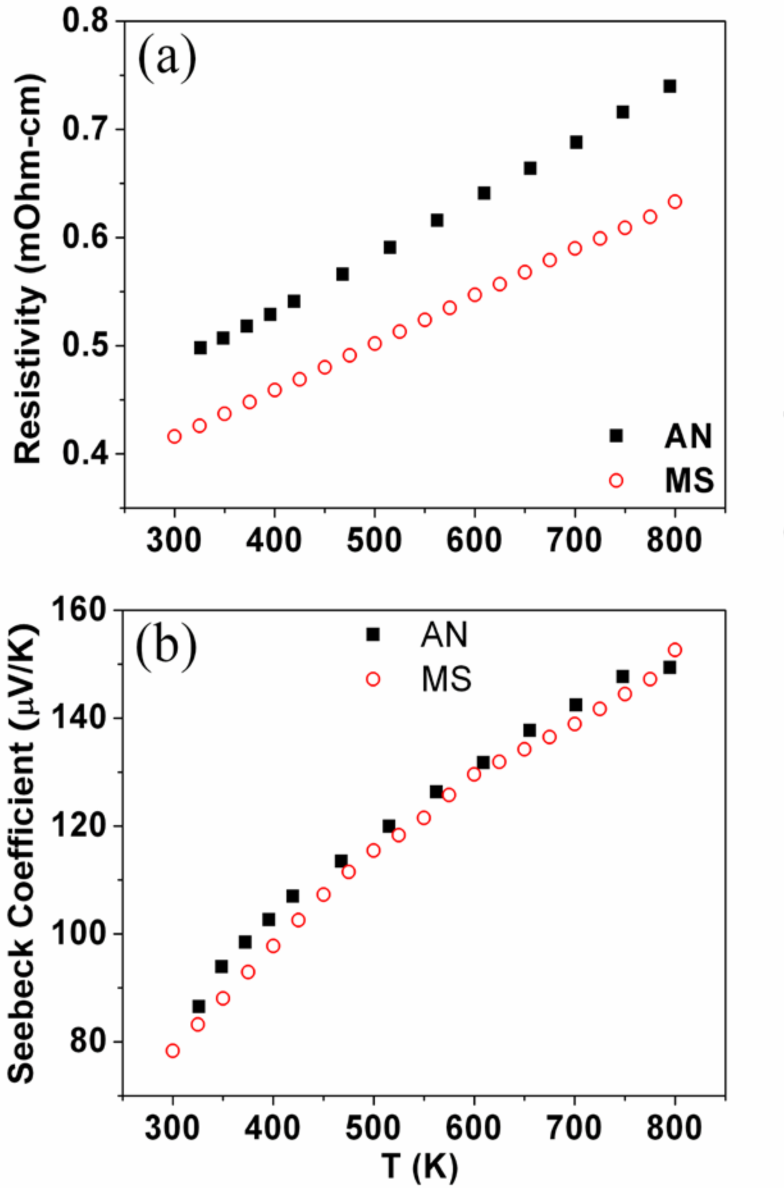
Melt Spin + SPS



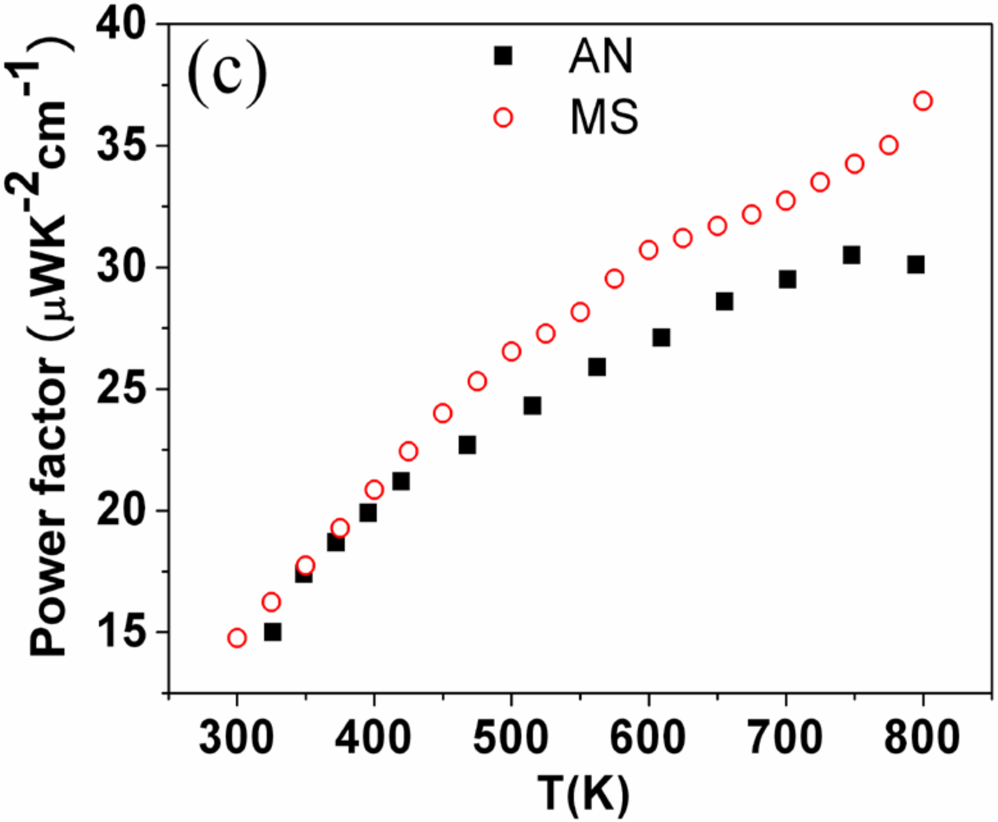
Anneal + SPS

- Grain size ~ 150-500nm
- Better fracture toughness could be expected

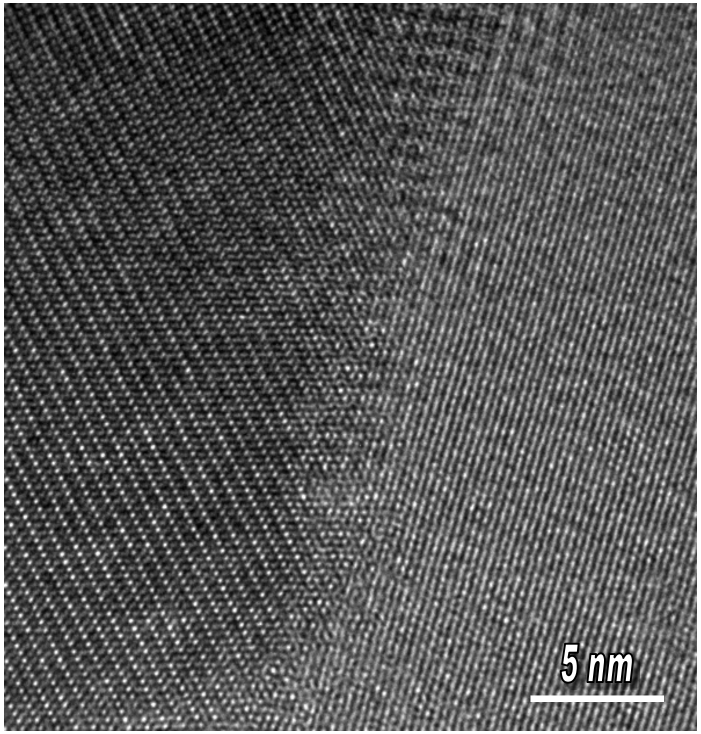
Electrical Transport Properties - $Ce_{1.05}Fe_4Sb_{12.04}$



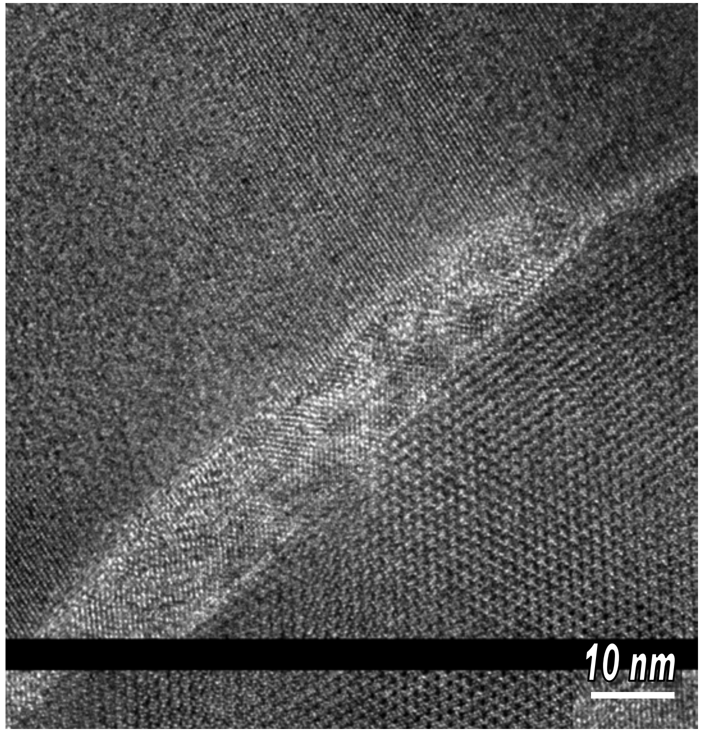
- Much lower resistivity
- Close Seebeck Coefficient
- **20%** improvement on PF



HRTEM grain boundary images of melt-spun+SPS and LT annealed +SPS $CeFe_4Sb_{12}$ Samples



Melt Spin + SPS



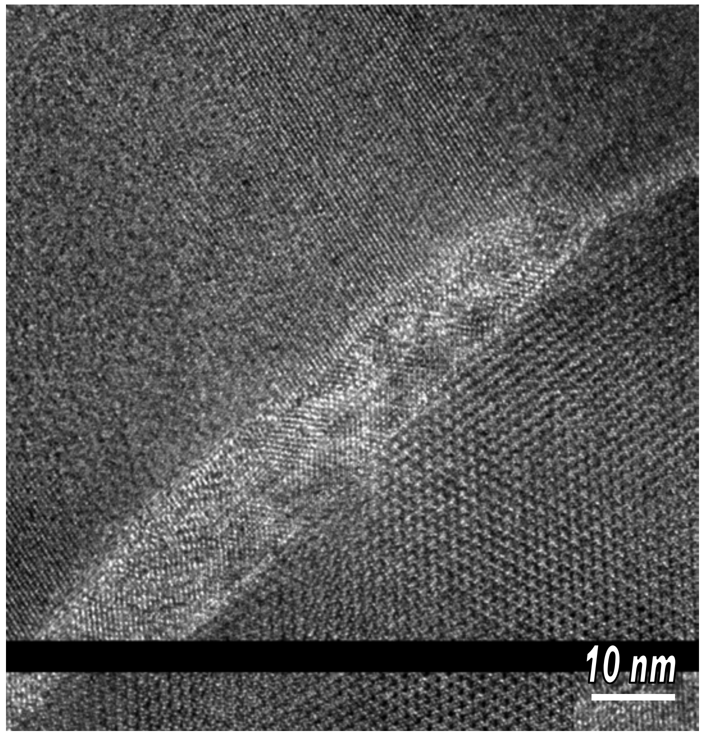
Anneal + SPS

Grain and grain boundary composition analysis of LT annealed +SPS $CeFe_4Sb_{12}$ samples

<u>Grain boundaries: Ce-rich (as much as 5-10 times higher).</u>

For example:
In two grain boundaries:
Ce:Fe:Sb: 58.5 : 1.5 : 40
39.2 : 8.1 : 52.7

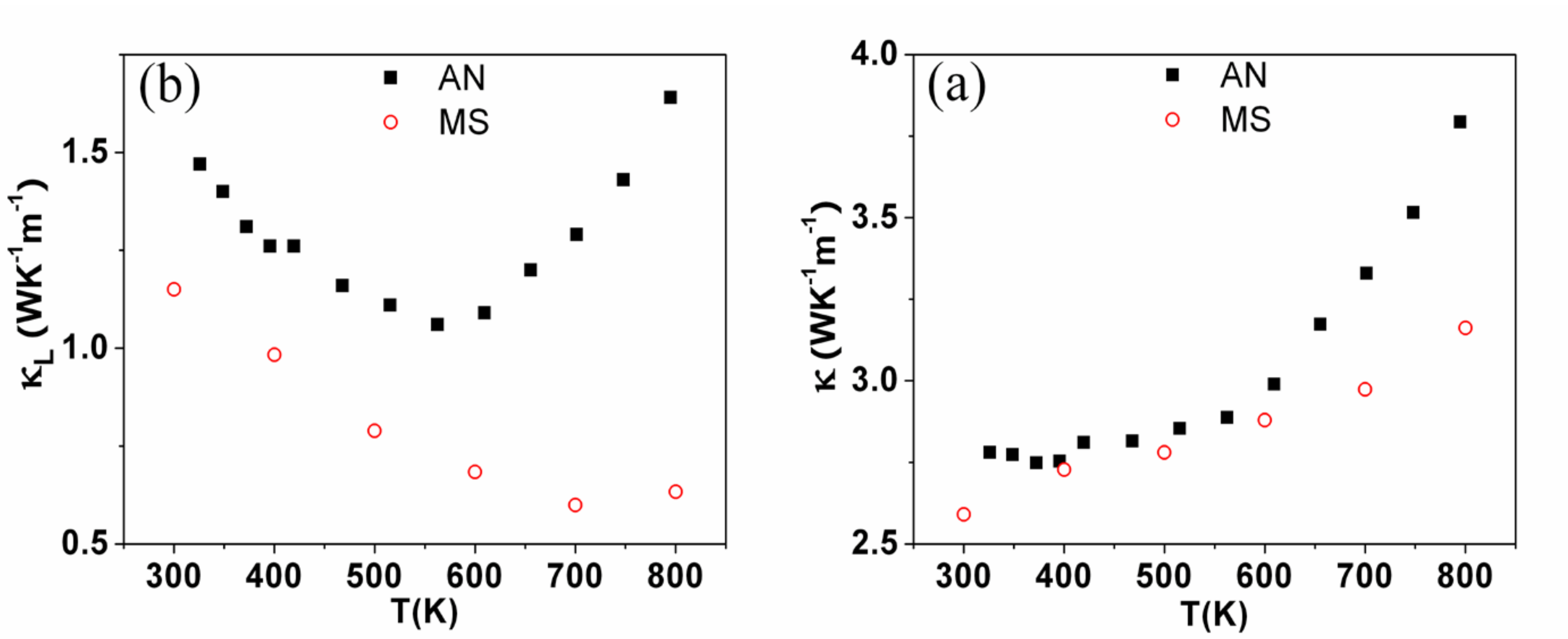
Within each grain
Ce:Fe:Sb: 5.9 : 23.5 : 70.6
very close to stoichiometric $CeFe_4Sb_{12}$



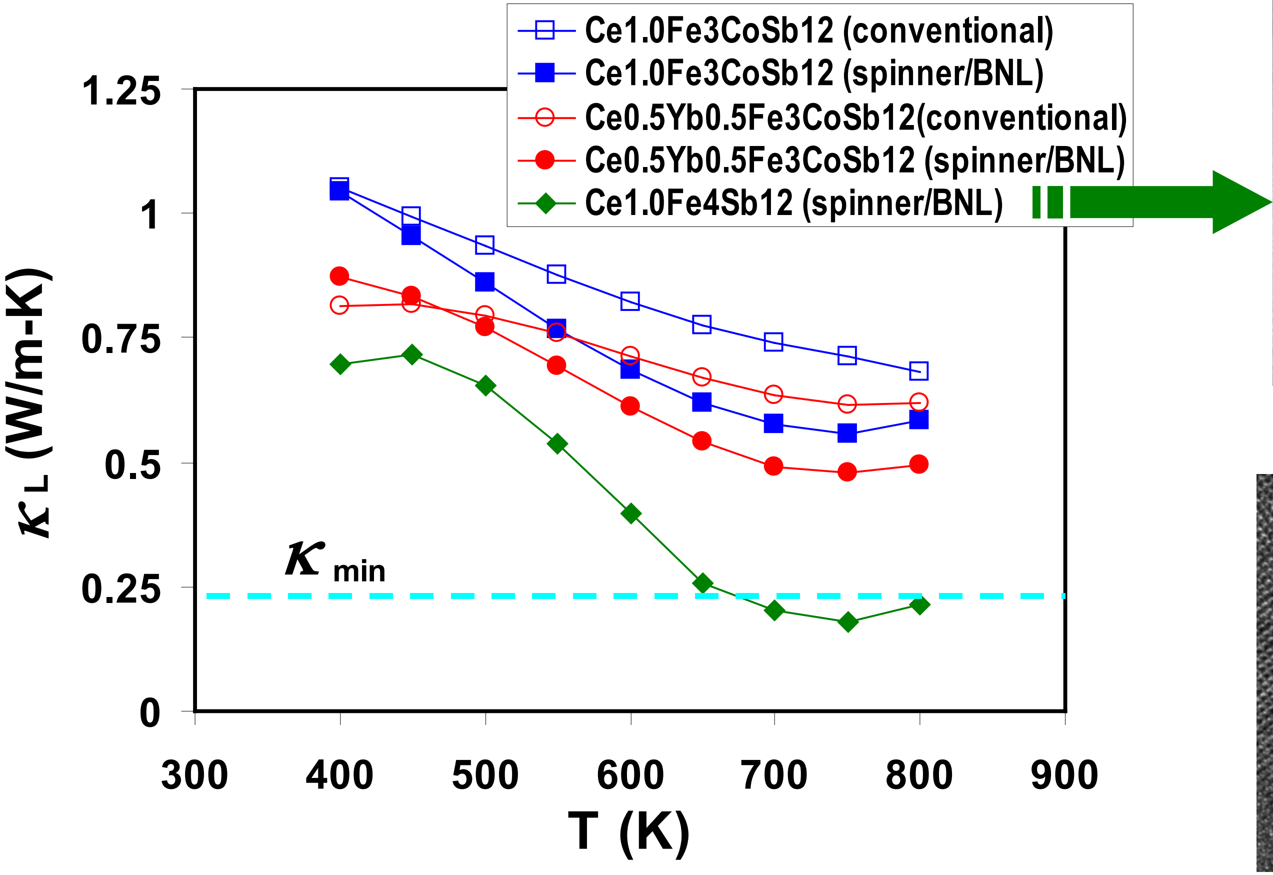
Anneal + SPS

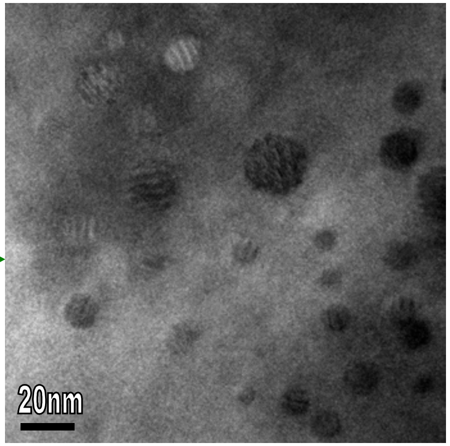
Thermal Conductivity - $Ce_{1.05}Fe_4Sb_{12.04}$

- **Much lower κ_L**

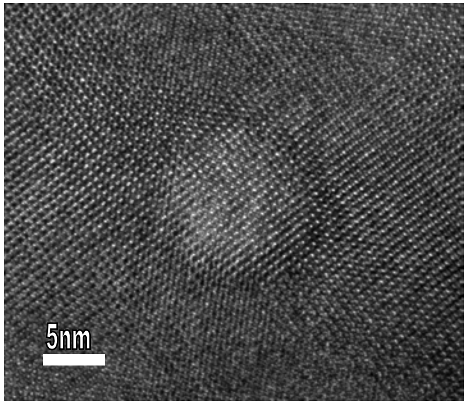


Low Lattice Thermal Conductivity





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

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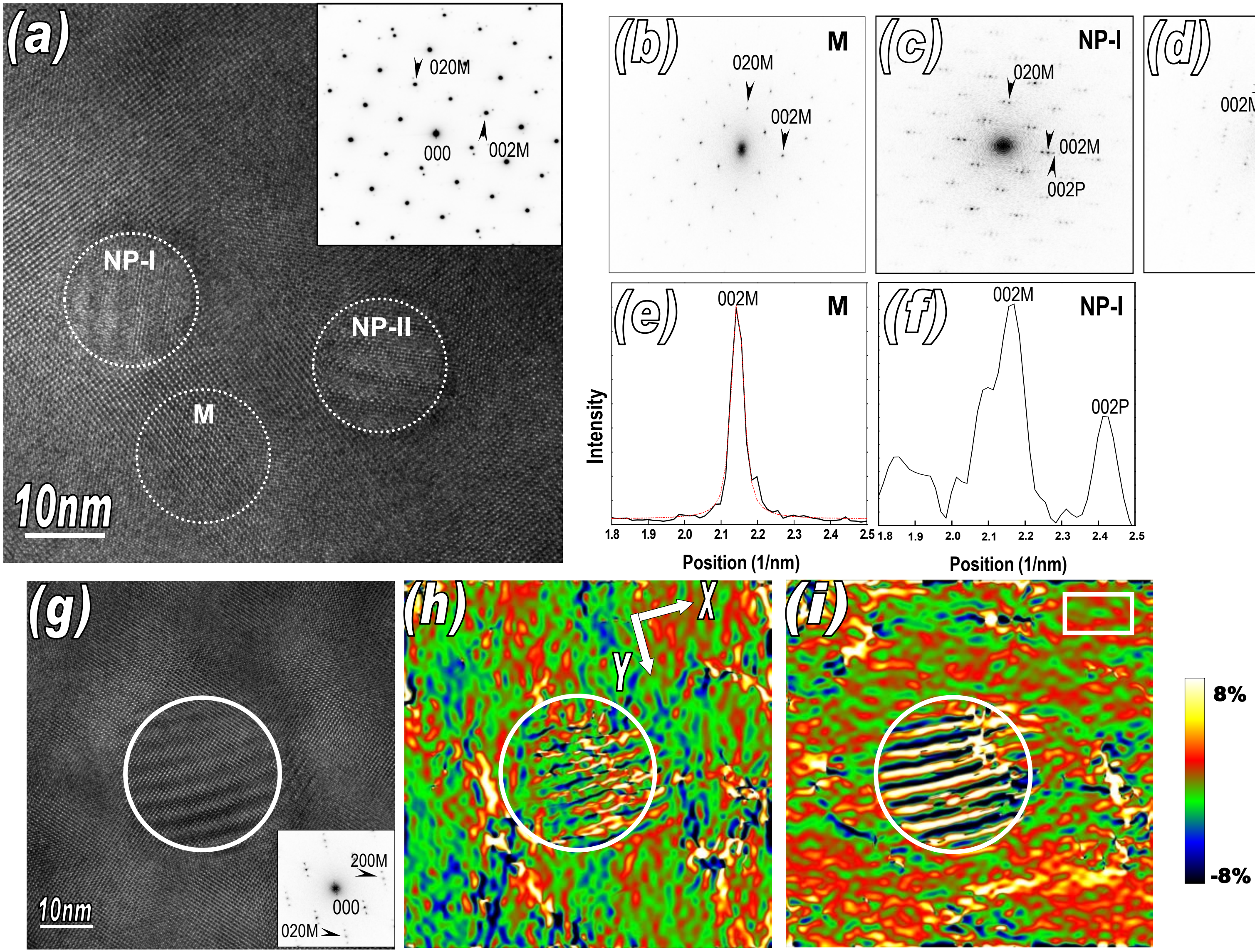
Nanostructures in melt-spun+SPS $CeFe_4Sb_{12}$ samples



strain map

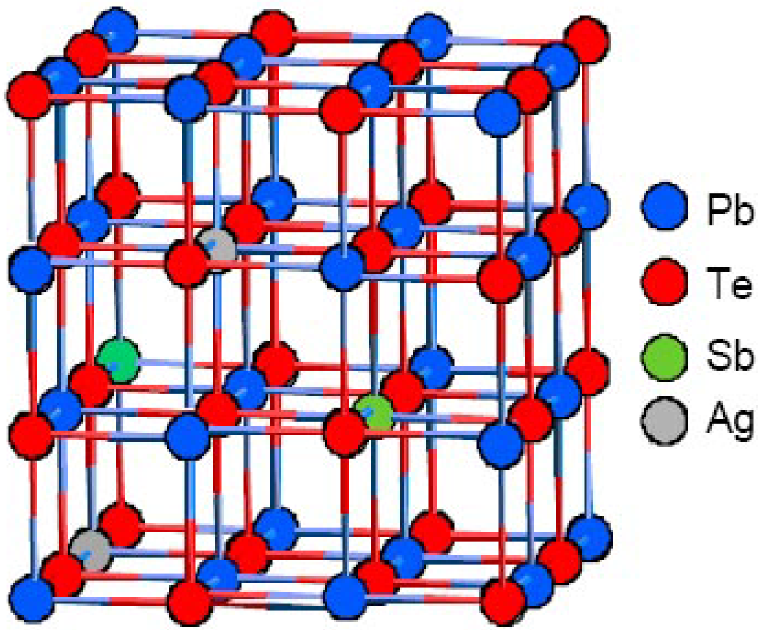
ε_{xx} and ε_{yy}

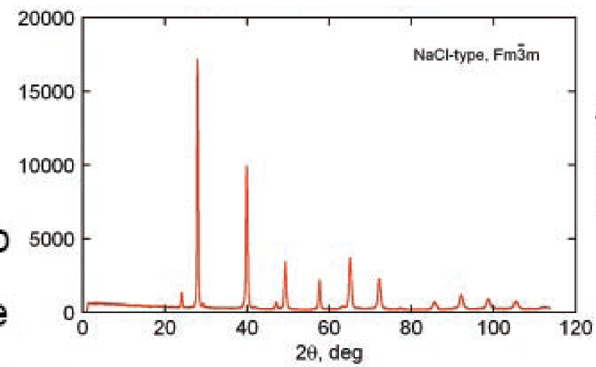
Matrix: CeFe4Sb12, Body centered cubic

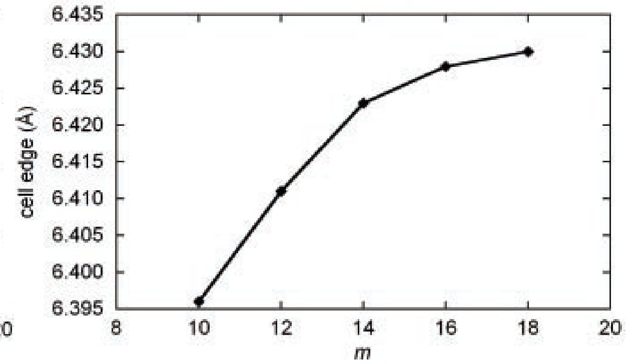
NP-I and NP-II: Sb rich, primitive tetragonal

<u>Orientation relationship:</u> $(001)_{NP\text{-}I}//(001)_M$, $(010)_{NP\text{-}I}//(010)_M$, $(010)_{NP\text{-}II}//(001)_M$, $(001)_{NP\text{-}II}//(010)_M$

Crystal Structure of LAST-m Compounds

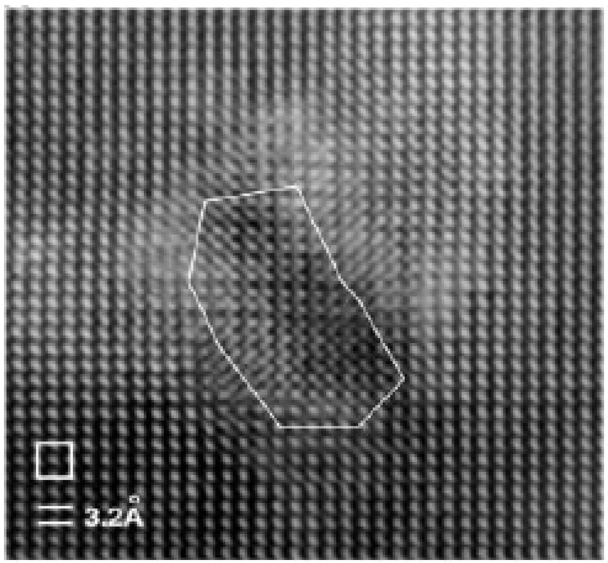






LAST-m: $(PbTe)_{1-x}(AgPbTe_2)_x$

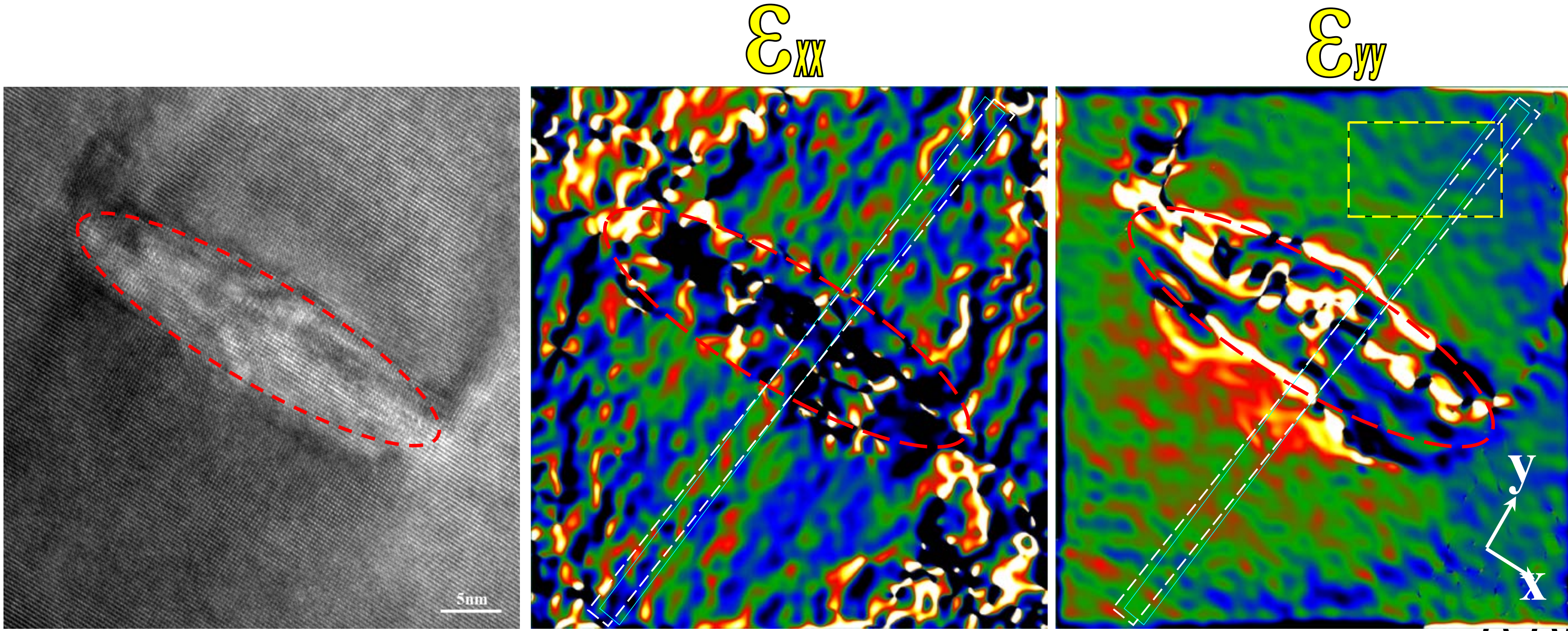
- **Average NaCl FCC structure**

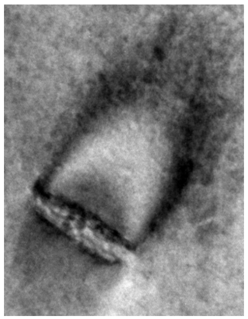


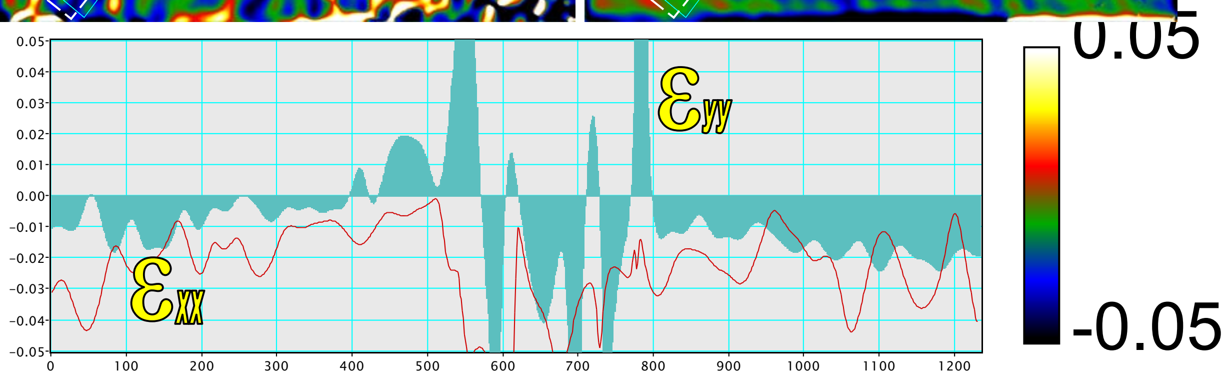
Host materials containing nanostructures

K. F. Hsu, S. Loo, F. Guo etc., Science, 2004. 303 (5659): p. 818-821.
E. Quarez, K. F. Hsu, R. Pcionek etc., J. Am. Chem. Soc., 2005. 127 (25): p. 9177-9190.

Strain Map Around the Nanoprecipitate





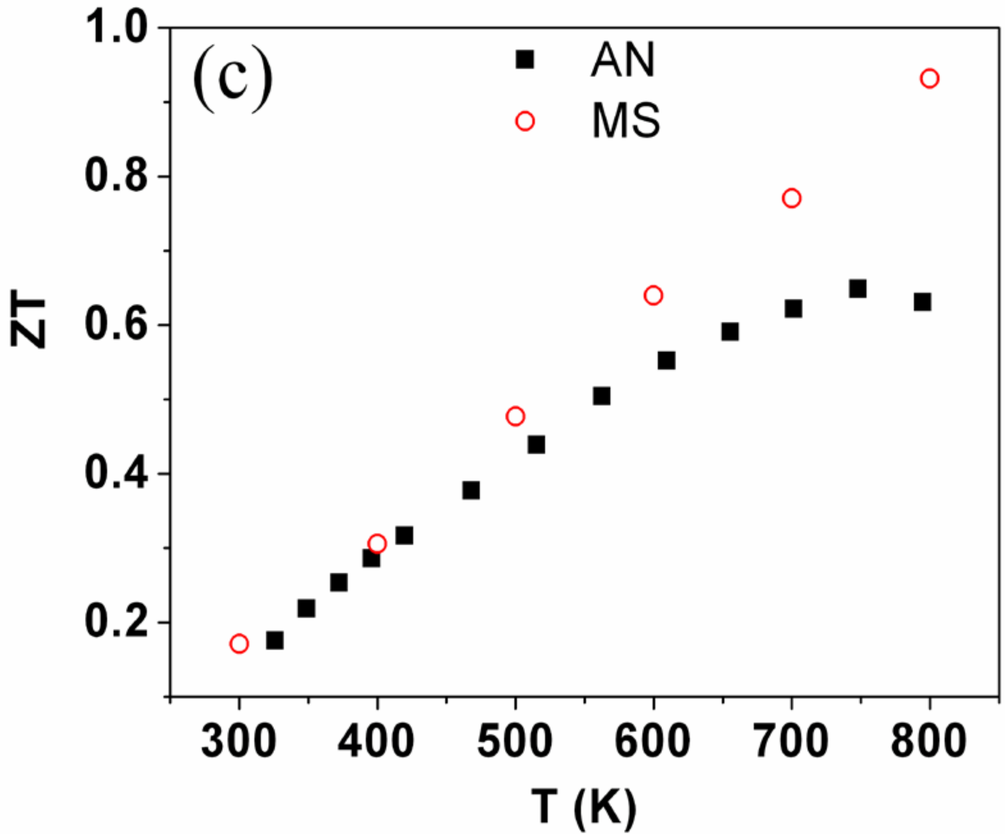


- ε_{xx}: Negative strain in matrix and NP
- ε_{yy}: Positive & negative strain in NP long-range, asymmetric in matrix

L. Wu, Q. Li et al – JAP (2009)

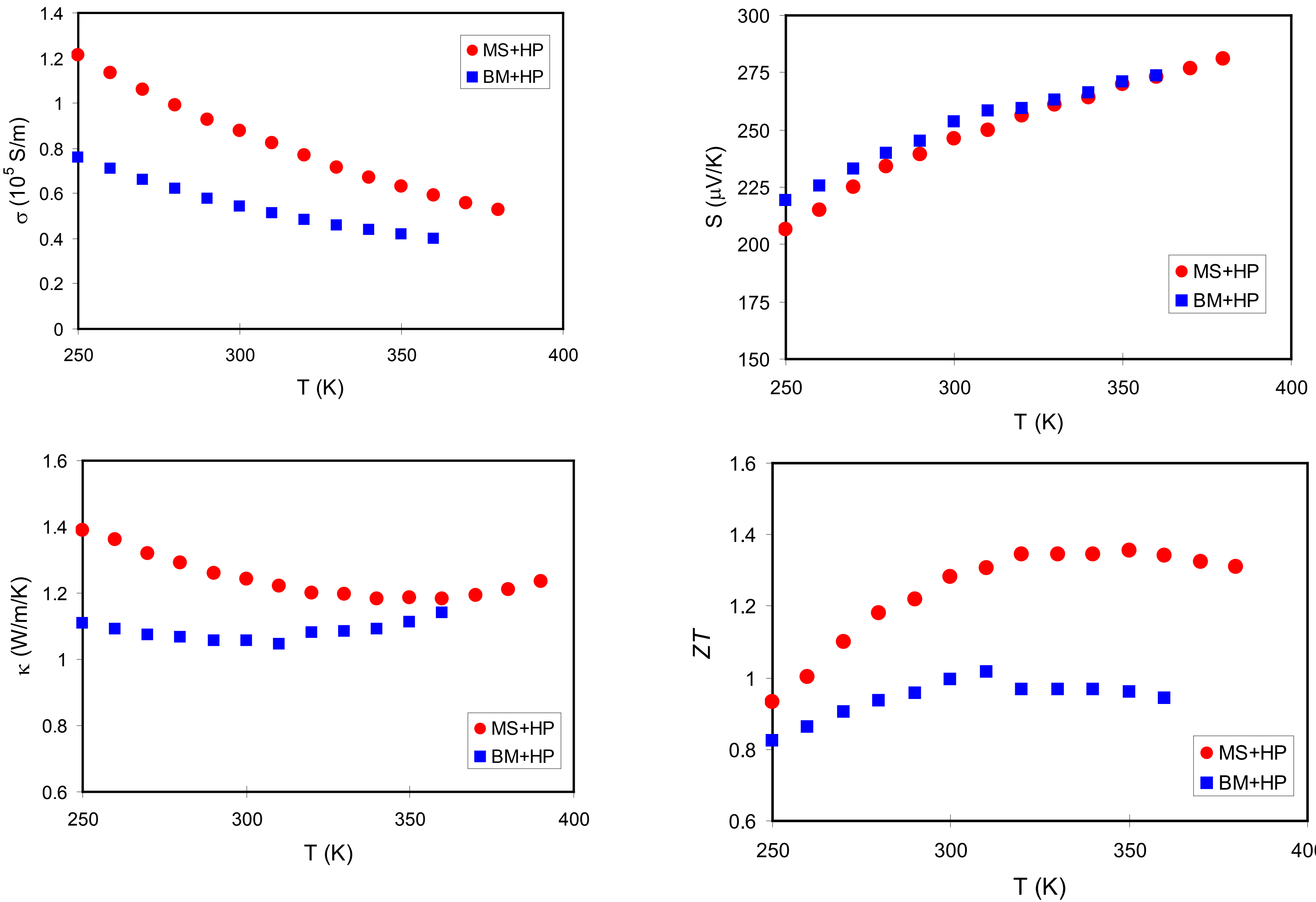
He, et al JACS & Adv. Func. Mat. (2009), (2010)

ZT - $Ce_{1.05}Fe_4Sb_{12.04}$



❖ **50%** **improvement on ZT at 800K**

TE Properties of MS+HP processed $Bi_{0.52}Sb_{1.48}Te_3$*



*Measured along the same direction: I//ΔT

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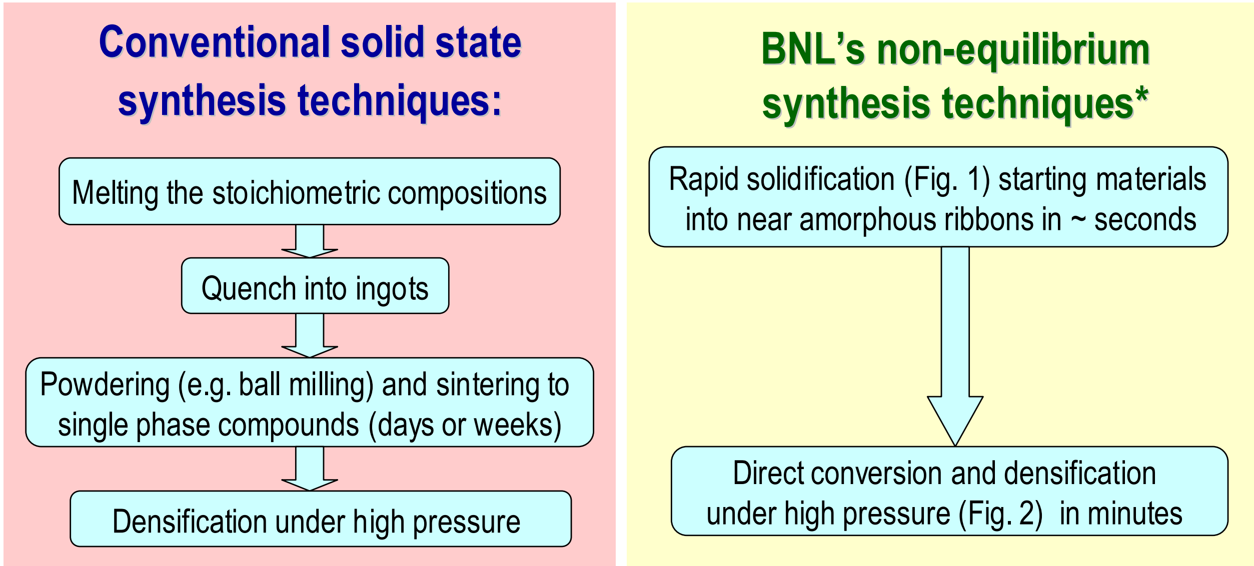
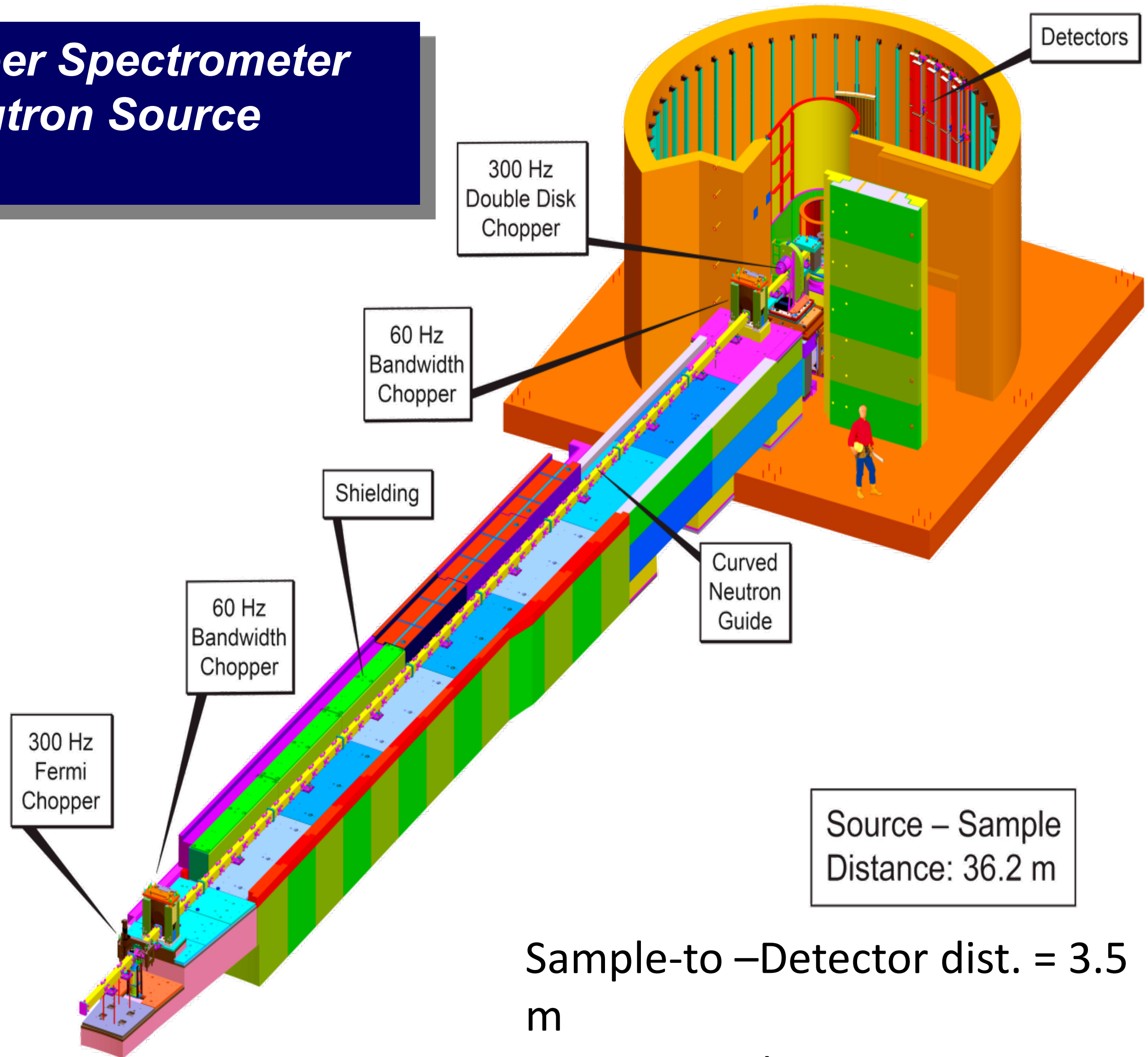
Advantages of non-equilibrium process



- 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

Inelastic Neutron Scattering Experiments

Cold Neutron Chopper Spectrometer at the Spallation Neutron Source ORNL



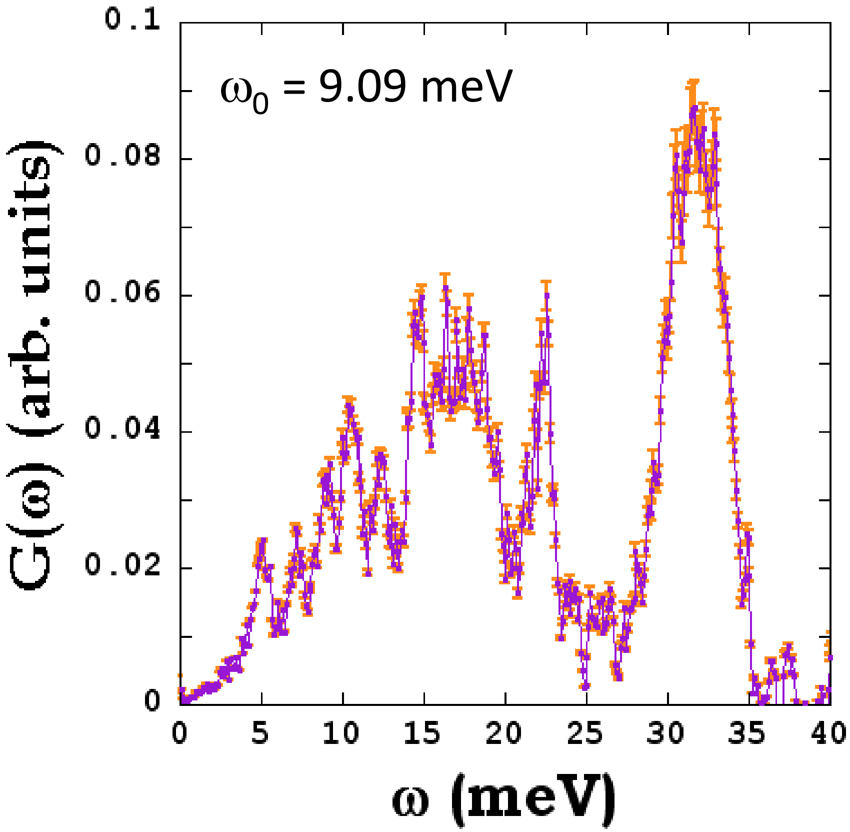
Experimental Parameters:

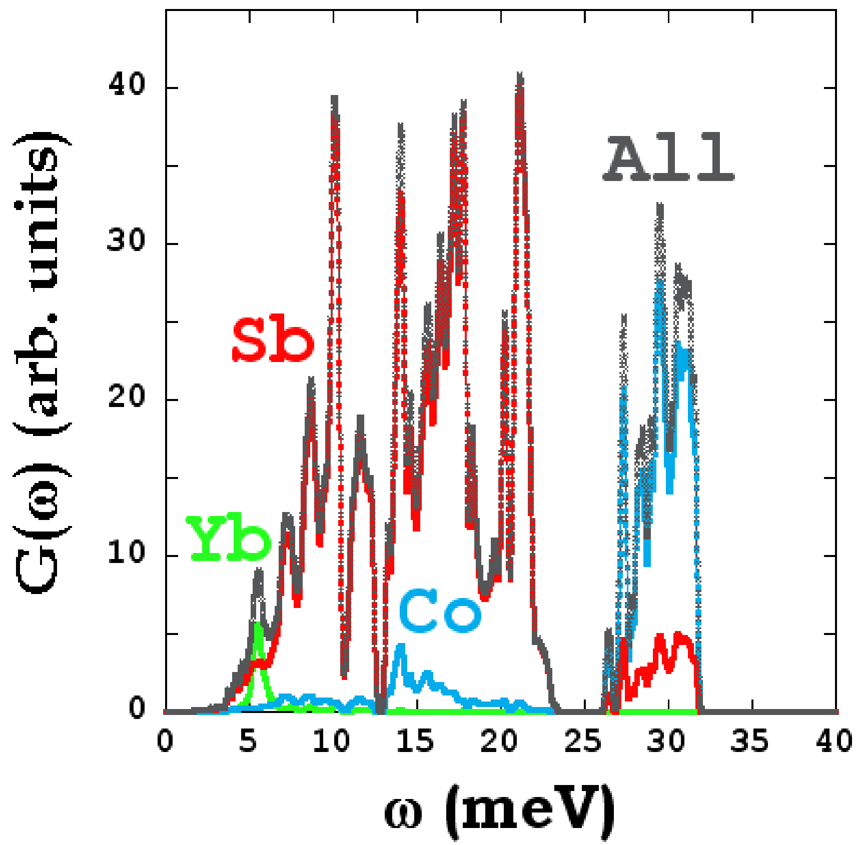
High Resolution Mode
ω_0 = 9.09 meV
$\Delta\omega(\omega=0)$ = 0.186 meV
T ≈ 300 K
t = 8 hr

Source – Sample Distance: 36.2 m

Sample-to –Detector dist. = 3.5 m
Energy Resolution = 10-500μeV
Incident E range = 2-50meV
Q-range = 0.05-10 A^{-1}

DOS of $Yb_{0.2}Co_4Sb_{12}$ from Inelastic Neutron Time-of-Flight Scattering and DFPT Calculation

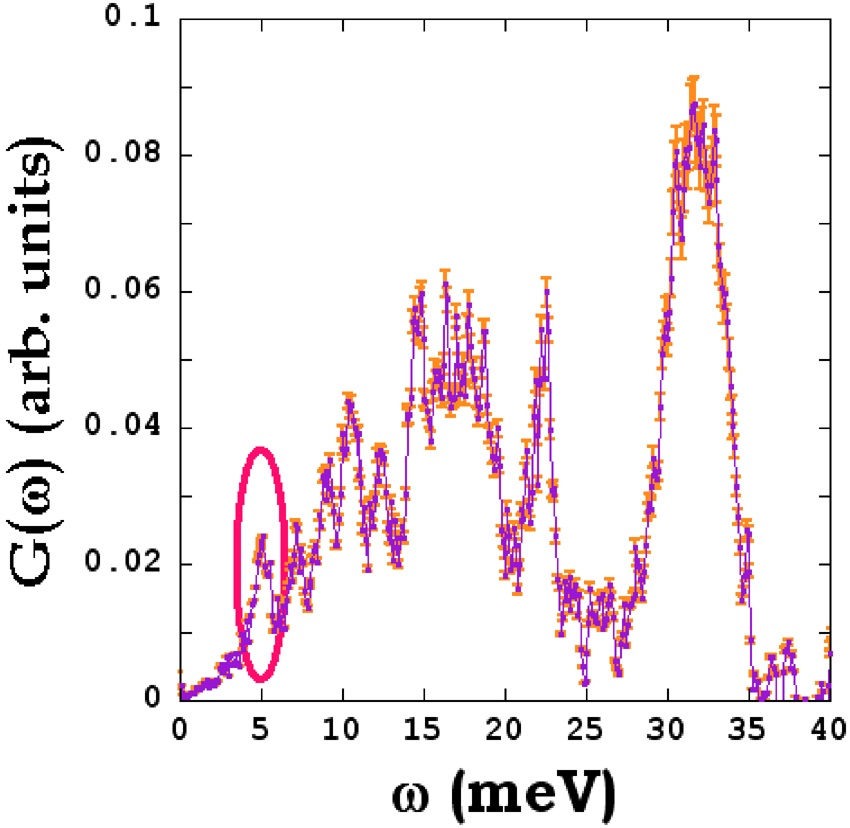


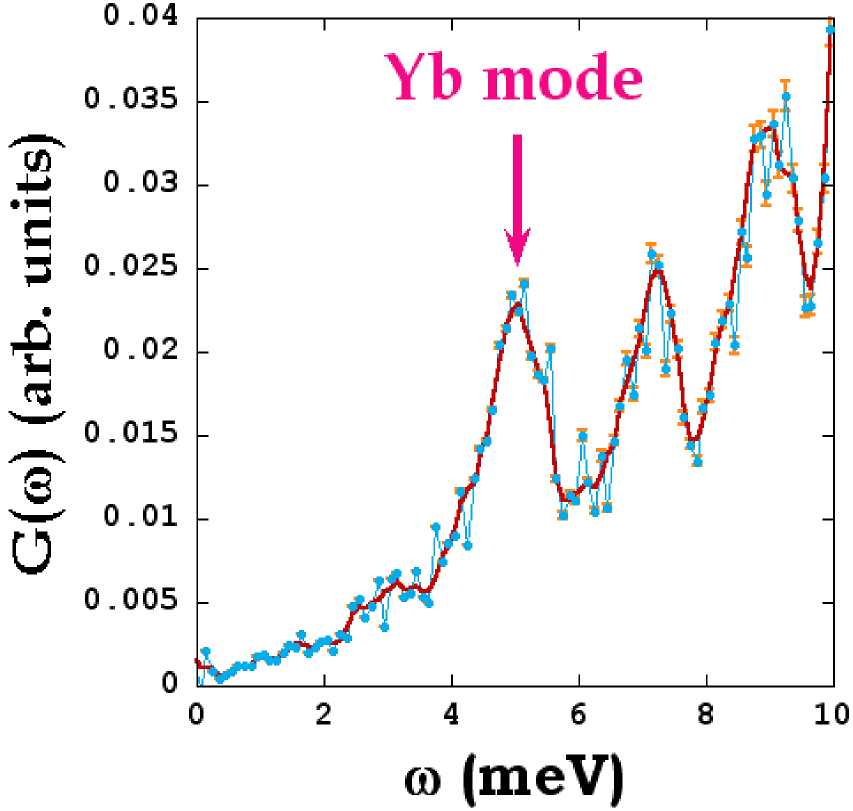


- Feature-by-feature correspondence between experiment and theory
- Novel observations
- Comparison with heat capacity data
- Evolving understanding of the "rattling mode scenario"

I. K. Dimitrov, M. E. Manley, S. M. Shapiro, J. Yang, W. Zhang, L. D. Chen, Q. Jie, G. Ehlers, A. Podlesnyak, J. Camacho, and Qiang Li, Phys. Rev. B **82**, 174301 (2010)

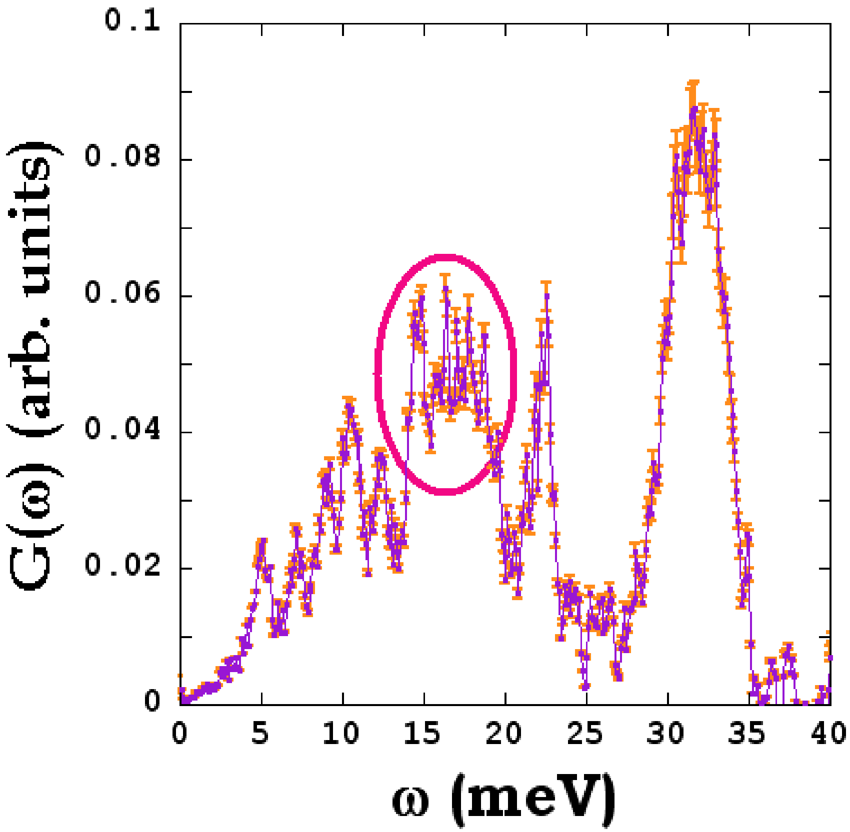
Low Transfer Energy Effects – Yb Peak at ω≈ 5 meV

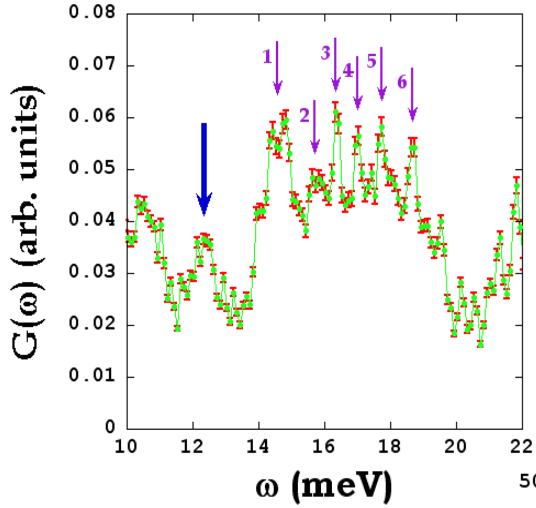




- Confirmation of the filler signature in the DOS of filled skutterudites
- Theoretical agreement

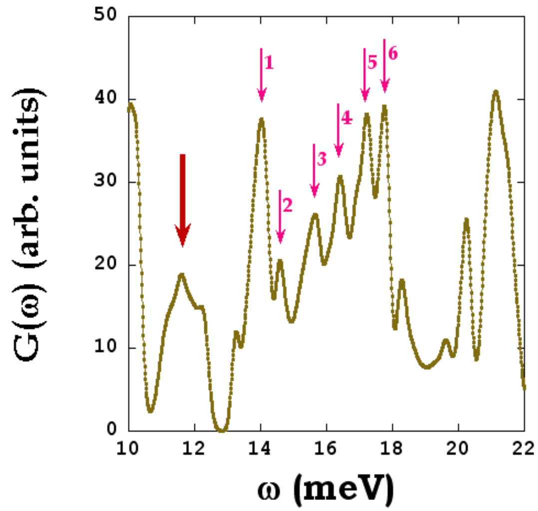
Intermediate Transfer Energy Effects – Local Modes at 10 meV ≤ ω ≤ 20 meV





Experimental Data

DFPT Calculation



- Observation of a well-pronounced feature at ω ≈ 12 meV (blue and red arrows) corresponding to Θ_{E1} and Θ_{E2} from the heat capacity data.
- Sharp local modes present at 14 meV ≤ ω ≤ 20 meV (**novel observation**)
- Local mode #1 – evidence for Co & Sb hybridization

In-situ high pressure synchrotron X-ray study of filled skutterudites

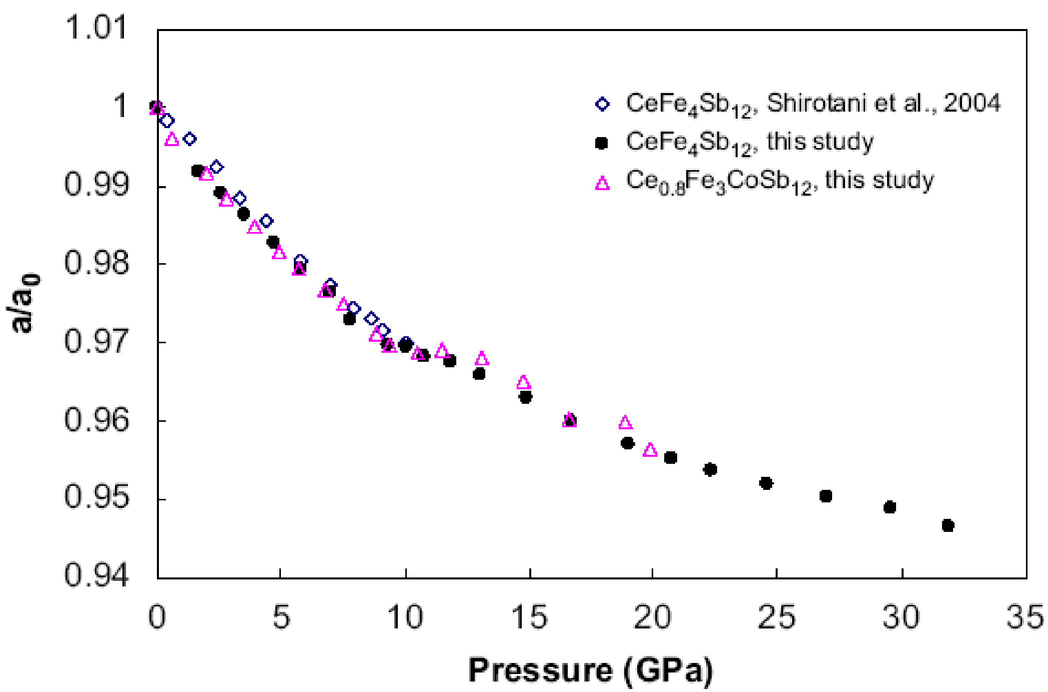
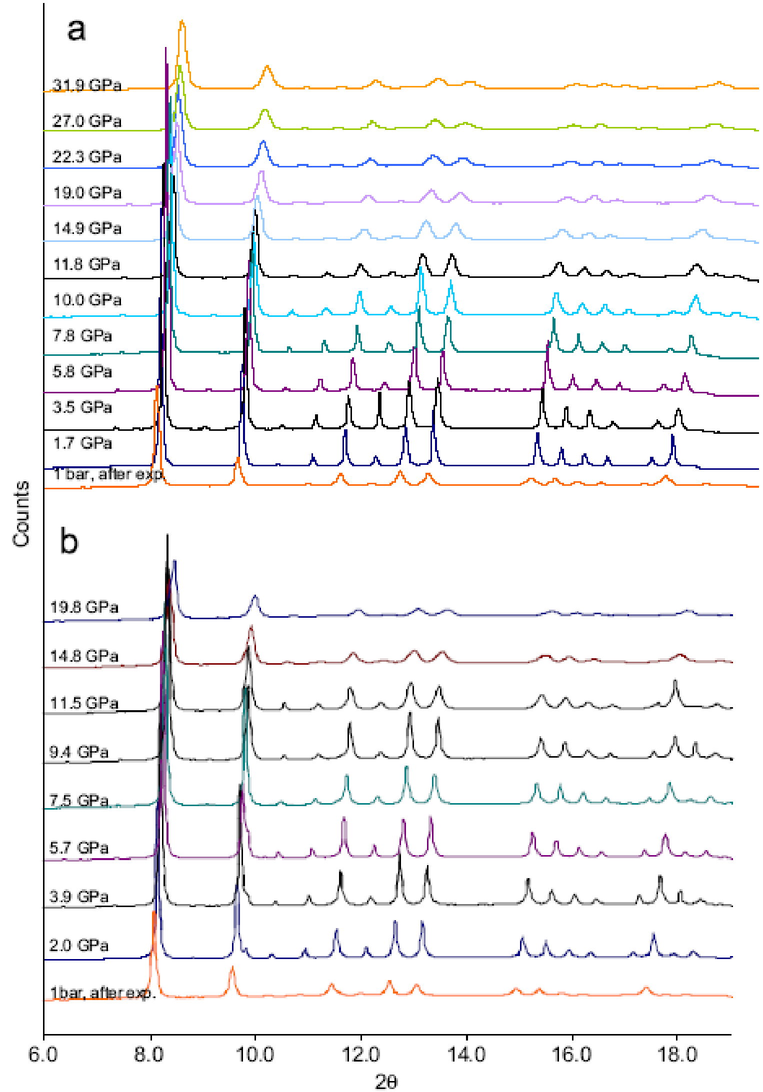


Fig. 3. Normalized lattice constants of $CeFe_4Sb_{12}$ and $Ce_{0.8}Fe_3CoSb_{12}$ at room temperature. The error bars are less than the symbols.



W. Liu, Z. Chen, B. Li (SBU) and Q. Jie Q. Li (BNL), Physica B **53** 406 (2011)

X-ray diffraction pattern of $CeFe_4Sb_{12}$ (a) and $Ce_{0.8}Fe_3CoSb_{12}$ (b) obtained up to 32 and 20 GPa at room temperature, respectively.

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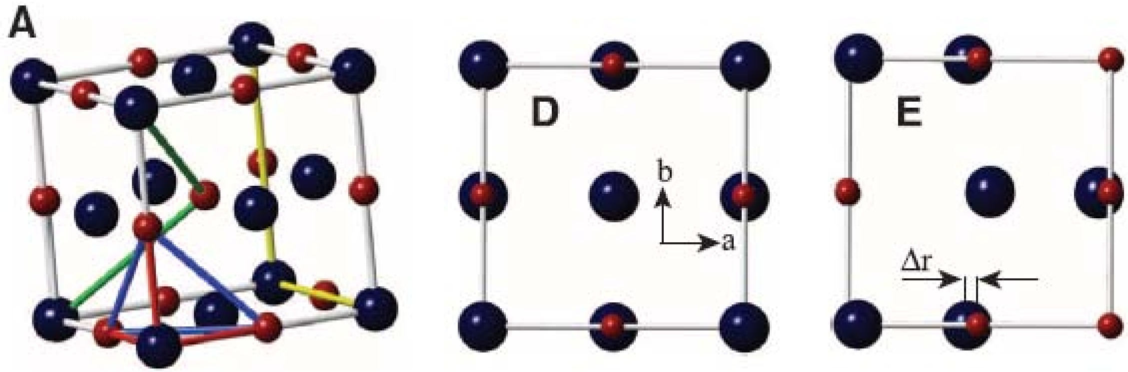
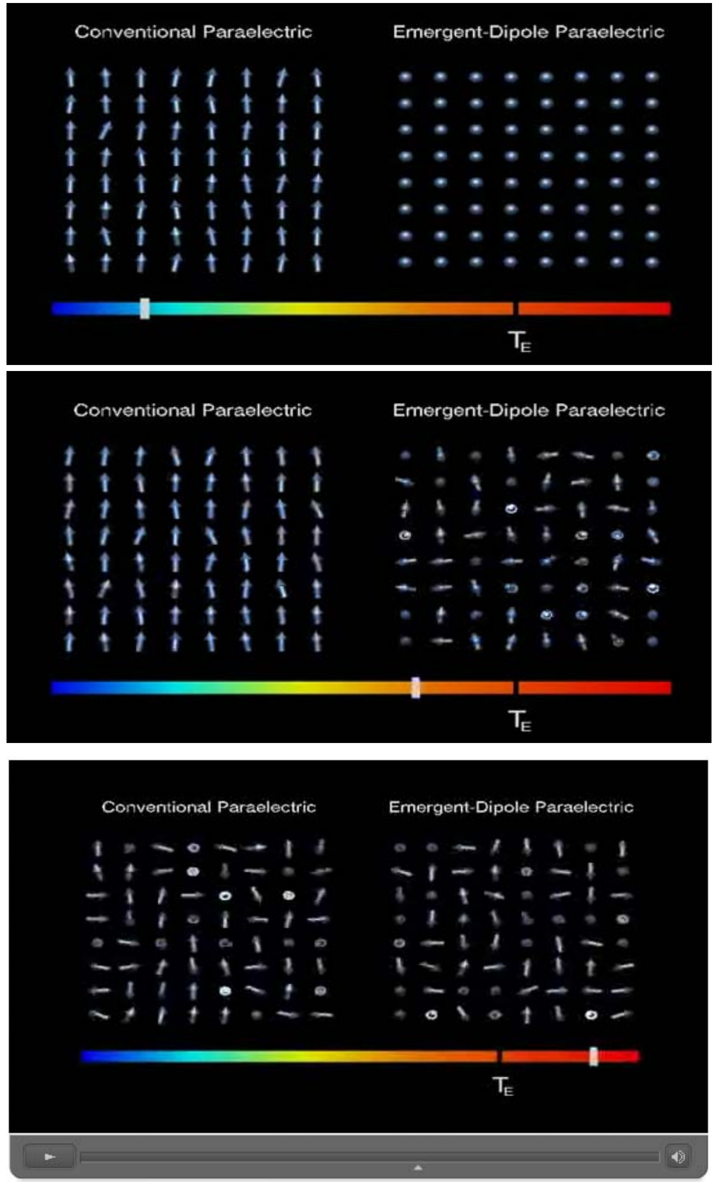
Entropically Stabilized Local Dipole Formation in Lead Chalcogenides

Bozin, Billinge (BNL) et al Science **330** 1660 (2010)



"New thermoelectrics should be sought among materials that, like PbTe, are close to a ferroelectric instability"



As the emergent-dipole material (right) is warmed, fluctuating local dipoles appear from an undisturbed ground state (i.e., from "nothing"). This is in contrast to the conventional material (left), which has aligned dipoles at low temperatures. The flip-flopping displacements impede the movement of heat through the material, allowing a strong temperature gradient to be maintained. Heat on one side of the material can then induce a flow of electrons from the hot to the cooler side. Capturing this current could put waste heat to work.

Conclusions

- Robust and higher thermoelectric performance materials can be prepared by the non-equilibrium process.

- Analytical TEM, in-situ high pressure synchrotron-based x-ray diffraction/scattering and neutron scattering experiments are powerful techniques for exploring electron transport and phonon dynamics, that again calls for more realistic theoretical modeling