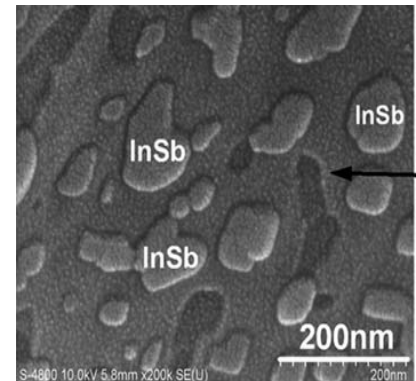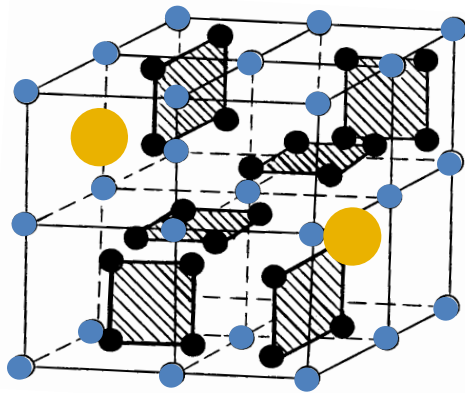# Nanostructures in Skutterudites

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Collaborators:
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Dr. Jihui Yang (GM)

InSb
InSb
InSb
200nm
S-4800 10.0kV 5.8mm x200k SE(U)

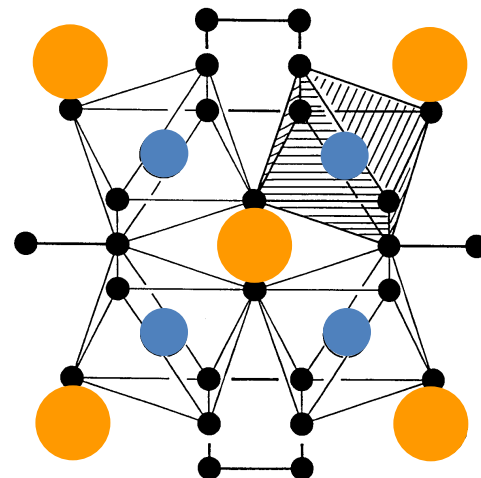2011 DoE Thermoelectrics Workshop
January 3 - 6, 2011
San Diego, CA

Skutterudite compounds

Chemical formula MX_3 M = Co, Rh, Ir   X = P, As, Sb

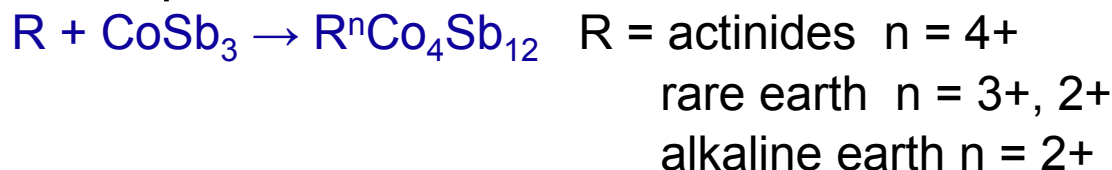Cubic structure with eight MX_3 groups in the unit cell $\Rightarrow$ 32 atoms/unit cell

- Co
- Sb
- Filler

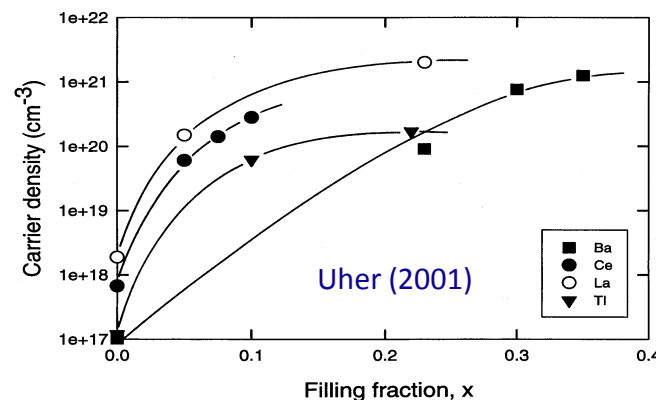$CoSb_3 \Leftrightarrow \square_2Co_8Sb_{24} \Leftrightarrow \square\, Co_4Sb_{12}$
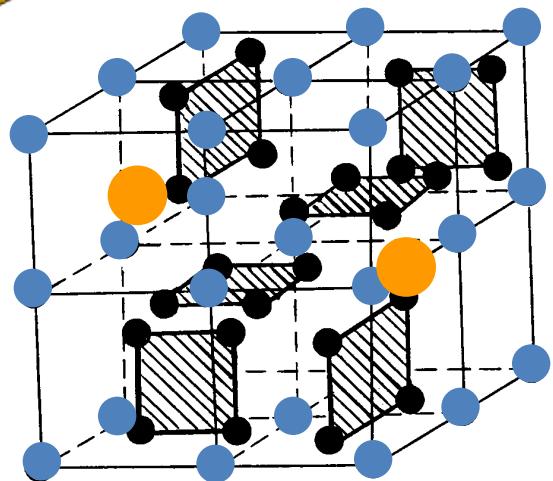
Cages can be filled with foreign ions $\Leftrightarrow$ **Filled skutterites** Jeitschko (1977)

Filler species donate electrons

$R + CoSb_3 \rightarrow R^nCo_4Sb_{12}$ R = actinides n = 4+

rare earth n = 3+, 2+

alkaline earth n = 2+

Filling drives skutterudites strongly **n-type**,

➡ limiting occupancy of voids.

Carrier density (cm^{-3}) vs Filling fraction, x — Uher (2001)
Legend: Ba, Ce, La, Tl

P-type skutterudites obtained by charge compensation $Ce_yFe_{4-x}Co_xSb_{12}$
or by doping on the pnicogen site with the group IV elements.
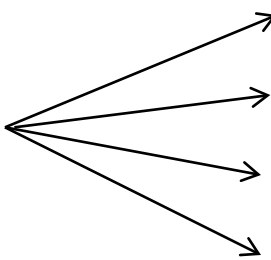
Status of n-type skutterudites
$R_yCo_4Sb_{12}$

- Fillers considered early were mostly rare earths Ce^{3+} and La^{3+}, low filling fraction, particularly for Ce ($y < 0.1$), ZT ~ 0.6 at 800K.

- **Anno et al.** (2000) and **Nolas et al.** (2000) tried Yb, a mixed valence ion, larger filling fraction ($y \sim 0.25$), ZT ~ 1.1 at 800K.

- **Chen et al.** (2001) introduced alkaline earths, notably Ba, strictly divalent ions, large filling fraction ($y \sim 0.45$), ZT ~ 1.2 at 800K.

- **Shi et al.** (2005) & (2007) developed theory for calculation of filling fraction limits.

- **Yang et al.** (2007) calculated resonant phonon frequencies for filler ions.

- **Shi et al.** (2008) synthesized double-filled $Ba_xYb_yCo_4Sb_{12}$, a large contrast in resonant frequencies of Ba and Yb, ZT = 1.36 at 800K.

- **Li et al.** (2008) used a rapid melt-spinning technique on $Yb_{0.3}Co_4Sb_{12+y}$ that cuts synthesis time and forms nanostructure resulting in ZT=1.3 at 800K.

- **Li et al.** (2009) observed *in-situ* forming nanostructured InSb phase in $In_xCe_yCo_4Sb_{12}$ prepared by melt-spinning & spark plasma, ZT = 1.43 at 800K.

Nanometer-scale inclusions in the bulk matrix (nanocomposites) seem to be very important!

The role of nanostructures in bulk skutterudites?

The critical issue is a relative size of the
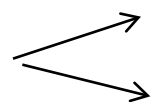
nanostructure vs.
- carrier de Broglie wavelength, Λ_c
- carrier mean-free path, L_c
- phonon wavelength, λ_p
- phonon mean-free path, ℓ_p

Ideal situation:

Nanostructure enhances electronic properties (carrier confinement or energy filtering) while it impedes phonon transport.

Reality:

Must make sure that nanostructuring does not degrade electronic transport while it strongly scatters phonons.

Nanostructure should
- be coherent with the matrix
- present no charge imbalance on the scale $\geq \Lambda_c \sim$ 1-2 nm

Filled skutterudites: $L_c \leq 10$ nm $\Longrightarrow$ only fine nanograins will impede carrier transport.

Nanostructure effects on phonons:

$$\kappa_p(T) = \frac{1}{3}\int C(\lambda,T)v(\lambda)\ell_p(\lambda,T)\,d\lambda$$

I. Quantum size effects: changes in phonon dispersion (e.g., branches of bulk dispersion folding over) resulting in a reduction of the specific heat or decrease of the group velocity. This requires nanostructure size $\leq \lambda_p \approx$ 1-2 nm and phonon coherence over several unit cells. While marginally possible in very short period superlattices, this is not realistic in nanocomposites .

II. Classical size effects: enhanced phonon scattering at interfaces and boundaries resulting in a reduction in phonon mean-free path. Short wavelength phonons have effectively been taken care of by atomic disorder. The idea is to attack the heat-carrying phonons. At this stage, one usually calculates the bulk mean-free path $\ell_p = \frac{3\kappa}{vC_p}$ which, for filled skutterudites, yields about 50nm. This may seem a short mfp, but Dames and Chen (CRC Handbook, 2006) show that, in fact, the range of mfp's of phonons carrying heat is quite large and a large fraction of heat is carried by phonons with mfp an order of magnitude larger. **Thus, it makes sense to use nanostructuring to lower κ_p.**

Principal Means of Forming Bulk Nanocomposite Materials

I. Intrinsic processes during cooling of the melt

Spinodal decomposition   (Androulakis et al., 2007)

Nucleation and growth (Heremans et al, 2005)

Matrix encapsulation (Sootsman et al., 2006)

Compound formation (Li et al., 2009)

Compensating double doping (Liu et al. 2008)

II. Extrinsic processes of preparing nanosized powders by

Grinding

Milling   (Poudel et al., 2008)

Wet chemistry   (Bertini et al., 2003)

followed by compacting into pellets/ingots.

While both approaches successfully form nanocomposite structures, the intrinsic routes are far superior especially for power generation TE materials that will have to withstand extended exposure to high-T environment.

The stability of the nanostructure matters!

Nanostructures in Bulk Skutterudites
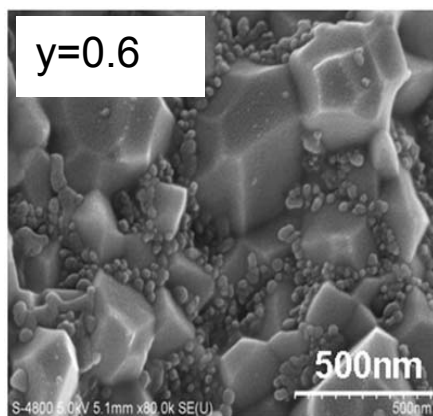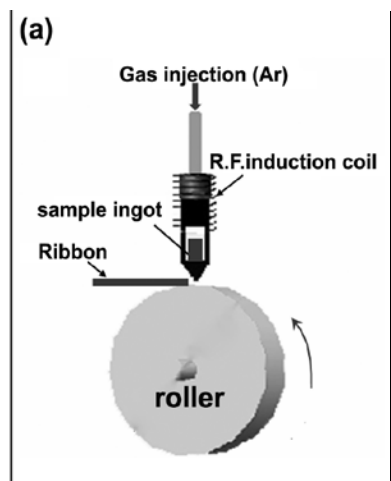
a) Consolidate precipitated nanopowders:

not a very effective route as the grains grow rapidly during thermal processing and the benefits are gradually annealed out!

Bertini et al. (2003)

b) Quench-in the nanostructure by melt spinning: H. Li et al. (2008)
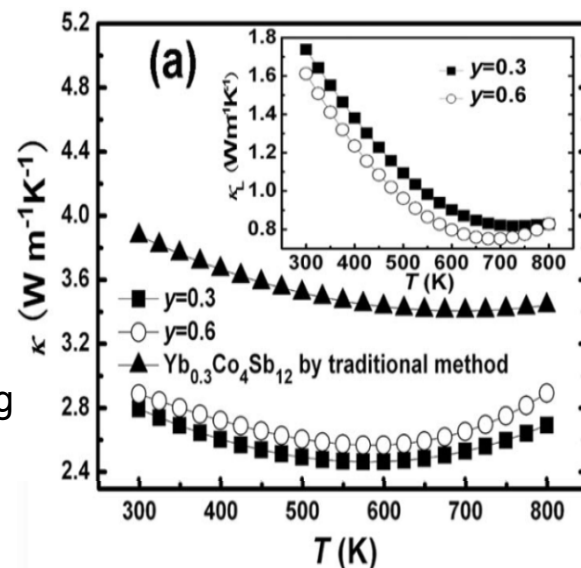
Tang et al. (2007)

Qiang Li et al. (2008)

y=0.6

H. Li et al. APL (2008)

$Yb_{0.3}Co_4Sb_{12+y}$

Very rapid synthesis.
Larger content of Yb
κ strongly reduced
ZT = 1.3 at 800K
Reproducible on cycling

H. Li et al. APL (2008)

Nanostructures in Bulk Skutterudites

c) In-situ formed nanostructure: H. Li et al. (2009)

According to Shi et al. (2005), filling of cages requires

$$X_{Sb} - X_{imp} > 0.80$$

Indium clearly does not satisfy this condition since

$$X_{Sb} - X_{In} = 2.05 - 1.78 = 0.27 \,!$$

Yet, Indium-filled skutterudites have been reported on.

He et al. (2006)
Jung et al. (2008)
Peng et al. (2008)

In collaboration with WUT we were interested what happens if **melt-spinning** is used in the synthesis of double-filled skutterudites containing Indium as one of the fillers.

$In_xCe_yCo_4Sb_{12+z}$ (x = 0.15, 0.2; y = 0.15, 0.20; z = 0, 0.3) by **melt-spinning**

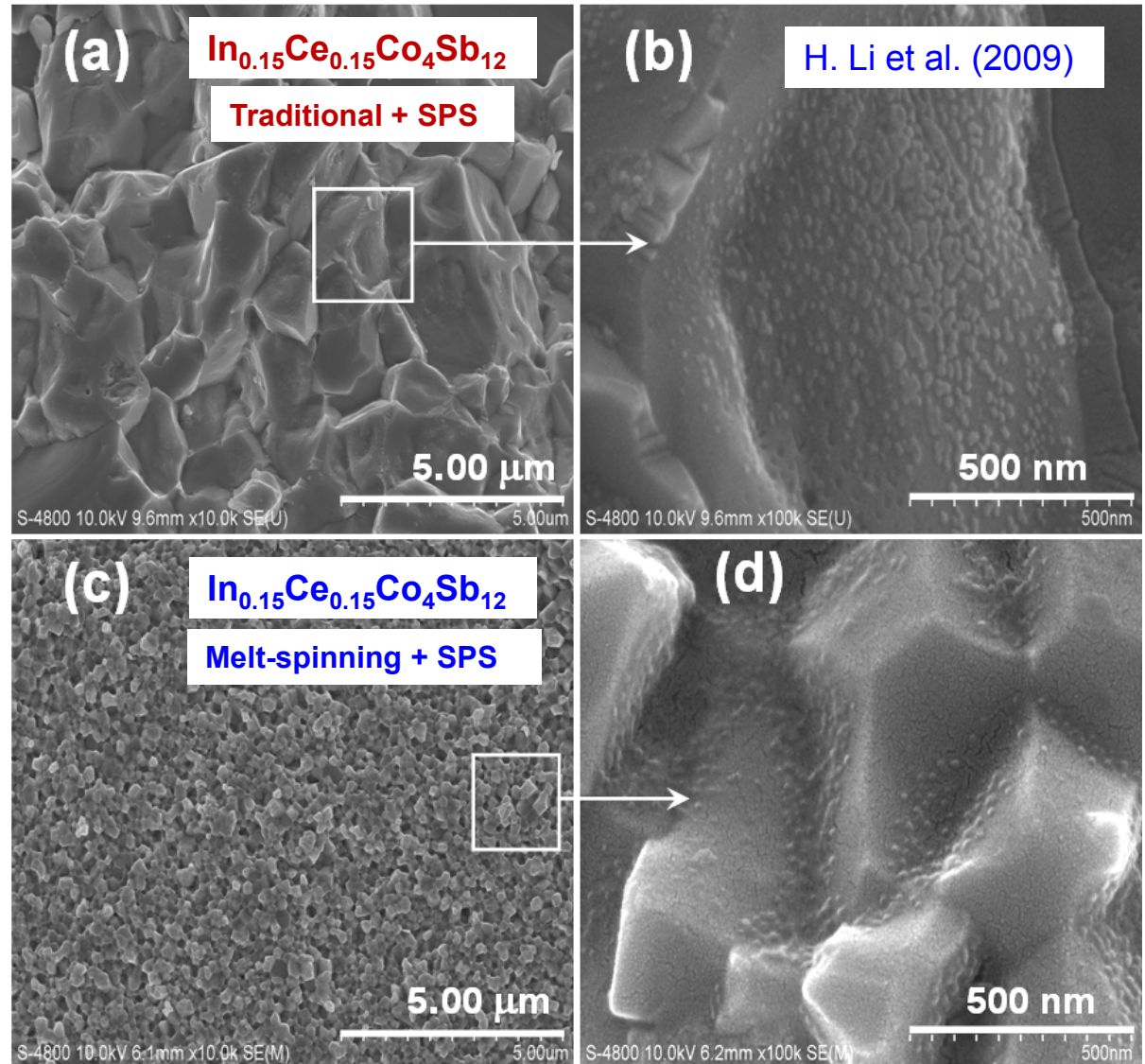$In_{0.15}Ce_{0.15}Co_4Sb_{12}$ reference sample by **traditional** method for comparison

Nanostructure in Bulk Skutterudites

Field emission scanning electron microscopy

Traditional + SPS process

Course matrix grains ~ 1-3 µm
Nanoparticles ~ 20-100 nm

Melt-spinning + SPS

Much finer matrix ~ 300 nm
Very fine nanostructure
~ 10-15 nm

(a) $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ **Traditional + SPS** — 5.00 µm

(b) H. Li et al. (2009) — 500 nm

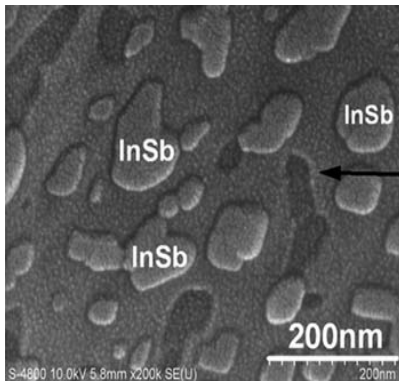(c) $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ **Melt-spinning + SPS** — 5.00 µm

(d) — 500 nm

Nanostructure in Bulk Skutterudites

High Resolution Transmission Electron Microscopy + EDS

Nanoparticles are InSb !

Domains I, II, III ⟺ Ce-filled $CoSb_3$
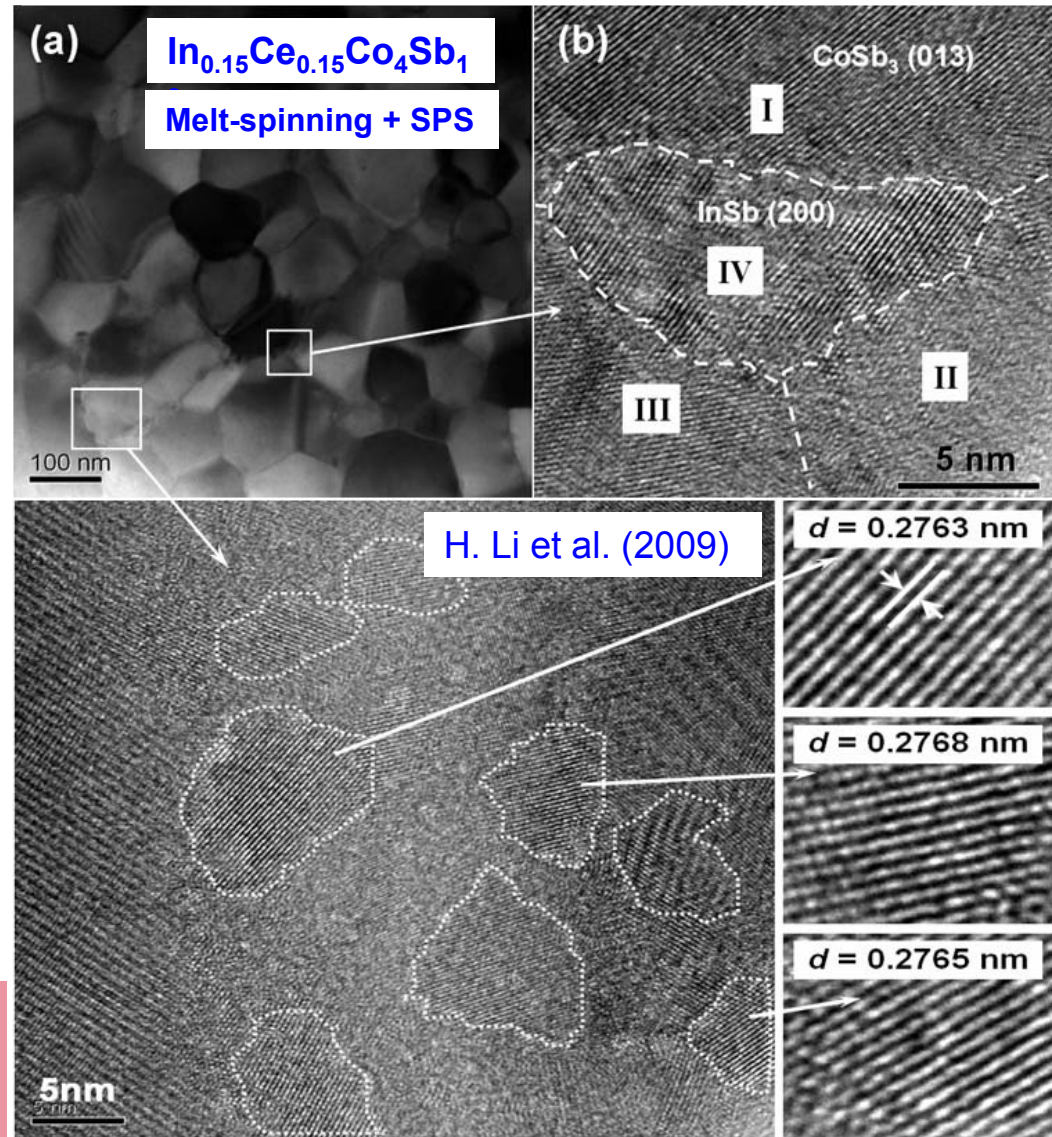In not detected

Domain IV ⟺ InSb (200)

Interlayer distances correspond to
InSb (101)

Indium forms a fine InSb nanostructure in skutterudites!

$In_{0.15}Ce_{0.15}Co_4Sb_1$
Melt-spinning + SPS

H. Li et al. (2009)

$d = 0.2763$ nm
$d = 0.2768$ nm
$d = 0.2765$ nm

Nanostructure in Bulk Skutterudites

Effect of InSb nanostructure on the electronic properties:
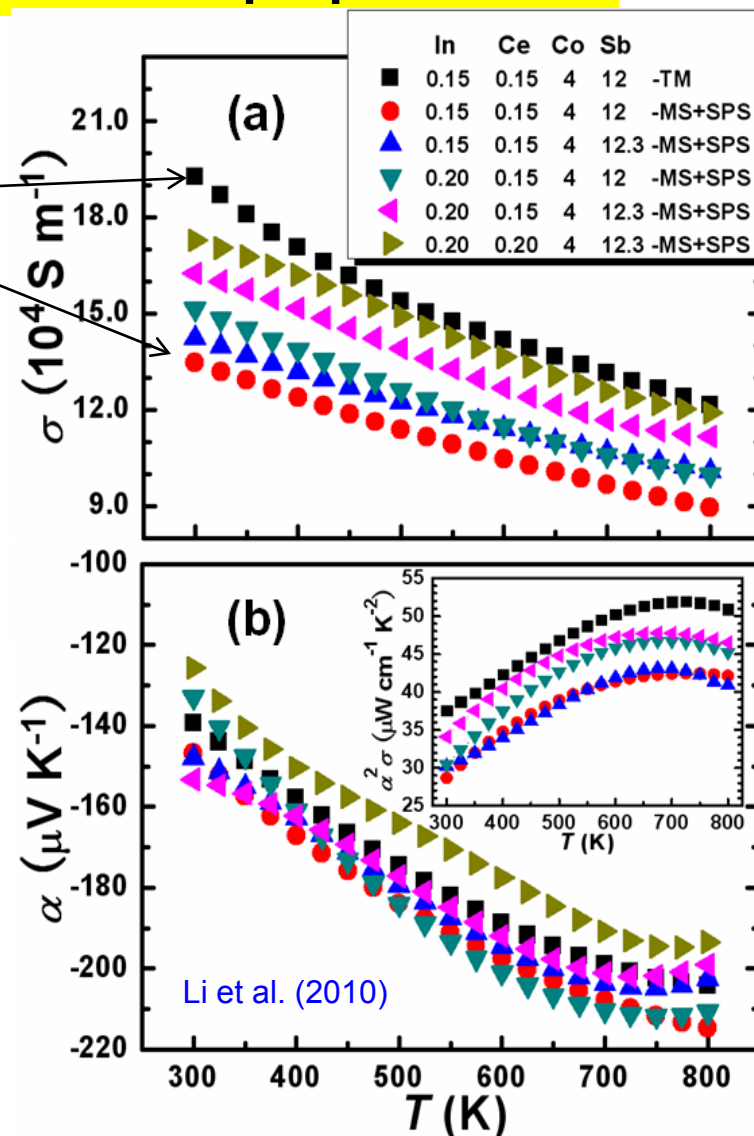
● Fine nanostructure of MS-SPS scatters electrons

compare $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ TM
with $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ MS-SPS

● With increasing x, y, and z, ⟶ σ increases

● For the same composition, Seebeck coefficient of MS-SPS higher than that of TM

● Power factor of MS-SPS smaller than for TM

● Nanostructure indeed scatters charge carriers !

In	Ce	Co	Sb	
0.15	0.15	4	12	-TM
0.15	0.15	4	12	-MS+SPS
0.15	0.15	4	12.3	-MS+SPS
0.20	0.15	4	12	-MS+SPS
0.20	0.15	4	12.3	-MS+SPS
0.20	0.20	4	12.3	-MS+SPS

(a)

(b)

Li et al. (2010)

Nanostructures in Bulk Skutterudites

Effect InSb nanostructure on thermal properties:

● Nanostructure of MS-SPS strongly scatters phonons

compare $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ TM
with $In_{0.15}Ce_{0.15}Co_4Sb_{12}$ MS-SPS

● κ of MS-SPS some 35% lower than for TM

● Greater density of InSb (more In) ⟹ lower κ_L

● Excess of Sb increases κ_L

● Vacancies on the Sb lattice may be further reducing κ_l

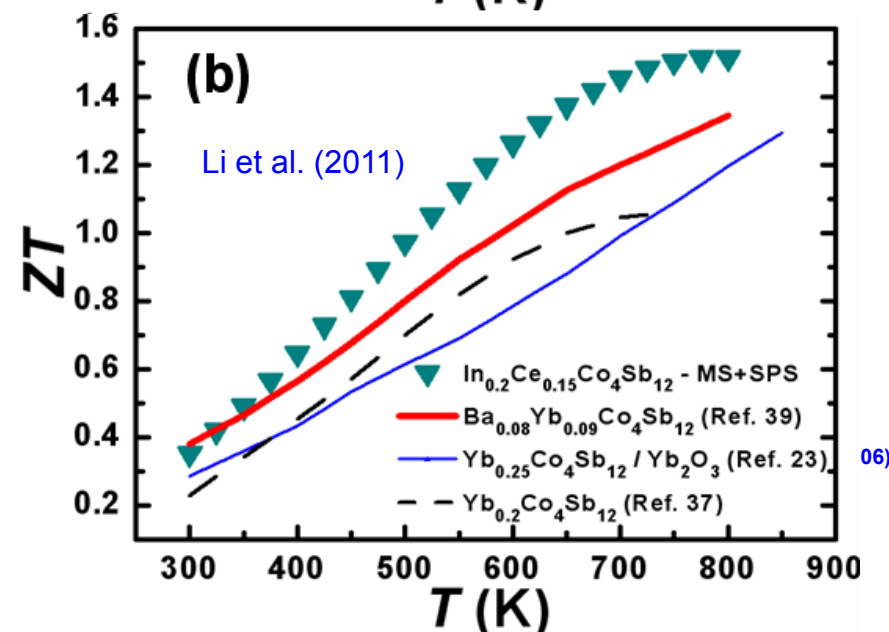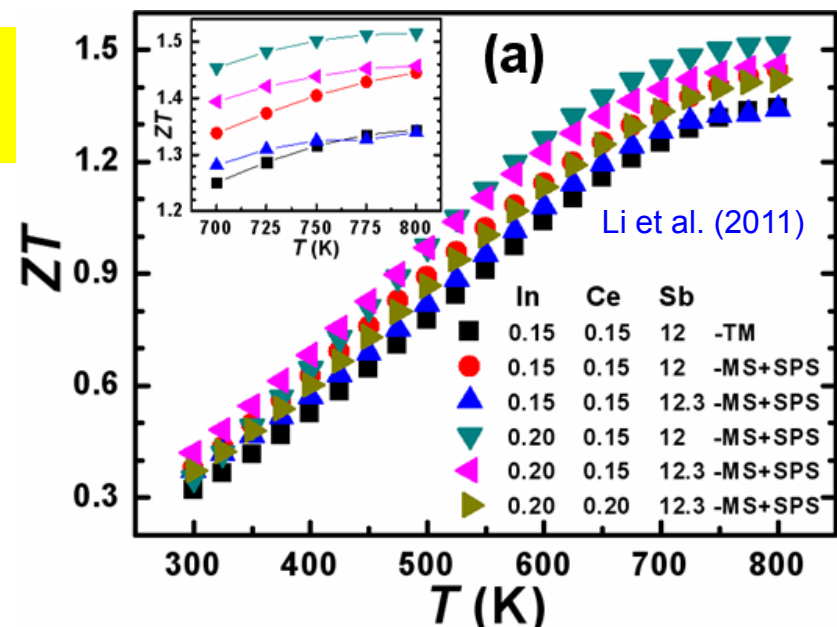| In	Ce	Co	Sb	
0.15	0.15	4	12	-TM
0.15	0.15	4	12	-MS+SPS
0.15	0.15	4	12.3	-MS+SPS
0.20	0.15	4	12	-MS+SPS
0.20	0.15	4	12.3	-MS+SPS
0.20	0.20	4	12.3	-MS+SPS

Li et al. (2011)
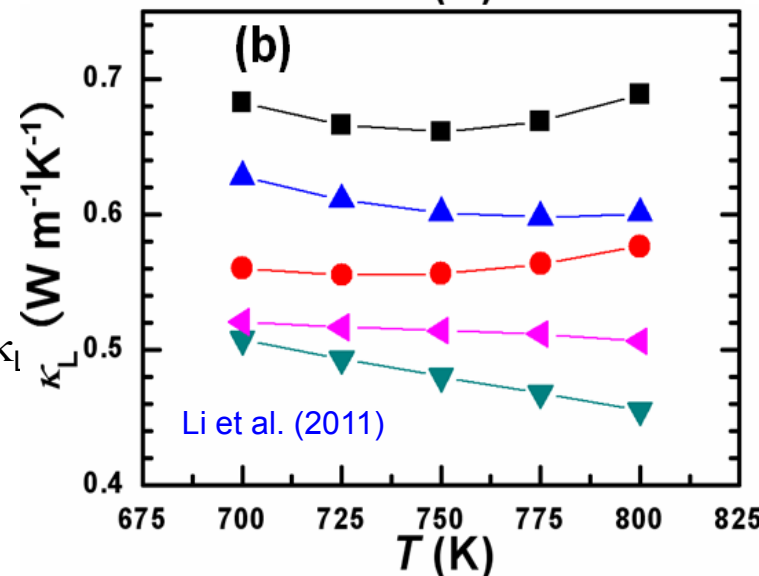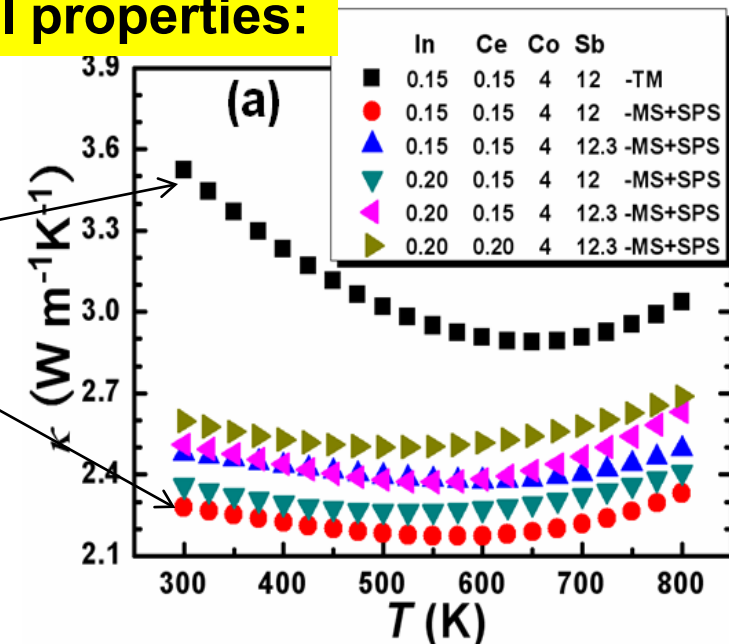
Nanostructures in Bulk Skutterudites

Effect of InSb nanostructure on TE properties:

- ZT of MS-SPS 10% higher than TM

- Highest ZT > 1.5 at 800K

- ZT > 1 above 500K
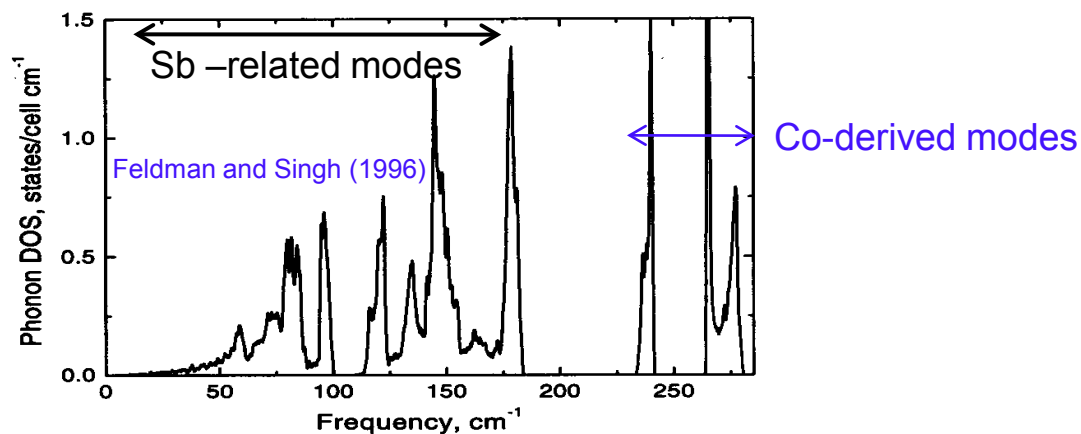
Excellent n-type skutterudites with

ZT ~ 1.5 at 800K

Li et al. (2011)

Li et al. (2011)

Nanostructures in Bulk Skutterudites

d) Compensating double-doping: (Liu et al., 2008), (Su et al. 2011)

Feldman and Singh (1996)

Sb –related modes

Co-derived modes

Heat in $CoSb_3$ is carried by Sb modes!

To lower thermal conductivity ⟷ must mess up the Sb ring structure!
Doping is a way to do it.

For n-type skutterudites, one uses elements such as Te to form $CoSb_{3-x}Te_x$.
Each Te (valency = 6) at the site of Sb (valency = 5) brings in 1 electron.
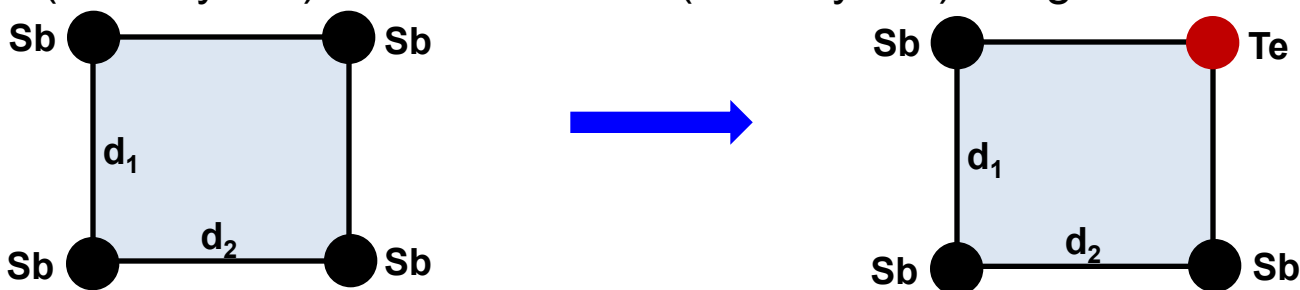
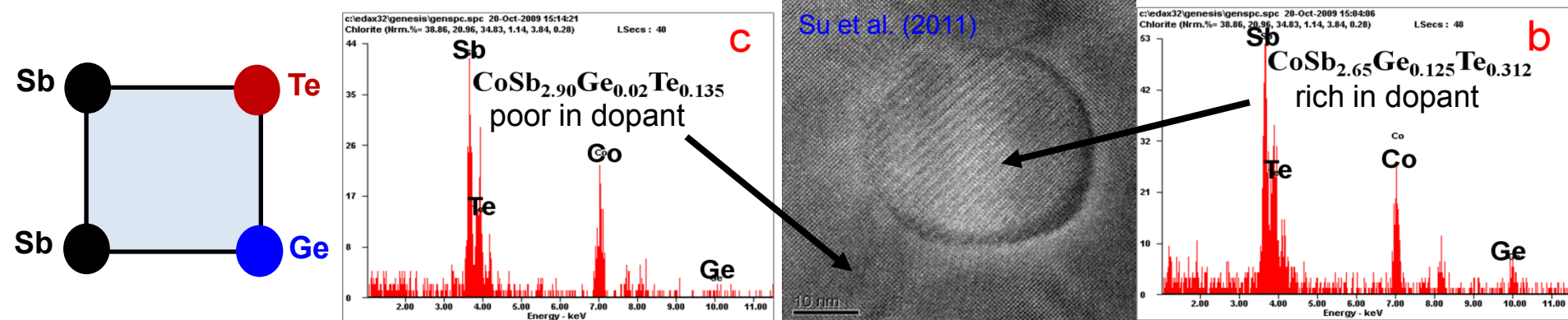Skutterudite is soon saturated with negative charge ⟹ solubility of Te limited to x~0.15.

Nanostructures in Bulk Skutterudites

To increase the solubility limit of Te, co-dope Te with a group IV element, e.g., Sn to form $CoSb_{3-x-y}Sn_yTe_x$. Nanostructured samples produced by **mechanical alloying**, grain size ~ 140 nm. Liu et al. (2008)

- Te solubility increased to x = 0.2
- Sn partly charge compensates
- Sn also partly size compensates   Sn(1.72Å); Sb(1.53Å) and Te(1.42Å)

ZT approaches 1.1 at 825K!

Most recently, similar enhancement in ZT obtained with **$CoSb_{2.75}Ge_{0.25-x}Te_x$** prepared by melt-quench-anneal-SPS technique. Su et al. (2011)

$CoSb_{2.90}Ge_{0.02}Te_{0.135}$ poor in dopant

Su et al. (2011)

$CoSb_{2.65}Ge_{0.125}Te_{0.312}$ rich in dopant

The nanostructure has similar origin as in the LAST materials.
Dominant scattering from point defects but nanostructure also contributes.
Values of ZT = 1.1 are comparable to those of filled n-type skutterudites!

Conclusions

- Tremendous progress in the development of n-type skutterudites, ZT~1.5.

- Formation of stable, robust nanostructures a major contribution to high ZT values.

- Nanocomposites were formed by intrinsic processes such as *in-situ* compound formation and compensating double-doping on the pnicogen site.

- The primary role of nanostructures in bulk matrices is to strongly enhance phonon boundary scattering while preserving good electronic properties.

- Issues to be explored further: what other kinds of nanostructures are possible? long-term stability of nanocomposite structures?

- MS + SPS processing a major advance in terms of time, energy, scale-up potential.

- Major effort needed to advance p-type skutterudites!!

- Outstanding mechanical properties bode well for applications. (Salvador et al. 2009)

- The most recent PRL (Kim et al., 105, 265901 (2010)) addresses the topology and order-disorder transitions of the filler species, the issue relevant to heat transport.

Skutterudites are likely to be the first of the novel thermoelectrics in practical power generation applications.