Proactive Design of *n*-Type (In,Ce) Filled Skutterudites Enabling High-Temperature Waste Heat Recovery

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Team Members

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Acknowledgements

Outline

- Motivation
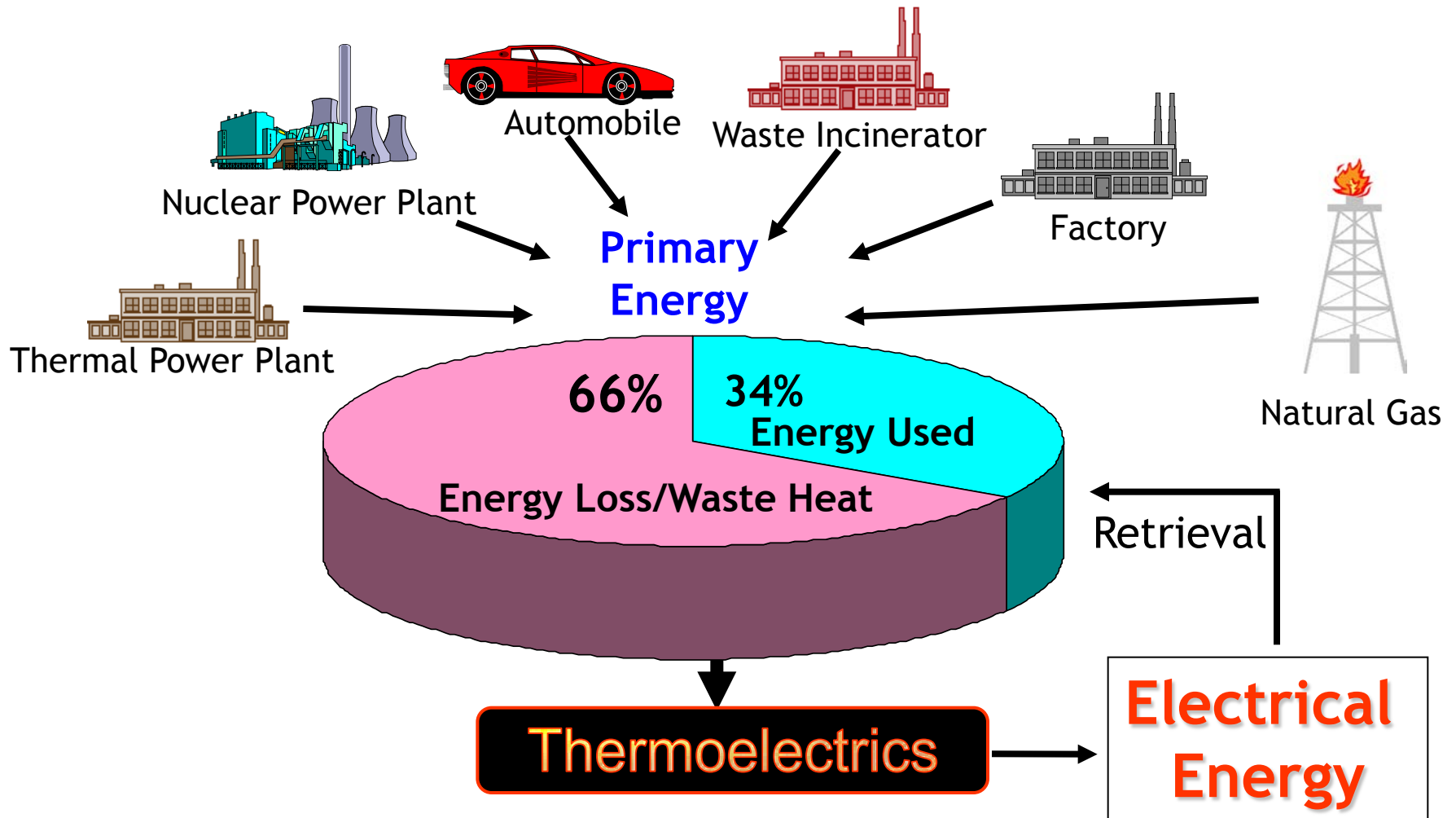
- TE characterization - challenges

- Filled skutterudites (single and multiple filled)

  - Indium and Rare earths

  - Thermoelectric properties

  - Structural properties

- Summary

Motivation

Nuclear Power Plant

Automobile

Waste Incinerator

Factory

Thermal Power Plant

Primary Energy

Natural Gas

66% **34%**

Energy Used

Energy Loss/Waste Heat

Retrieval

Thermoelectrics

Electrical Energy

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Waste Energy Recovery
Magnitude of the Opportunity

Transportation Sector

➢ **Light-Duty Passenger Vehicles + Light-Duty Vans/Trucks (SUVs)**

  2004: ~135 billion gallons of gasoline

  ~ 4.5 quads/yr exhausted down the tail pipe

  ~ 5.5 quads/yr rejected in coolant system

➢ **Heavy-Duty Vehicles**

  2004: ~32 billion gallons of diesel

  ~1.45 quads/yr exhausted down the tail pipe

  ~1 quad/yr rejected in coolant system (~1 quad)

➢ **Hybrid Electric Vehicles**

  Move Toward Electrification – Micro, Mild, and Full

  Needs for Power Generation

  Needs for Electric-Driven Cooling

Industrial Sector

  Glass, Aluminum, Cement, Paper, Chemical

  Another 10 quads – 1.8 quads recoverable

TE materials performance:
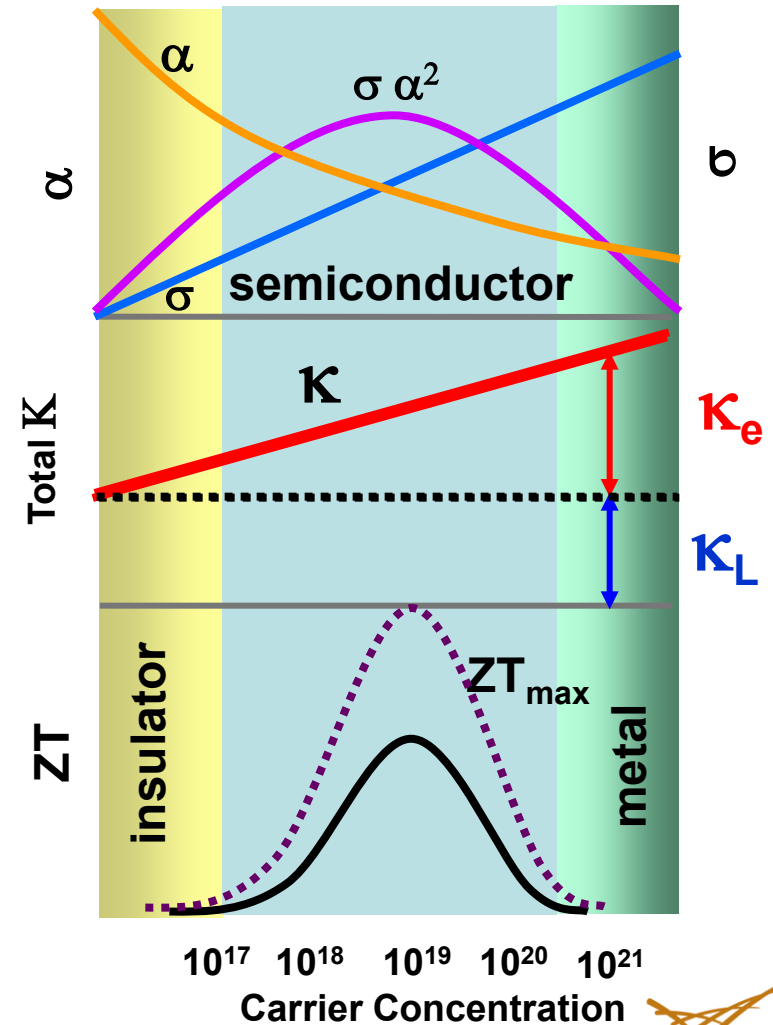## *Figure of Merit*

Electrical conductivity

Seebeck coefficient or thermopower ($\Delta V / \Delta T$)

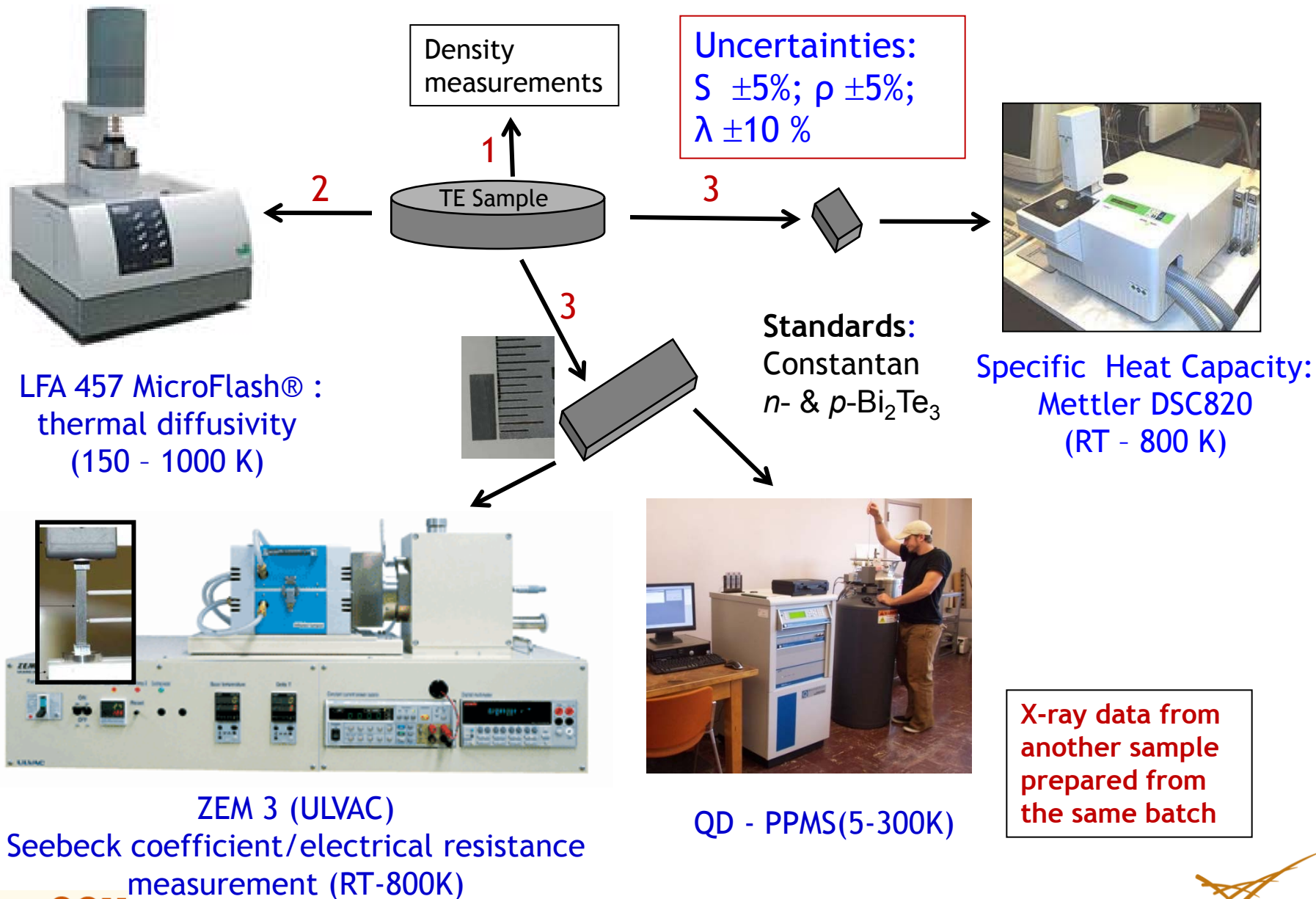$$ZT = \frac{\sigma \; \alpha^2}{(\kappa_e + \kappa_L)} \cdot T$$

Total thermal conductivity

No upper limit for ZT

Contraindicated Properties

TE Properties Characterization

Density measurements

Uncertainties:
S $\pm 5\%$; ρ $\pm 5\%$;
λ $\pm 10\%$

1
2
TE Sample
3
3

Standards:
Constantan
n- & p-Bi_2Te_3

LFA 457 MicroFlash® :
thermal diffusivity
(150 – 1000 K)

Specific Heat Capacity:
Mettler DSC820
(RT – 800 K)

ZEM 3 (ULVAC)
Seebeck coefficient/electrical resistance
measurement (RT-800K)

QD - PPMS(5-300K)

X-ray data from another sample prepared from the same batch

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ZT Values – A Word of Caution

Table 1. Effect of instrument accuracy on ZT

Sample A: ZT = 1.4, T = 575 K, S = 300 μV/K, ρ = 3 mΩ.cm, κ = 1.23 W/mK

Instrumental Error[1]	ZT_{Max}[2]	ZT	ZT_{Min}[3]	$ZT_{Max} - ZT_{Min}$
± 1%	1.46	1.4	1.35	0.11
± 2%	1.52	1.4	1.29	0.23
± 5%	1.71	1.4	1.15	0.56
± 10%	2.10	1.4	0.94	1.16

Sample B: ZT = 1.2, T = 575 K, S = 280 μV/K, ρ = 3 mΩ.cm, κ = 1.25 W/mK

Instrumental Error[1]	ZT_{Max}[2]	ZT	ZT_{Min}[3]	$ZT_{Max} - ZT_{Min}$
± 1%	1.25	1.2	1.15	0.1
± 2%	1.30	1.2	1.11	0.19
± 5%	1.47	1.2	0.98	0.49
± 10%	1.80	1.2	0.80	1.0

1. Assume S, ρ, and κ have the same degree of instrumental errors.
2. ZT_{Max} is calculated using S_{Max}, ρ_{Min}, κ_{Min}.
3. ZT_{Min} is calculated using S_{Min}, ρ_{Max}, κ_{Max}.

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Research strategies to increase ZT

Lowering Lattice thermal conductivity - Scatter Acoustic Phonons
Heavy Atoms with Complex Structure
Anisotropic Thermal Vibrations
Atomic Disorder
"Rattlers" filled Cage Structure
Defects & Grain Boundary Scattering
Superlattice structures
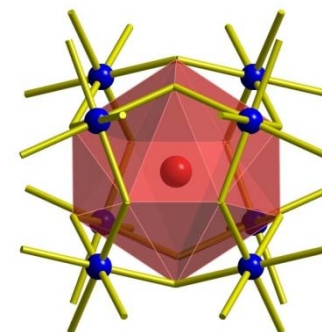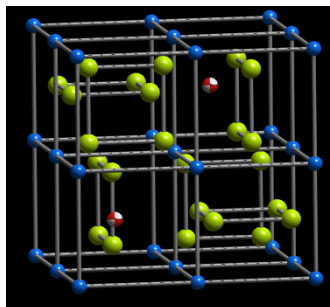
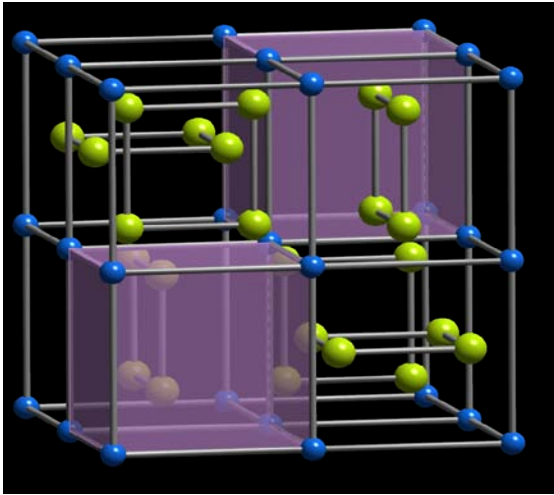$$ZT = \frac{\uparrow \alpha^2 \sigma T}{\downarrow (\kappa_E + \kappa_L)}$$

Increasing Seebeck (α)
Bandgap tuning
Large density of states at E_F
Large Effective Mass (M_{EFF})

Increasing Electrical Conductivity (σ)
High Mobility Charge Carriers
Narrow Gap Semiconductors
Lower Electron Scattering

Crystal Structure of Skutterudite

CoSb$_3$ [Co$_8$(Sb$_4$)$_6$]

R$_x$Co$_4$Sb$_{12}$

- Cobalt atoms form a *fcc* cubic lattice
- Antimony atoms are arranged as a square planar rings
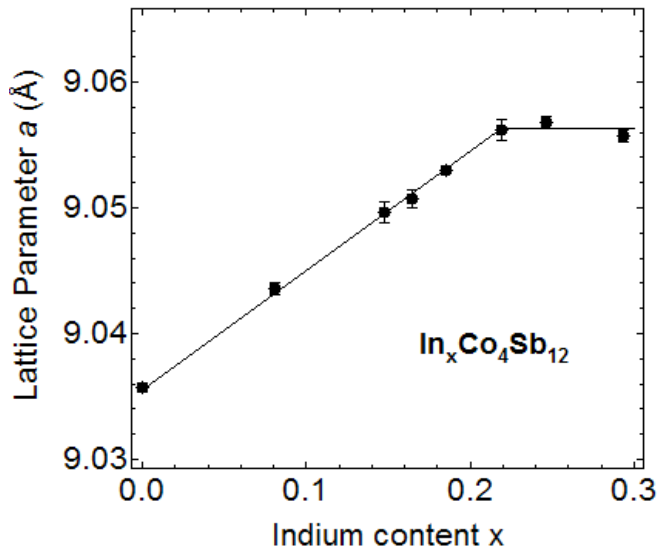- There are 8 spaces for the Sb$_4$ units; 6 are filled and 2 are empty
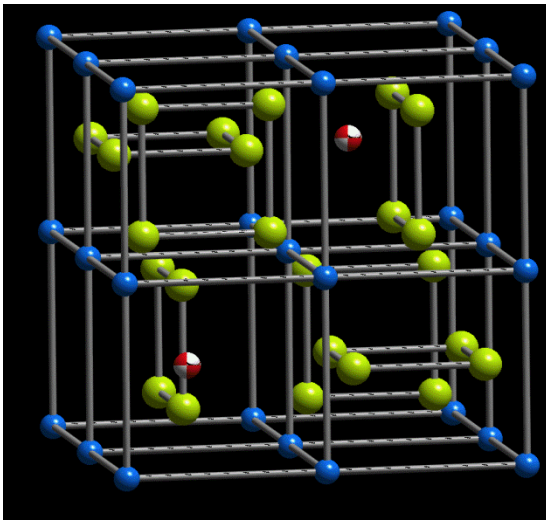
Atoms can be inserted into empty sites. Atoms can "rattle" in these sites – scatter phonons and lower the lattice thermal conductivity.

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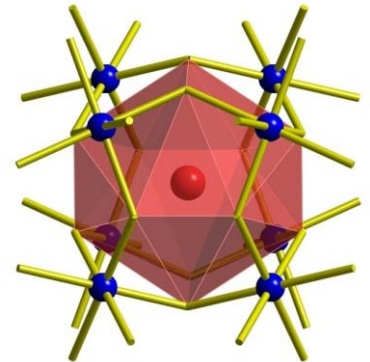
Indium Filled Skutterudites: $In_xCo_4Sb_{12}$

- ❖ $CoSb_3$: a = 9.0357 Å
  - ✓ Agrees with reported a = 9.0345 Å for $CoSb_3$ single crystal
- ❖ Indium solubility limit x = 0.22
  - ➤ $a \sim$ 9.0563 Å
  - ➤ x > 0.25, InSb mpurity

$In_xCo_4Sb_{12}$: ZT~0.8-1.2 @ 600K

He, Chen, Rosenfeld and Subramanian,
Chem. Mater. 18, 759, (2006)

Subramanian US 7,462,217
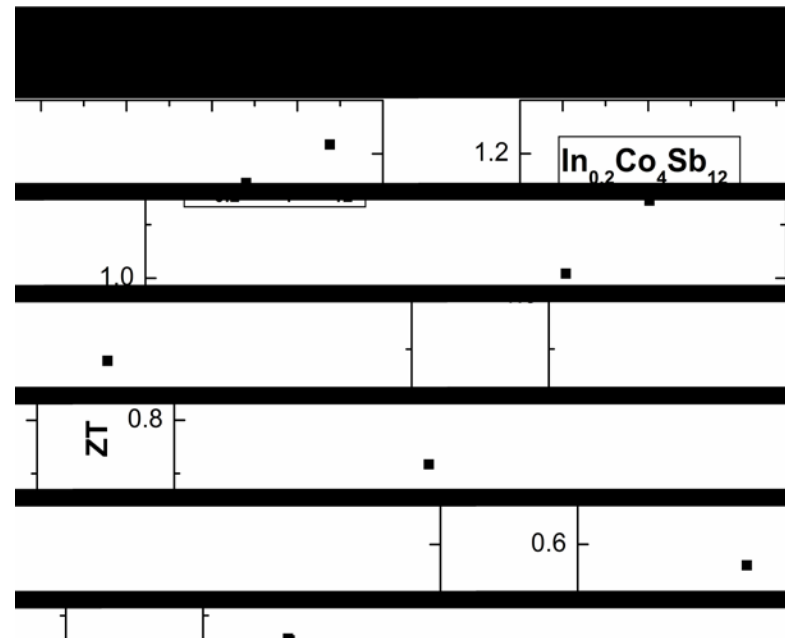
Rare-Earth Intermediate Valence Intermetallics

✦ Intermetallics with rare earths in intermediate valence states

    ✦ $Yb^{2+,3+}$ ($4f^{13}$-$4f^{14}$) ; $Ce^{3+,4+}$ ($4f^1$-$4f^0$)
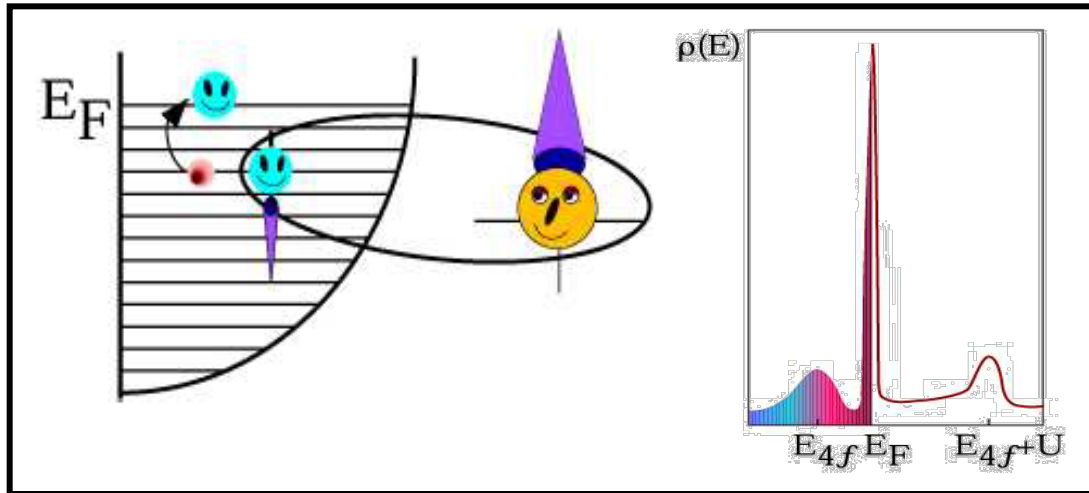
    ✦ Large Density of States at the Fermi Level

        - interaction between conduction electrons (*s*, *p* or *d* state) and partially localized 4f electrons leads to large α

        - very large numerator (power factor)

        - large denominator (thermal conductivity) – low ZT

$$ZT = \frac{\sigma\,\alpha^2}{(\kappa_e + \kappa_L)} \bullet T$$

Examples: $YbAl_3$ and $CePd_3$

(G. Mahan)

TE based on Skutterudites with Dual Rattlers: $In_{0.15}R_{0.10}Co_4Sb_{12}$[1]

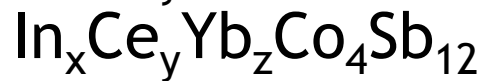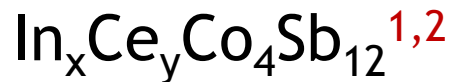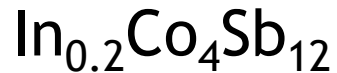**Rattlers** $\longrightarrow$ R: Rare Earth (La, Ce, Nd, Er, Yb etc.)

Co $\longrightarrow$ Mn, Fe, Ni, Cu, Pd, Pt, Rh, Ru

Current Focus:
$In_{0.2}Co_4Sb_{12}$
$In_xCe_yCo_4Sb_{12}$[1,2]
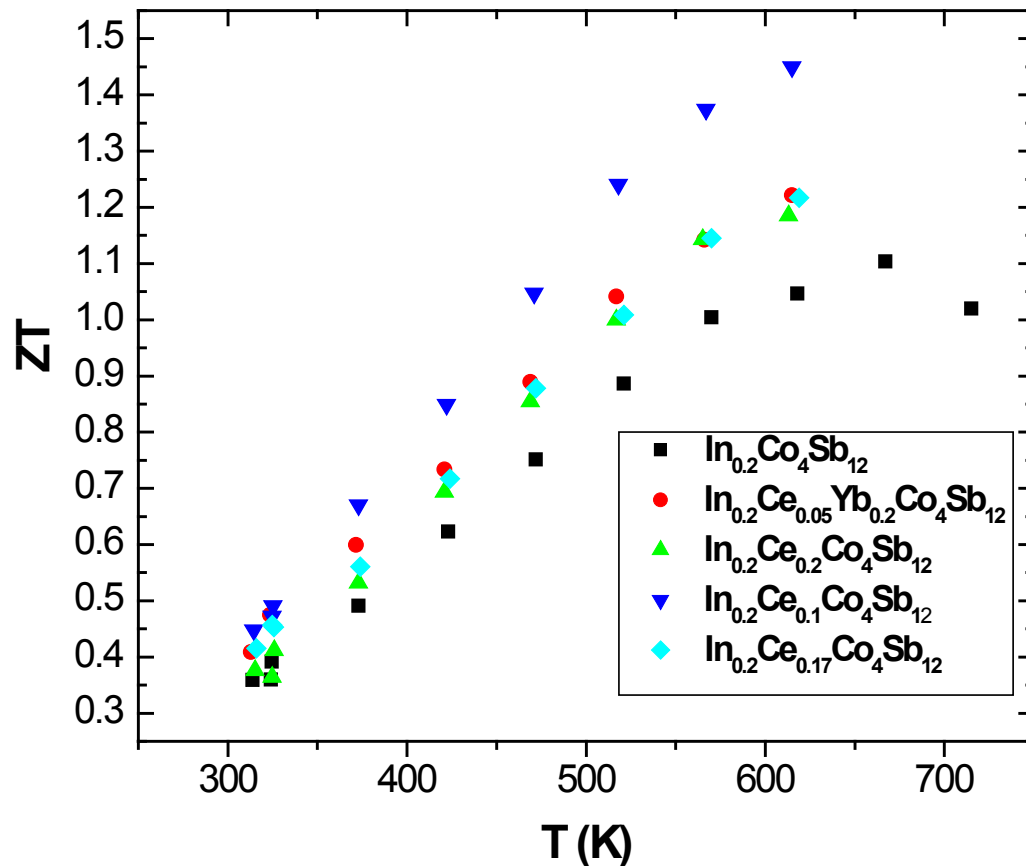$In_xCe_yYb_zCo_4Sb_{12}$

$In_xR_yCo_4Sb_{12}$

[1]Subramanian et al. US patent 7,723,607
(Filed: April 2005; Issued: May 25, 2010)
[2]Li e al. *Appl. Phys. Lett.*, 94, 102114, (2009).
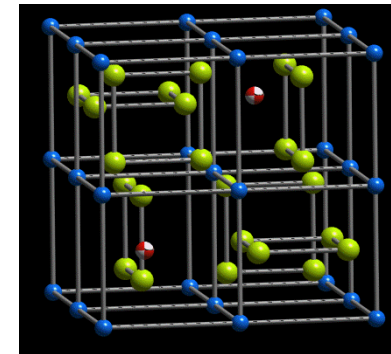
$In_xCe_yCo_4Sb_{12}$ Skutterudites

- $In_{0.2}Co_4Sb_{12}$ ZT ~ 1.1 @ 600 K (highly reproducible).

- There is an enhancement of ZT when Ce is co-filled with In.

- Cerium (Ce^{3+}, Ce^{4+}) mixed valiancy may play a role. - Enhancement of Seebeck values.

- $In_{0.2}Ce_{0.15}Co_4Sb_{12}$ showed ZT ~ 1.5 – 1.6 around 500 K, but not reproducible.

Legend:
- ■ $In_{0.2}Co_4Sb_{12}$
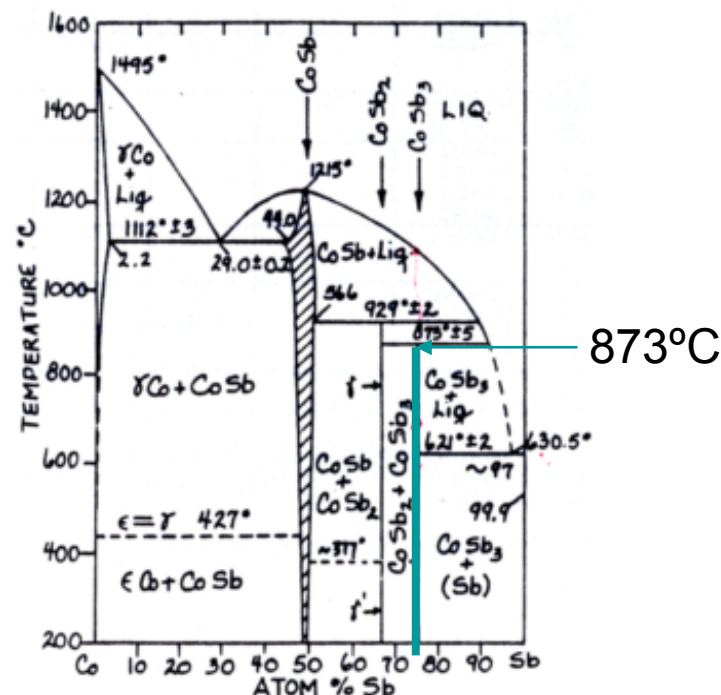- ● $In_{0.2}Ce_{0.05}Yb_{0.2}Co_4Sb_{12}$
- ▲ $In_{0.2}Ce_{0.2}Co_4Sb_{12}$
- ▼ $In_{0.2}Ce_{0.1}Co_4Sb_{12}$
- ◆ $In_{0.2}Ce_{0.17}Co_4Sb_{12}$

$In_xCe_yCo_4Sb_{12}$ - Synthesis

Two Methods

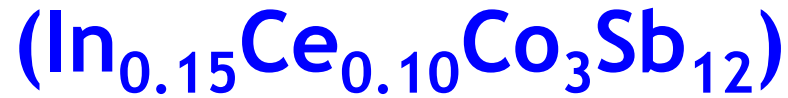(1) Rare earth metal (Ce) reacted with preformed $In_{0.15}Co_3Sb_{12}$

(2) Starting from elemental rare earth, In, Co, Sb in stoichiometric ratios

The powders were calcined at 610°C for 12 hours, and then 675°C for 36 hours under a gas mixture of 5% H_2 and 95% Ar. Reground, pelletized, sintered at 750°C for 4 hours under the same gas mixture.
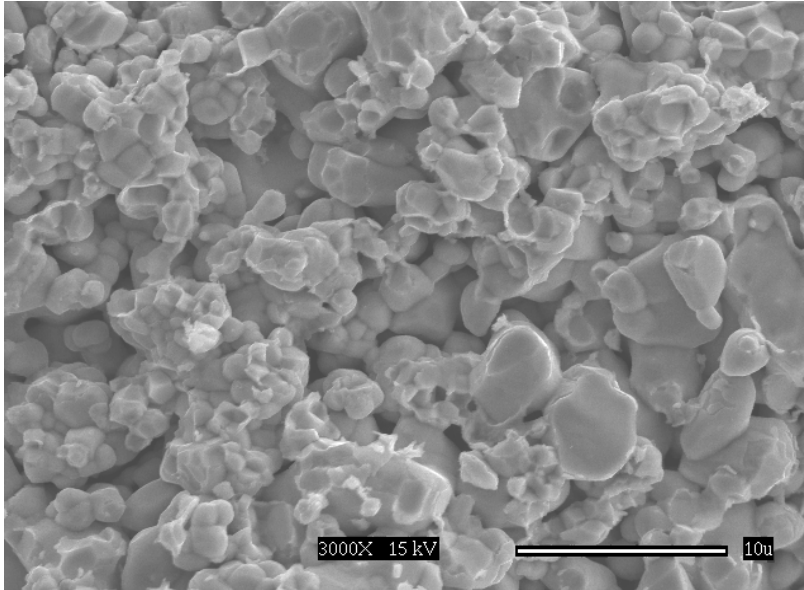

873°C

(Pellets are of 75 – 85% theoretical density)

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ZT Dependence on Microstructure ($In_{0.15}Ce_{0.10}Co_3Sb_{12}$)
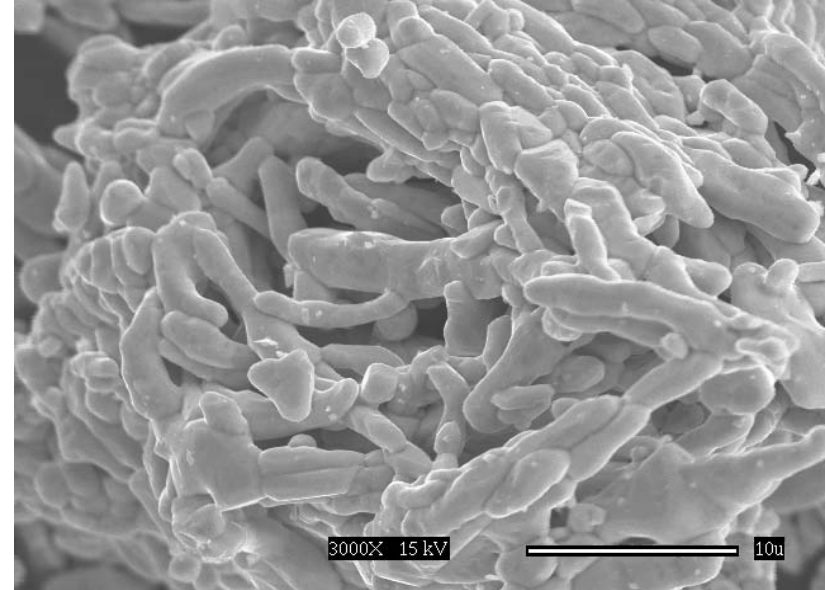
ZT ~ 1.4 @ 600 K　　　　　　**ZT ~ 1.1 @ 600 K**

Synthetic Method - 1　　　　　**Synthetic Method - 2**

In addition to chemical composition and crystal structure, for ceramic samples, the ZT also depends on microstructure, grain-morphology etc.
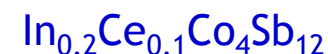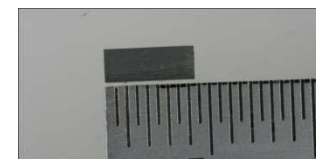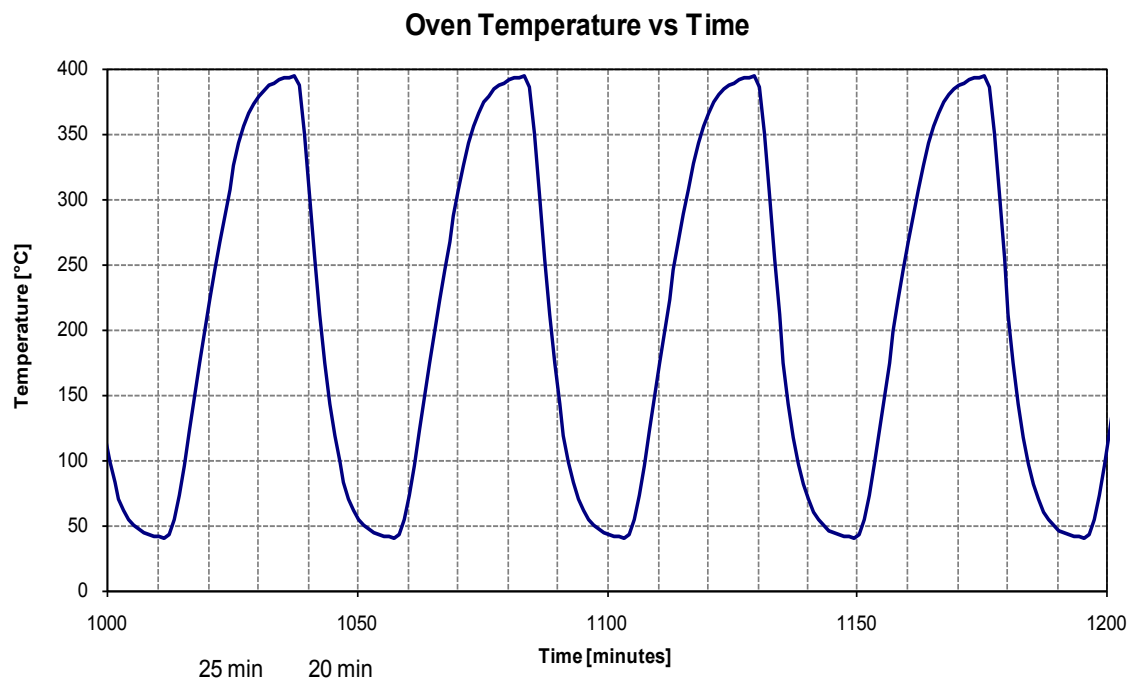
Structural Properties:
Resonant Ultrasound Spectroscopy

Specimen Label and Comments	ρ, density (g/cm^3)	υ, Poisson's ratio	CTE (10^{-6} / C) (300-673K)	E, Elastic Modulus (10^{11} N/m^2)	ZT (@ 600 K)
Bi$_2$Te$_3$ Alloys (Literature)		0.21-0.37	14 -21 (Anisotropic)	0.40-0.47	0.0-0.1
CoSb$_3$ (Literature)		0.222		1.396	0.6
CoSb$_3$		0.225-0.226	12.8	1.391-1.398	
In$_{0.1}$Co$_4$Sb$_{12}$		0.227	8.37	1.396	
In$_{0.15}$Ce$_{0.1}$Co$_4$Sb$_{12}$	7.314		8.30-8.83		
In$_{0.15}$Ce$_{0.1}$Co$_4$Sb$_{12}$ – PNNL3	7.314	0.185	8.61	1.339	1.0
In$_{0.15}$Ce$_{0.1}$Co$_4$Sb$_{12}$ - LB1	7.304	0.215	8.56	1.348	1.0
In$_{0.15}$Ce$_{0.1}$Co$_4$Sb$_{12}$ - LB2	7.264	0.204	8.26	1.326	1.0
In$_{0.2}$Ce$_{0.1}$Co$_4$Sb$_{12}$	7.019	0.210-0.214	8.11-8.44	1.182-1.185	1.4
In$_{0.2}$Co$_4$Sb$_{12}$	7.06-7.10	0.208-.218	8.27-8.34	1.178-1.238	1.1
In$_{0.2}$Yb$_{0.1}$Ce$_{0.05}$Co$_4$Sb$_{12}$	6.421	0.207	7.06-9.7	0.895	1.1

PNNL3-G1B, LB1 and LB2 are codes for samples cut from the same bar

Thermal Cycling Tests

- Materials subjected to thermal cycling tests at temperatures representative of waste heat recovery applications
  - Ar atmosphere
- Temperature profile shown below
  - 40°C to 400°C
  - Limited to 200 cycles

Oven Temperature vs Time

25 min   20 min

$In_{0.2}Ce_{0.1}Co_4Sb_{12}$

Thermal Cycling Results

	Temp [°C]	Before Thermal Cycling		After Thermal Cycling	
		Young's Modulus, E 10^9 [N/m^2]	Poisson's Ratio, ν	Young's Modulus, E 10^9 [N/m^2]	Poisson's Ratio, ν
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL1) – n-type	20-22	134.8	0.215	134.4	0.204
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL2) – n-type	20-22	132.6	0.204	131.9	0.200
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (PNNL3-G1B) n-type	20-22	133.9	0.185	135.8	0.194
$In_{0.2}Ce_{0.15}Co_4Sb_{12}$ n-type	20.6	124.5	0.213	125.7	0.214
$In_{0.2}Ce_{0.1}Co_4Sb_{12}$	20.5	123.1	0.197	125.1	0.217
$In_{0.2}Ce_{0.17}Co_4Sb_{12}$	19.9	109.5	0.213	108.5	0.210
$In_{0.2}Ce_{0.05}Yb_{0.1}Co_4Sb_{12}$	20-22	89.5	0.208	85.9	0.207

- Minimal thermal cycling impact on structural properties
- Indicates little or no micro-crack growth or initiation
- Thermal stability critical to TE devices and systems

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Thermal Cycling Impacts Power Factor

➢ $In_{0.15}Ce_{0.1}Co_4Sb_{12}$ showed significant increases in power factor after thermal cycling

➢ Effect in the right direction – Big impact on Seebeck coefficient

➢ Could not check thermal conductivity however (incorrect sample size and shape to re-run κ tests)

➢ Requires further investigation with other (InCe)-based compounds and with statistically-significant sample numbers

	Temperature [K]	Before Thermal Cycling Power Factor [$\mu W/cm\text{-}K^2$]	After Thermal Cycling Power Factor [$\mu W/cm\text{-}K^2$]
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL1) n-type	510	28.7	39.2 (+36.6%)
$In_{0.15}Ce_{0.1}Co_4Sb_{12}$ (LBL2) n-type	510	28.7	32.7 (+13.9%)

➢ X-ray data before and after thermal cycling indicates no sign of decomposition or change in the cubic lattice parameter

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Thermal Cycling Impacts on Power Factor

➢ $In_{0.2}Ce_{0.17}Co_4Sb_{12}$ showed ~ 35 % increase in PF @ ~ 500-600K
➢ Similar behavior seen in other dual filled $(In,Ce)Co_4Sb_{12}$ samples
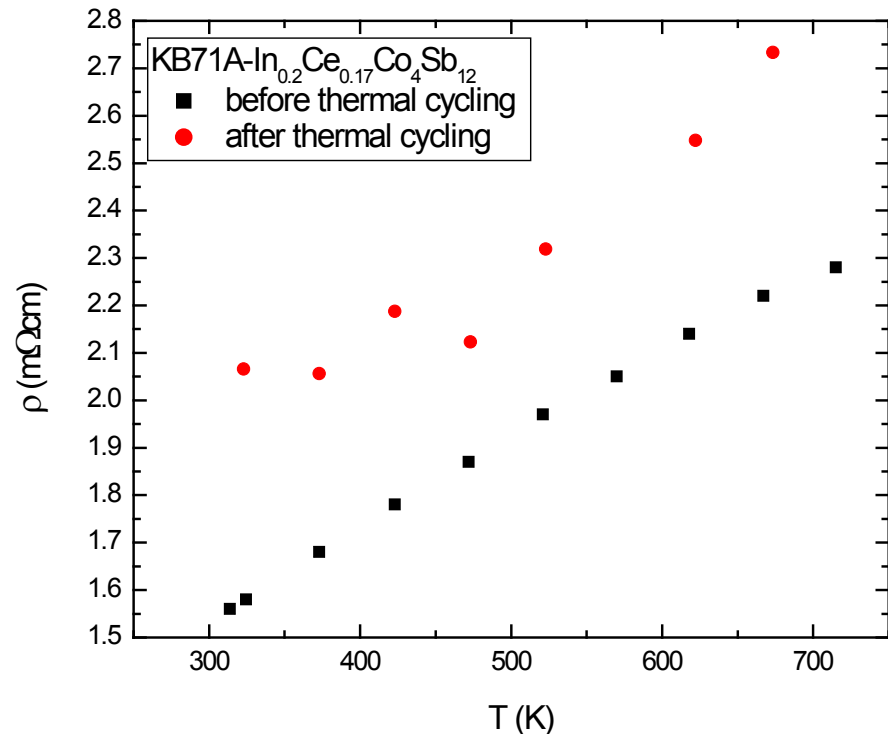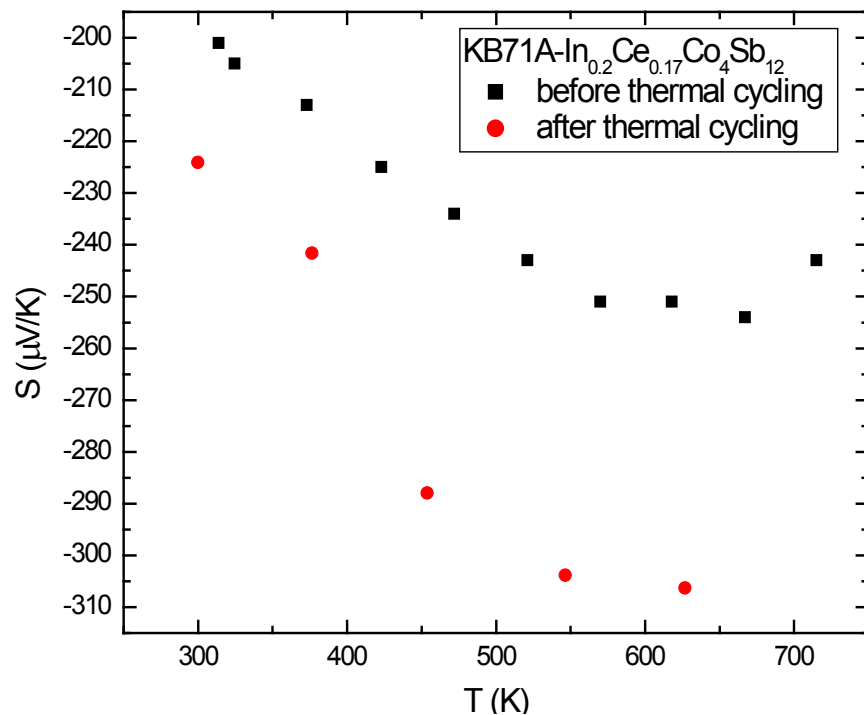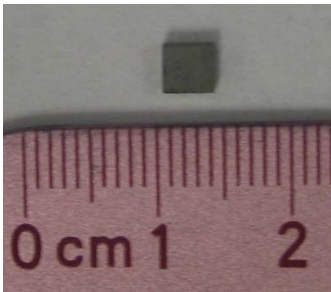
Thermal Cycling Impacts on Power Factor

➢ $In_{0.2}Ce_{0.05}Yb_{0.1}Co_4Sb_{12}$ showed ~30% <u>decrease</u> in PF @ ~ 500-600 K
➢ Materials that behave this way after thermal cycling may be an issue.
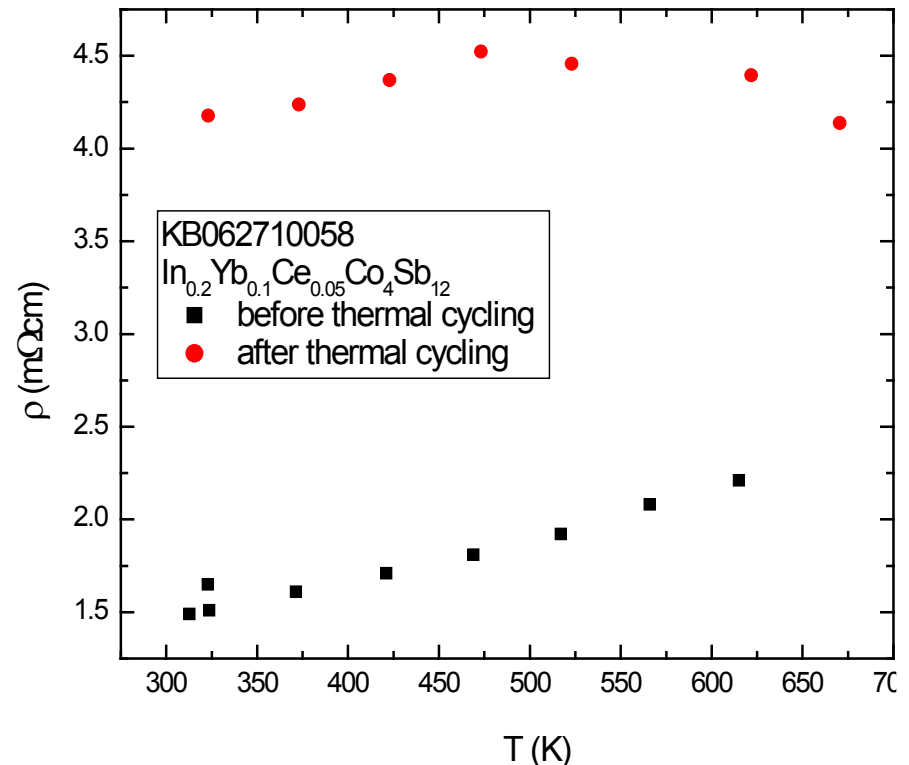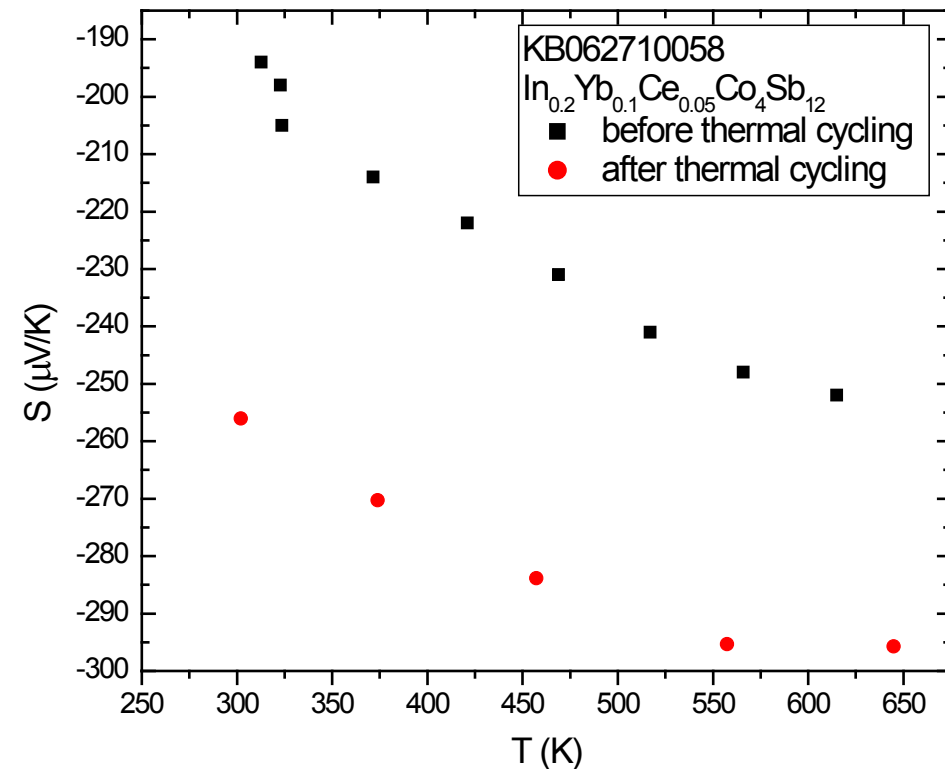
Summary

- Several *n*-type (InCe)-based skutterudite compounds fabricated and their TE and structural properties characterized
  - $In_{0.2}Co_4Sb_{12}$, $In_xCe_yCo_4Sb_{12}$ & $In_xCe_yYb_zCo_4Sb_{12}$
  - ZT_{peak} ~ 1.0 - 1.4 @ ~ 600K
  - Young's modulus generally lower than base Co_4Sb_{12} material, but higher than conventional TE materials
  - Poisson's ratio lower than base Co_4Sb_{12} material and conventional TE materials
  - CTE (25 to 400°C) is lower than base Co_4Sb_{12} material and conventional TE materials
- *n*-type (In,Ce)-based skutterudites showing good structural stability after thermal cycling
  - 313 K to 673 K (200 cycles)
- Power factor increases after thermal cycling compounds in $In_xCe_yCo_4Sb_{12}$
  - Thermal cycling may be major differentiator in skutterudites
- *p*-type materials development $(In,Ce)Fe_xCo_{4-x}Sb_{12}$ (ZT ~ 0.5 at 600K)
- Validation of TE properties with third party testing (ORNL)

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Thank You!

$(In, Ce)Co_4Sb_{12}$ diced samples