Filled Skutterudites for Efficient Power Conversion Applications

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Novel bulk thermoelectric materials:

β-$FeSi_2$

Clathrates ($Sr_8Ga_{16}Ge_{30}$)

Complex chalcogenides ($CsBi_4Te_6$)

Half-Heusler alloys (ZrNiSn)

Oxide materials ($Na_xCo_2O_4$)

Pentatellurides ($HfTe_5$)

Sb-Zn system (Sb_3Zn_4)

Skutterudites ($R_yCo_4Sb_{12}$)

Skutterudite Compounds

Compounds of the form MX_3

M = Co, Rh, Ir (Ni)

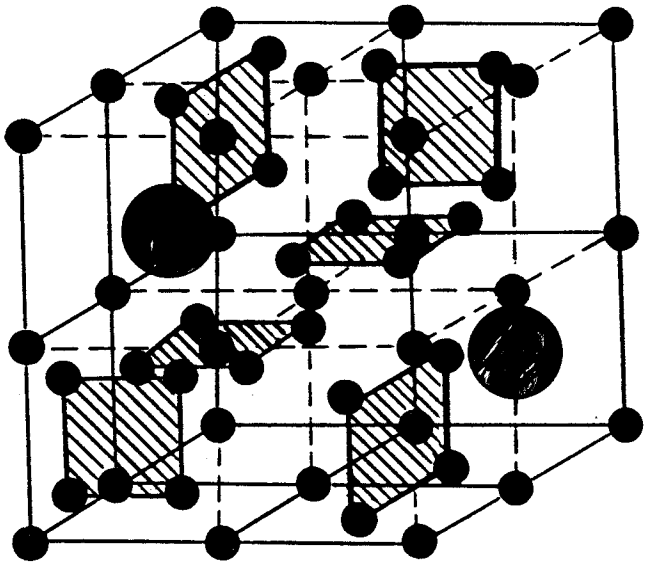
X = P, As, Sb

Crystallize with the bcc structure, space group Im3.

Eight MX_3 units in the unit cell ⇒ 32 atoms/ unit cell.

Skutterudite structure identified by Oftedal in 1928.

$CoSb_3$



● Co
● Sb

Two empty "cages" in the structure

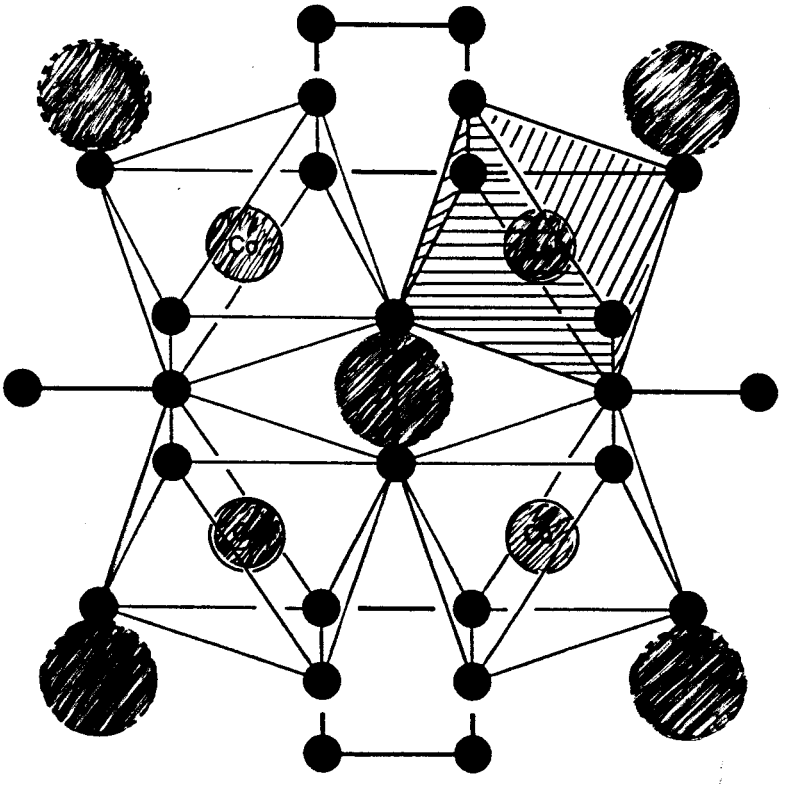
$$CoSb_3 \Leftrightarrow \square_2Co_8Sb_{24} \Leftrightarrow \square Co_4Sb_{12}$$

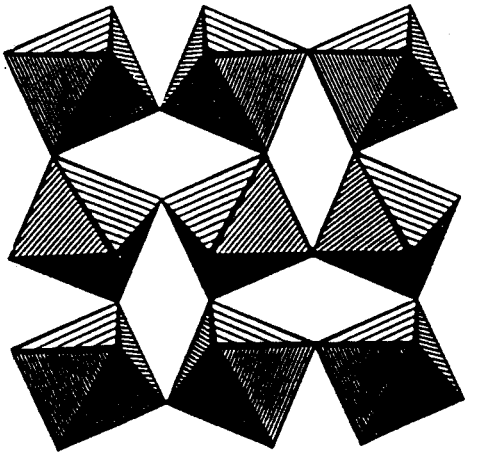
Cages can be filled with rare-earth atoms:

Filled Skutterudites

Semiconductors & Semimetals
Vol. 69, 139-253 (2001)

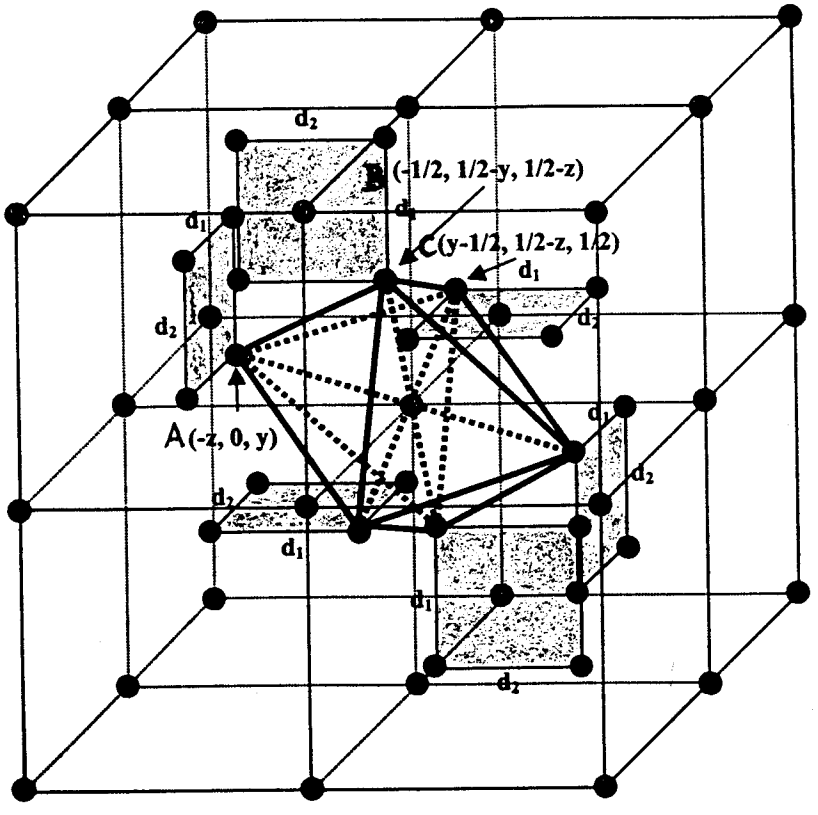
Skutterudites





MX_6 cluster

Not a regular octahedron.
Trigonal antiprismatic distortion.

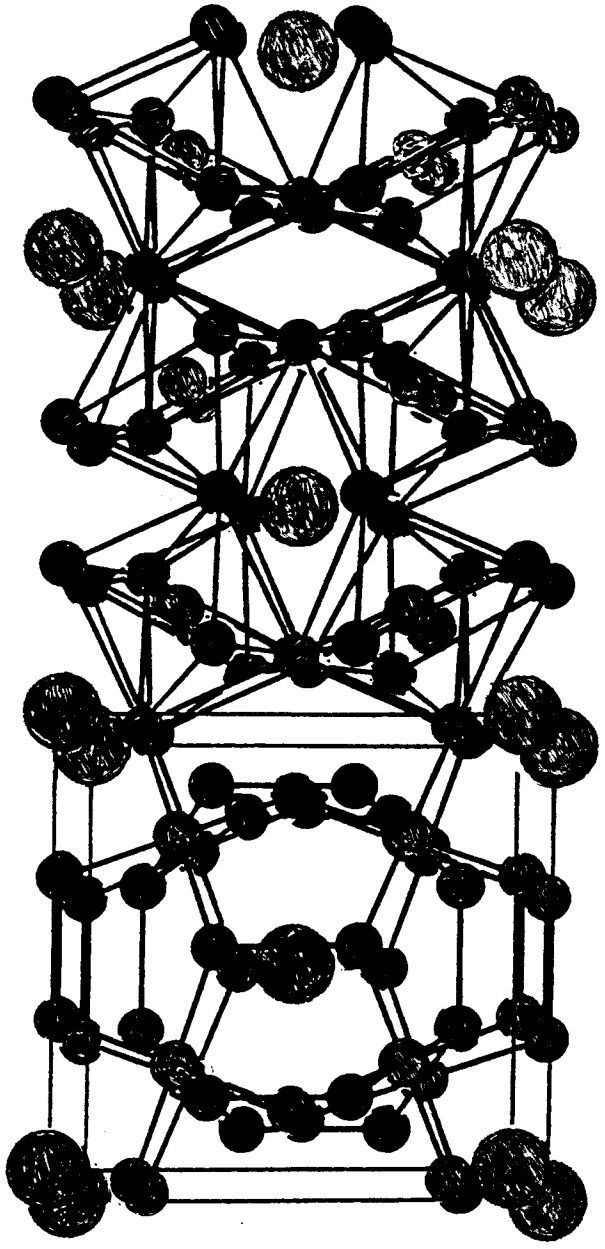


Comparing distances (edge lengths) of the octahedron:

$A(-z,0,y)$ to $B(-\frac{1}{2},\frac{1}{2}-y,\frac{1}{2}-z) = [(z-\frac{1}{2})^2 + (y-\frac{1}{2})^2 + (y+z-\frac{1}{2})^2]^{1/2}$
$B(-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z)$ to $C(y-\frac{1}{2}, \frac{1}{2}-z, \frac{1}{2}) = [(y^2 + (z-y)^2 + z^2]^{1/2}$

$$AB \neq BC$$

Distortions might be healed by adding a small amount of Ni.



1992—JPL identified skutterudites as potential advanced thermoelectric materials.

- Large unit cell
- Reasonably large atomic masses
- Exceptionally high mobilities

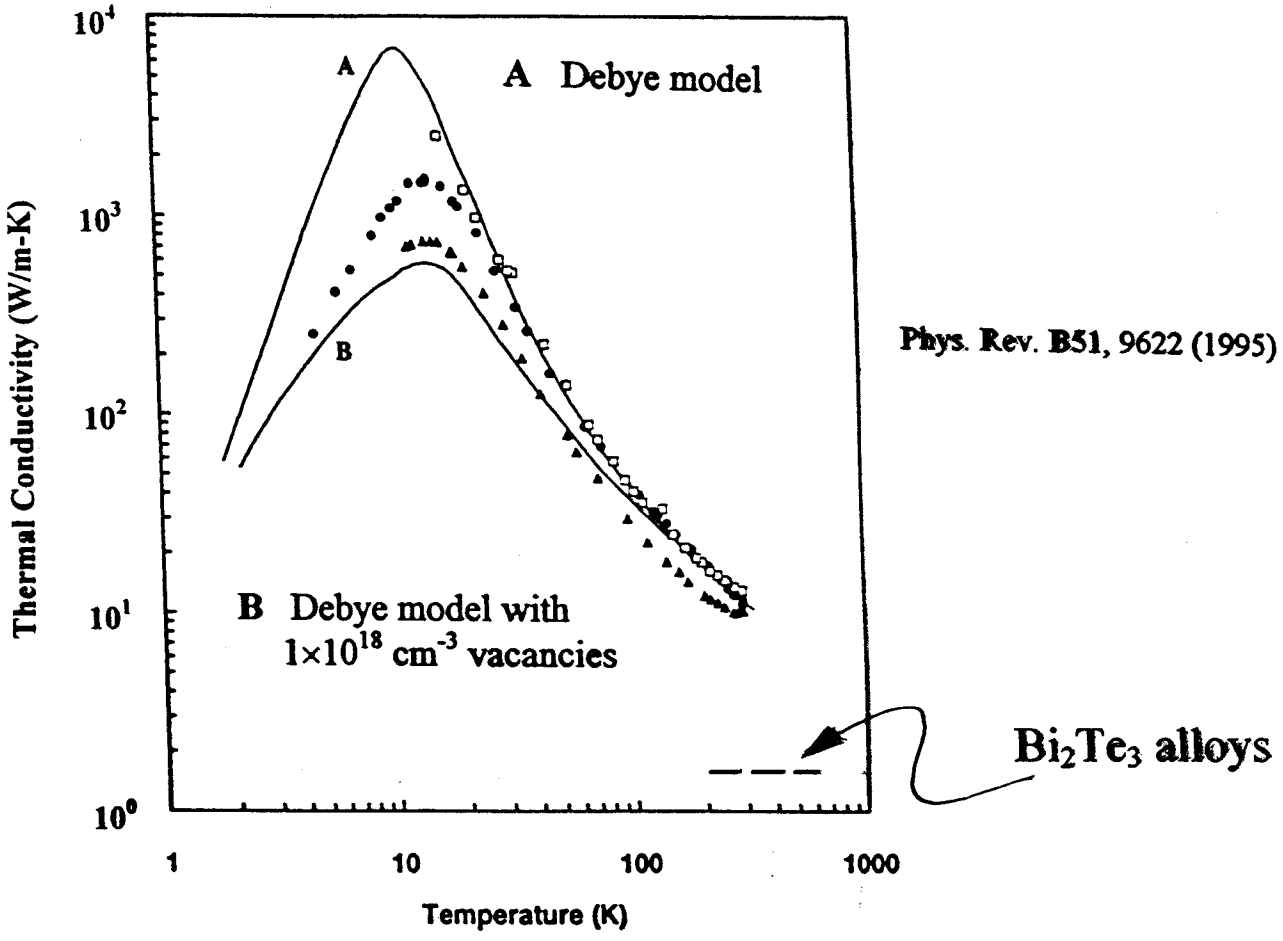
$$P \sim \mu\,(m^*)^{3/2}$$

$$\kappa_p \sim M^{-1/2} N^{-2/3}$$

Thus far, primary focus on $CoSb_3$

- $M_{Sb} > M_{As} > M_P \Rightarrow$ antimonides have lowest thermal conductivity.
- Antimonide skutterudites have the largest cage.
- Cobalt and antimony are inexpensive.
- Relatively easy to synthesize via a solid or liquid phase diffusion.
- Minimal hazard to people or environment.
- Other skutterudites, notably $IrSb_3$ and arsenides offer specific advantages, e.g., higher T_p.

Thermal Conductivity of $CoSb_3$



Phys. Rev. B51, 9622 (1995)

- Classic phonon heat conduction behavior.
- Strong exponential rise below 300K.
- Very high conductivity at low temperatures.
- Essentially no electronic contribution.

Crucial to reduce lattice conductivity by an order of magnitude!

Traditional ways of reducing thermal conductivity

Let phonons scatter on:

- charge carriers
- point defects (impurities)
- structural defects (grain boundaries)
- mixed-valency ions

Effective but not quite enough for skutterudites.

1994 – Slack: filler ions act as "rattlers":

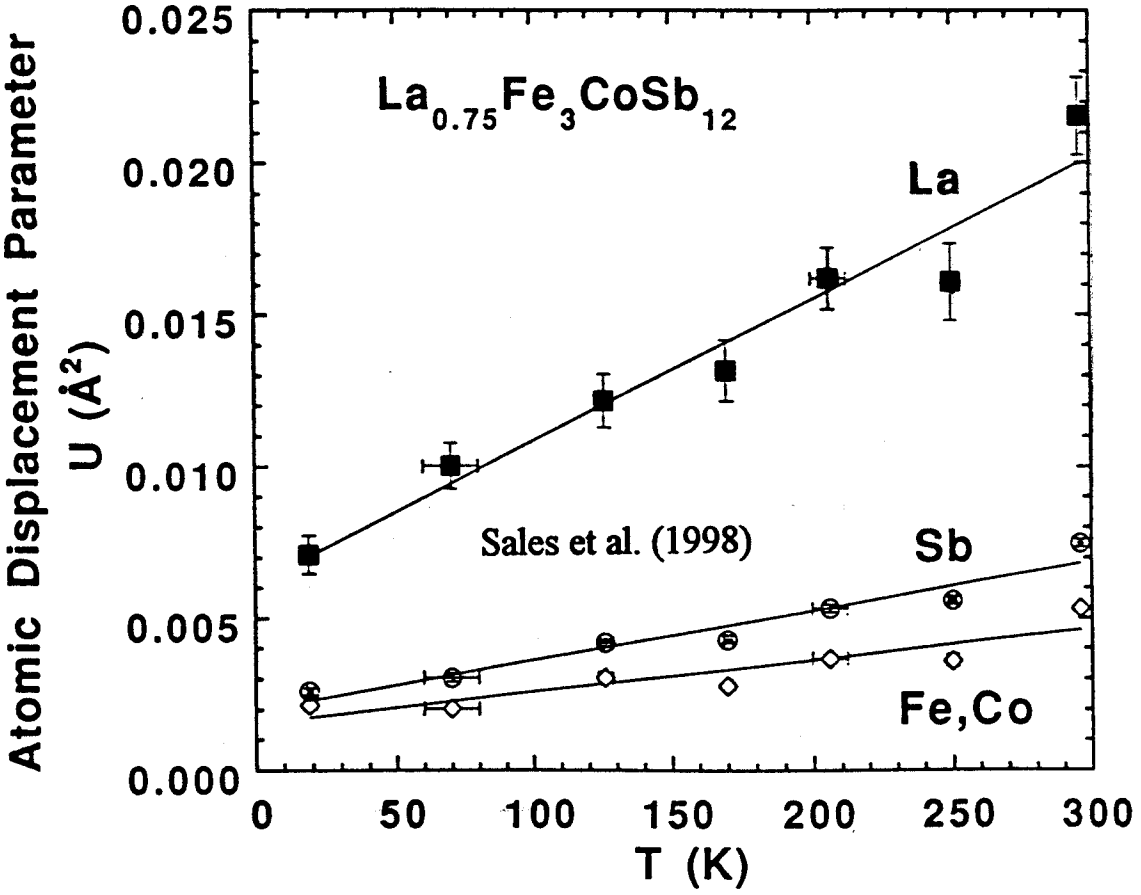
drastic reduction of κ_p & due to weak bonding

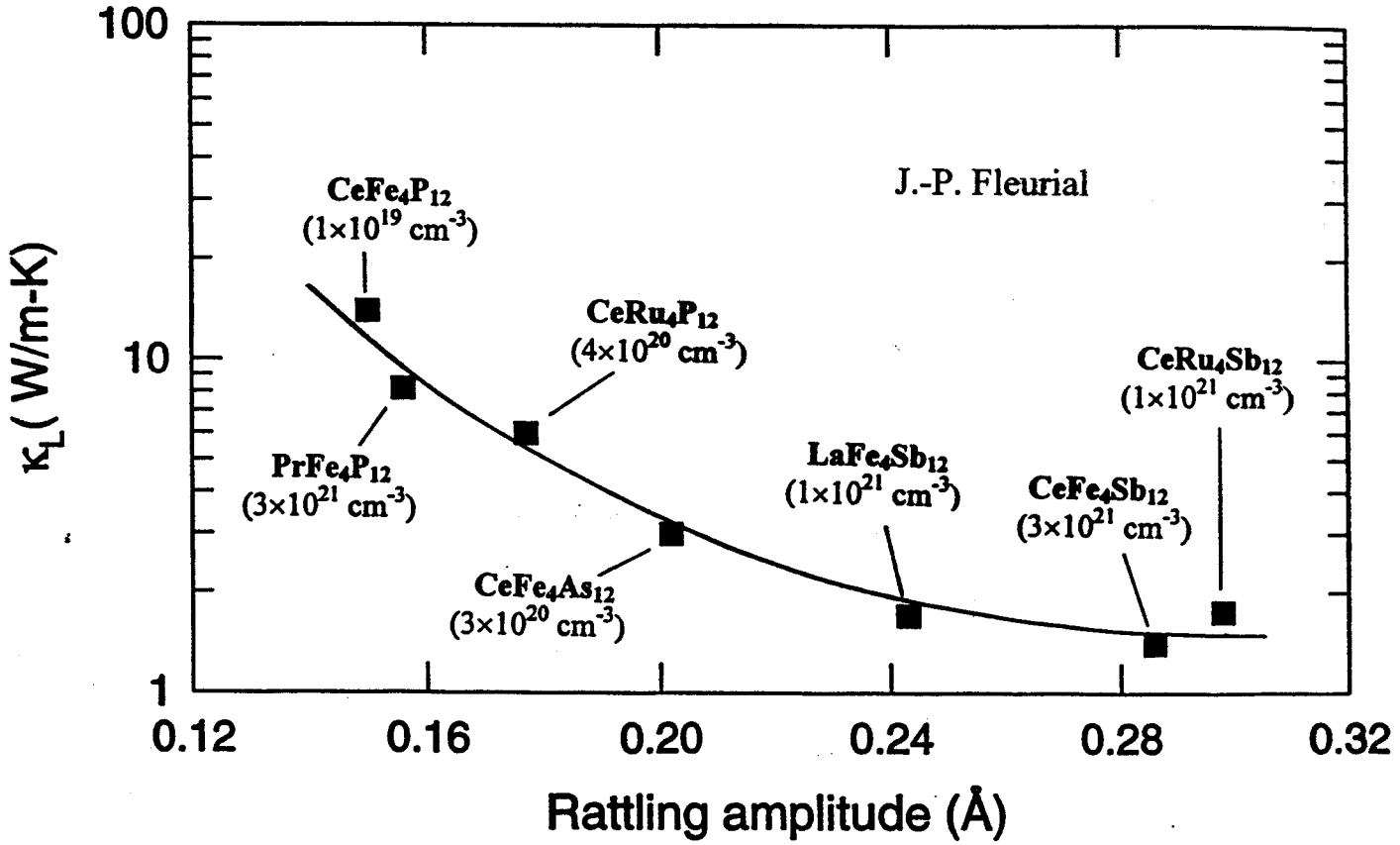
$\Downarrow$

filled skutterudites a **PGEC** system?

Low κ_p demonstrated by Morelli & Meisner (1995).

Evidence for Cage Rattling




100
10
1
0.12
0.16
0.20
0.24
0.28
0.32
κ_L (W/m-K)
Rattling amplitude (Å)
J.-P. Fleurial
$CeFe_4P_{12}$ (1×10^{19} cm^{-3})
$CeRu_4P_{12}$ (4×10^{20} cm^{-3})
$CeRu_4Sb_{12}$ (1×10^{21} cm^{-3})
$PrFe_4P_{12}$ (3×10^{21} cm^{-3})
$LaFe_4Sb_{12}$ (1×10^{21} cm^{-3})
$CeFe_4Sb_{12}$ (3×10^{21} cm^{-3})
$CeFe_4As_{12}$ (3×10^{20} cm^{-3})

Suitable filler species for skutterudites:

- rare-earths (Ce, La, Yb, ...)
- alkaline-earths (Ba, Ca, Sr)
- actinides (U, Th)
- elements (Tl, Sn)

Fillers do not enter as neutral atoms but donate electrons:

AE^{2+}
RE^{3+} (usually, with a few exceptions)
U^{4+}

The structure is rapidly saturated with negative charge

↓

Limits to void occupancy.

Occupancy limits:

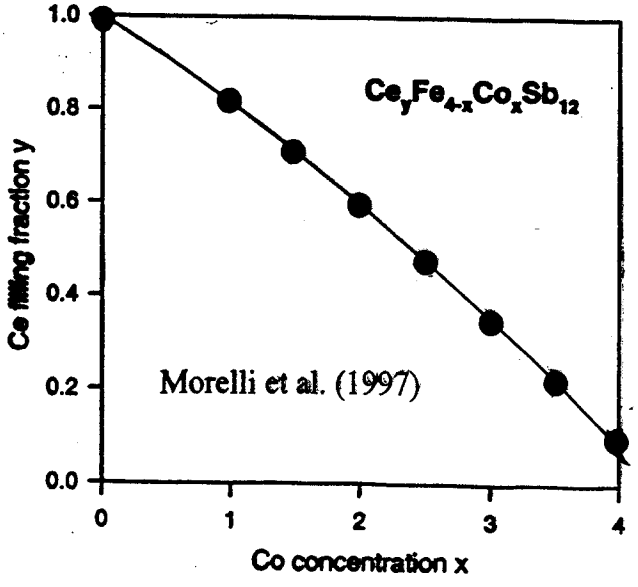
$Ce_yCo_4Sb_{12}$	$y_{max} \approx 0.1$	(Chen et al. 1997)
$Tl_yCo_4Sb_{12}$	$y_{max} \approx 0.22$	(Sales et al. 2000)
$La_yCo_4Sb_{12}$	$y_{max} \approx 0.23$	(Nolas et al. 1998)
$Yb_yCo_4Sb_{12}$	$y_{max} \approx 0.25$	(Anno et al. 2000)
$Ba_yCo_4Sb_{12}$	$y_{max} \approx 0.45$	(Chen et. al. 2001)
$Eu_yCo_4Sb_{12}$	$y_{max} \approx 0.54$	(Berger et al. 2001)

To increase void occupancy ⇔ charge compensate

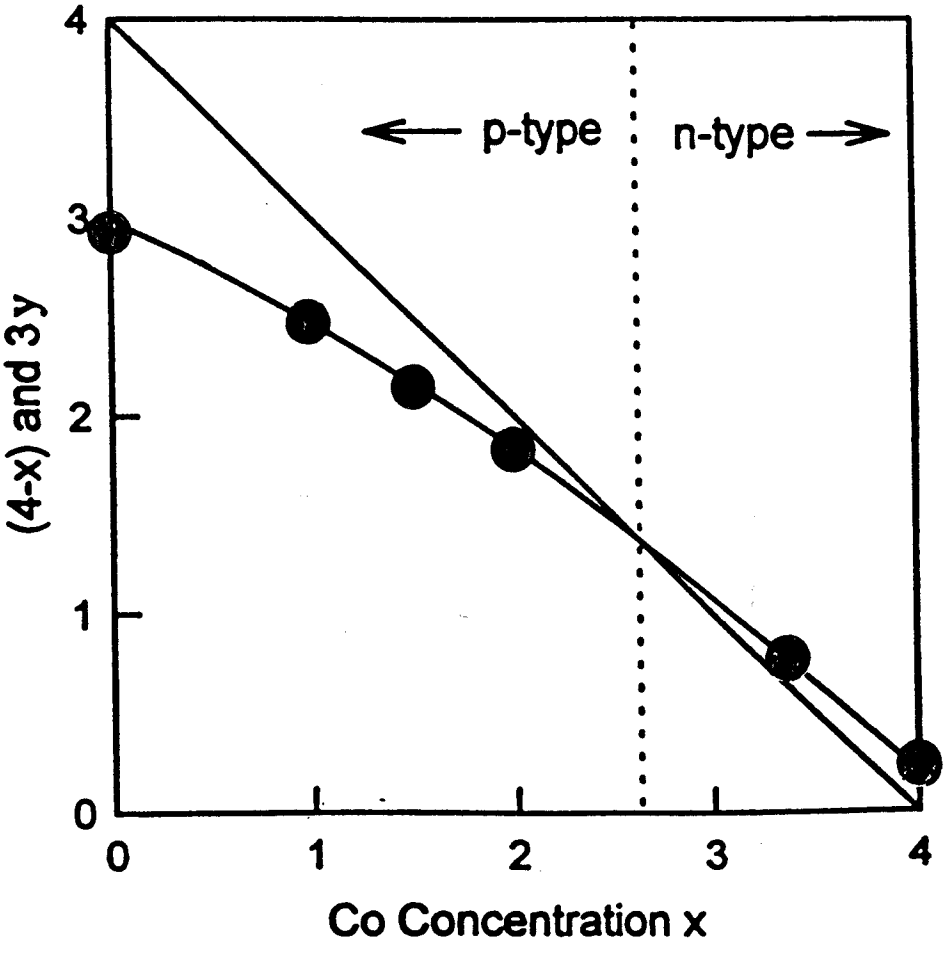
Fe^{26}
$2-8-14-2$
$3d^6 4s^2$

Co^{27}
$2-8-15-2$
$3d^7 4s^2$

$Ce_yFe_{4-x}Co_xSb_{12}$
$La_yFe_{4-x}Co_xSb_{12}$



$Ce_yFe_{4-x}Co_xSb_{12}$

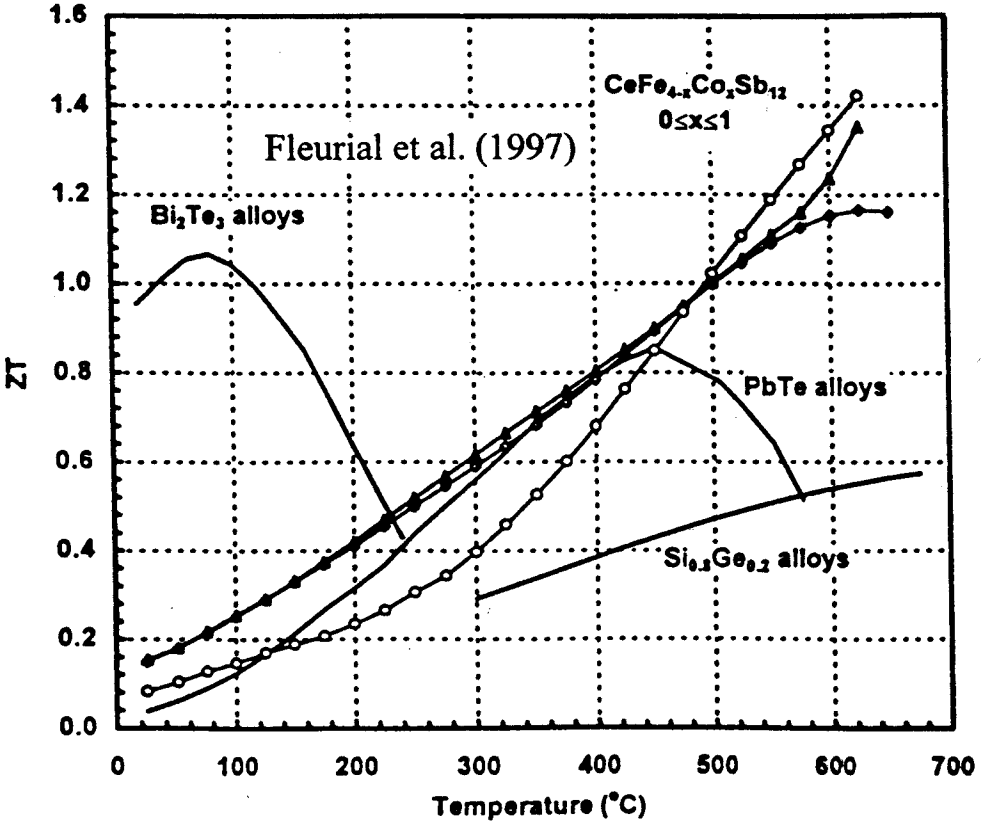


Similar phase diagrams describe other filler species.

Low κ_p & good electronic properties of

$$RFe_{4-x}Co_xSb_{12} \qquad x \leq 1$$

- exceptionally high ZT values
- p-type thermoelectric
- operational range 700K – 1000K



Can high ZT be achieved with n-type skutterudites?

Difficulties:

- Compensation drives the system p-type.
- Cage occupancy for R^{3+} ions is very limited.
- Smaller and heavier rare earths (Ho, Lu) do not go in.

Remedies:

- Try innovative synthesis/fabrication approaches.
- Explore rare earths with intermediate valence (Eu, Yb).
- Look beyond rare earth ions.

● Looking beyond Rare-Earth ions

$Tl_yCo_4Sb_{12}$ (Sales et al., 2000) $y_{max} \approx 0.22$

$ZT \approx 0.75$ near 750 K

$Ba_yCo_4Sb_{12}$ (Collaboration: U of Michigan
Tohoku University
Shanghai Inst. Ceramics)

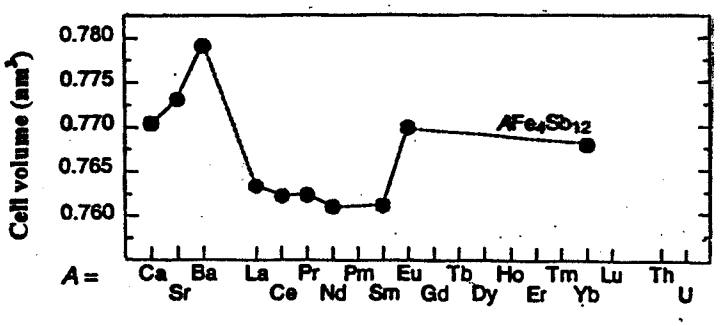
Ba is strictly a divalent ion.

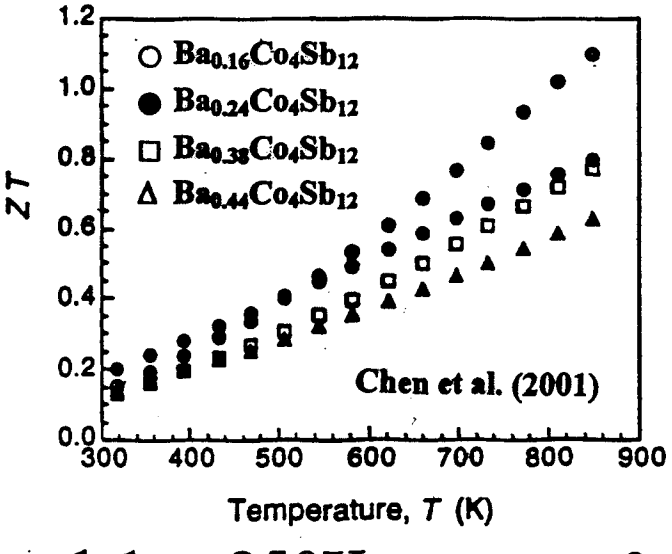
Large void occupancy up to $y \approx 0.45$.

Even larger occupancy if charge compensated by Fe.

Ba^{2+} is a large ion.

No intermediate valence state.





Best $ZT \approx 1.1$ at 850K near $y = 0.2$-0.3.

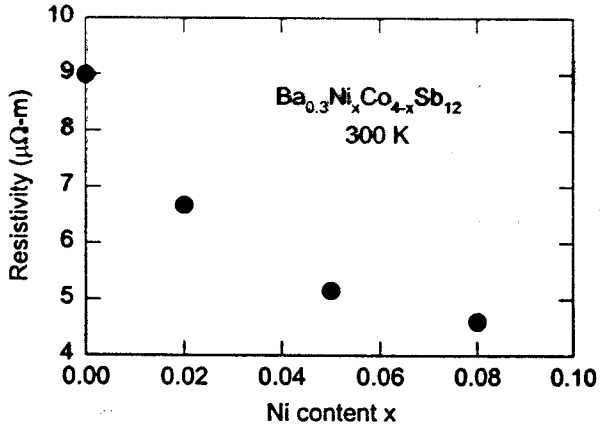
An improvement of $Ba_yCo_4Sb_{12}$ by Ni doping

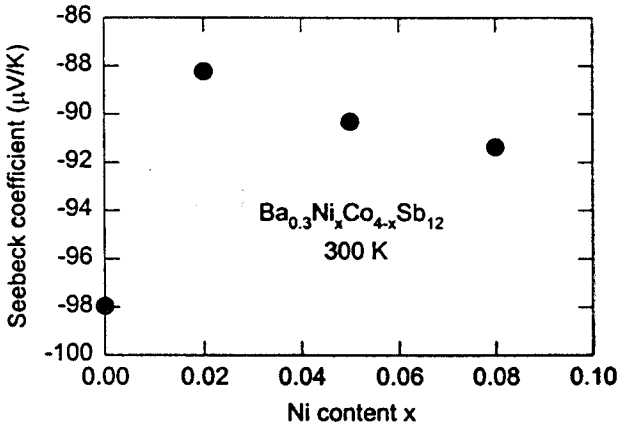
(Dyck et al., JAP (2002))

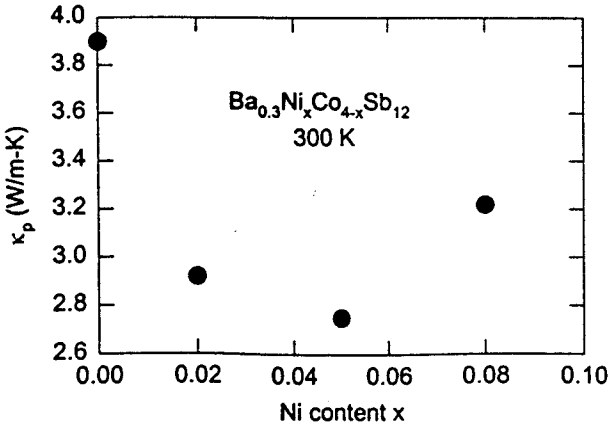
Small amount of Ni improves $CoSb_3$ (Uher et al. (2000)).

Ni donates an electron to the conduction band (Ni^{4+});
lowers electrical resistivity;
reduces lattice thermal conductivity;
increases effective mass ⇒ keeps Seebeck large.

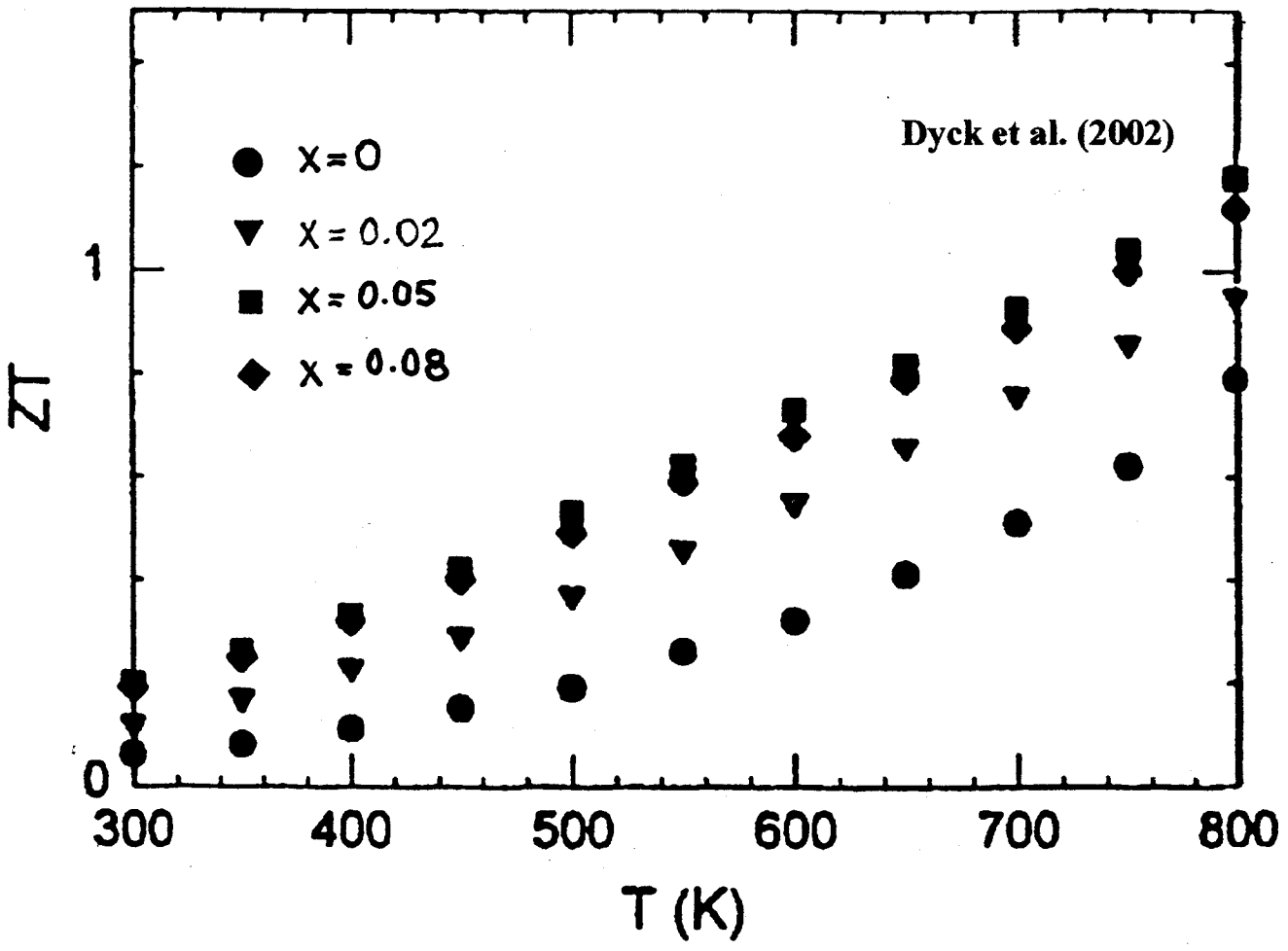
Would this work also for $Ba_yCo_4Sb_{12}$?
$Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$ with $0 \leq x \leq 0.1$







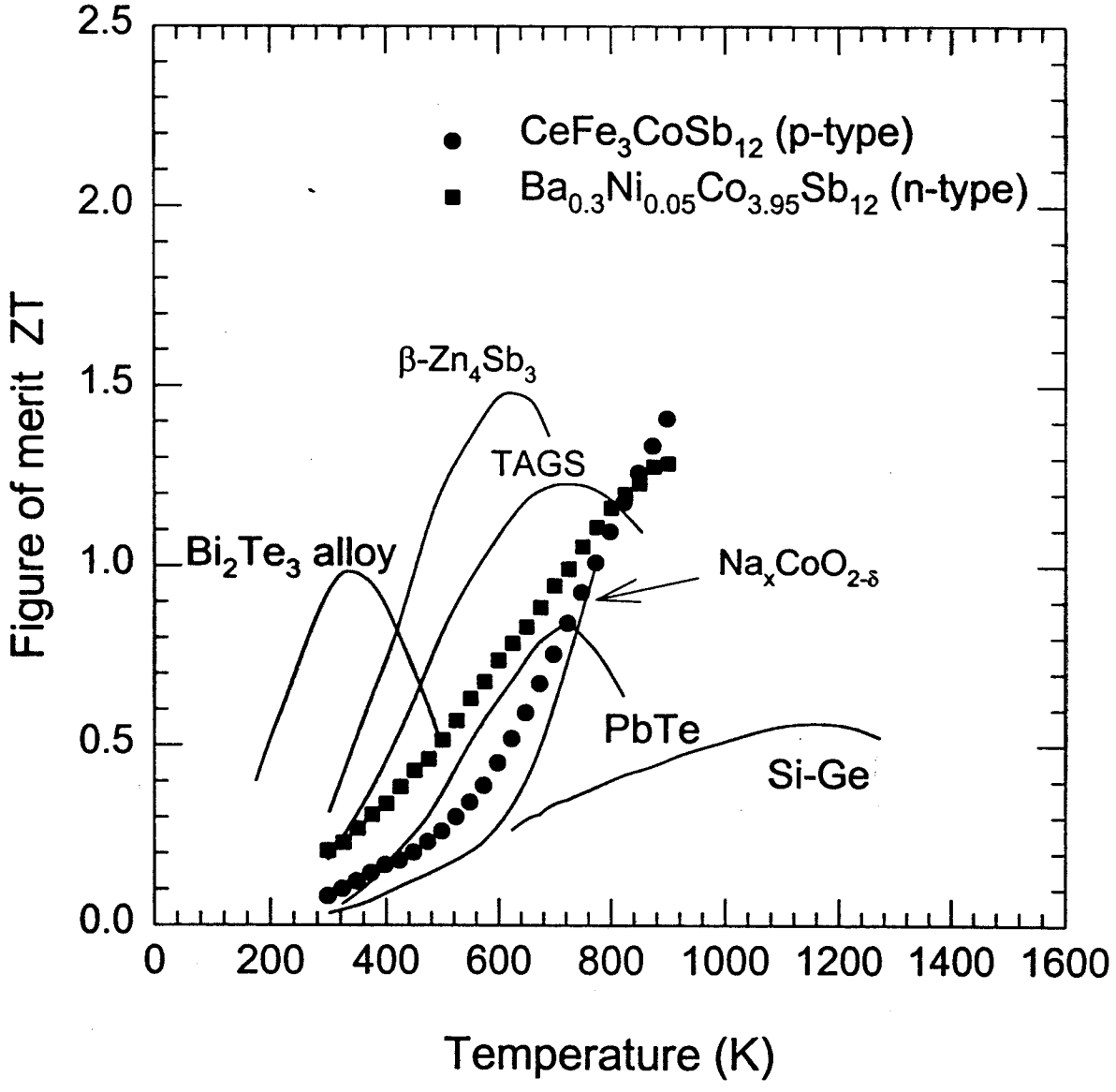
$Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$



ZT > 1 for x = 0.05 and x = 0.08 above 750K.

ZT = 1.2 for x = 0.05 at 800K.

Alkaline earths–based n-type skutterudites are very promising.


2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
Figure of merit ZT
Temperature (K)
CeFe3CoSb12 (p-type)
Ba0.3Ni0.05Co3.95Sb12 (n-type)
β-Zn4Sb3
TAGS
Bi2Te3 alloy
NaxCoO2-δ
PbTe
Si-Ge

SOLID SOLUTIONS OF FILLED SKUTTERUDITES

Most of the successful thermoelectrics are solid solutions

Maximize point defect scattering ⇒ small κ_L
Alter the cage size ⇒ broader range of filler species
Enhance T_p ⇒ wider operational range

Apply the concept to filled skutterudites

$$R_yCo_4(Sb_{1-x}As_x)_{12}$$
$$R_y(Co_{1-x}Ir_x)_4Sb_{12}$$

Critical issues: range of solid solubility
miscibility gaps exist
so far successful for $x \leq 0.1$

Currently filling solid solutions with Ce and Ba.

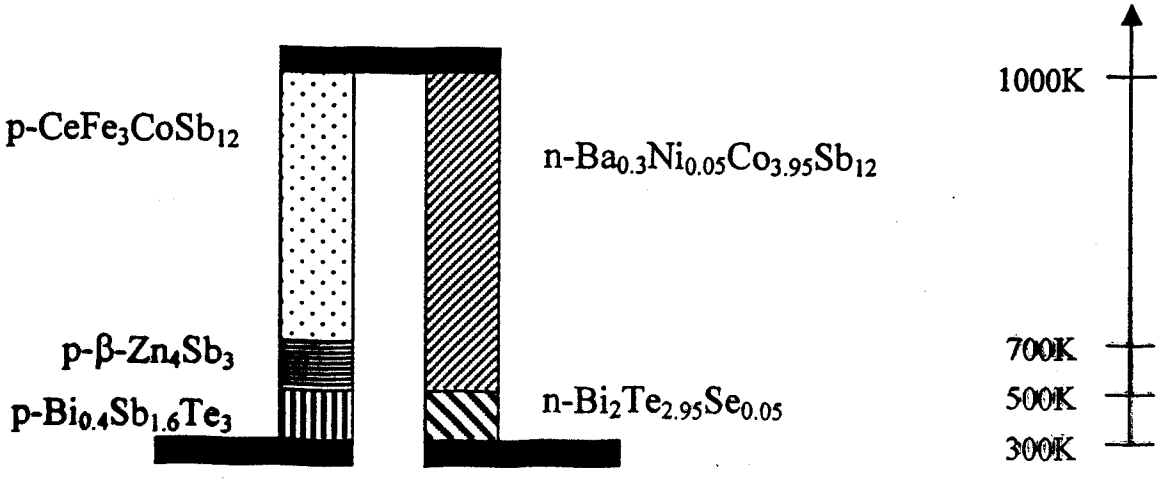
Integral part of the project:
high temperature property measurements facility

i. electrical resistivity and Seebeck apparatus to 1000 °C
ii. Flashline 5000 thermal diffusivity to 1500 °C
iii. Air-bore, 3" dia., 9 T superconducting magnet for Hall

Excellent, university-based high temperature transport characterization facility.

Summary

- Both p- and n-type filled skutterudites with ZT > 1 available.
- Operational range 700K – 1000K, the best bulk thermoelectrics.
- Most of the work focused on the cobalt triantimonide matrix.
- Great prospects for further improvement leading to:
  - enhanced ZT,
  - expanded operational range.
- We have barely scratched the surface of the problem.
- Several promising approaches still unexplored:
  - multiple filling,
  - doping studies,
  - nanostructure-size matrix
  - solid solution of filled skutterudites
- Filled skutterudites already used in segmented unicouples.



Skutterudites are for real!