Low-Cost and Non-Toxic Zn-Sb Zintl Compounds for Thermoelectrics

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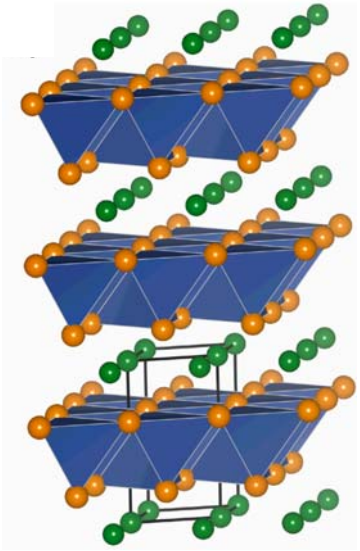

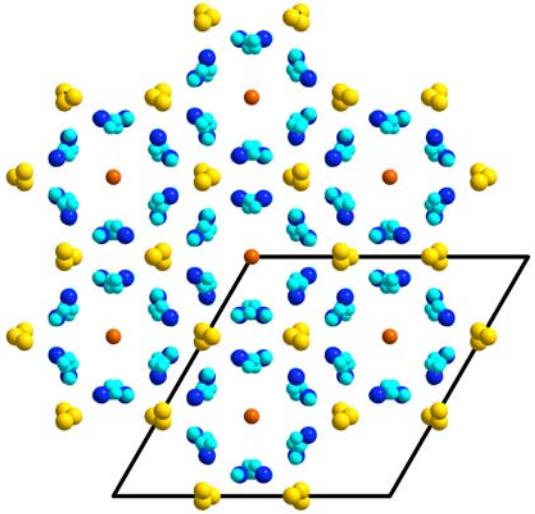

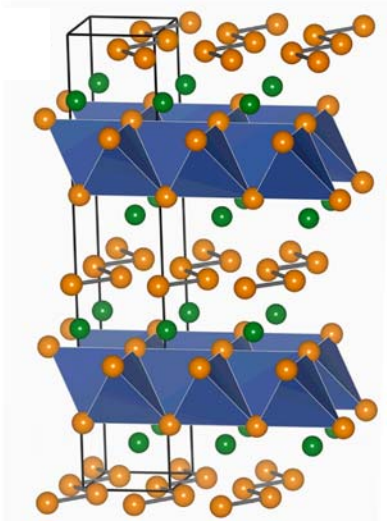

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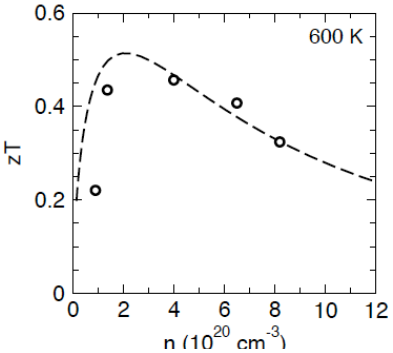
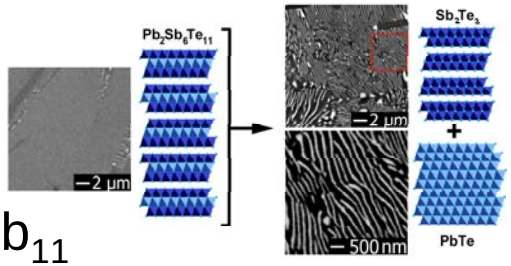
Snyder et. al. ***Nature Materials, 7***, p. 105, (2008)

Caltech Thermoelectrics

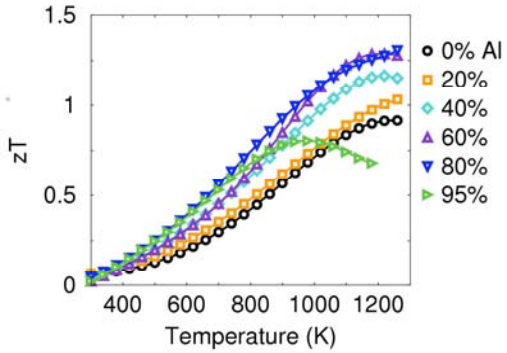
2009 Group BBQ



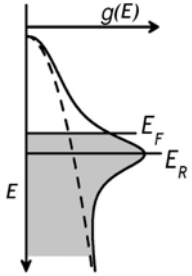
Clathrates



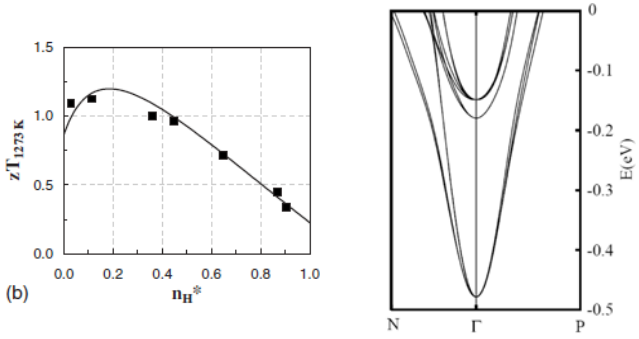
Nanostructures



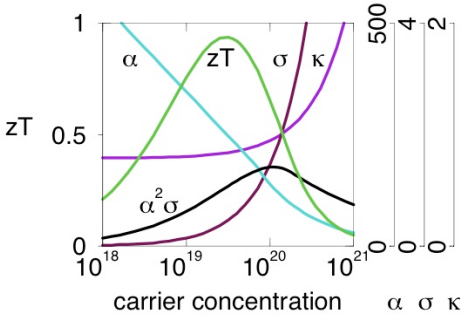
$Yb_{14}MnSb_{11}$
Zintl compounds



PbTe:Tl
Resonant states



La_3Te_4



Review Articles

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Zinc and Antimony

Low Cost

Iron < $1/kg

Zinc $2/kg

Silicon $2/kg

Aluminum $2/kg

Lead $2/kg

Magnesium $3/kg

Ca, Sr, Ba < $5/kg

Cadmium $5/kg

Antimony $6/kg

Copper $6/kg

Ce, La $8/kg

Tin $15/kg

Cobalt $40/kg

Selenium $50/kg

Lithium $70/kg

Tellurium $140/kg

Indium $500/kg

Gallium $500/kg

Germanium $1000/kg

Non Toxic

Both elements used as flame retardants in consumer products

- Antimony Oxide Sb_2O_3
- Zinc Oxide Borate

  $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$

Both used as synergistic co-additives in combination with halogen compounds

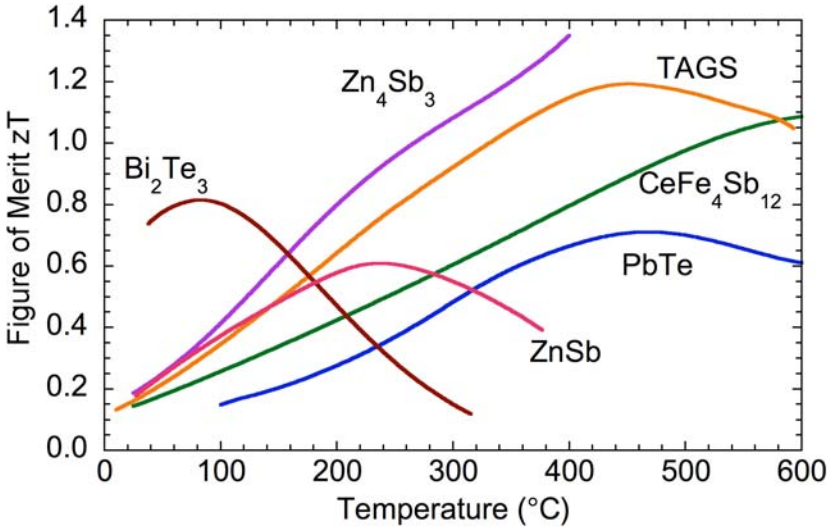
- most concern over polybrominated biphenyl

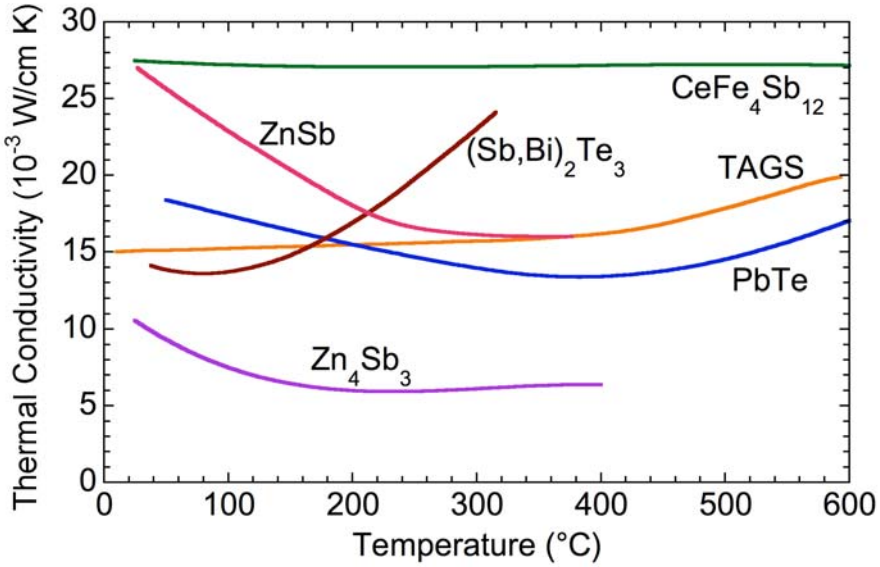
http://www.inchem.org/documents/ehc/ehc/ehc192.htm

High zT Zn_4Sb_3

Zn_4Sb_3
Highest TE Figure of Merit

Because of exceptionally low thermal conductivity





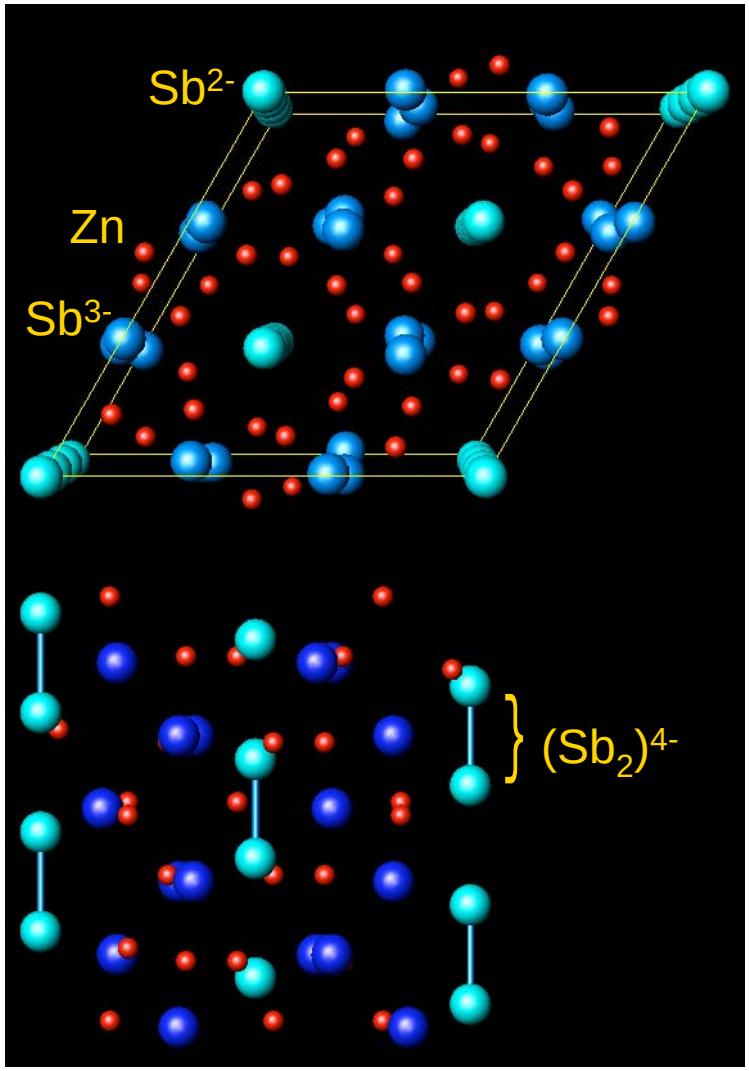
Crystal structure should explain thermal properties

- complex crystal structure, disorder, grain structure, composite microstructure ?

Crystal structure should explain electronic properties

- Valence compound from Zintl chemistry

Zn_4Sb_3 Core Structure



Contains two types of Sb

- Single Bonded Sb^{2-} dimers (1.2/f.u.)
- Isolated Sb^{3-}(1.8/f.u.)
- Valence balance: $Zn_{3.9}Sb_3$ (Zn^{2+})

One Zn site

- 4Sb + 1Zn coordination
- Will only fit $Zn_{3.6}Sb_3$

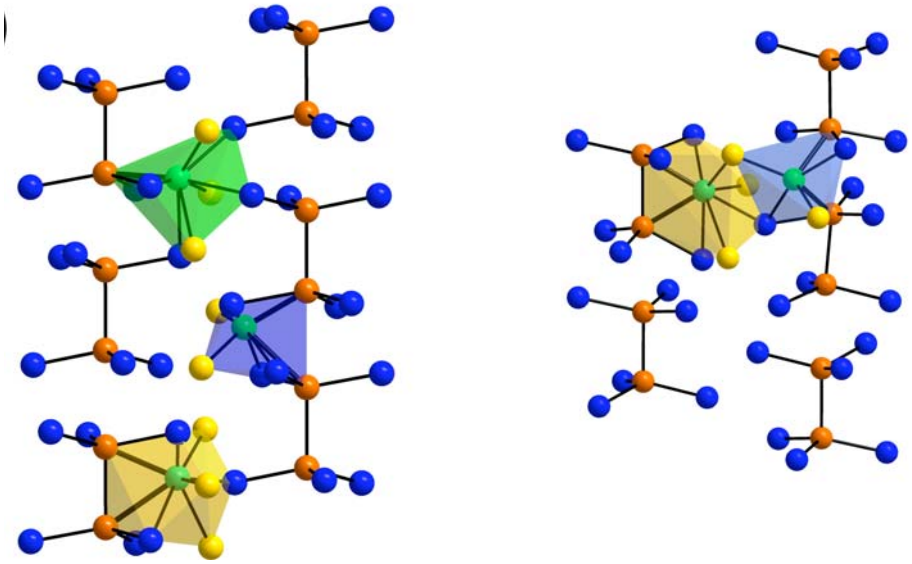
Where is extra Zinc?

- Chemical analysis: $Zn_{3.95(5)}Sb_3$
- p-type Semi. Con: $Zn_{3.9-\delta}Sb_3$

Interstitial Zn in Zn_4Sb_3

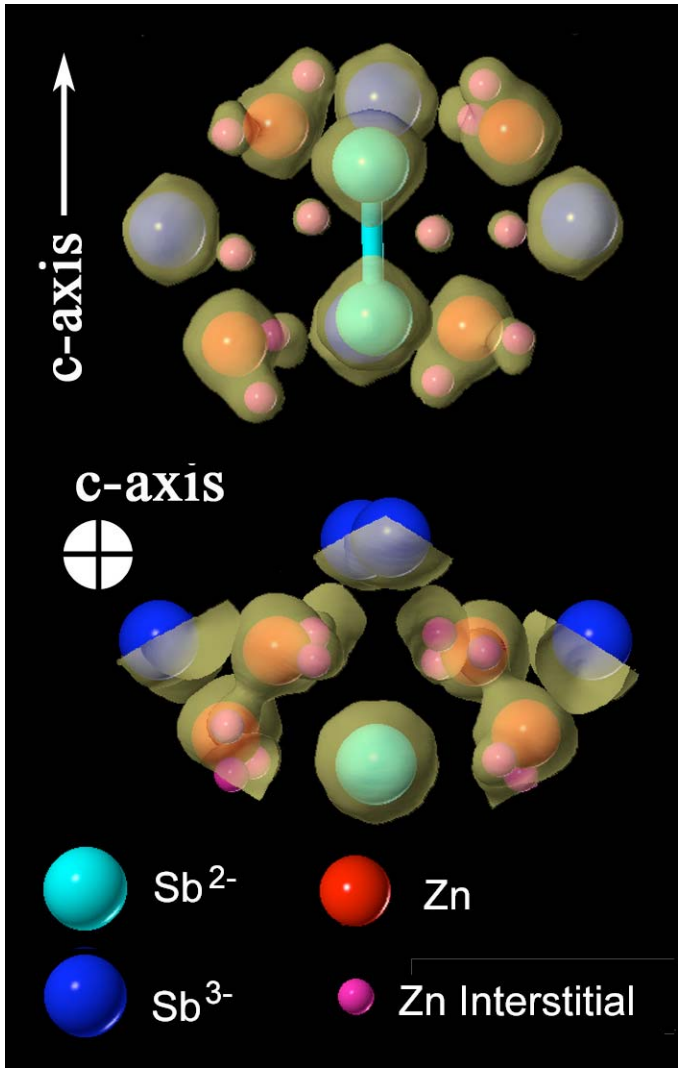
Zn interstitial sites

- Three unequivocal regions of excess electron density in XRD
  - Maximum Entropy Method & Bader Topological Analysis
- Coupled to vacancy on primary Zn site (10% vacancies)
- 20% of Zn is interstitial
- Many configurations, sites may be possible



3 interstitial types (300K) **Coupled interstitials (100K)**

Toberer et al. *Phys. Stat. Sol.-RRL* **3,** 458 (2004)
Boström, et al. *J. Alloys Compounds*, **376**, 49 (2004)



Snyder et al. *Nature Materials* **3,** 458 (2004)
Chem. Eur. **10** 3862 (2004)

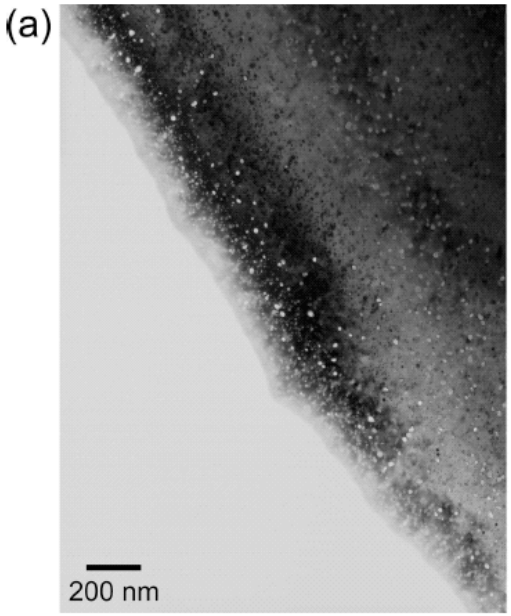
Nanoparticles discovered in Zn_4Sb_3

10-20nm Zn particles found in Zn_4Sb_3

- likely to be an additional mechanism for reduced thermal conductivity in Zn_4Sb_3

Must be due to a phase instability: likely a (coherent) solid-solid precipitation

- Unknown orientation relationship of Zn particles in Zn_4Sb_3



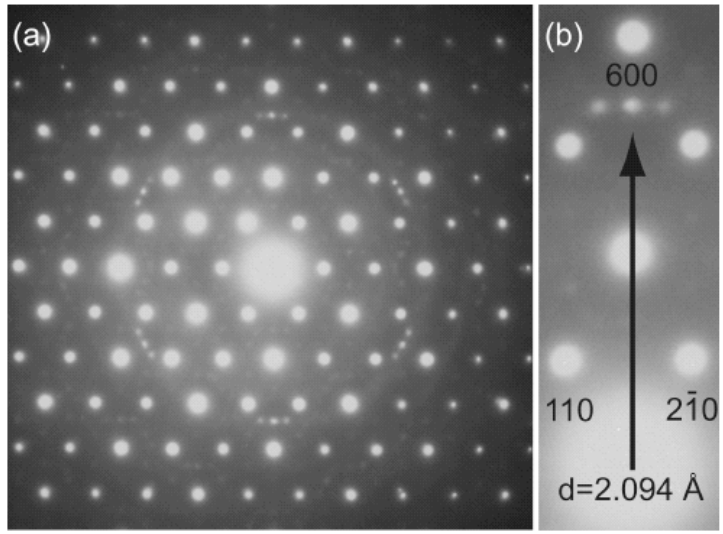
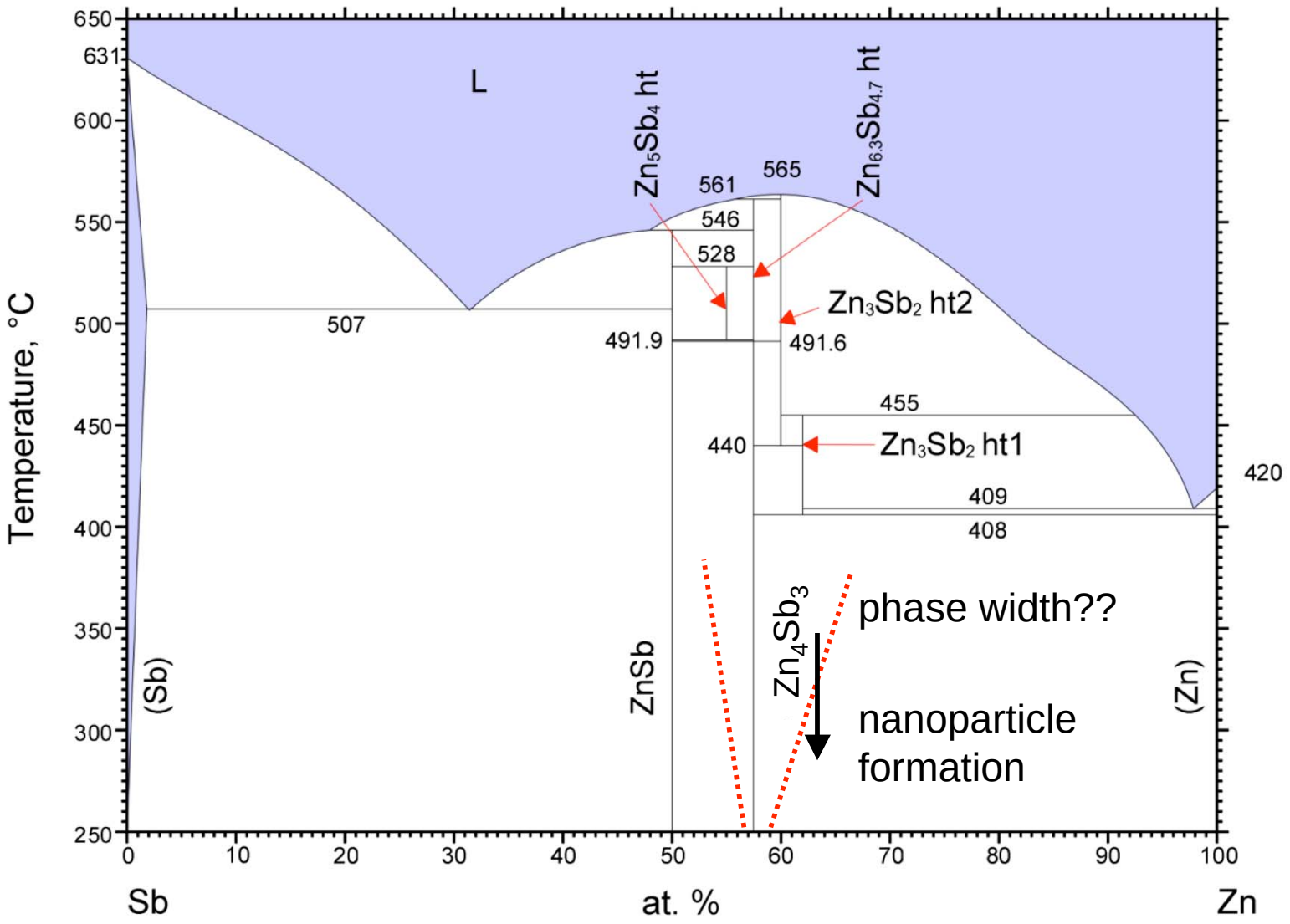


FIG. 3: (a)Selected area diffraction pattern taken with a long exposure time in the [001] projection of the Zn_4Sb_3 phase.

Prytz, et al, *Philosophical Magazine Letters*, **V 89**, p362 (2009)

Zn-Sb Phase Diagram



Lattice Thermal Conductivity in Zn_4Sb_3

Mechanisms for low κ_l in Zn_4Sb_3

1. Large Unit Cell

   κ_l ~ 1/Primitive cell 309 Å^3

   Low Temp α-Zn_4Sb_3 cell 2135 Å^3

2. local distortion microstructure

   (~10Å)

   Kim, et al, *Phys. Rev. B*, **75**, 134103 (2007)

3. Interstitial disorder (point defect)

   Toberer, *Phys. Stat. Sol.-RRL* **3,** 458 (2004)

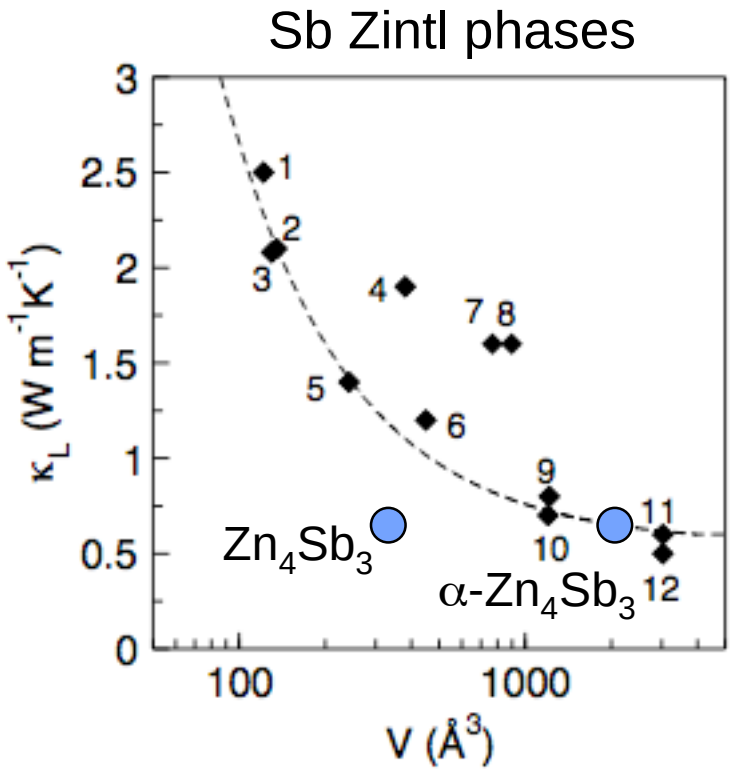
4. Interstitial motion

   liquid like diffusivity

   Chaflin, *Sol. State Ionics*, **178**, 447 (2007)

5. Nanoparticles

   Prytz, et al, *Phil. Mag. Lett.*, **89**, p362 (2009)



These also complicate stability, lifetime during use.

Require better understanding before commercialization

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Caillat, *J. Phys. Chem. Sol.*, **58**, 1119 (1997)

Substructure Approach to TE

Separate *Phonon Glass* from *Electron Crystal*

Use complexity to disrupt phonons more than electrons

- length scale: e- mean-fee-path < phonon mean-free-path
- chemistry: minimize disruption of atoms contributing to bands at E_f
- physics: mass (vs. bonding) complexity has more impact on phonons than e^-

Zintl Phases

Valence Balance provides band gap

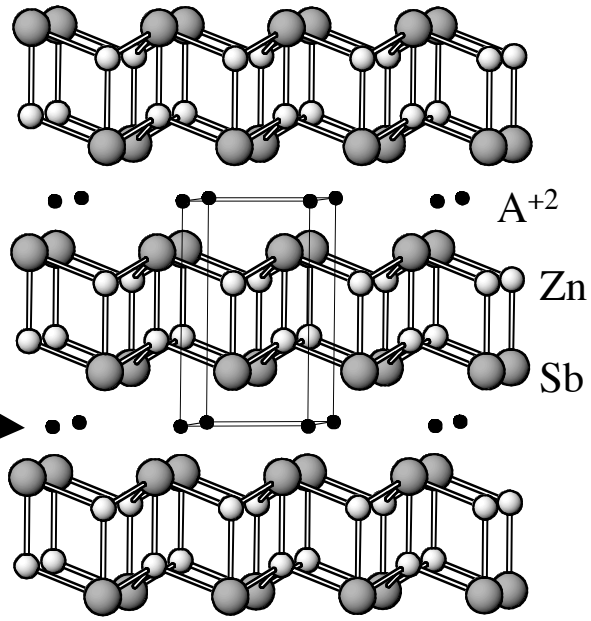
- e.g. $Ca^{+2}_{x}Yb^{+2}_{1-x}Zn^{+2}_{2}Sb^{-3}_{2}$

Distinct Anionic & Cationic regions

- Anionic framework
  - Center for electron transport

  Electron crystal
- Cations
  - Site for dopants - control carrier conc.
  - Provide opportunity for disorder
  - Packing Arrangement complicated for large cell

  Phonon Glass



Ternary A-Zn-Sb

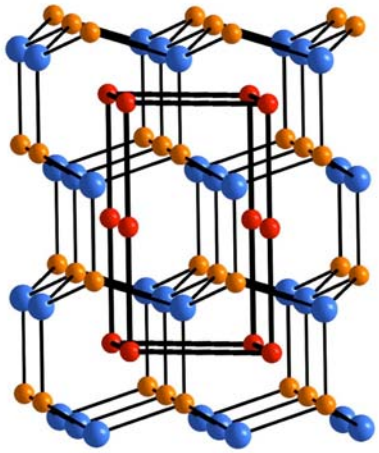
Many A-Zn-Sb phases considered

- Typically p-type

Sensitivity to air increases with

- reactivity of A
- content of A

LiZnSb
Predicted high zT
for n-type



Compound	Seebeck (300K)
$CaZn_2Sb_2$	+120
$SrZn_2Sb_2$	+125
$BaZn_2Sb_2$	+125
$YbZn_2Sb_2$	+48
$EuZn_2Sb_2$	+120
$SrZnSb_2$	+30
LiZnSb	+50
KZnSb	? too reactive
$Ca_9Zn_{4.5}Sb_9$	?
$Yb_{14}ZnSb_{11}$	+30

Toberer *Dalton Trans*, in press (2009)
Gascoin, *Adv. Funct. Mat.* **15,** 1860 (2005)
Wang, *APL*, **90**, 232107 (2007)
Toberer *JAP*, **105**, 063701, (2009)
May *JAP*, **106**, 013706, (2009)

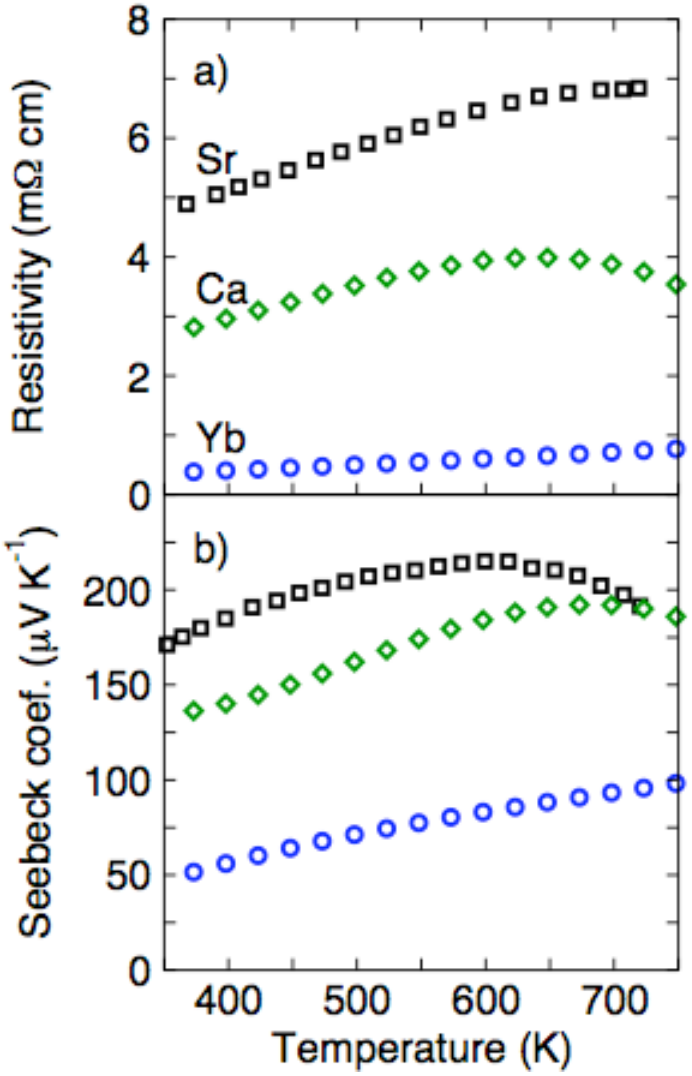
$A^{+2}Zn_2Sb_2$

$A^{+2}Zn_2Sb_2$ Phases

- Same nominal electron count
  - Sr^{+2}, Ca^{+2}, Yb^{+2}, Eu^{+2}
- Metallic to Semiconducting
- High Thermopower
- Promising thermoelectrics
  - Peak zT 0.5 to ~1 (Eu, Yb-Cd)

Why are properties different ?

- Band Gap
- Band Structure (effective mass)
- Mobility
- **Carrier Concentration**



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Gascoin et. al. ***Adv. Funct. Mat., 15***, p. 1860, (2005)

$A^{+2}Zn_2Sb_2$ Band Structure

$A^{+2}Zn_2Sb_2$ DFT calculations

Valence band (holes)

- mostly Sb character
- similar effective mass

Similar band gap

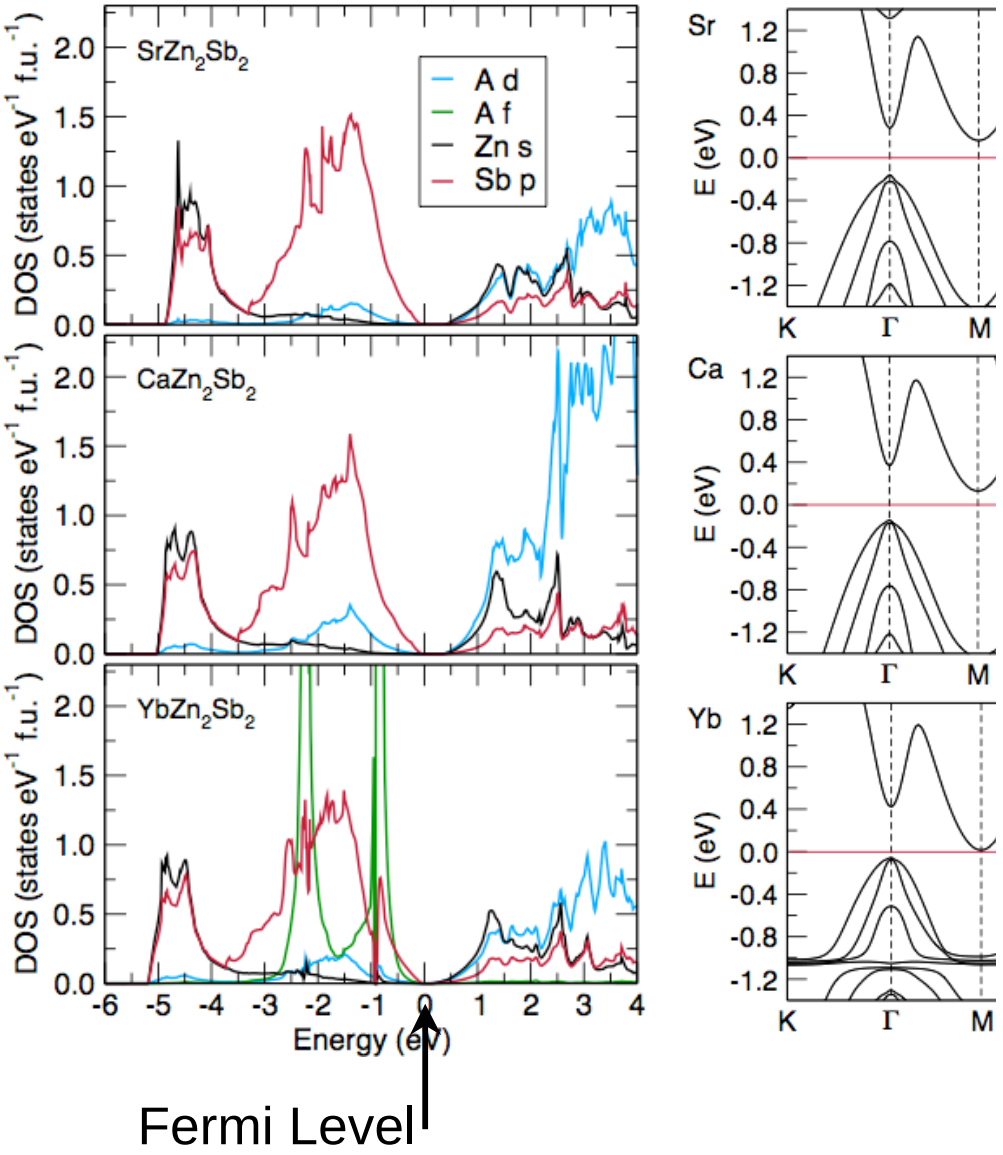
- Ca, Sr

Predict similar transport

- A^{+2} influences conduction band (e^-)

Fermi Level at valence band edge

- No intrinsic holes (0K)
- A^{+2} does not change total number of valence states



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$A^{+2}Zn_2Sb_2$ Carrier Concentration

Transport properties of $A^{+2}Zn_2Sb_2$

Trend with Carrier Concentration

- Carrier (hole) conc. from n_H

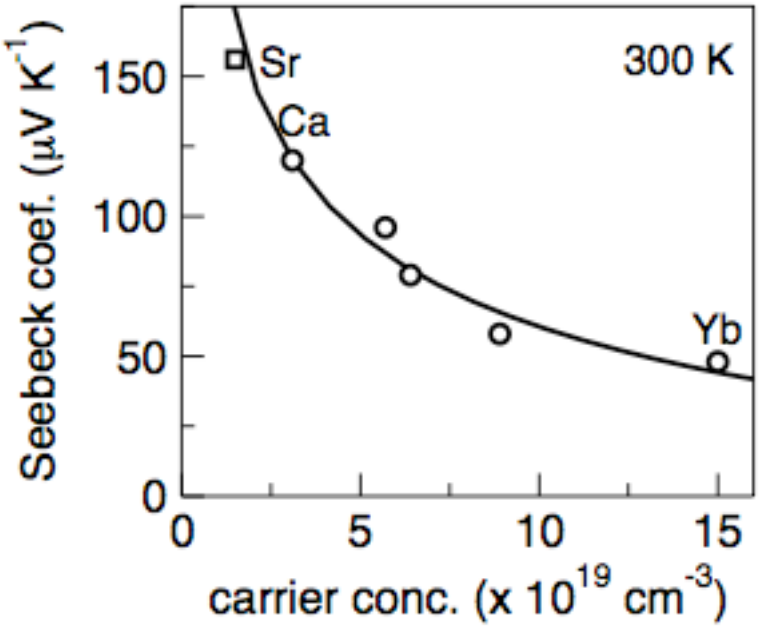
Seebeck Coefficient

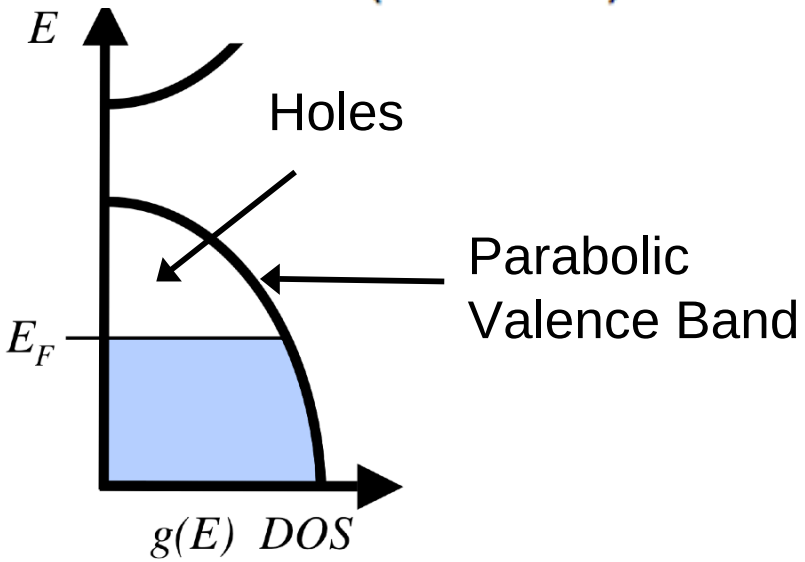
$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

For common band approx

Parabolic bands

- constant effect mass $m^* = 0.6\, m_e$
- Itinerant conductors
  - degenerate *eq*. shown above
- Band Gap $E_g = 0.3$ eV





Toberer, *Dalton Trans.* in press (2009)

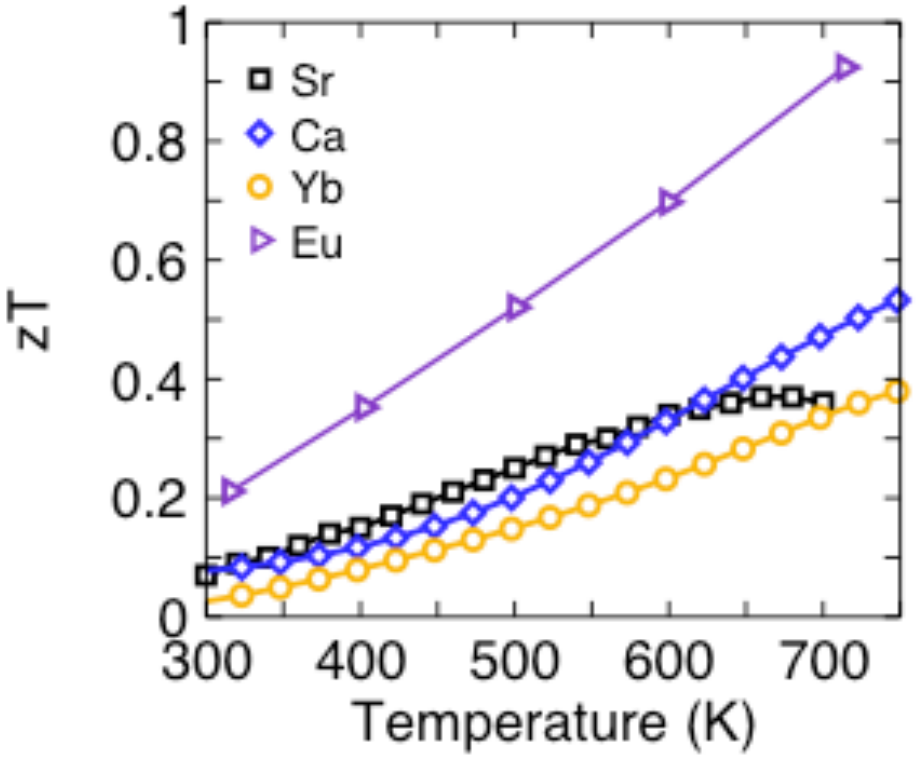
Gascoin et. al. *Adv. Funct. Mat.*, ***15***, p. 1860, (2005)

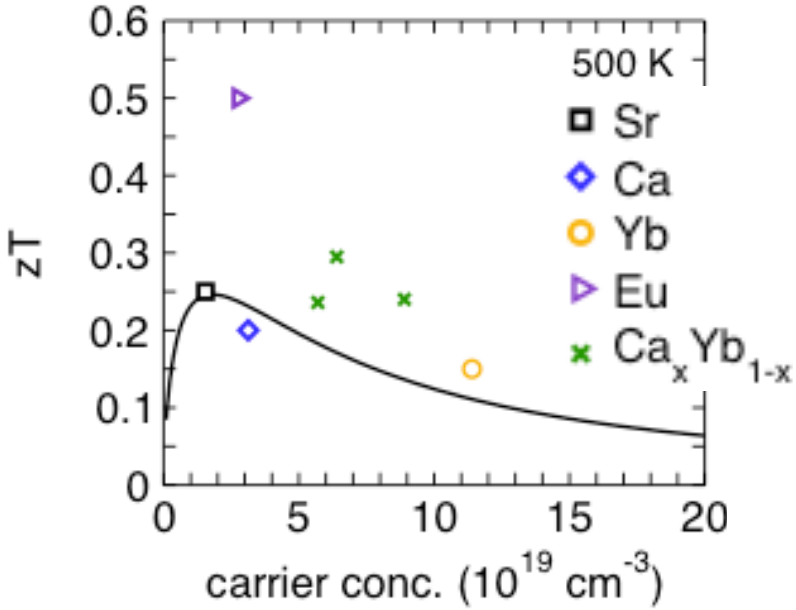
$A^{+2}Zn_2Sb_2$ zT

Tuning n changes transport properties; Sr, Ca, Eu near peak zT

$EuZn_2Sb_2$ high $zT \sim 1$. (due to mobility)

Lattice thermal conductivity should be reduced for higher zT





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Gascoin et. al. ***Adv. Funct. Mat., 15***, p. 1860, (2005)

Zhang et. al. ***J. Chem. Phys., 129***, p. 164713, (2008)

Mass contrast

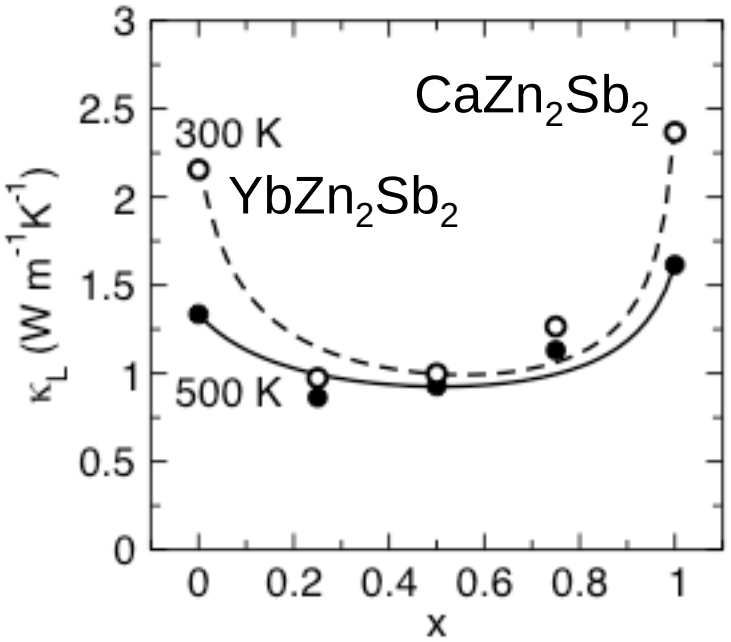
Mass contrast to lower the lattice thermal conductivity.

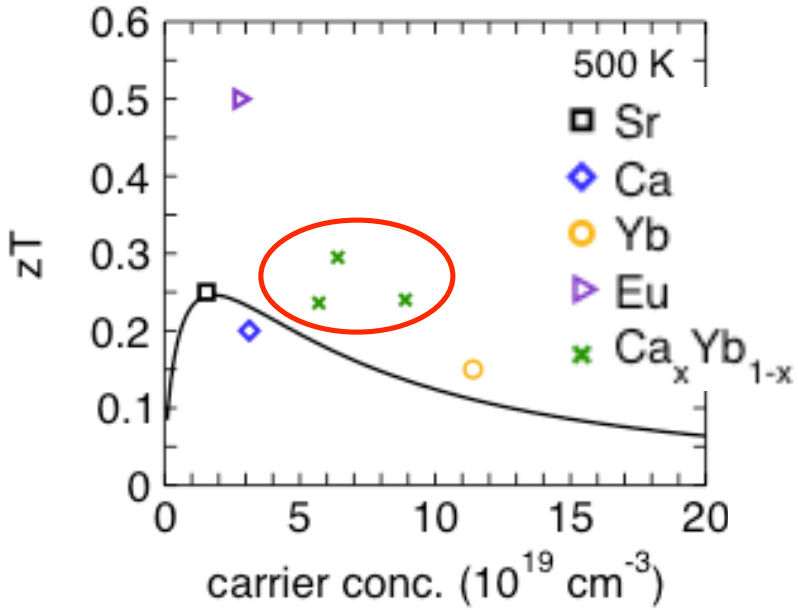
Example: $Ca_xYb_{1-x}Zn_2Sb_2$ isoelectronic solid solution

Curves predicted from mass contrast and end member properties

(κ_L, θ_D, v)

At high T, acoustic phonon scattering reduces effect

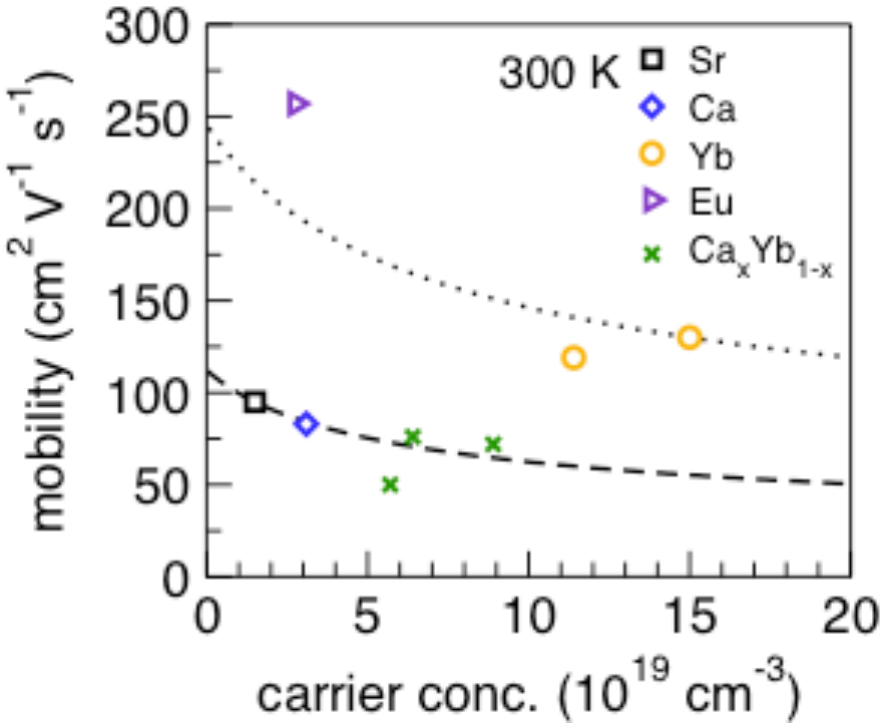




Mobility

Despite constant m^*, intrinsic mobility significantly higher for A = Eu, Yb

- Rare earth f levels - Yb, Eu
  - new mechanism for enhanced mobility?
- microstructure ? - grain boundaries, alignment

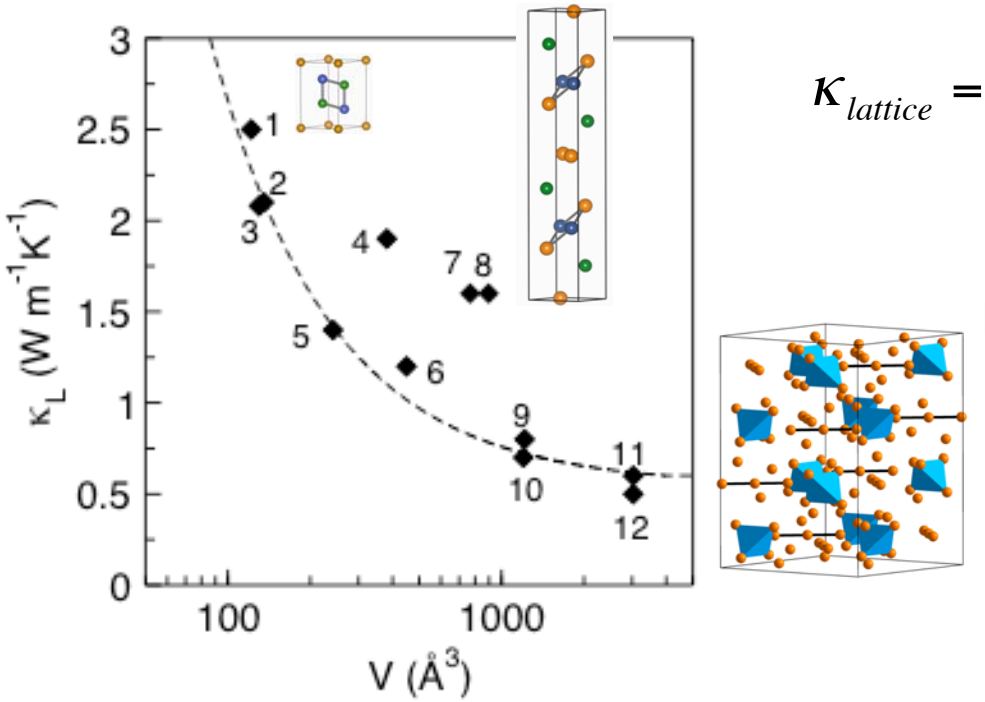


Cell Volume Trend in κ-lattice

Where to look for new high *zT* compounds?

- unit cell volume (V)

Primitive unit cell volume (V)
good indicator for
lattice thermal conductivity



$$\kappa_{lattice} = \frac{1}{3} C v l$$

C - heat capacity
v - speed of sound
l - phonon mean free path

If only acoustic modes contribute:

3 acoustic modes out of 3N in cell

V = Cell Volume

$$C_{ac} = 3k_B/V$$

$$\kappa_l = v l k_B / V$$

Dashed line: $V^{-1} + \kappa_{min}$

1 - LiZnSb
2 - $SrZn_2Sb_2$
3 - Mg_3Sb_2
4 $CeFe_4Sb_{12}$
5 - $BaZn_2Sb_2$
6 - $SrZnSb_2$
7 - $Yb_5In_2Sb_6$
8- $Ba_4In_8Sb_{16}$
9 - $Yb_{11}Sb_{10}$
10 - $Yb_{11}GaSb_9$
11 - $Yb_{14}AlSb_{11}$
12 - $Yb_{14}MnSb_{11}$

$SrZnSb_2$ thermal transport

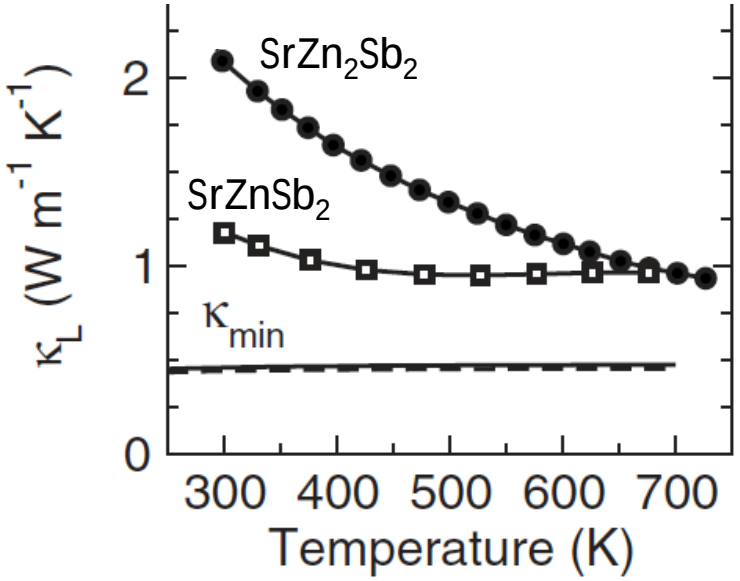
Similar bonding

- layers of covalently bound Zn-Sb
- Sr cationic layers

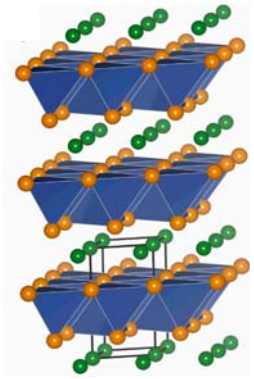
leads to similar speed of sound:

- $SrZnSb_2$ - 2040 m/s
- $SrZn_2Sb_2$ - 2010 m/s

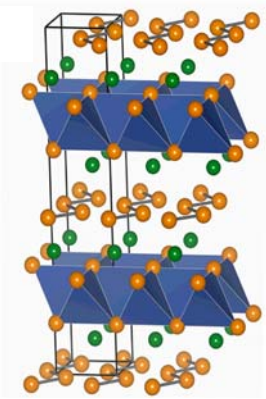
More complex $SrZnSb_2$
displays significantly lower κ_L



$SrZn_2Sb_2$



$SrZnSb_2$



May, *J. Applied Phys.*, **106**, 013706, (2009)

Summary

Zn-Sb phases

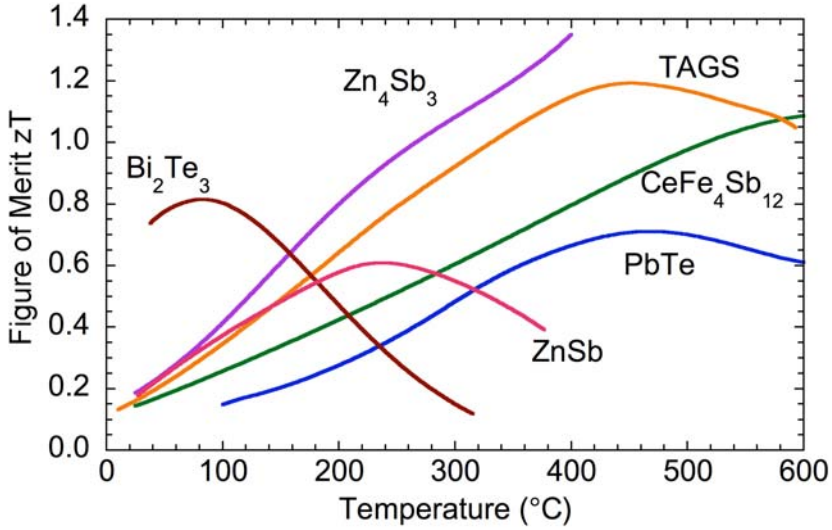
- low cost
- non-toxic
- good zT

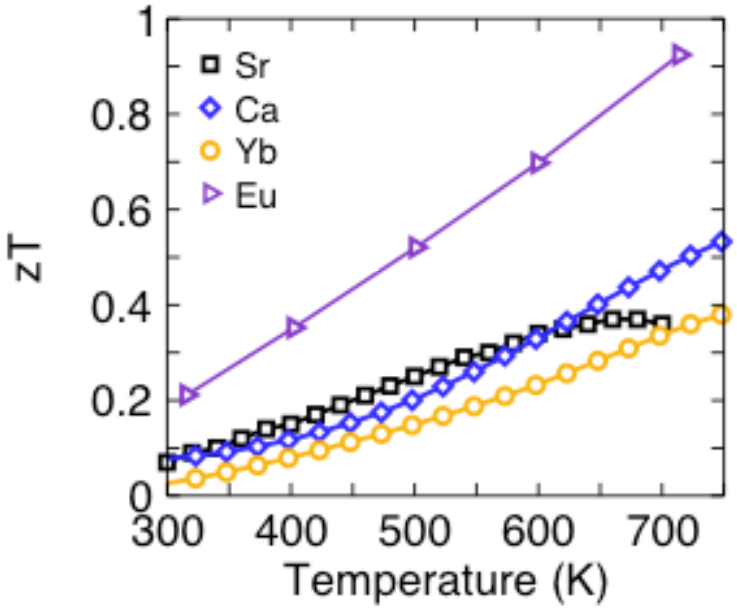
Zn_4Sb_3

- Promising for power generation
- need to understand
  - structure-property relationship
  - **stability (thermal, chemical, gradient)**

$A^{+2}Zn_2Sb_2$

- good example of Zn-Sb derivative
- High mobility, high *zT* In Rare Earth?
  - new mechanism for high *zT*?
  - $EuZn_2Sb_2$
- other complex Zn-Sb derivatives ?





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