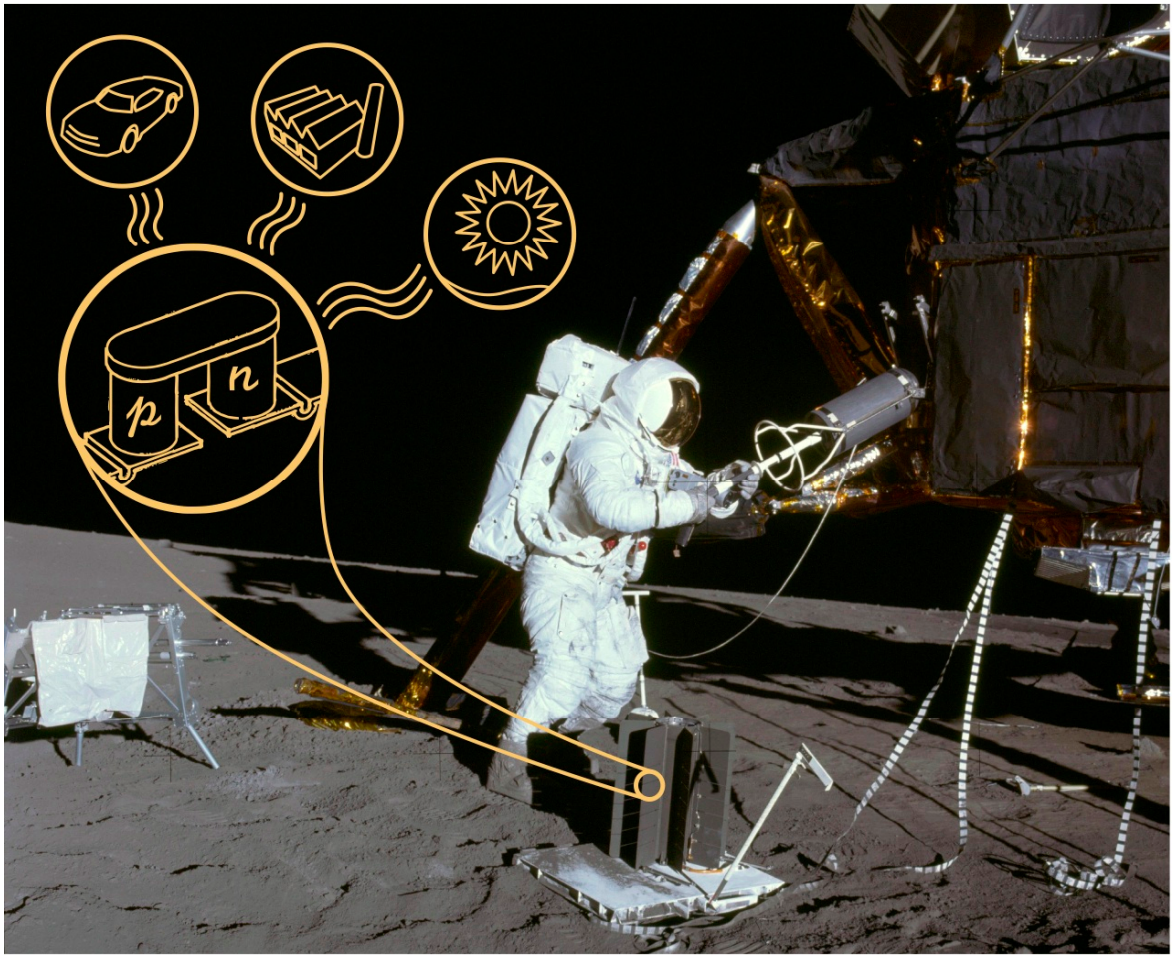
# *Electronic* Strategies for High Thermoelectric *zT* in Bulk Materials

*G. Jeffrey Snyder, Caltech*



# Successful Strategies for TE

| Zintl Phases | Band Engineering | nano-composite |
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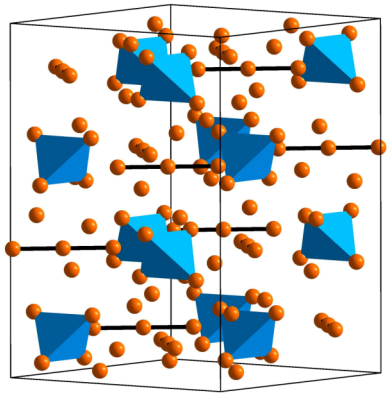
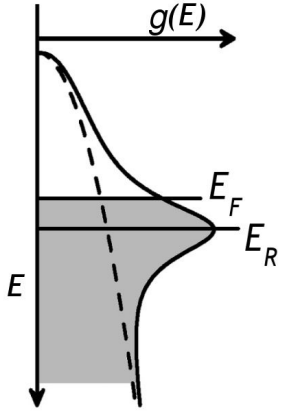
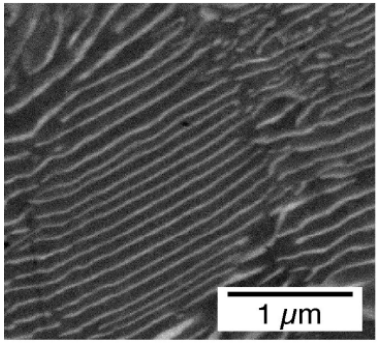
|  |   |   |
| Large Unit Cell | Band Structure | Nano Lamallae |

Three routes to high *zT*:

- Structural complexity - good for low $\kappa$
  - Different length scales ~ 1nm up to > 100nm
  - Eric Toberer 2:30pm
- **Band Structure Engineering - Electronic Properties**

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

# Conventional Thermoelectric Material

Desire High *zT* Figure of Merit

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

"Electron Crystal - Phonon Glass"

α Seebeck Coefficient

High in Crystalline Semiconductor

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

σ Electrical Conductivity

High In Crystalline Metal

$$\sigma = ne\mu = \frac{ne^2\tau}{m^*}$$

Carrier Concentration Tuning

Band Structure Engineering

κ Thermal Conductivity

Low for Glass

$$\kappa \approx \kappa_l + L\sigma T$$

See Eric Toberer 2:30

# Carrier Concentration

Desire High *zT* Figure of Merit

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

***Conflicting Materials Requirements***

α Seebeck Coefficient

Need small *n,* large *m**

- Semiconductor (Valence compound)

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

σ Electrical Conductivity

Need large *n*, high *μ*, low *m**

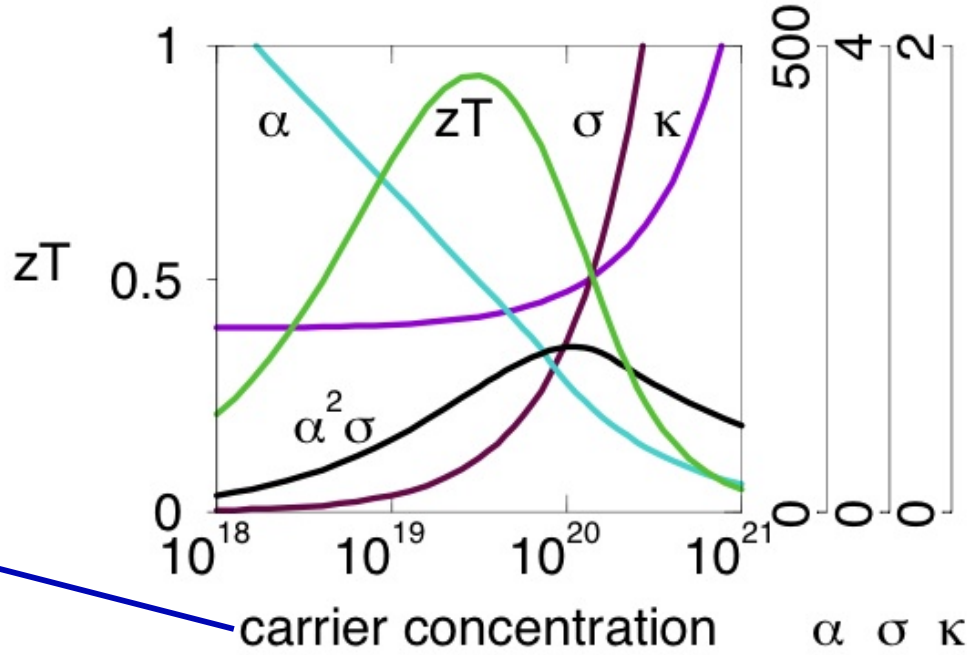
- Metal

$$\sigma = ne\mu$$

κ Thermal Conductivity

Desire small $\kappa_l$, small *n*

$$\kappa \approx \kappa_l + LTne\mu$$




Carrier Concentration Tuning using Zintl Chemistry

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# Valence Semiconductors

**General Valence Rule**

Accounts for

Number of electrons donated (+)

or needed (-) to fill valence band states

- $e$ valence electrons in atom
- each bond $b$ reduces |valence| by 1

$$V_c = e_c - b_c$$
$$V_a = e_a + b_a - 8$$

| | Valence Band | Conduction Band |
|---|---|---|
| Ionic | anion states | cation states |
| Polar Covalent | Either/Both Interpretation | |
| Covalent | bonding states | antibonding states |

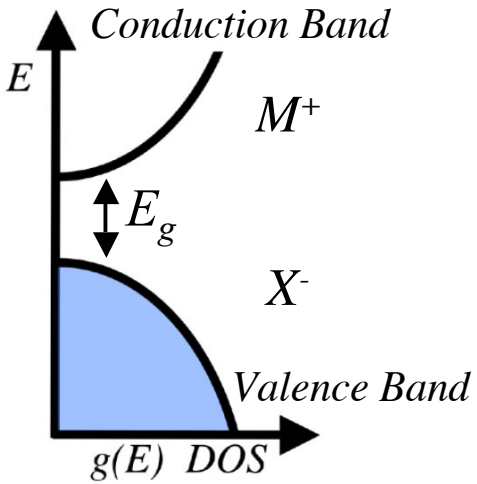
Valence Semiconductors

Stoichiometric balance of valences

- ionic $In^{3+}Sb^{3-}$; covalent $In^{1-}Sb^{1+}$

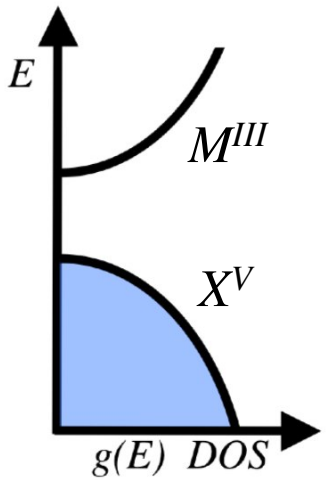
Ionic MX

$La^{3+}{}_2Te^{2-}{}_3$



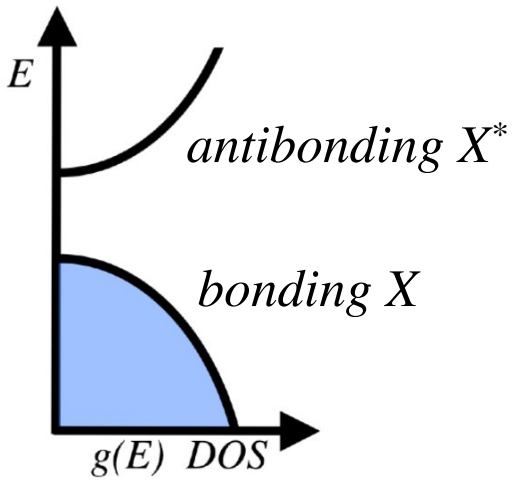

Polar SC MX

InSb $E_g \sim 0.2$ eV




Semicond. X

$Ge^0$ $E_g \sim 0.7$ eV

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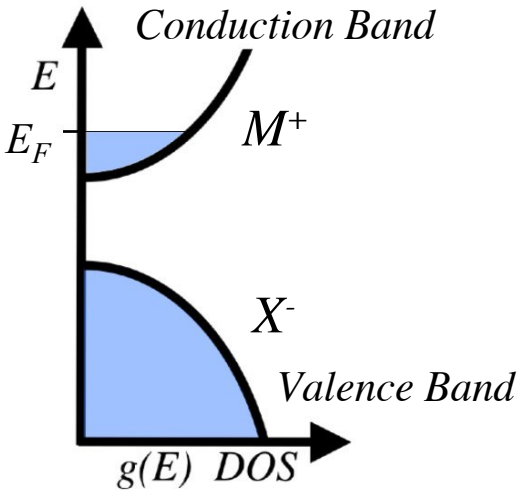
Toberer, May, Snyder ***Chem. Mat., 22,*** p. 624 (2010)

# TE: Valence Metals with Band Gap

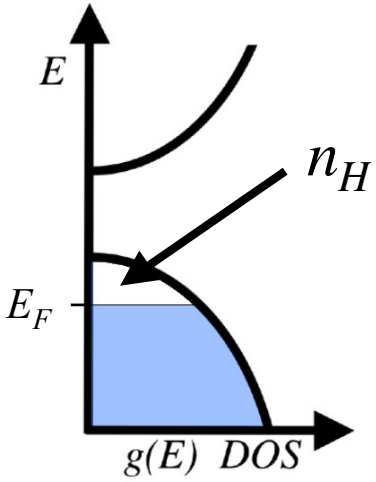
Thermoelectric materials are typically:

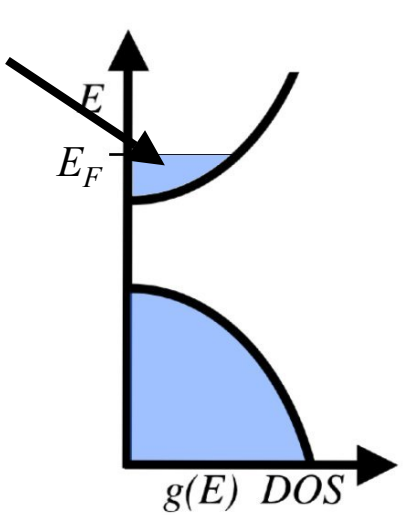
- Off Valence Balance compounds
- Where ***concentration of valence imbalance = free carrier concentration***
  - free Carrier Concentration measured by Hall Effect $n_H$
- Transport properties are metallic
  - Heavily doped, degenerate semiconductors
- Zintl electron counting rules apply
  - Poly anions, Metal-Metal bonding

Ionic MX
$La_3Te_4$




Polar MX
"$Zn_4Sb_3$"




Semicond. X
Ge-clathrates

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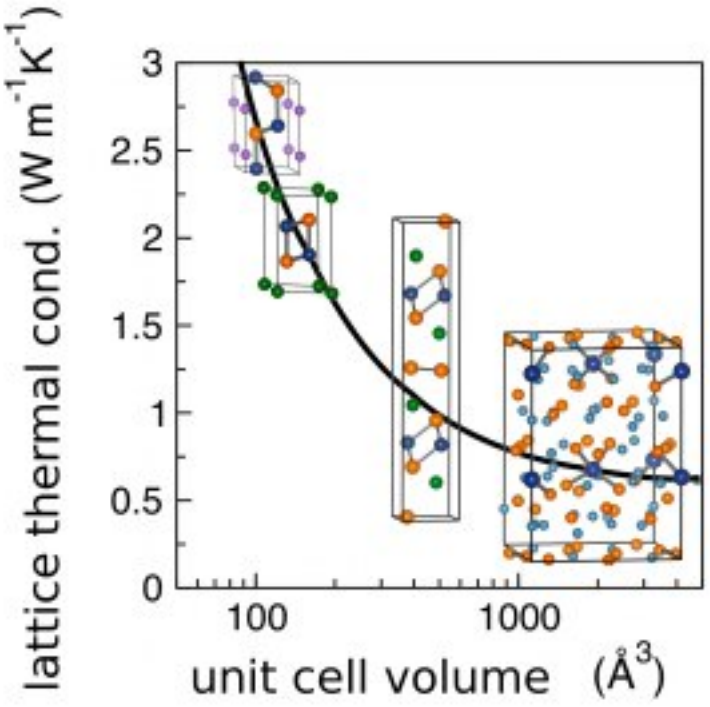
Toberer, May, Snyder ***Chem. Mat., 22,*** p. 624 (2010)

# Zintl Phases
# for
# Low Cost Thermoelectrics



# $Ca_5Al_2Sb_6$ valence balance

Zintl-Klemm valence counting gives valence balanced structure

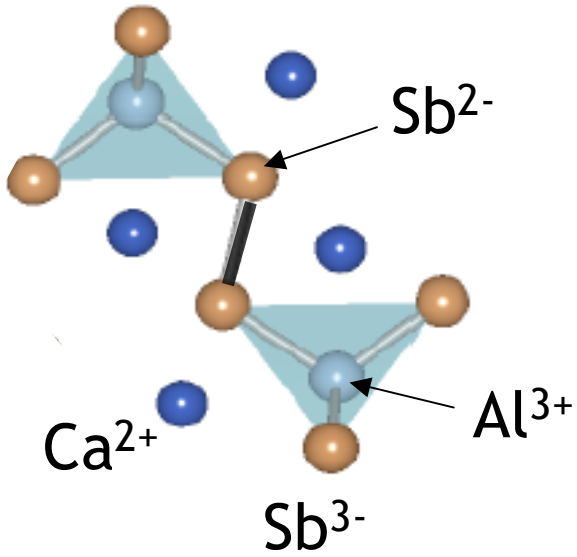
Cation Valence = electron - bonds

Anion Valence = electrons + bonds - 8

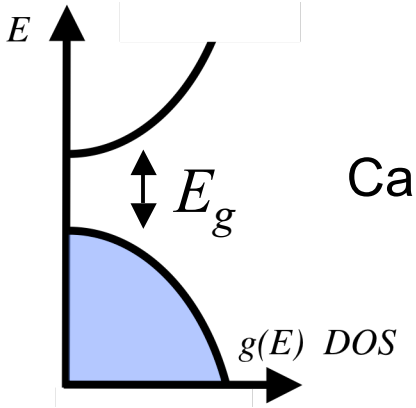
Al as cation

| | Ca | Al | $Sb^{1,2}$ | $Sb^3$ |
|---|---|---|---|---|
| electrons | 2 | 3 | 5 | 5 |
| bonds | 0 | 0 | 0 | 1 |
| valence | 2 | 3 | -3 | -2 |
| total | 10 | 6 | -12 | -4 |

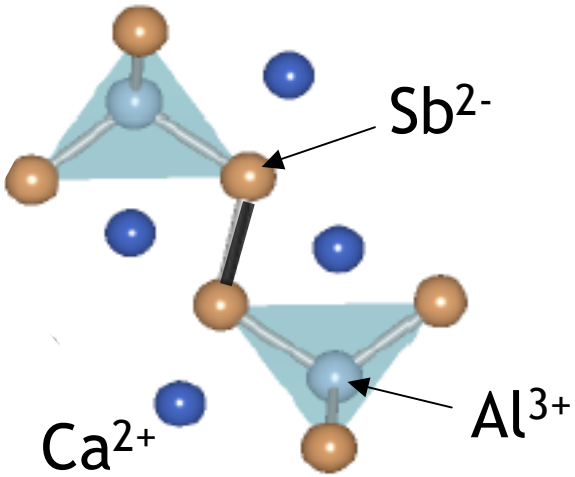
Net Valence = 0

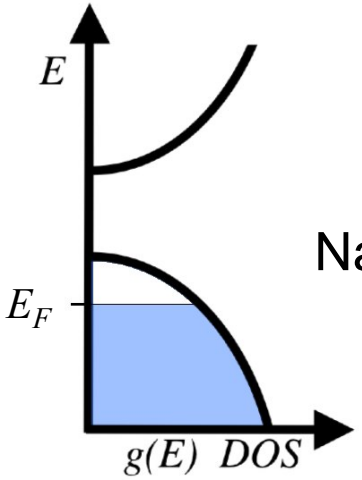


# $Ca_5Al_2Sb_6$ cation doping




$Ca_5Al_2Sb_6$



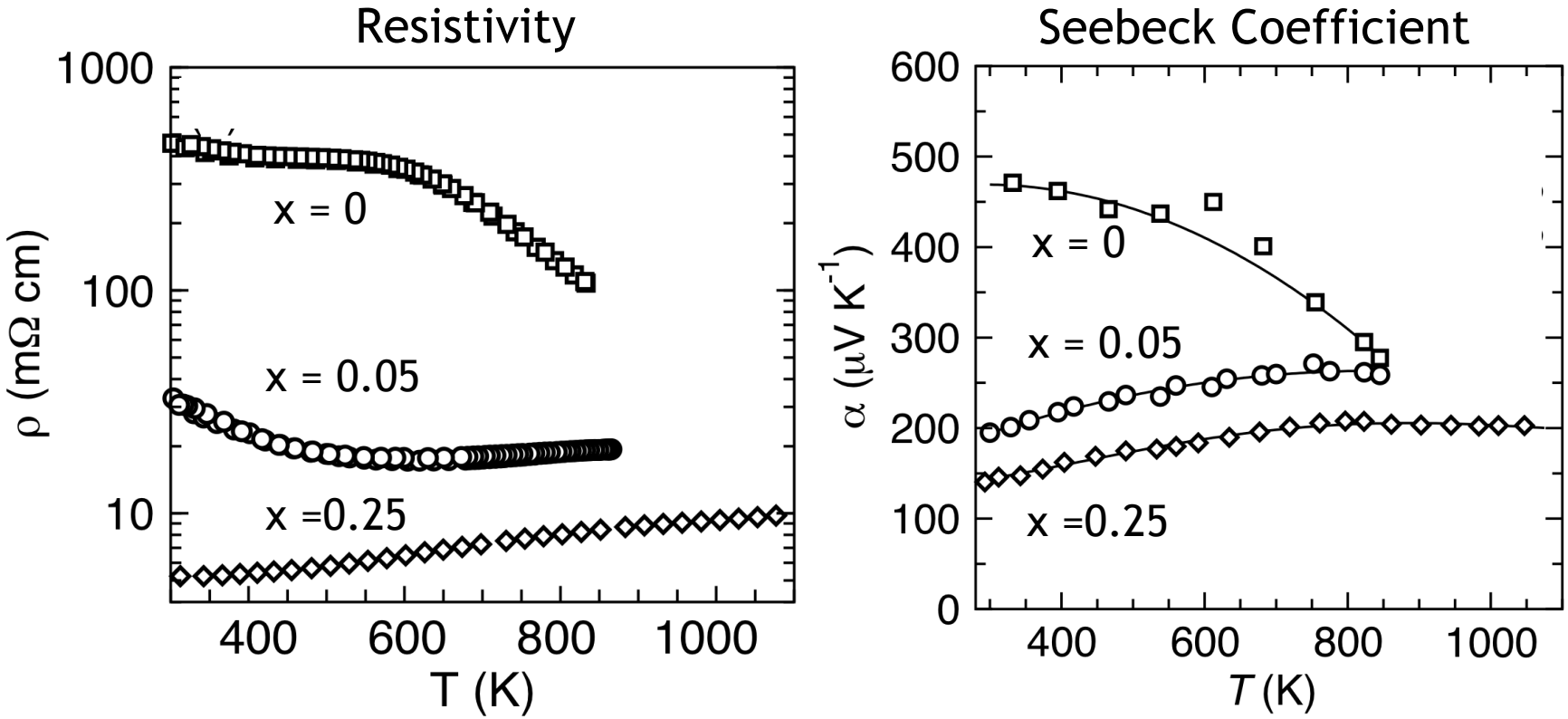

$Na_xCa_{5-x}Al_2Sb_6$

Replace with

$Na^{1+}$ + $hole^{+}$

Induces free carriers

# Resistivity and Seebeck Coefficient

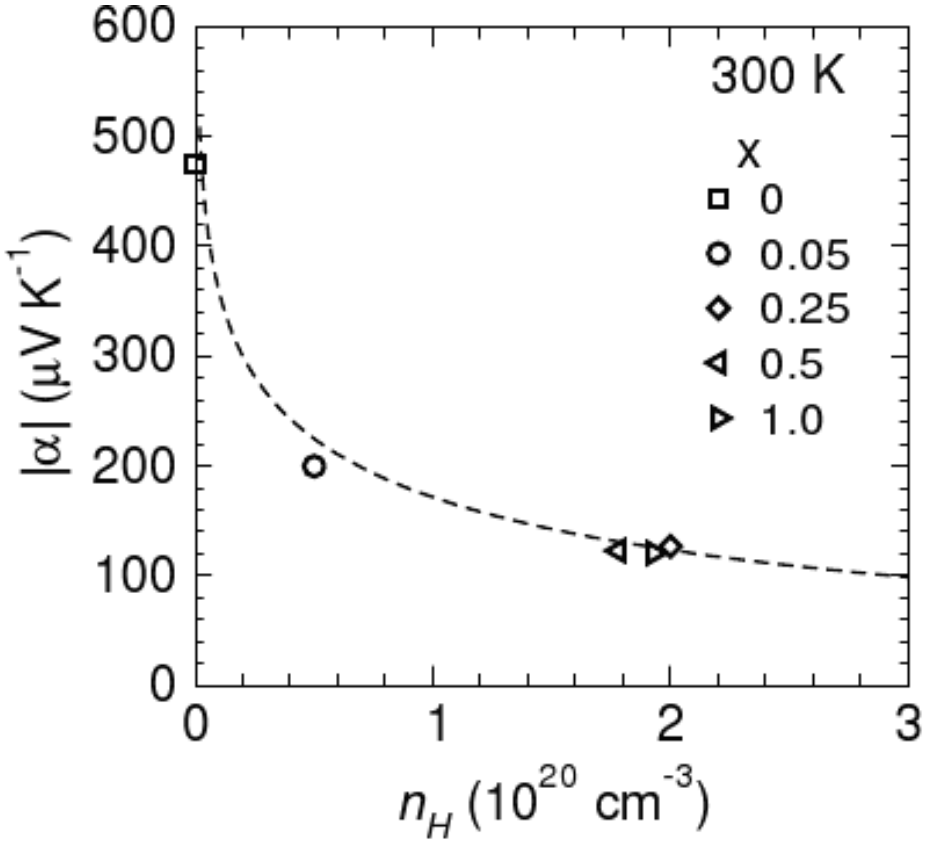



Heavily doped semiconductor: linear resistivity and Seebeck with T

- x=0.05: Seebeck peak at 800K gives $E_g$ = 0.4 eV

$$E_g = 2eT_{\max}\alpha_{\max}$$

# Seebeck vs. Carrier Concentration




Effective mass: $m^* = 2.2m_e$

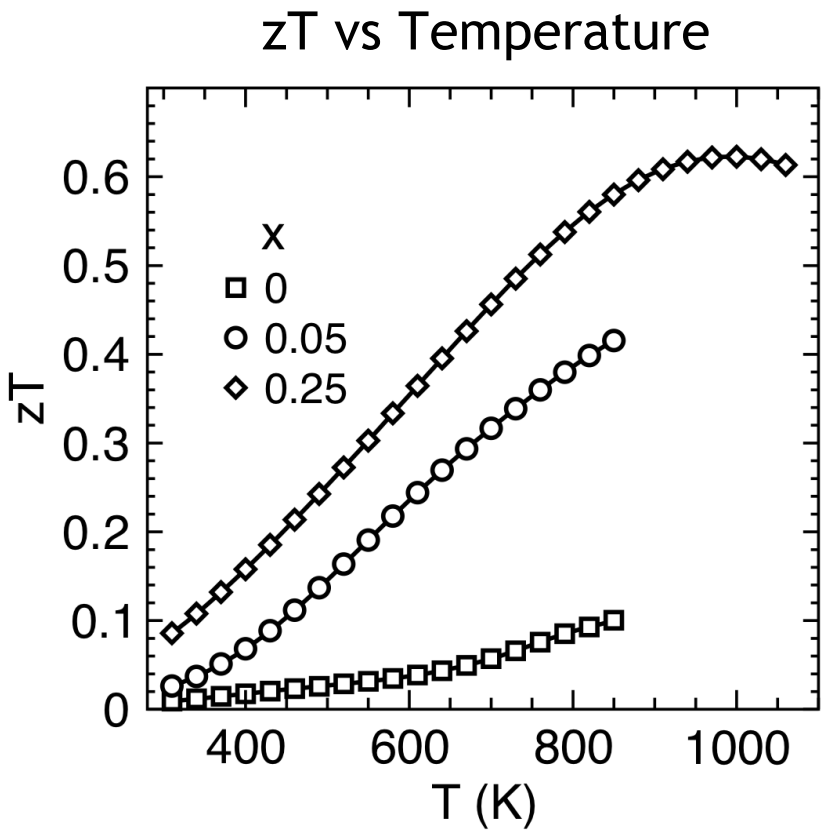
$$\alpha = \frac{k}{e}\left(\frac{(2+\lambda)F_{1+\lambda}(\eta)}{(1+\lambda)F_{\lambda}(\eta)} - \eta\right)$$

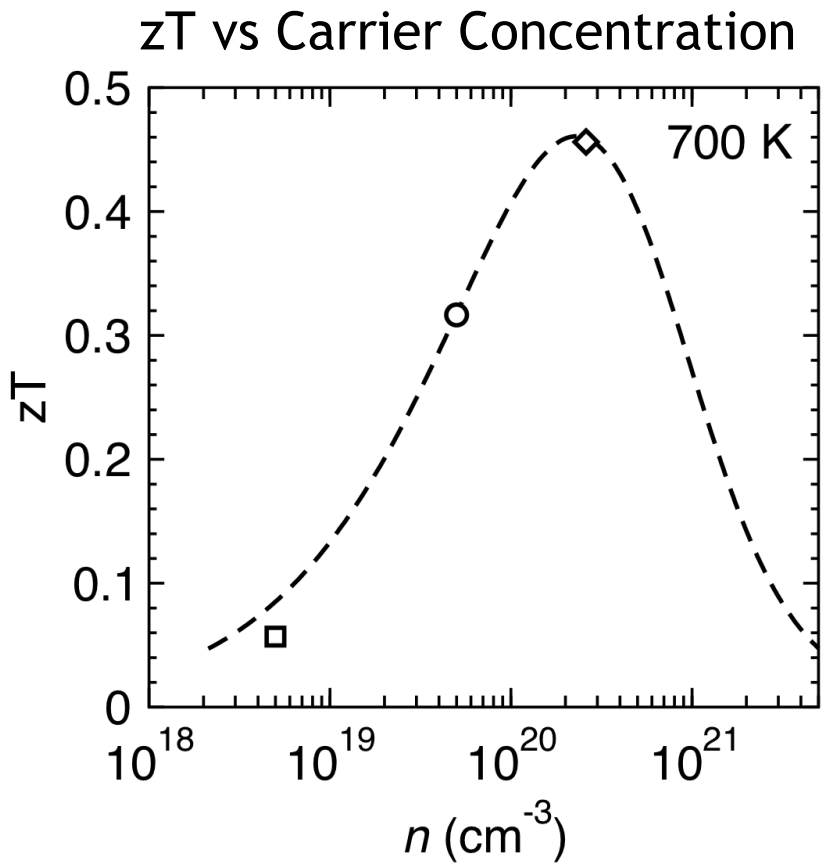
$$F_r(\eta) = \int_0^\infty \zeta^r f_o(\eta) d\zeta$$

$$n = \frac{4}{\sqrt{\pi}}\left(\frac{2\pi m^* kT}{\hbar^2}\right)^{3/2} F_{1/2}(\eta)$$

Assumptions: Single parabolic band, acoustic phonon scattering

# $Na_xCa_{5-x}Al_2Sb_6$ *zT*




zT greater than 0.6 at 1000K for heavily doped sample

Input from x=0.25 sample: $m^*=1.9m_e$ $\mu_o=4.7\ cm^2/Vs$ $\kappa_l=0.76\ W/mK$

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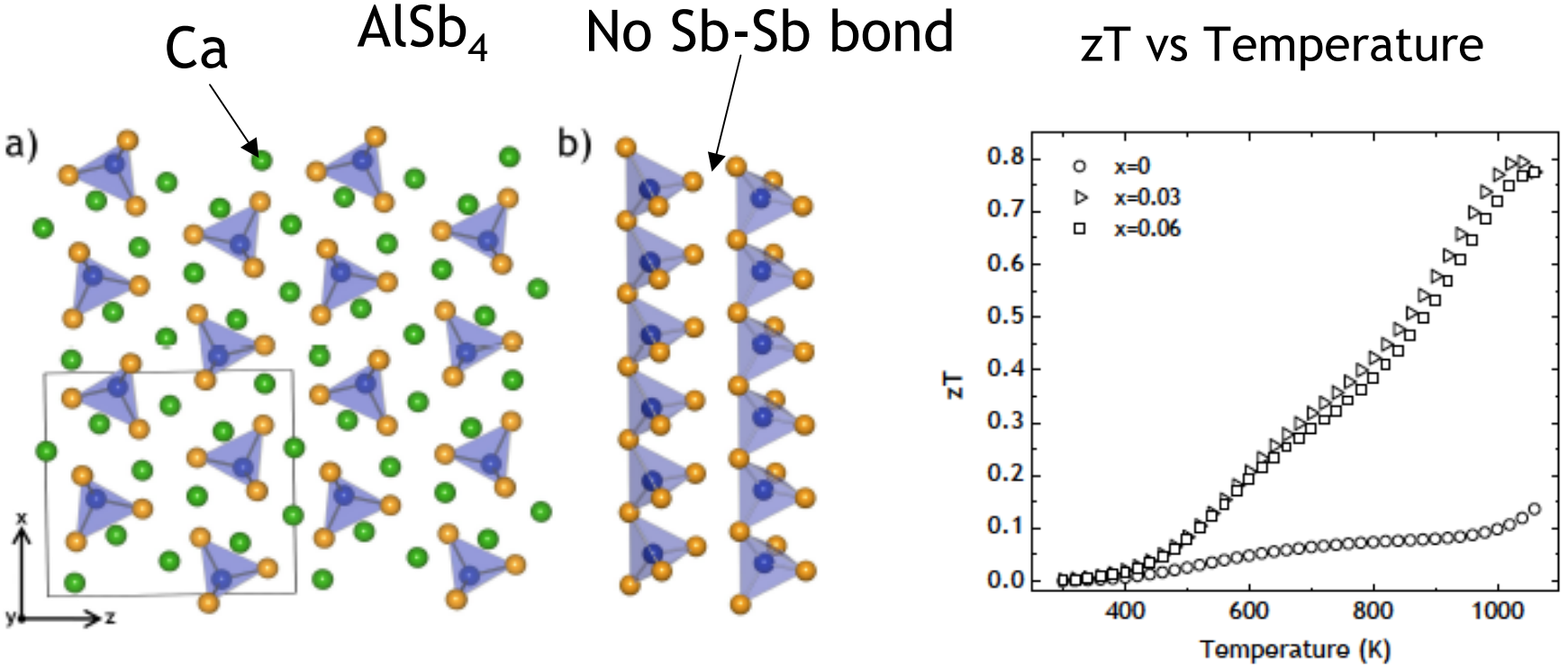
Toberer, Zevalkink, Snyder ***Adv. Funct. Mat.,*** (2010) 201000970

# $Na_xCa_{3-x}AlSb_3$



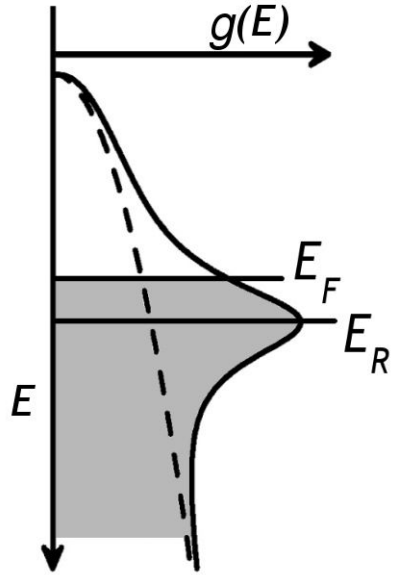

Similar structure and chemistry to $Ca_5Al_2Sb_6$, except for no Sb-Sb bond higher mobility, lower effective mass leads to higher zT

$Ca_3Al_1Sb_3$: $m^* = 0.8\ m_e$ $\mu_o = 15\ cm^2/Vs$ $\kappa_l = 0.78\ W/mK$
$Ca_5Al_2Sb_6$: $m^* = 1.9\ m_e$ $\mu_o = 4.7\ cm^2/Vs$ $\kappa_l = 0.76\ W/mK$



Zevalkink, Toberer, Snyder ***Energy. Environ. Sci.,*** (2010)

# High Efficiency from Band Structure Engineering



# Enhancing Thermopower


## Seebeck

Typically described by *effective* $m^*$

- Single Parabolic Band

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

degenerate limit,
acoustic phonon scattering

- Need carrier concentration $n$
  - Typically use Hall $n_H$

## Thermopower increased by

1. Larger band mass $m^*$

   But reduces mobility

$$\sigma = ne\mu = \frac{ne^2\tau}{m^*}$$

2. Greater band degeneracy $N_V$

   multiple parabolic bands

$$m^* = m^*_{band} N_V^{2/3}$$

3. Scattering

   Energy dependence of $\tau$

# p-PbTe Pisarenko Plot

Thermopower depends on carrier conc. $n$

parabolic band metal $\alpha \propto n^{-2/3}$

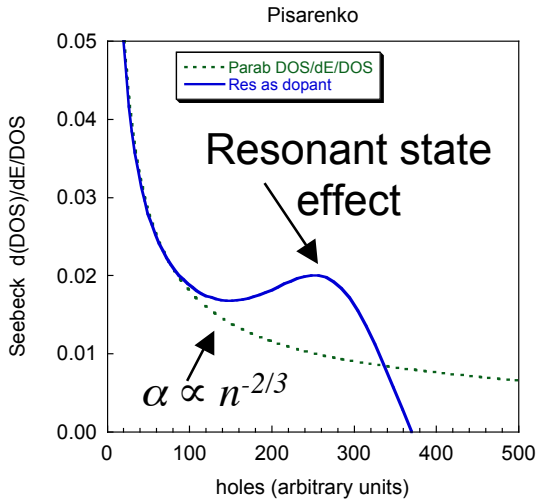
$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

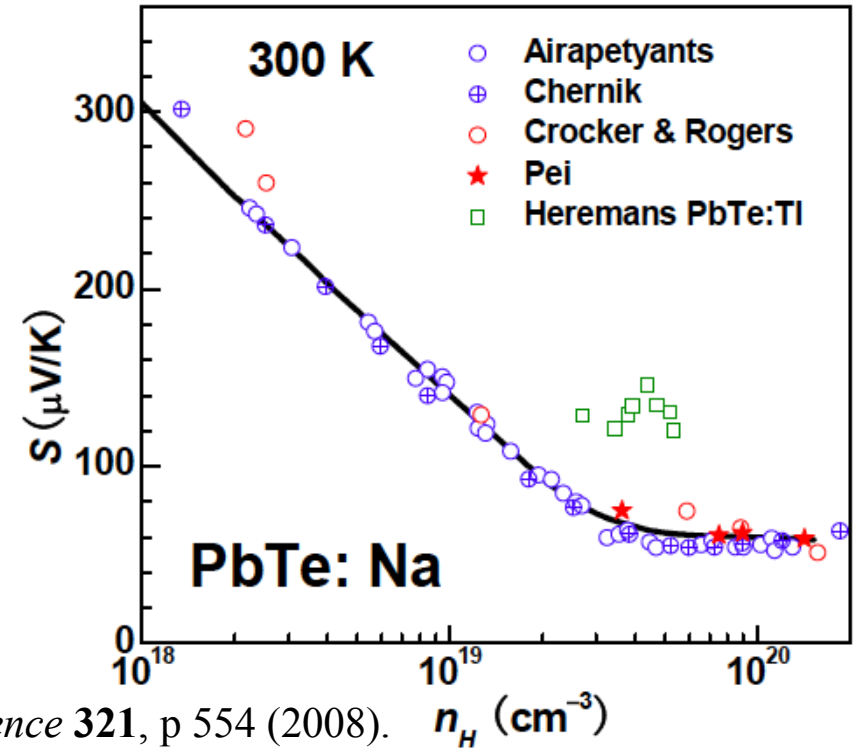
$m^*$ is the single Parabolic Band effective mass

PbTe:Tl shows higher thermopower than other p-type dopants

- Resonant state should alter thermopower from increased DOS

Change in slope $\alpha$ *vs*. $n$ in PbTe:Na indicates multiple band behavior






Heremans, et al.. *Science* **321**, p 554 (2008).

# Thermoelectric $La_{3-x}Te_4$

$La_{3-x}Te_4$ has high $zT$ at high $T$

Higher than SiGe used by NASA

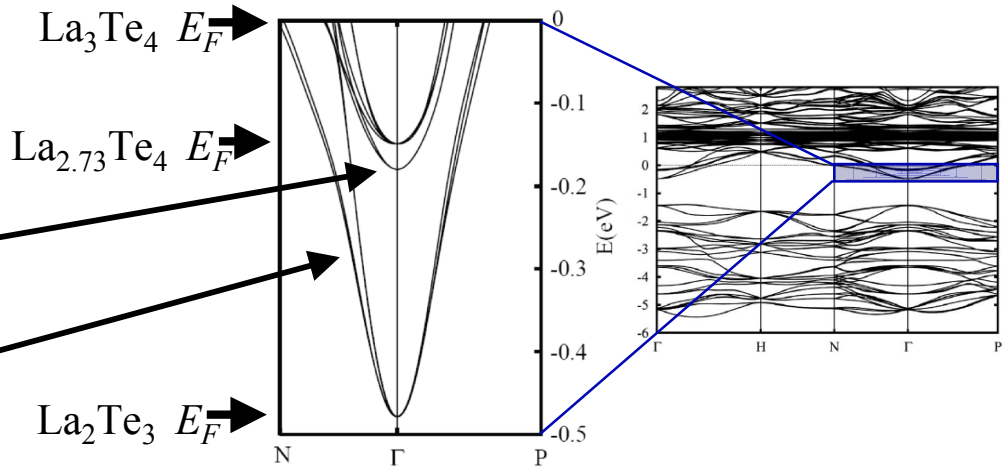
Highest $zT$ for $La_{2.73}Te_4$

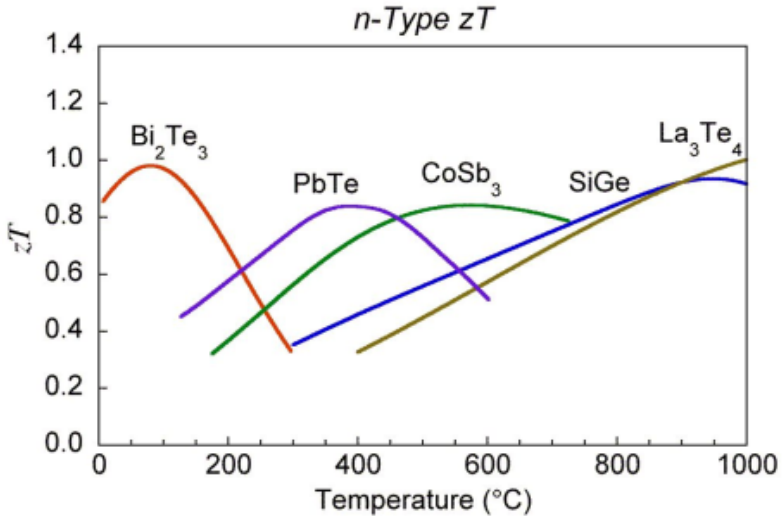
$E_F$ at edge of heavy band

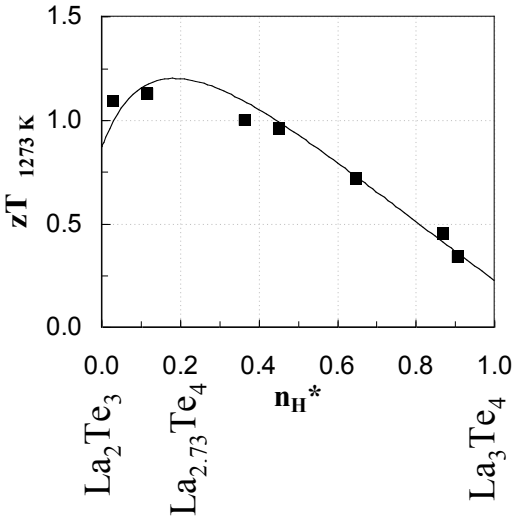
- $m^* \sim 3.5\, m_e$

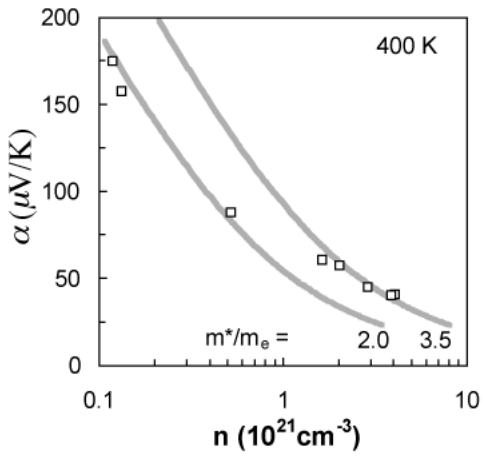
$E_F$ deep inside light band

- $m^* \sim 2\, m_e$




THERMOELECTRICS


May et. al. *Phys. Rev. B*, **78**, p. 125205, (2008)

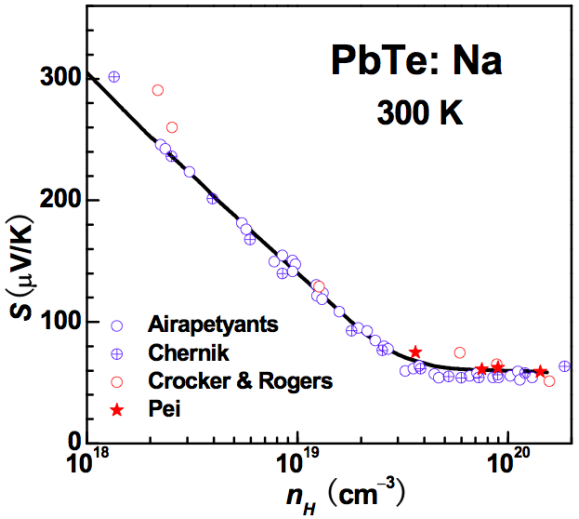
May et. al. *Phys. Rev. B*, **79**, p. 153101, (2009)

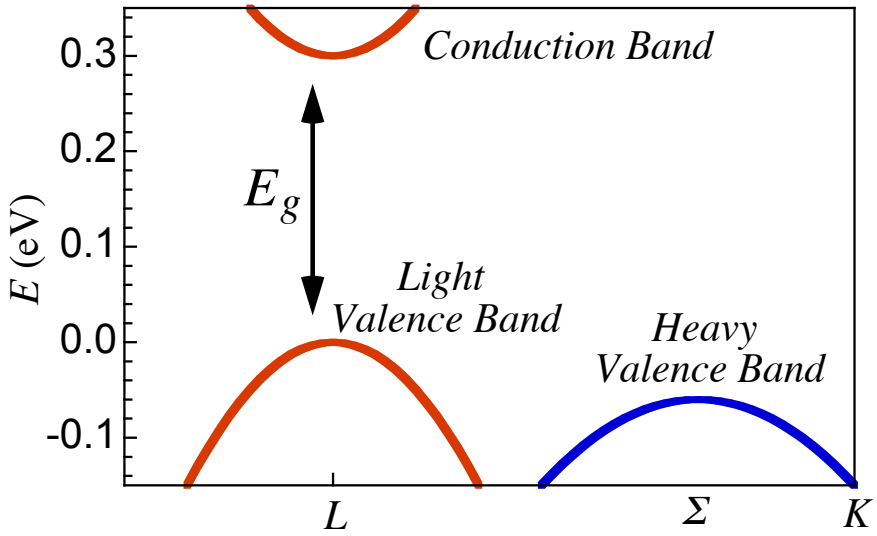
# Heavy and Light holes in PbTe

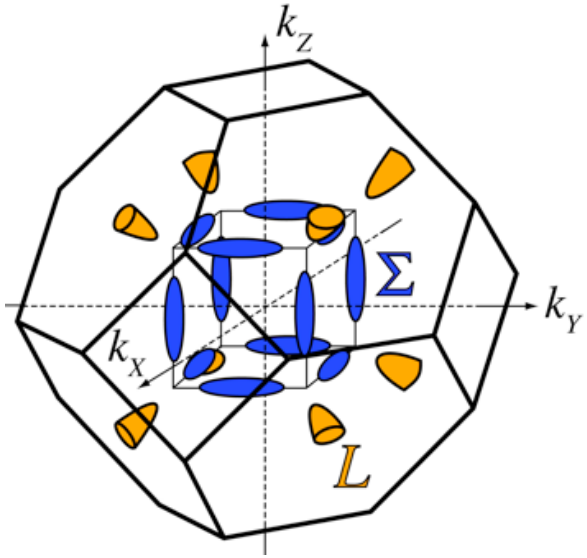
Valence Band Maximum is at *L* point
- "Light Band"

Second valence band occurs at $\Sigma$ line
- "Heavy Band"

Transition from single to multiple band occurs at $n_H \sim 3 \times 10^{19}$ holes/cm$^3$

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# *p*-PbTe *zT*

Light band has peak zT at low $n$

zT peak < 1

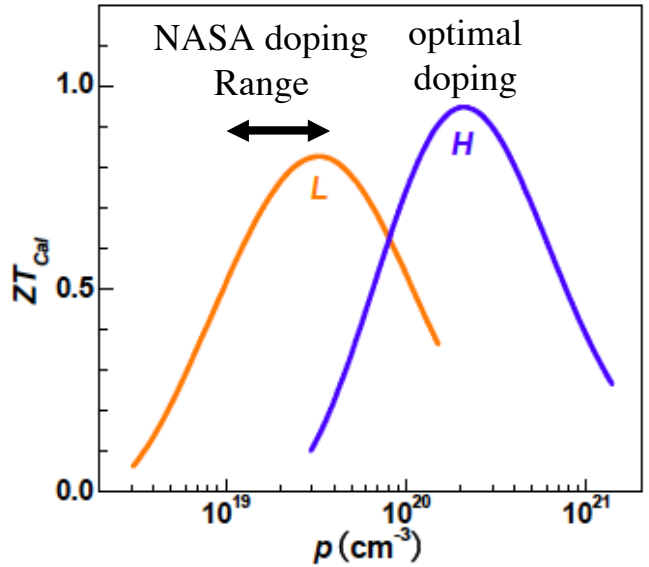
"2P-PbTe" used by NASA in 1960's

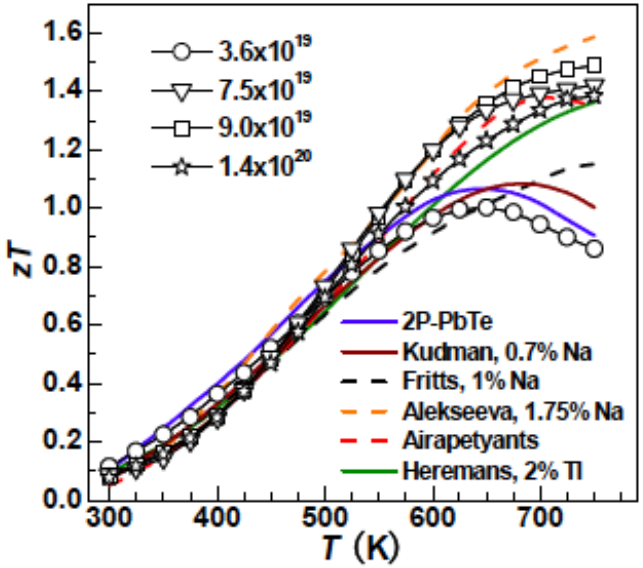
$n_H$ < 4 x $10^{19}$ holes/cm$^3$

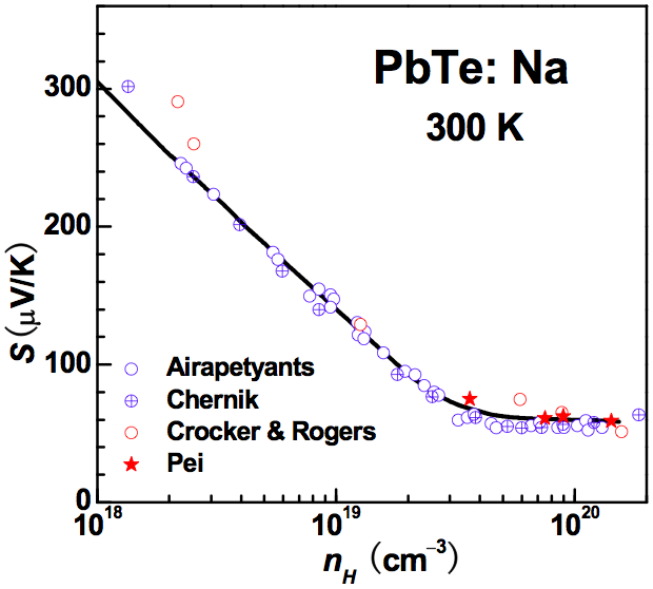
Heavy band requires high $n$

zT peak ~ 1.5

$n_H$ ≥ 1 x $10^{20}$ holes/cm$^3$

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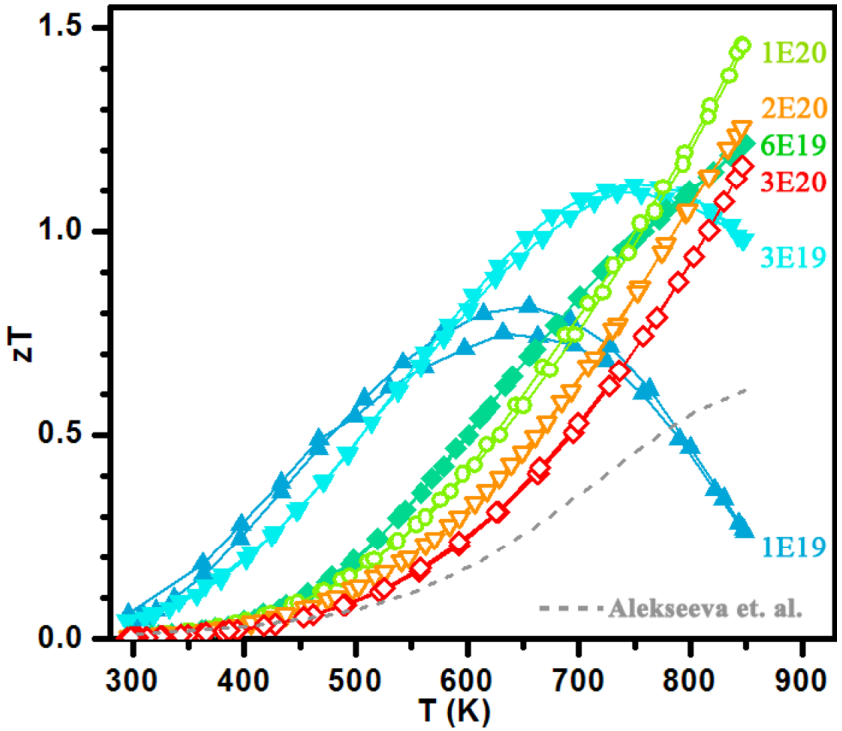
Pei, Snyder, et al.. *Energy Environ. Science* (in press).

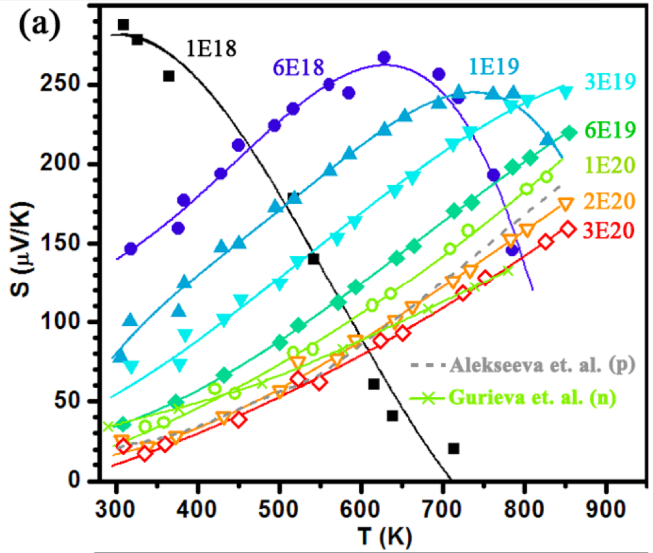
# p-PbSe

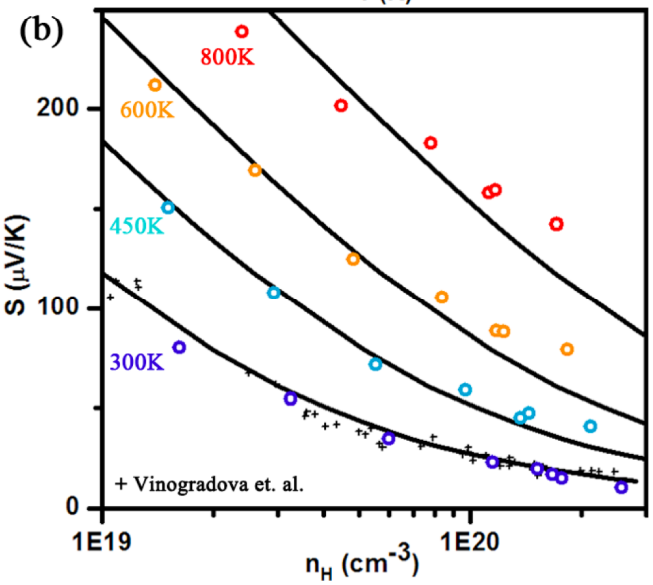
Similar light-band heavy-band in PbSe

Leads to zT > 1

without expense of Te!



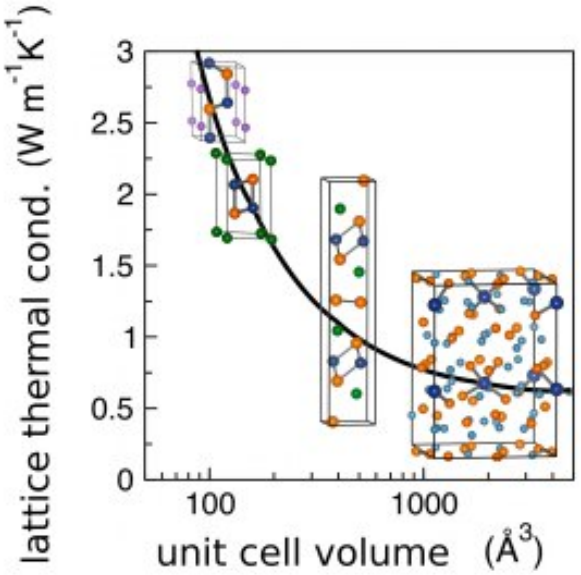

THERMOELECTRICS

Wang, Snyder, et al.. *Advanced Materials* (in press).

# Summary

Three Strategies for advanced TE

1. Zintl Phases
2. Band structure Engineering
3. Nano composites




Zintl Phases

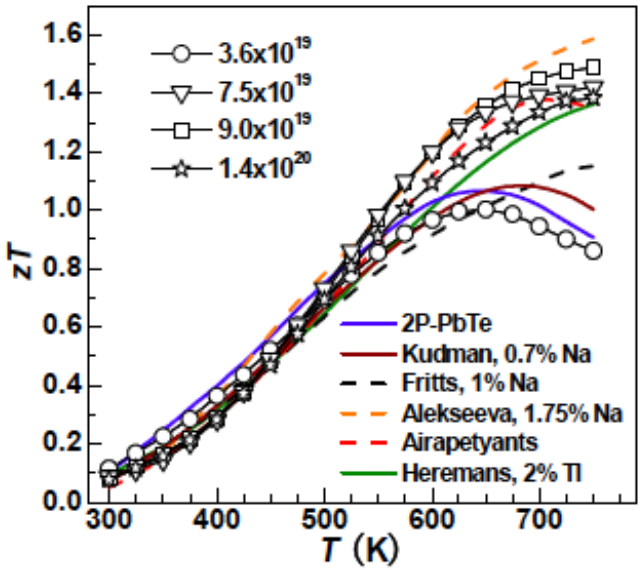
New low cost, non-toxic TE systems

- $Na_xCa_{5-x}Al_2Sb_6$ zT 0.6 at 1000K
- $Na_xCa_{3-x}Al_1Sb_3$ zT 0.8 at 1000K

PbTe structure materials

High *zT* without Tl or Te

- Na:PbTe zT ~ 1.5 at 750K
- Na:PbSe zT ~ 1.2 at 800K



# Acknowledgements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- Doug Medlin (Sandia CA) - TEM
- David Singh (ORNL)
- Axel van de Walle (Caltech)
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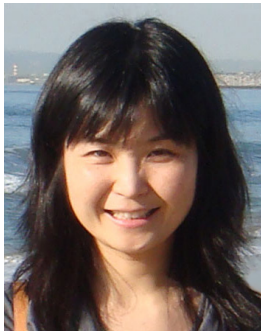
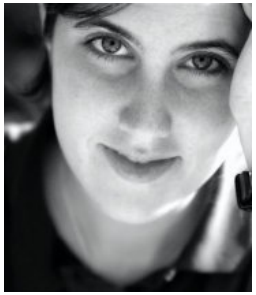

Shiho IWANAGA


Heng WANG


Alex Zevalkink


Nick Heinz


Greg Pomrhen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THERMOELECTRICS

# Actual band structure

Blue PbTe

Red Tl:PbTe (minus one band)

Supercell L is actually Gamma