Materials strategies for improving the overall device ZT

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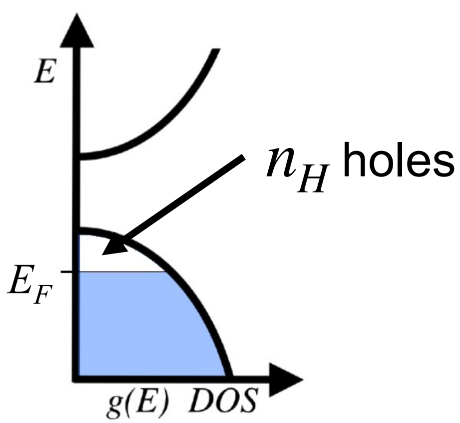

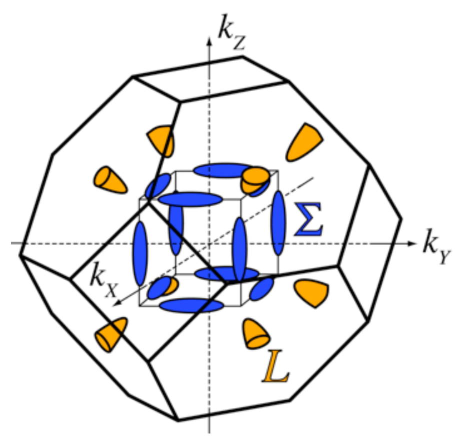

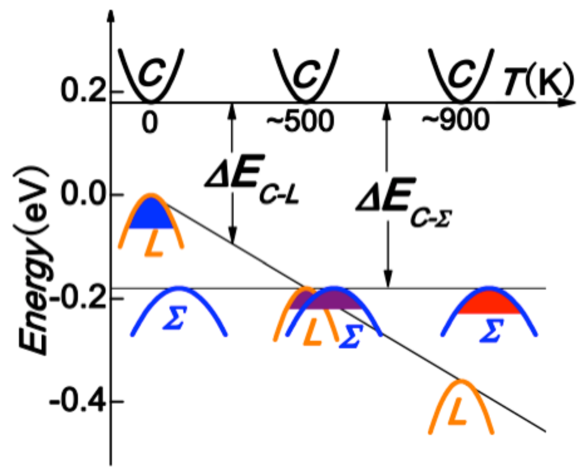

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Lalonde, Pei, Wang, Snyder, *Materials Today* **14** 526 (2011).

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*

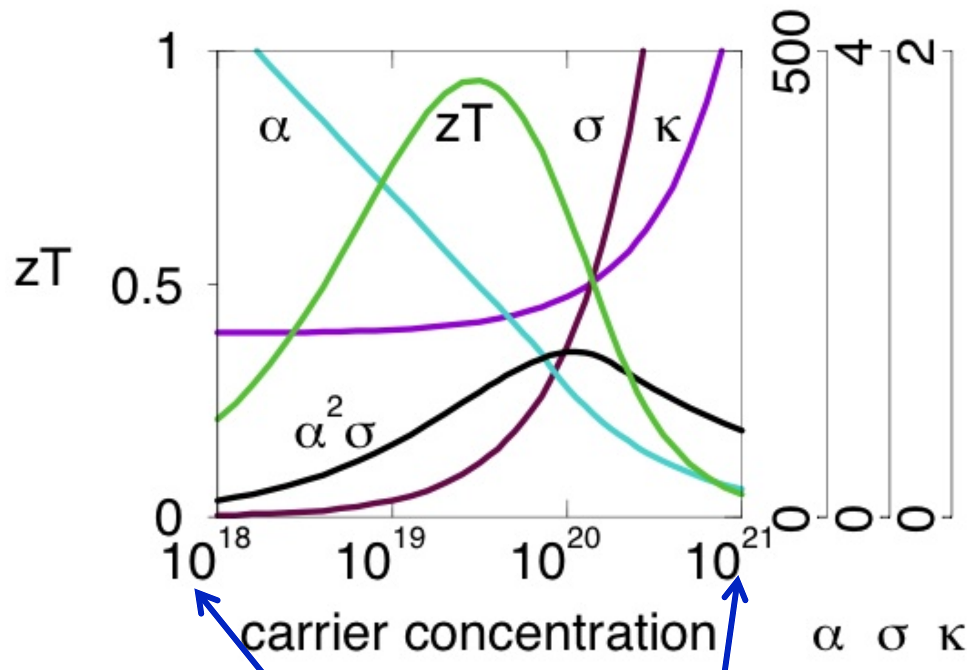
- Metal

$$\sigma = ne\mu$$

κ Thermal Conductivity

Desire small κ_l, small *n*

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



Optimum between Insulator and Metal

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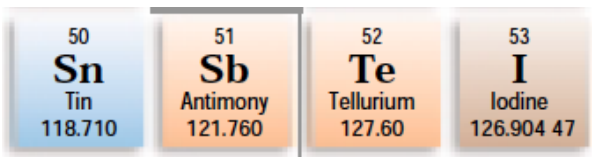
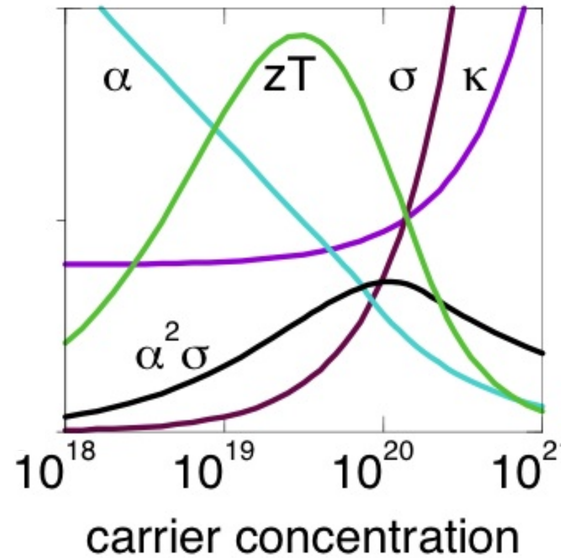
Snyder, Toberer Nature Materials ***7,*** *105 (2008)*

Carrier Concentration Tuning

$PbTe_{1-x}I_x$

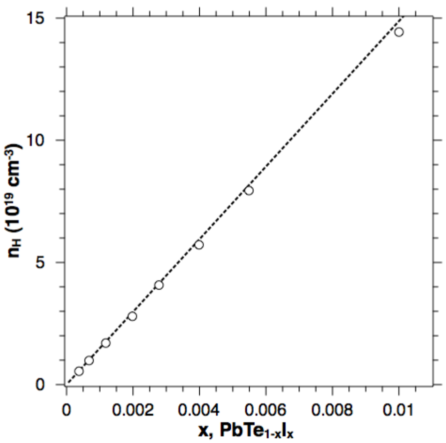
Iodine (I) supplies one more electron than Tellerium (TE)



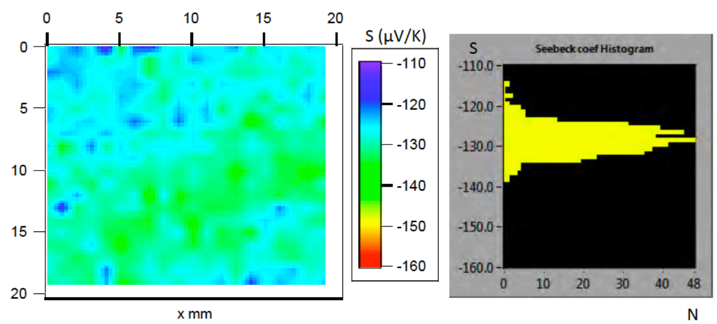


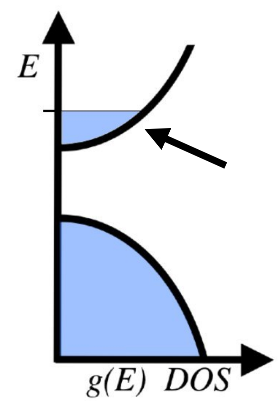
Iodine (I^-) replaces Te^{2-} producing 1 e^-

10^{18} - 10^{20} e^-/cm^3



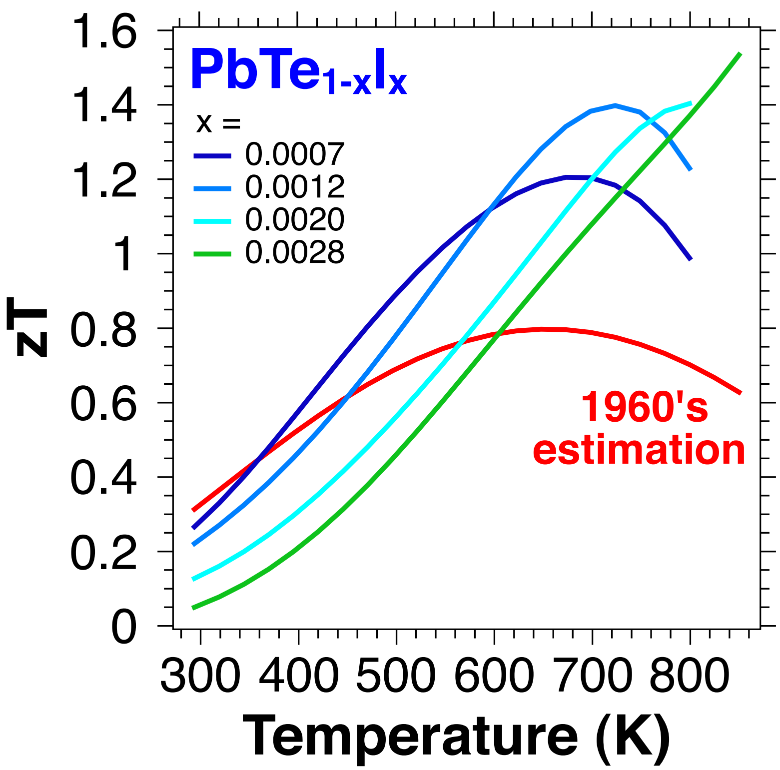
From Room Temperature Hall Effect

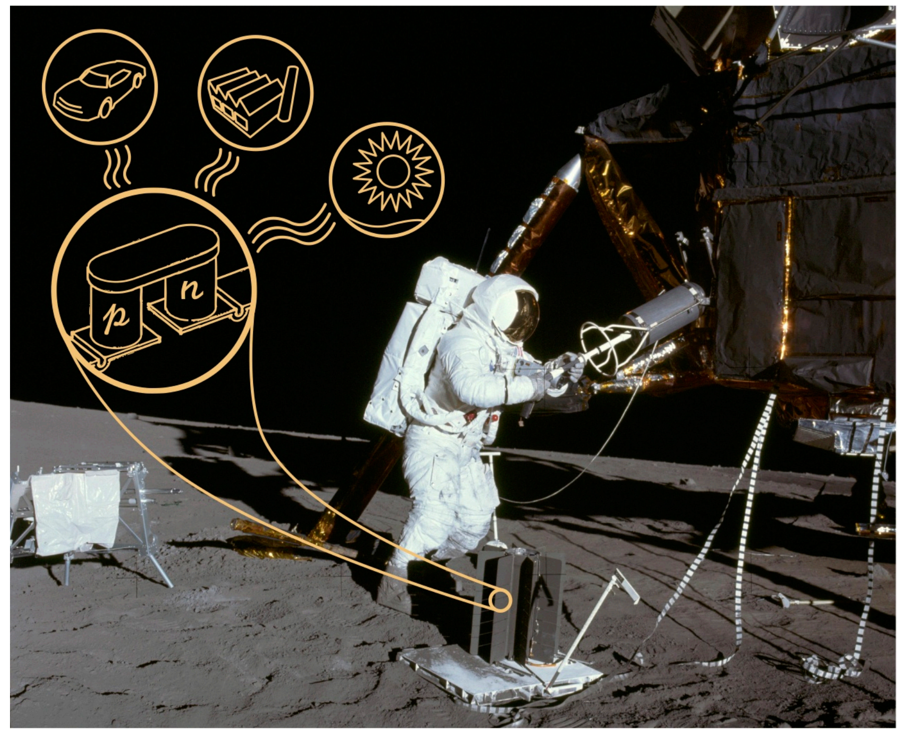




zT of n-type $PbTe_{1-x}I_x$

Peak zT ~ 1.4 at 800K due to low thermal conductivity





Unattended operation for over 10 years

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Lalonde, Pei, Snyder *Energy and Environmental Science* **4**, *2090* (2011)

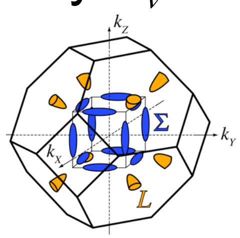
Quality Factor *and* n^*

Maximum zT depends on Quality Factor

$$\boxed{B \sim \frac{N_V}{m_b^* \kappa_L}}$$

Multi Valley Fermi Surface with Valley Degeneracy N_v

$$m^* = m_b^* N_V^{2/3}$$



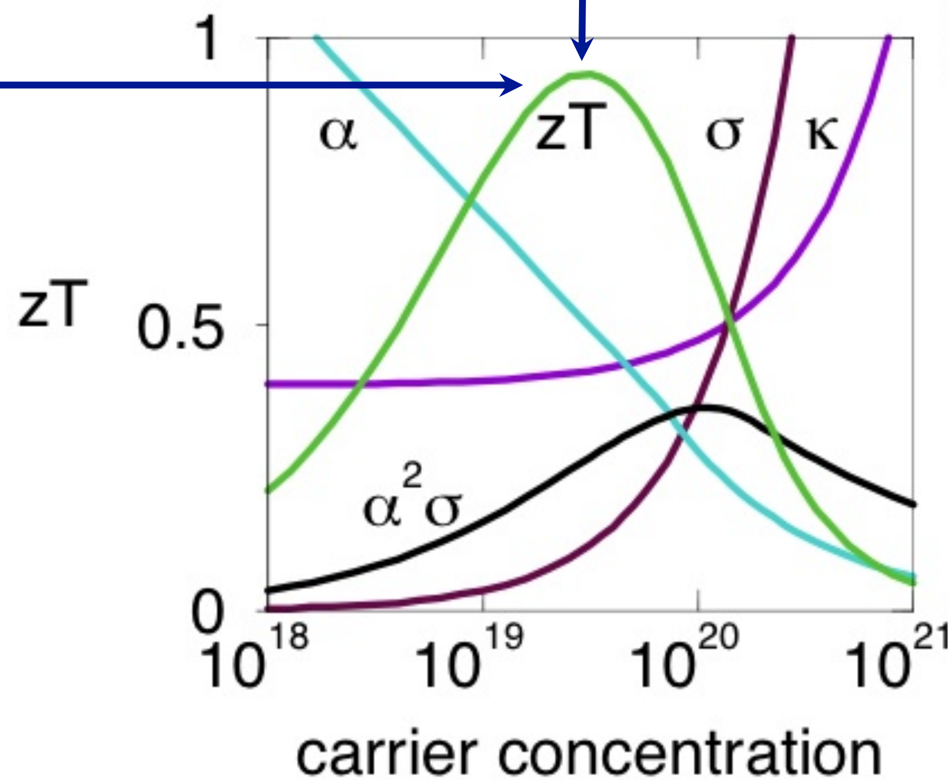
because μ decreases with m^*

$$\mu = \frac{e\tau}{m_b^*} \qquad \tau \propto \frac{1}{m_b^{*\,3/2}}$$

Acoustic Phonon Scattering

Optimized carrier concentration

$n^* \sim N_v^{2/3} m_b^* \, T^{3/2}$



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Lalonde, Pei, Wang, Snyder, *Materials Today* **14** 526 (2011).

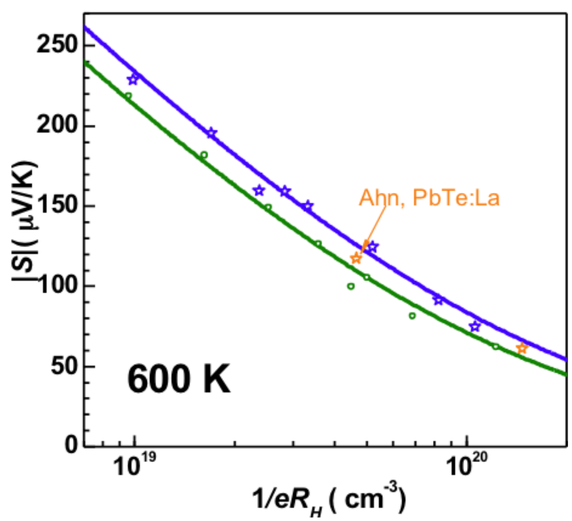
Mahan, “Good Thermoelectrics” *Solid State Physics* **51**, p 81 (1998).

Effective mass

$La_xPb_{1-x}Te$ vs. $PbTe_{1-x}I_x$

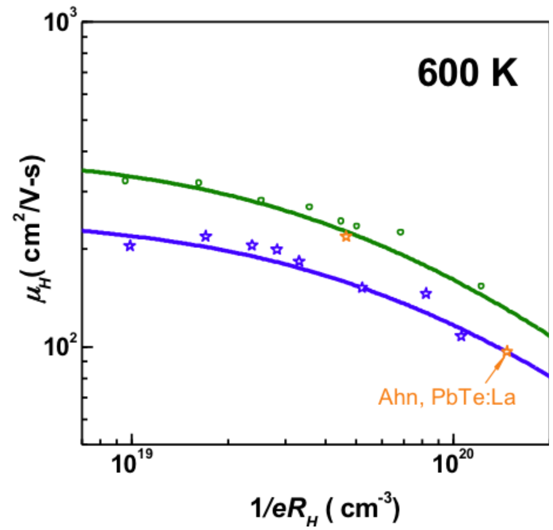
Both n-type L-band

20% lower m^*

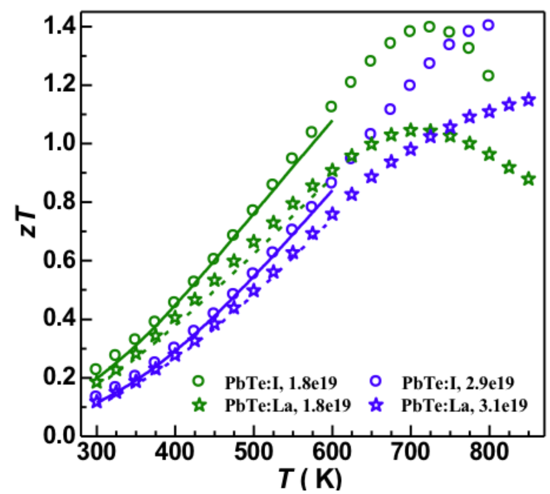


$$\mu \propto \frac{1}{m^{*5/2}_{b}} \qquad B \sim \frac{N_V}{m_b^* \kappa_L}$$

30% higher μ



20% Higher zT



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Heavy and Light holes in PbTe

Valence Band Maximum is at *L* point

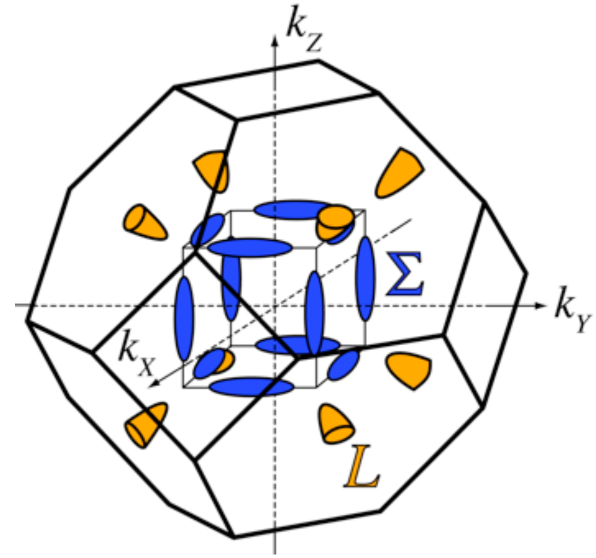
- "Light Band" $N_V = 4, \quad m_b^* = 0.14\, m_e$

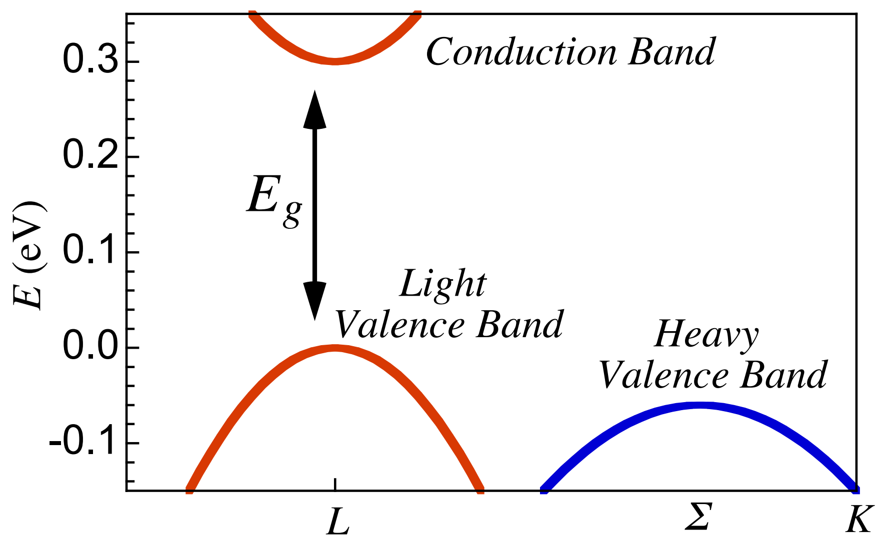
Second valence band occurs at Σ line

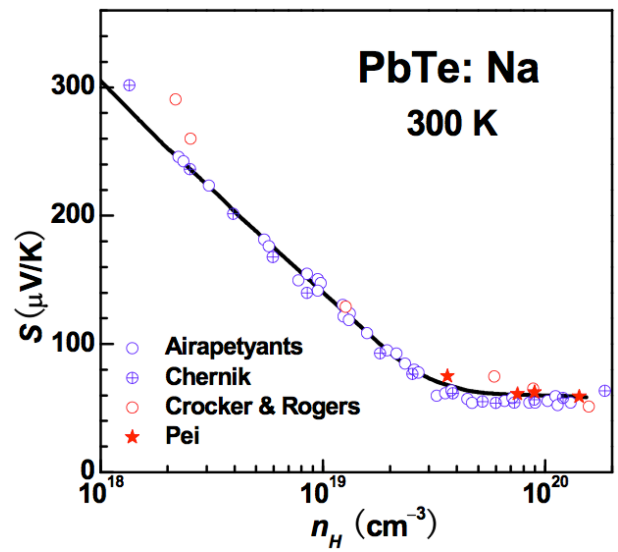
- "Heavy Band" $N_V = 12\,, \quad m_b^* = 0.28\, m_e$

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

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







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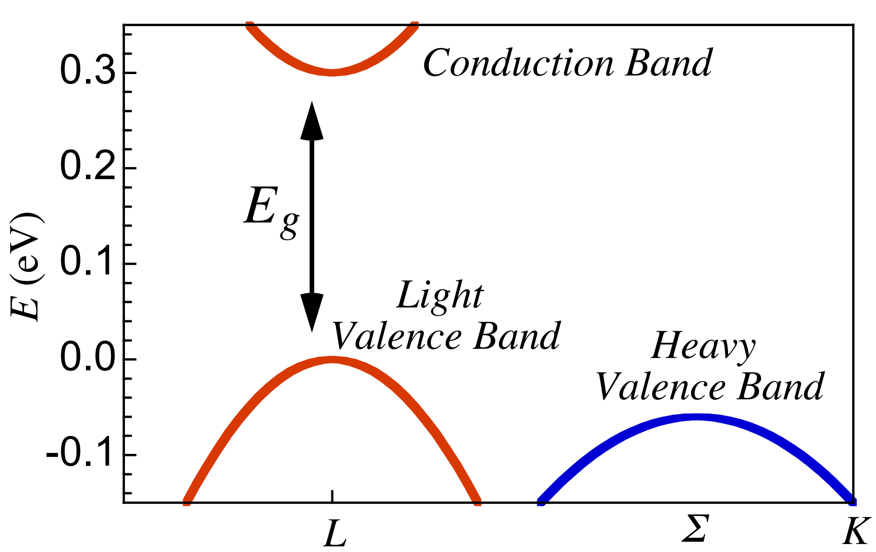
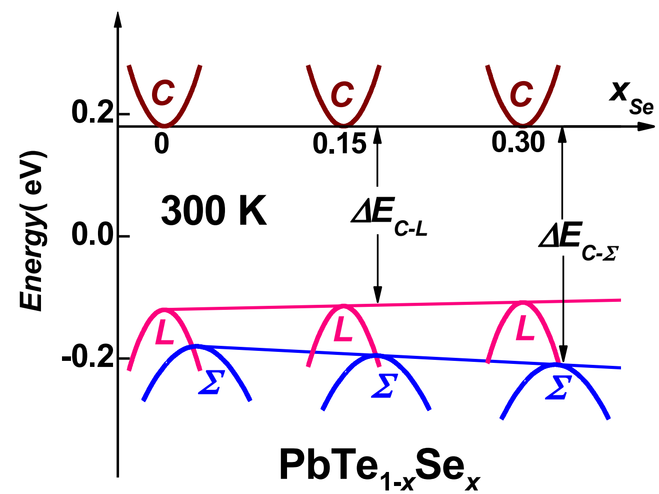
Pei, Snyder, et al.. *Energy Environ. Science* **4,** 2085 (2011).
Pei, Snyder, et al. *Nature* **473,** p66 (2011).

Valley Convergence with composition

PbTe convergence changes with alloying

- Slight shift in energy of C, L and Σ bands
- Will change Convergence Temperature
  - Increases T_{convg} with PbSe alloying
  - Decreases T_{convg} with MgTe alloying





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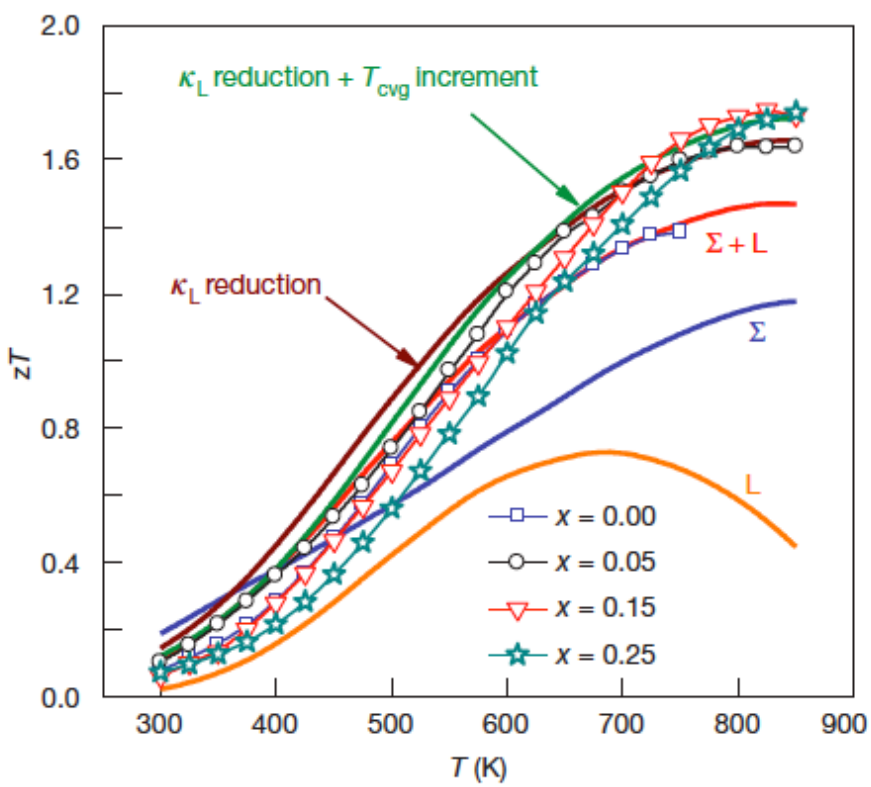
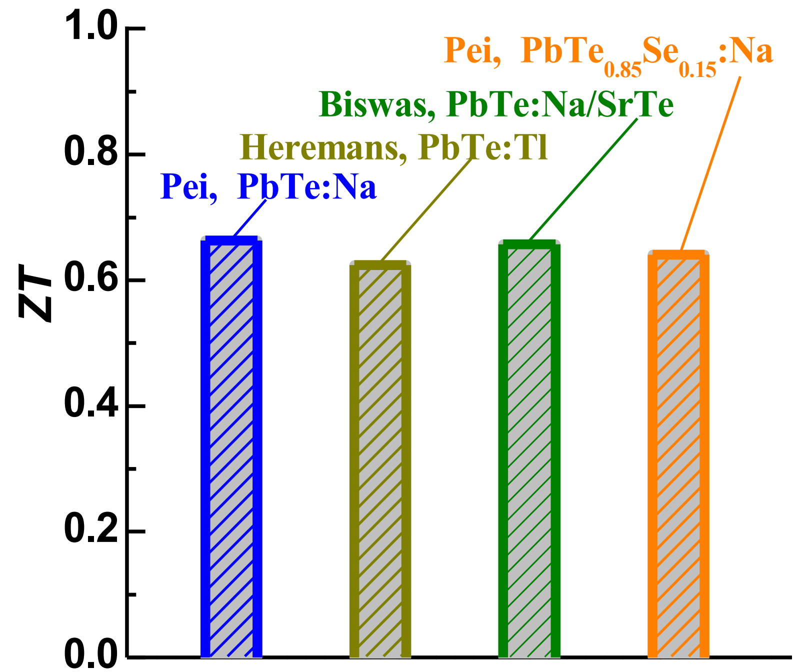
Pei, Snyder, et al. *Nature* **473,** p66 (2011).

p-type PbTe-PbSe ZT (average zT)

Peak zT is high but device ZT (average zT) is not really improved

zT at low temperature reduced by increasing T_{convg}!





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Pei, Snyder, et al. *Nature* **473,** p66 (2011).

zT vs. ZT

Materials figure of merit zT

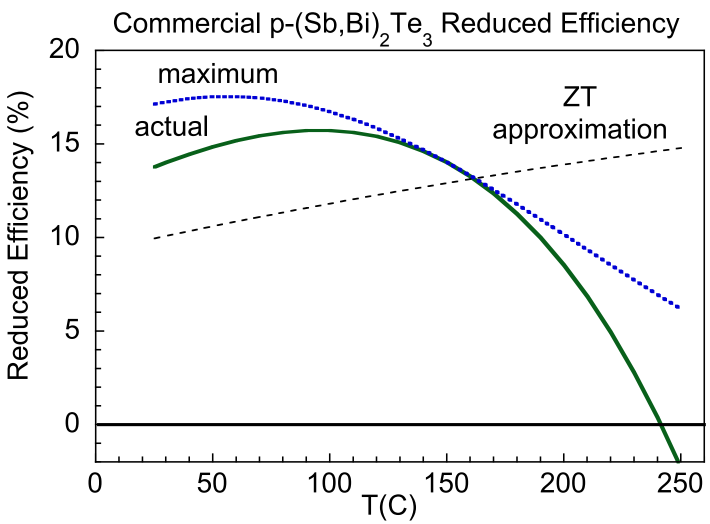
$$\boxed{zT = \frac{\alpha^2}{\rho\kappa} T}$$

Determines maximum reduced efficiency at any given point

$$\max \eta_r = \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + 1}$$

Actual efficiency is less

- series current not optimal everywhere

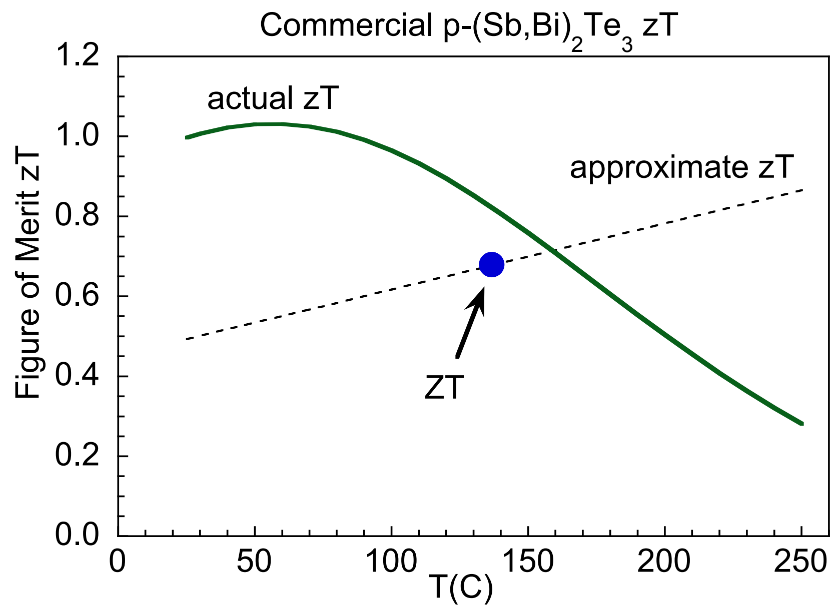


Device Figure of Merit ZT

$$\eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + T_c / T_h}$$

$ZT = zT$ is approximation for

$\alpha(T)$, $\rho(T)$, $\kappa(T)$, are constant



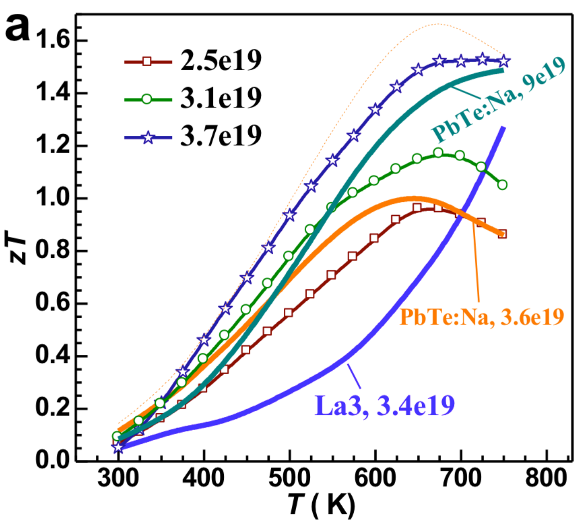
Real materials: $zT \neq ZT$

especially max $zT \neq ZT$

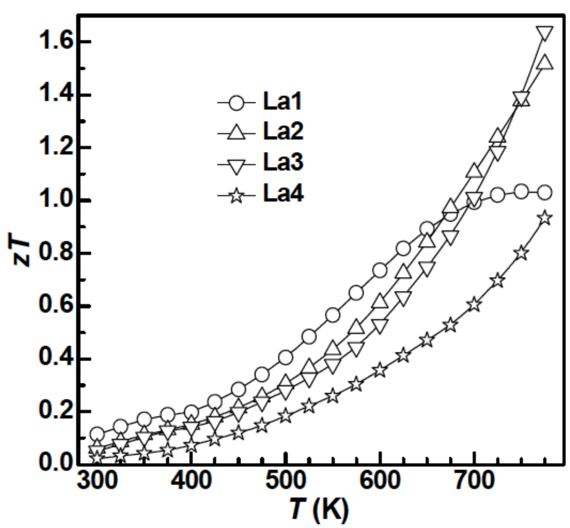
Beware conclusions about changing ΔT

Goldsmid, H. J. Applications of Thermoelectricity (Methuen, London, 1960).

Precipitates in PbTe can Increase *ZT*



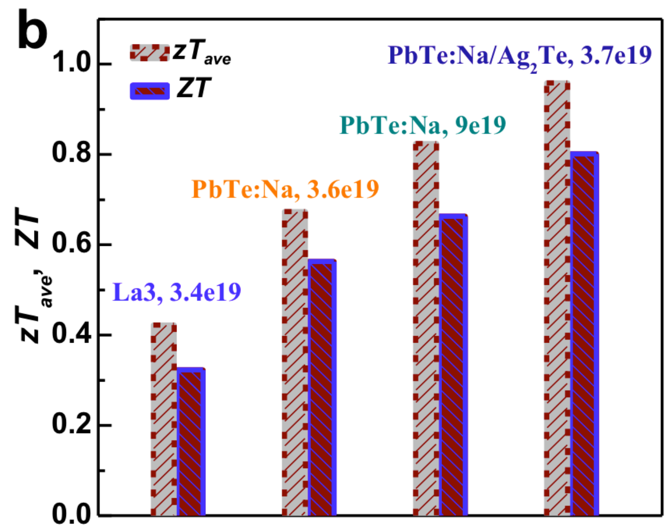
p-type

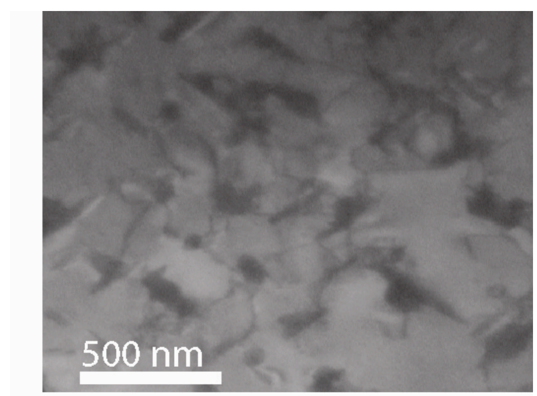


n-type

Higher average *zT*

Higher Device *ZT*





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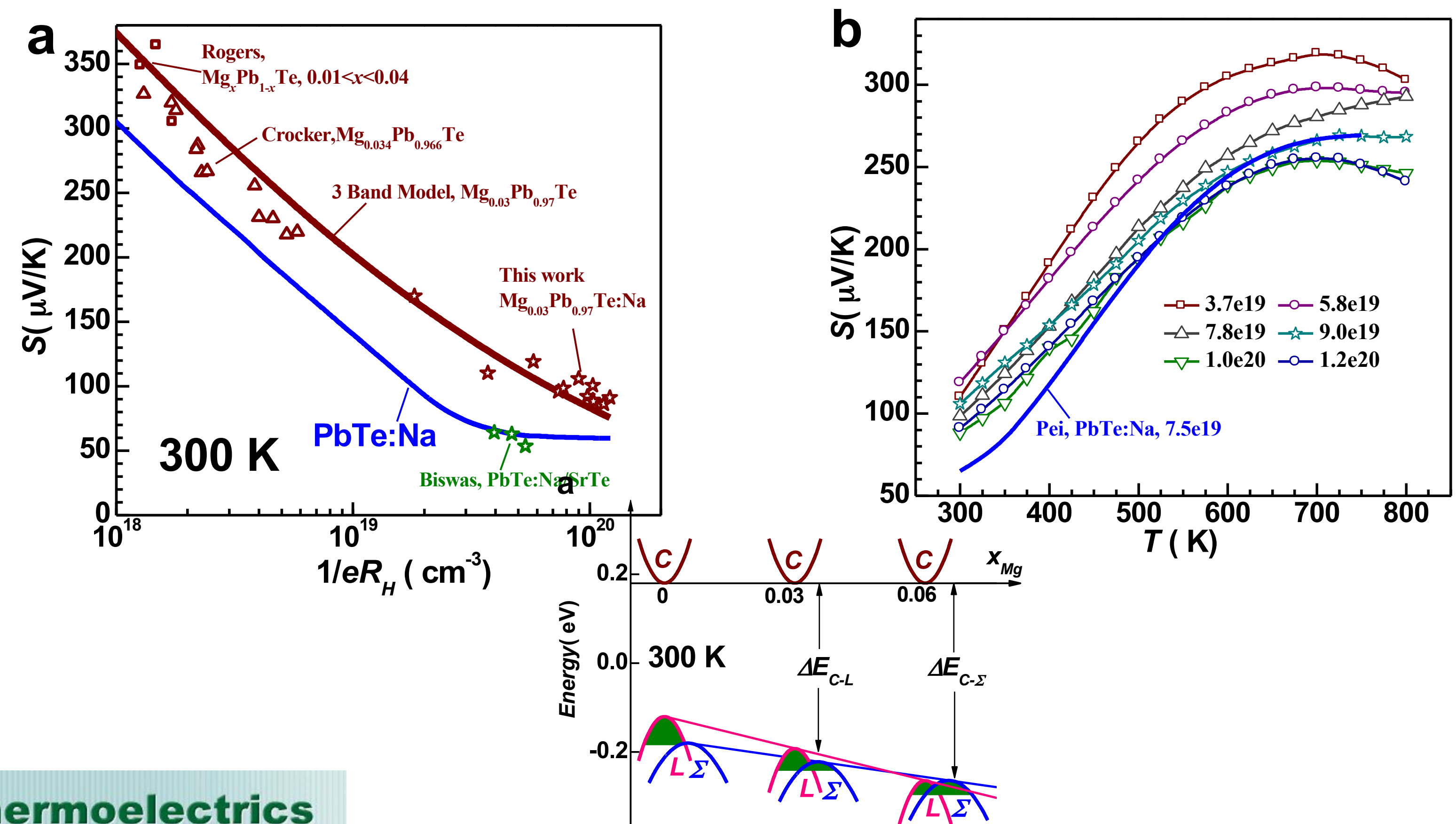
Pei, Snyder, et al, *Energy and Environmental Science* 4, 3640 (2011)

Pei, Snyder, et al, *Adv. Funct. Mat.*,**21,** 241 (2011)

Decreasing T_{convg} with Mg

- $Mg_xPb_{1-x}Te$ shifts valence L band to convergence with Σ at 300K
  - *S* vs *n* (Pisarenko) looks like single heavy band
- Continues to go below Σ at high temperature
  - But band gap (between C and Σ) increases, helps *S* at high *T*



Pei, Snyder, et al. *Advanced Materials* **23**, 5674 (2011)

Increasing ZT by stabilizing n^*

Lower T_{convg}:

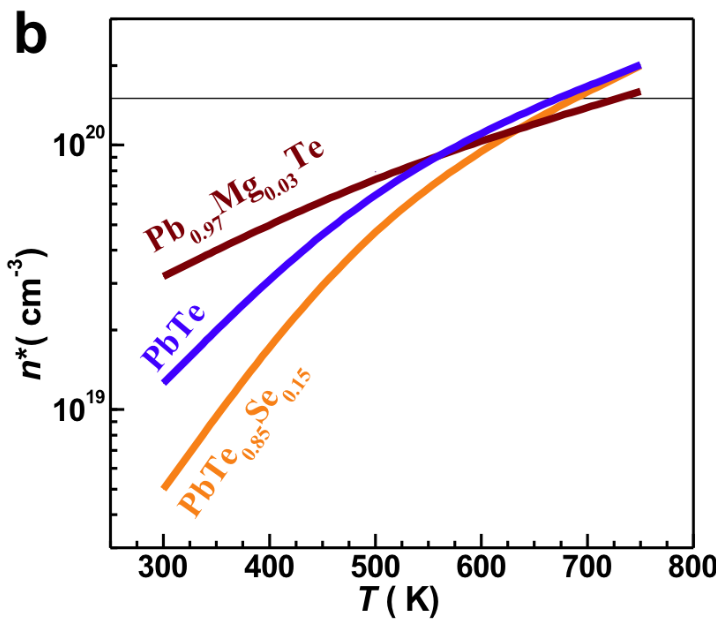
Reduces T of N_V enhancement

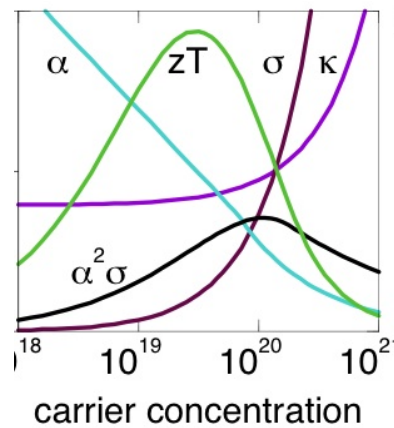
Keeps n^* from increasing with T so fast

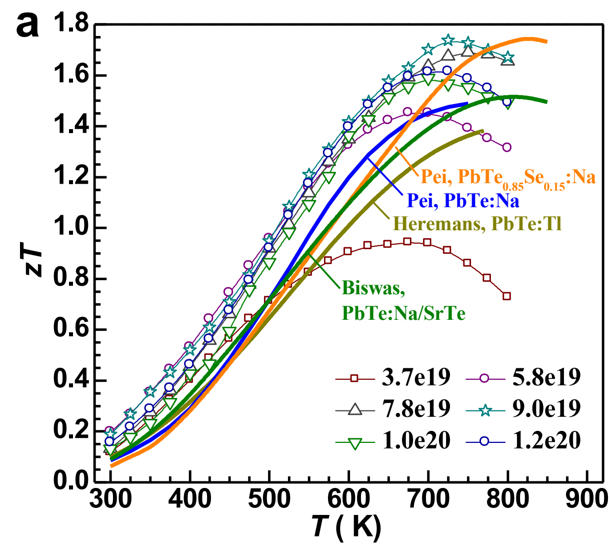
Higher average zT

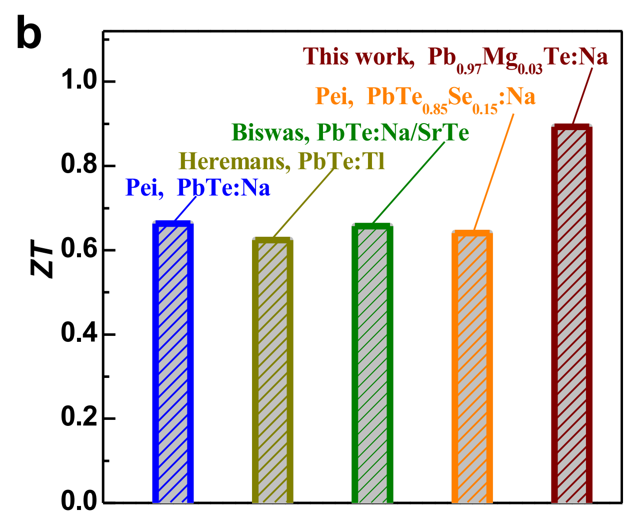
Optimized carrier concentration

$n \sim N_v^{2/3} m_b^* \, T^{3/2}$





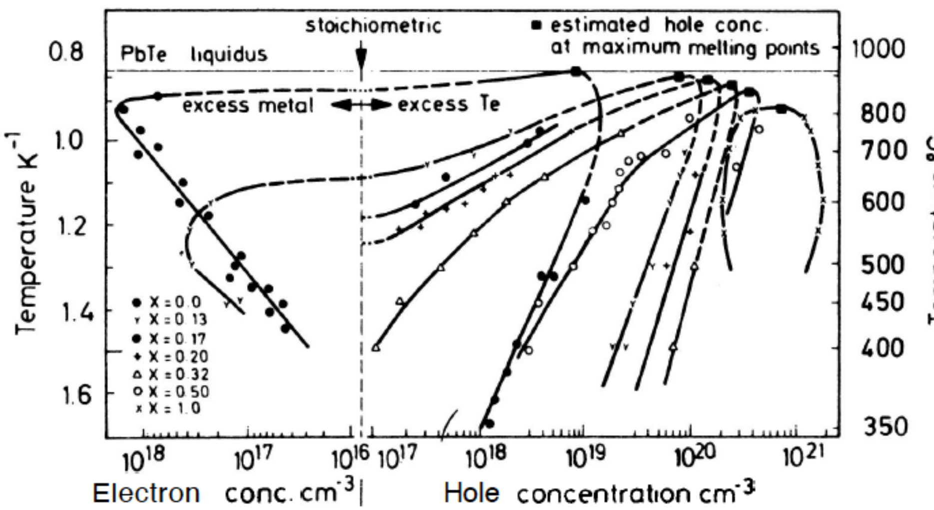




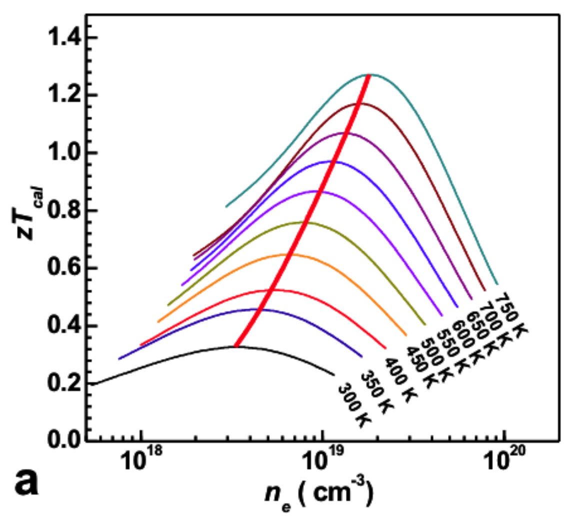
Pei, Snyder, et al. *Advanced Materials* **23**, 5674 (2011)

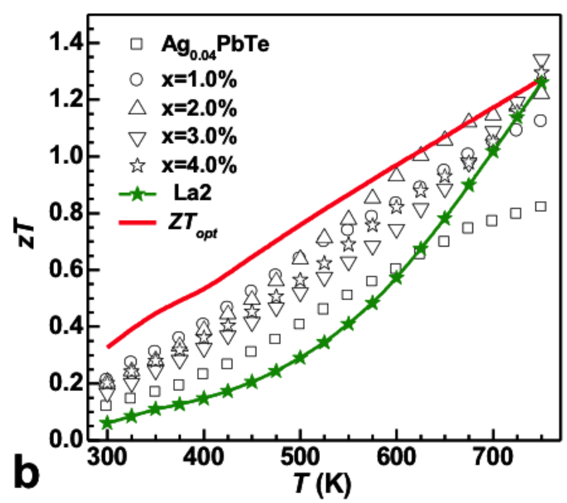
Self-Tuning n^* via Composites

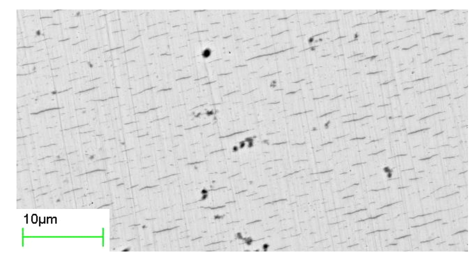
- Temperature dependent dopant solubility
  - Pb, Te, Ag, Cu in PbTe
  - B, P in SiGe
- At solubility limit, n increases with T



TE Handbook (1995)







Ag, Ag_2Te particles in PbTe

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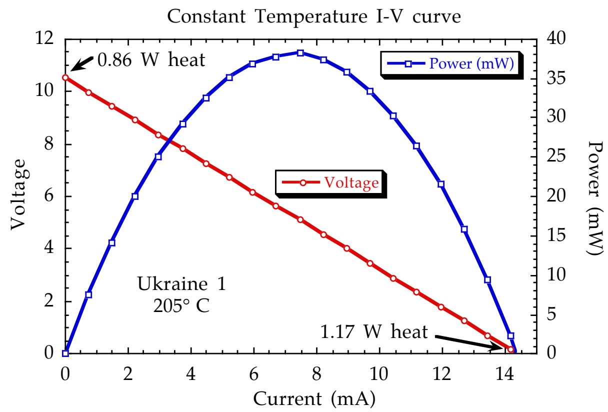
Pei, Snyder, et al. *Advanced Energy Materials* **1**, 291 (2011)

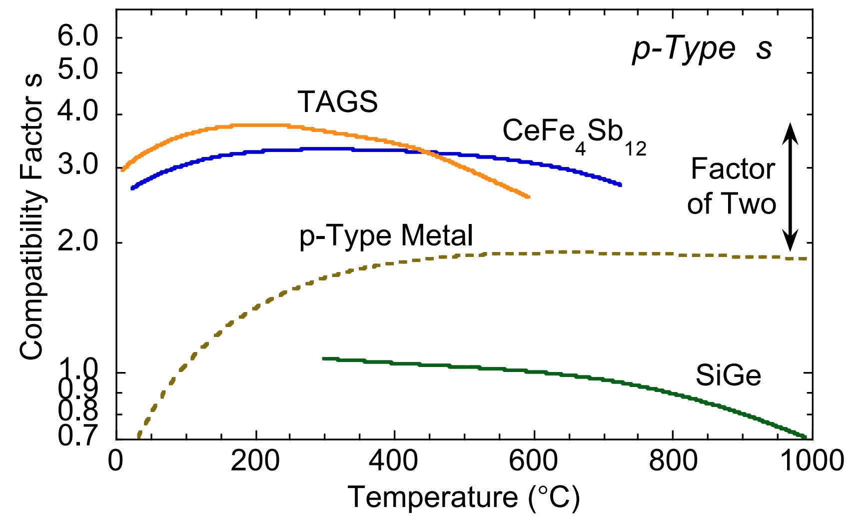
Compatibility Factor

High Efficiency from zT only with compatible s

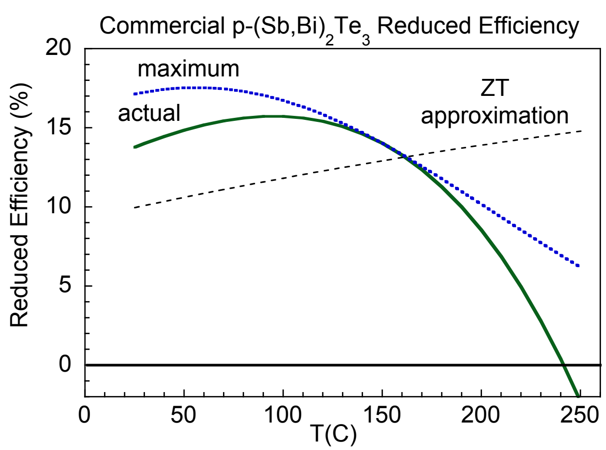
$$s = \frac{\sqrt{1+zT}-1}{\alpha T}$$

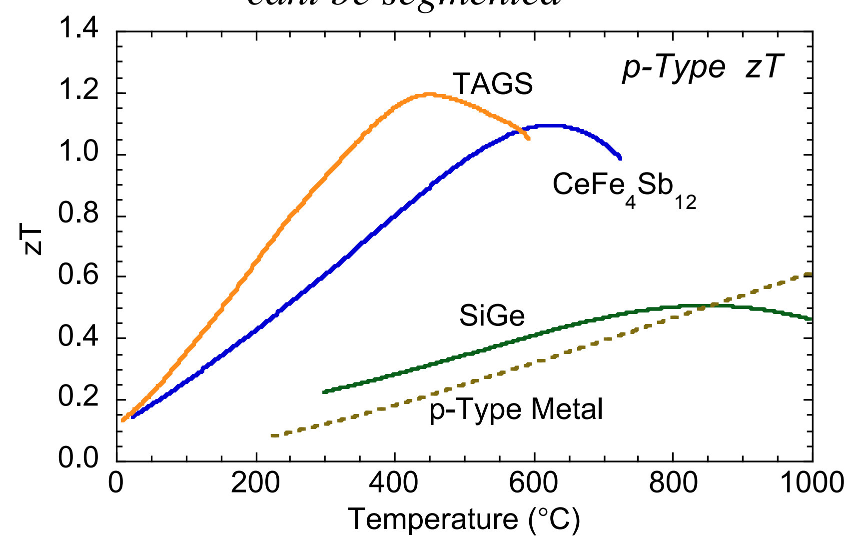
operating current must match





SiGe has small s compared to other TE cant be segmented





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Snyder *Applied Physics Letters* **84**, 2436 (2004)

Summary

Many levels of complexity for ZT

- higher order effects relevant for high efficiency applications

Peak zT

- carrier concentration for peak zT
- quality factor maximization

High average zT

- carrier conc. tuning
- functionally grading
- *self-tuning composites

Band Engr. for ZT

- quality factor engr for avg zT
- nanostructures for low temp
- *stabilizing n*

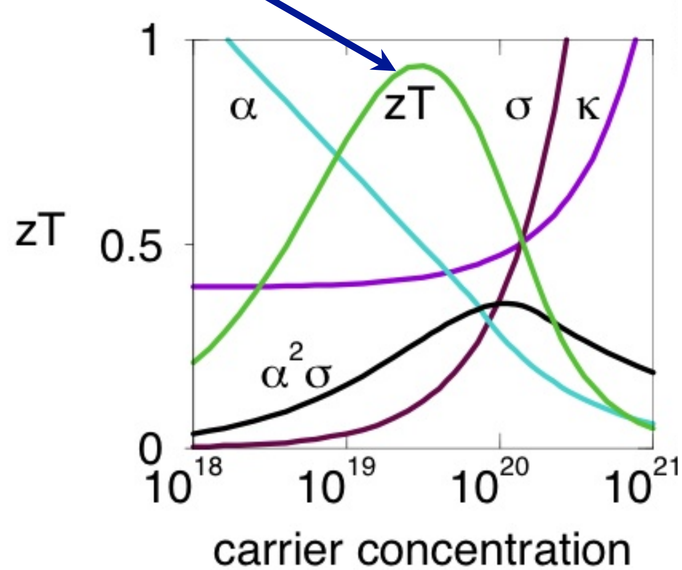
Compatibility effects

- ZT not a simple average of zT

$$\boxed{B \sim \frac{N_V}{m_b^* \kappa_L}}$$

Optimized carrier concentration

$n \sim N_v^{2/3} m_b^* \, T^{3/2}$



Pei, Snyder, et al. *Advanced Materials* **23**, 5674 (2011)
Pei, Snyder, et al. *Advanced Energy Materials* **1**, 291 (2011)
Lalonde, Pei, Wang, Snyder, *Materials Today* **14** 526 (2011)

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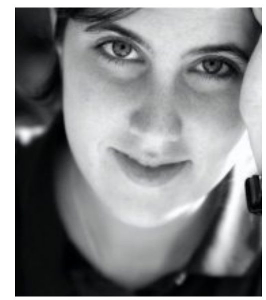
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