Complex Thermoelectric Materials

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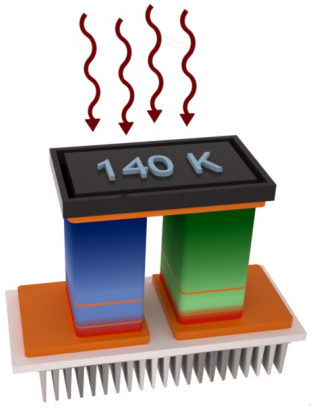
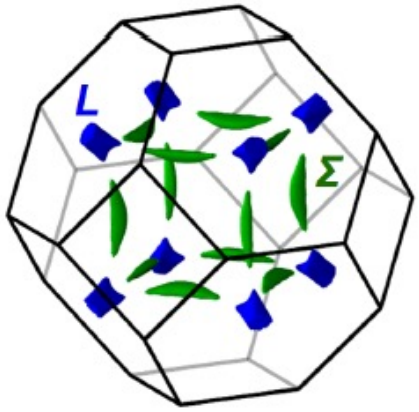
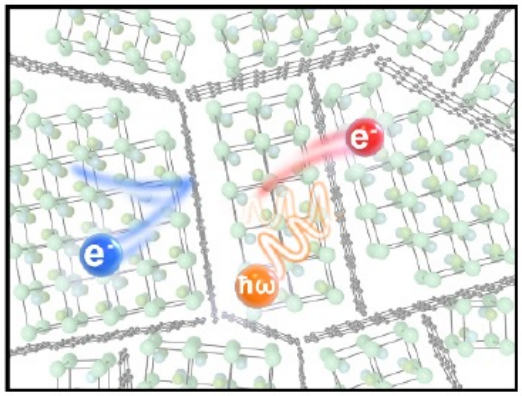
http://thermoelectrics.matsci.northwestern.edu

Device Engineering	Electron-Phonon Engr.	Interfaces
		
Compatibility	Complex Structures	Microstructures

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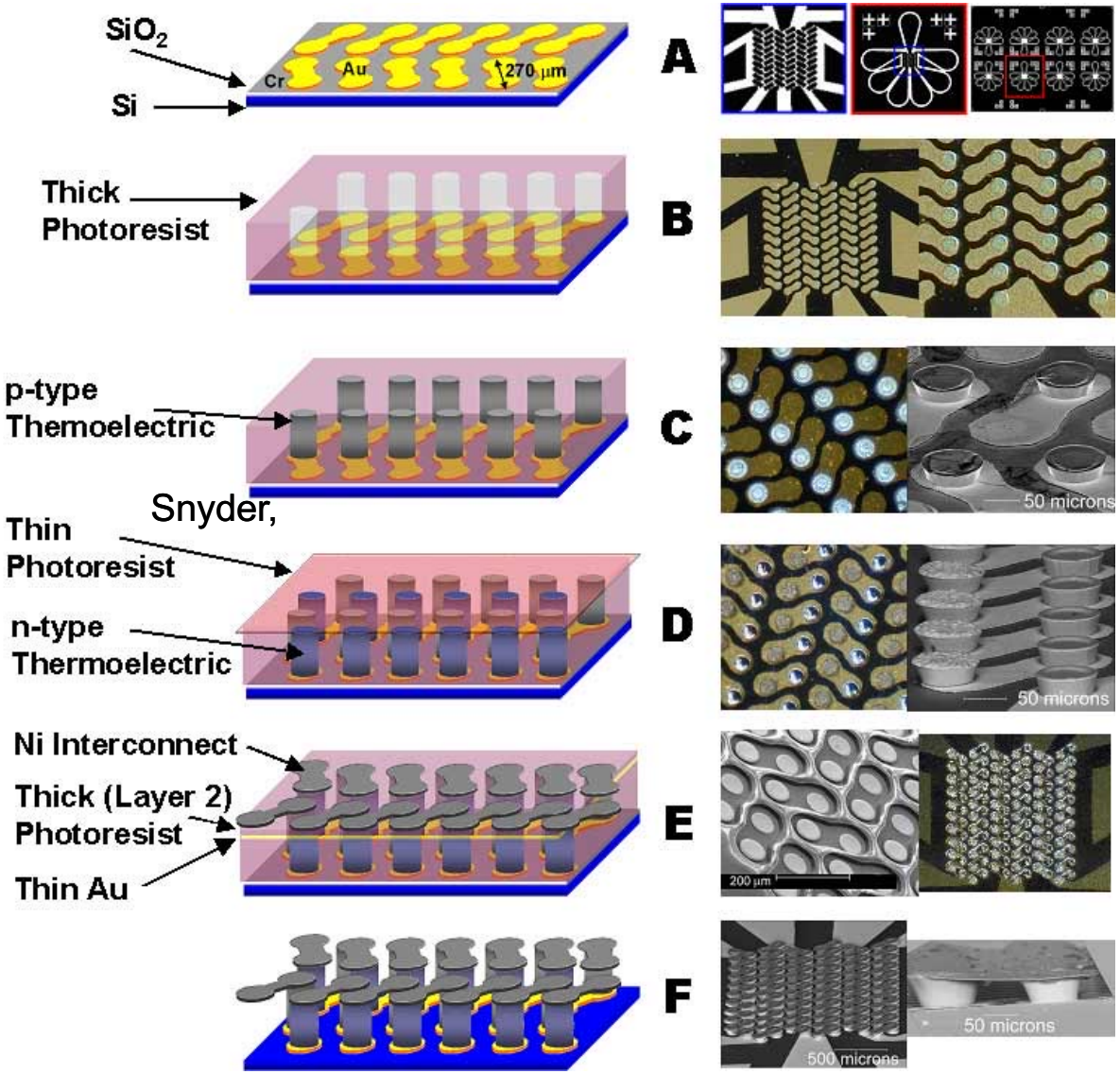
Snyder, Toberer *Nature Materials* **7,** 105 (2008)

JPL 1997-2006

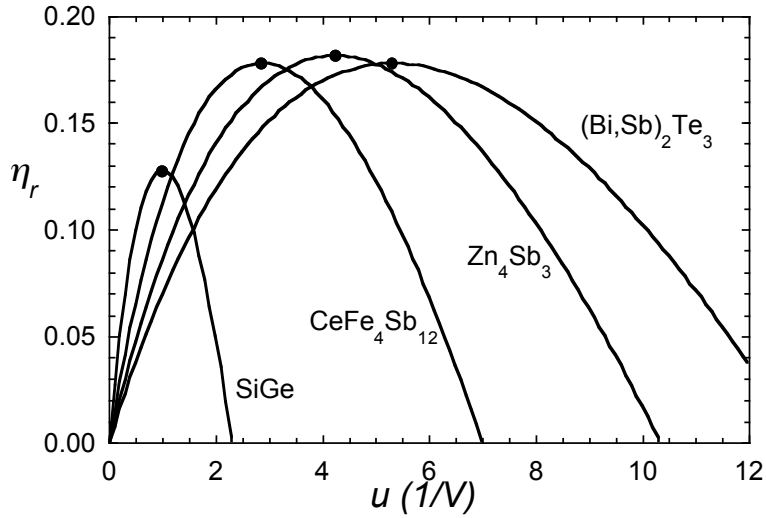
Electrochemical MEMS MicroDevice



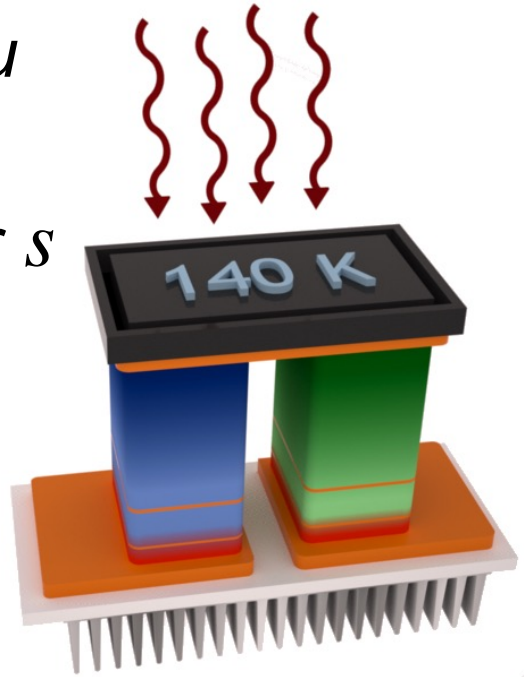
G. J. Snyder *et al.*, *Nature Materials* **Vol 2,** p. 528 (2003)

Compatibility Factor

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



- Power and efficiency depend on red. current *u*
  - not all *T* work at optimum efficiency
- Optimal reduced current is compatibility factor *s*
- *s* depends on material properties
- Leads to Thomson Cooler



G. J. Snyder and T. Ursell, *Phys. Rev. Lett.* ***91****, 148301 (2003)*
G. J. Snyder et al, *Phys. Rev. B.* , 86 045202 (2012)

ZT Calculator

Materials figure of merit

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

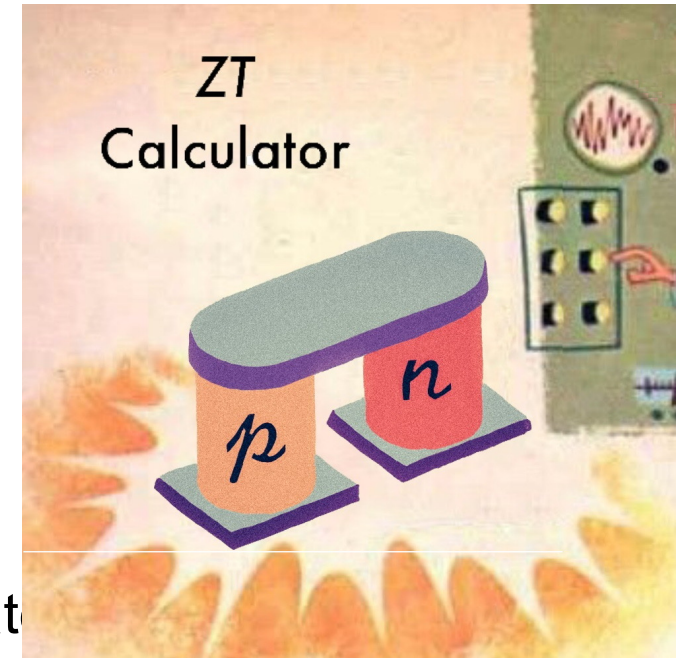
Efficiency comes from device ZT

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

Exact definition of ZT

Can be calculated from spreadsheet calculat

easy!



$$ZT = \left(\frac{T_h - T_c(1-\eta)}{T_h(1-\eta) - T_c}\right)^2 - 1$$

T (K)	Seebeck (μV/K)	resistivity (10-3 Ω cm)	thermal cond. (W/m K)	zT	max Red eff	s (1/V)	u (1/V)	Red eff	Φ (V)	efficiency	ZT
300	106	0.71	2.52	0.19	4.3%	2.83	2.7815	4.3%	0.391		
325	119	0.75	2.29	0.27	5.9%	3.26	2.8222	5.8%	0.393	0.4%	0.22
350	131	0.81	2.09	0.36	7.6%	3.58	2.8658	7.3%	0.395	0.9%	0.26
375	142	0.90	1.94	0.43	8.9%	3.70	2.9084	8.6%	0.397	1.4%	0.30
400	154	1.01	1.79	0.52	10.4%	3.79	2.9596	10.0%	0.399	2.0%	0.33
425	166	1.14	1.68	0.61	11.8%	3.81	3.0174	11.4%	0.402	2.7%	0.37
450	178	1.28	1.57	0.71	13.3%	3.84	3.0804	12.9%	0.405	3.3%	0.40
475	191	1.43	1.49	0.81	14.8%	3.83	3.1537	14.4%	0.408	4.0%	0.44
500	205	1.59	1.40	0.95	16.5%	3.86	3.2418	16.2%	0.411	4.8%	0.48
525	219	1.74	1.33	1.08	18.2%	3.87	3.3365	17.9%	0.414	5.6%	0.53
550	229	1.90	1.26	1.21	19.6%	3.85	3.4259	19.4%	0.418	6.4%	0.57
575	239	2.06	1.21	1.31	20.6%	3.79	3.5132	20.6%	0.422	7.2%	0.62
600	247	2.22	1.16	1.42	21.7%	3.74	3.6039	21.7%	0.426	8.1%	0.66
625	254	2.37	1.13	1.50	22.5%	3.66	3.6893	22.5%	0.430	8.9%	0.71
650	258	2.52	1.09	1.58	23.2%	3.60	3.7663	23.2%	0.433	9.7%	0.75
675	262	2.66	1.07	1.63	23.7%	3.51	3.8429	23.6%	0.437	10.5%	0.79
700	266	2.80	1.04	1.70	24.3%	3.45	3.9254	24.1%	0.441	11.3%	0.83
725	269	2.94	1.03	1.74	24.7%	3.35	4.0046	24.1%	0.445	12.0%	0.87
750	269	3.08	1.02	1.73	24.6%	3.23	4.0514	23.7%	0.448	12.8%	0.90
775	268	3.24	1.01	1.70	24.3%	3.10	4.0926	23.0%	0.452	13.4%	0.93
800	268	3.42	1.01	1.67	24.1%	2.95	4.1582	21.9%	0.455	**14.0%**	0.96

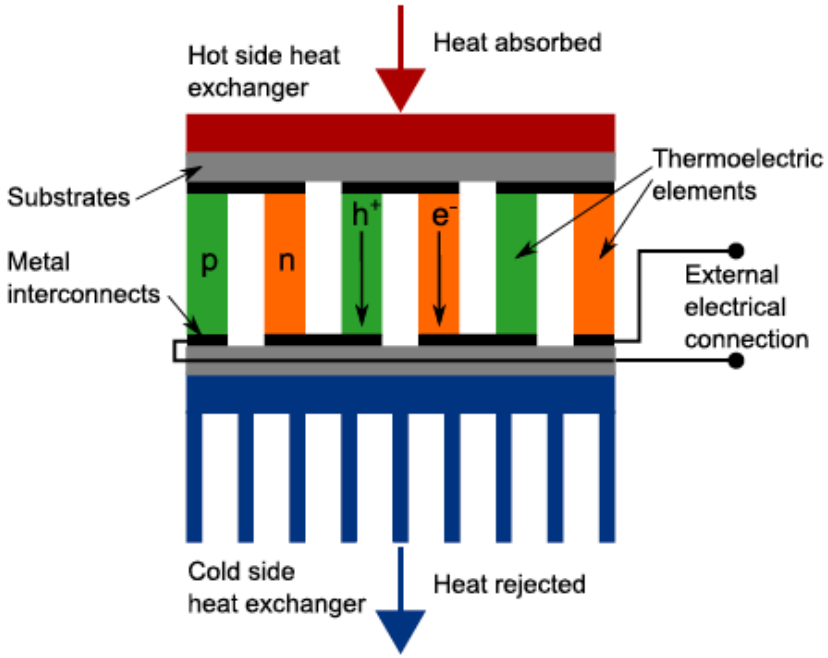
Snyder, *Energy and Environmental Science* **10**, 2280 (2017)
http://thermoelectrics.matsci.northwestern.edu/thermoelectrics/ztcalc.html

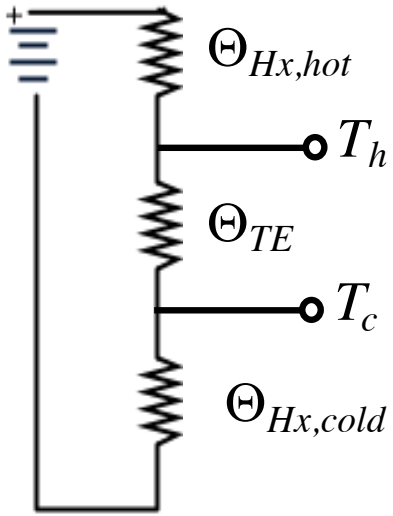
Leg Length from Thermal Impedance Match

Thermal Impedance match of Heat Exchanger

Effectively determines leg length of thermoelectric

$$\Theta_{TE} = \Theta_{\mathrm{Hx}}$$





$$\Theta_{TE} = \frac{l}{\kappa_{TE} A f}$$

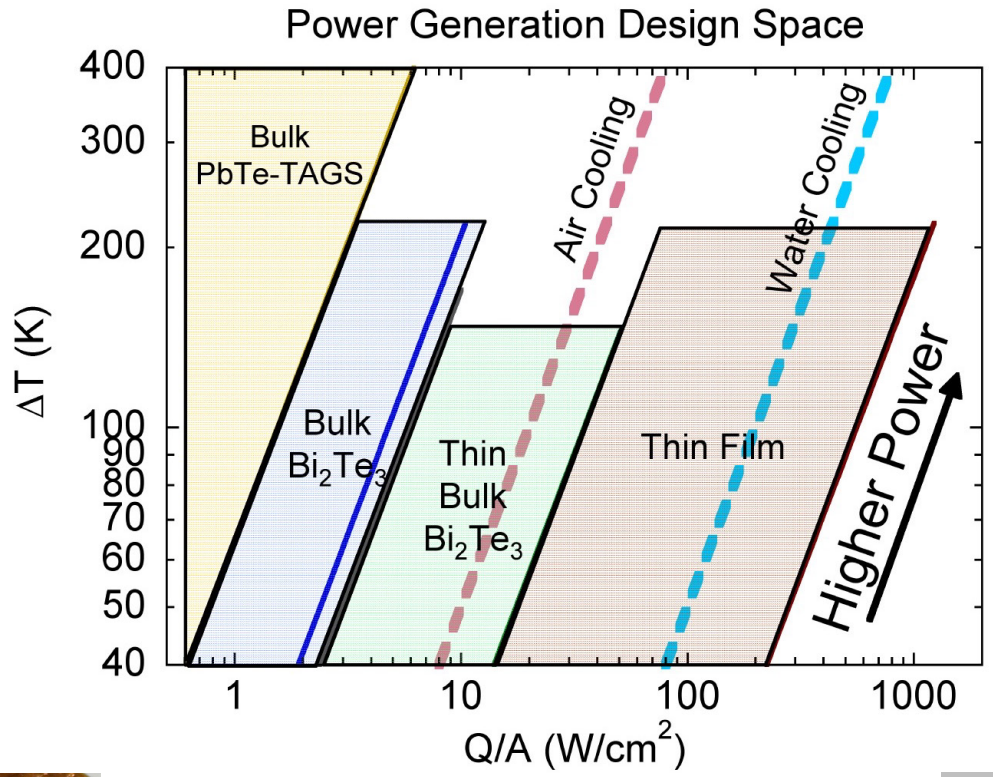
l = leg length

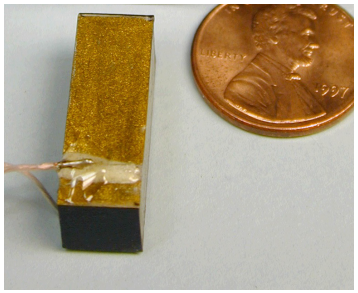
f = TE fill factor

A = area

Baranowski, Snyder et al, *J Applied Phys.* 113, 204904, (2013)

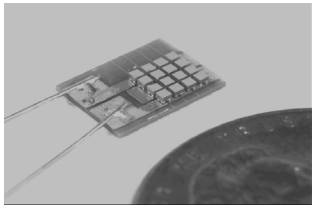
TE phase space





Thermopile
l ~ 20 mm

Commercial Module
l ~ 2 mm



Thin Film Device
l ~ 0.02 mm

ZT for maximum Power

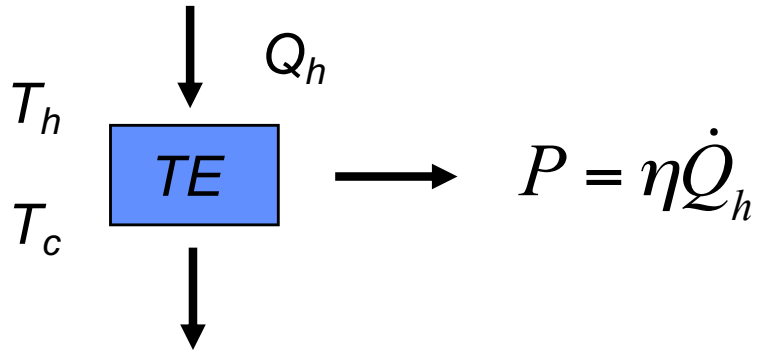
not 'power factor': Proof by Contradiction

1) Suppose material or device design based on power not *ZT* (lower efficiency η_P)

$$P = \alpha^2 \sigma \frac{A}{l} \Delta T^2 \frac{R_L / R_{TE}}{\left(1 + R_L / R_{TE}\right)}$$

$$\Theta_{TE} = \Theta_{Hx} = \frac{l}{\kappa_{TE} A f}$$

2) Take same System Design: same heat flux Q_h at same ΔT,
Use TE designed for efficiency (maximize ZT) η_{ZT}



3) Because $P = \eta Q_h$, *ZT* device produces more power

Baranowski, Snyder *et al, J Applied Phys.* 115, 126102, (2014)
Zavenelli, Snyder *J. Appl. Phys.* 131, 115101 (2022)

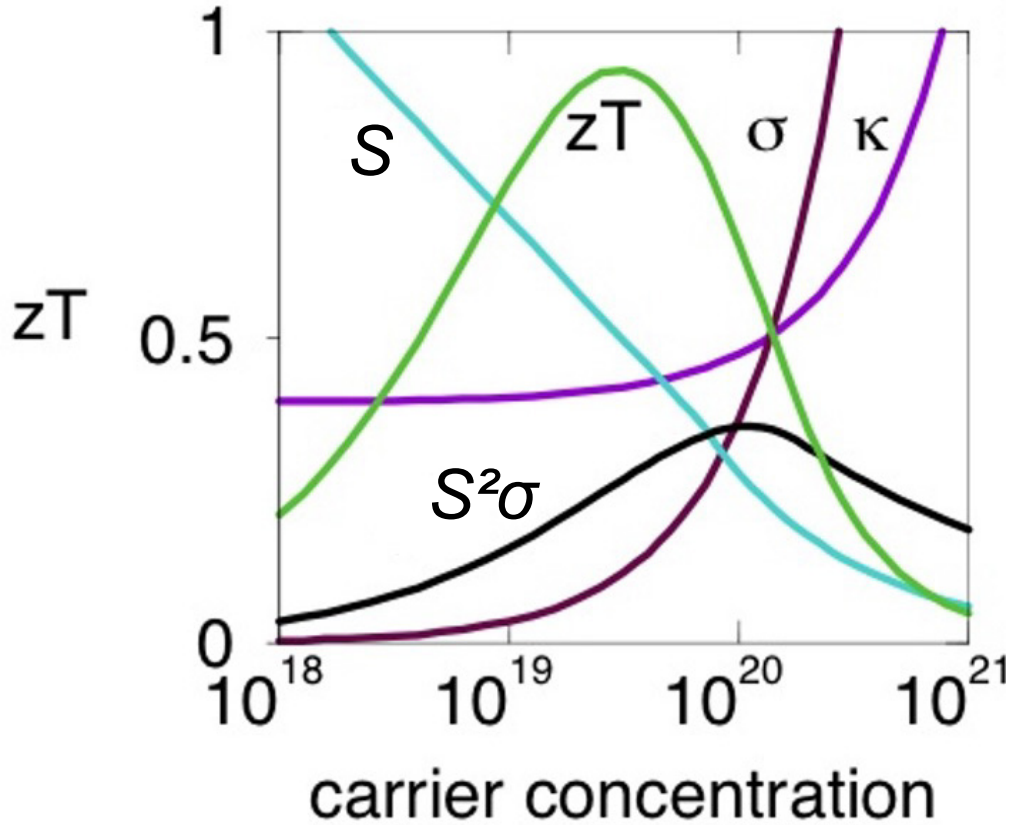
“Promising TE Material” ?

Maximum zT depends on Quality Factor, B

$$B \sim \frac{\mu_w}{\kappa_L}$$

Weighted Mobility

Lattice Thermal Conductivity



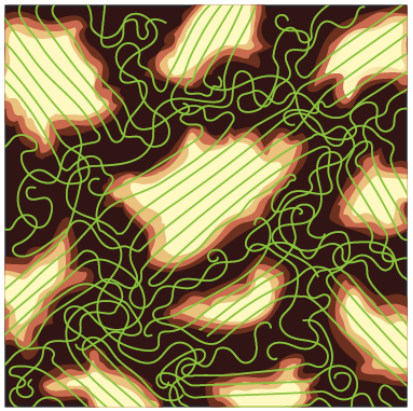
“Better Electronic Properties” = higher μ_W (not S, $S^2\sigma$)

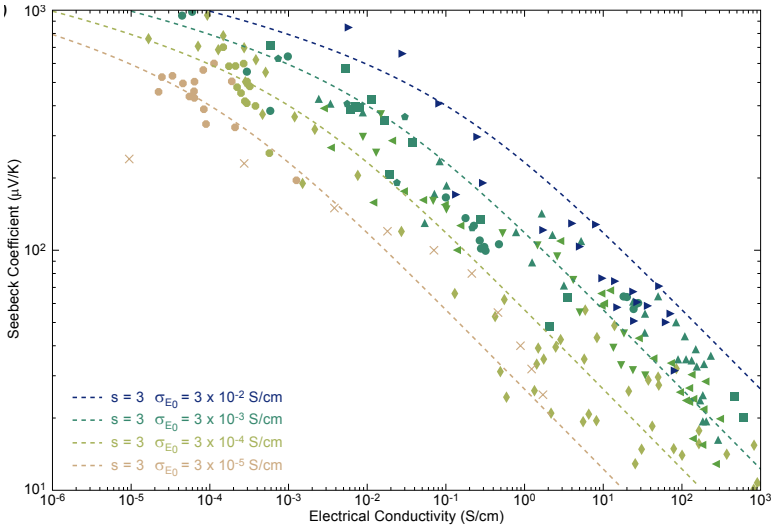
“Better Thermal Properties” = lower κ_L

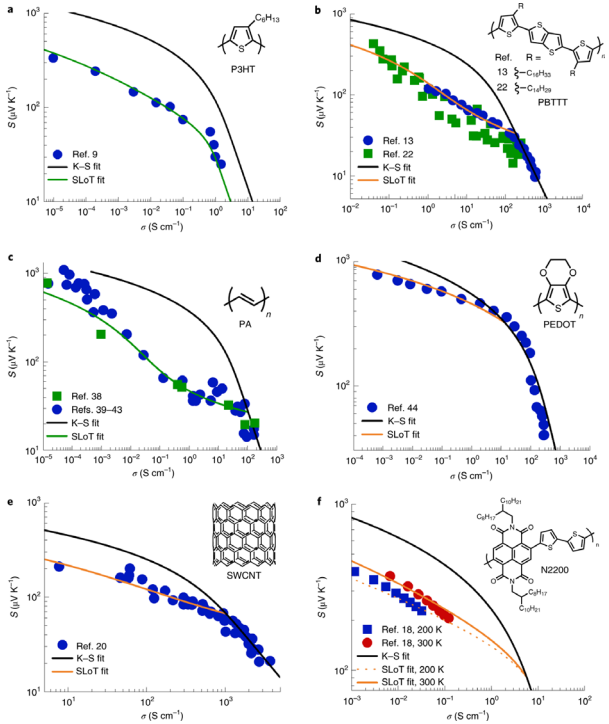
Snyder et. al. *Advanced Materials*, **32**, 2001537 (2020)
Pei, Wang, Snyder *Advanced Materials* **24**, 6125 (2012)

μ_W for Disordered Materials

- Model how properties change with doping
- Helps identify transport mechanism
- Quantify Localization
- Predicts peak *zT*







polyacetylene (◆); PBTTT (■◀); P2TDC17-FT4 (⬟)
P3HT (●▲); PDPP3T (▶); PSBTBT (▼); P3HTT (🛑)

S. Kang and Snyder, *Nature Materials* **16**, 252 (2017)
S. Gregory et al, *Nature Materials* **20**, 1414 (2021)
M Agne et al, *Matter* **4**, 2970 (2021)

Ball-Milling Synthesis

Complex alloys typically melt incongruently

melt produces inhomogeneous materials

Solution = Milling + Annealing of solid

Solid-state reaction diffusion limited

reaction time t

particle size l

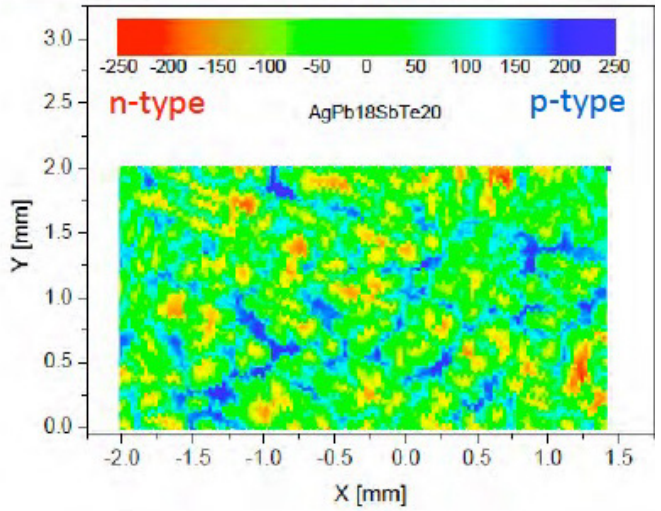
diffusion coefficient D

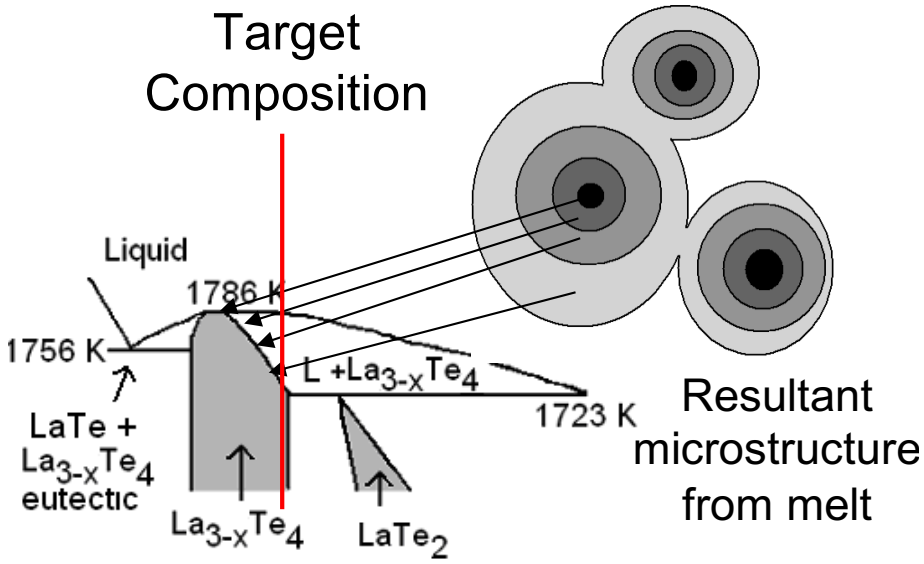
$$t \approx \frac{l^2}{D}$$

Mechanical Alloying - Ball Milling

Reduce particle size l to 10-100nm

speed reaction time at low temperature





Thermoelectrics
Northwestern Materials Science and Engineering

May, Snyder, *Phys. Rev. B* **78**, 125205 (2008)
Snyder, Müller et al., *Appl. Phys. Lett.*, **87**, *p.* 171903 (2005)

Rapid Hot Press vs SPS

Spark? Plasma?

Want to drive ions with DC current?

System	HP	SPS	RHP
Cost	Med	High	Low
System size	Med	Large	Small
Heating rate	Slow	Fast	Fast
Chemistry effect	None	Problem	None
Design flexibility	Med	Small	Large
Scale up	Easy	Hard	Easy

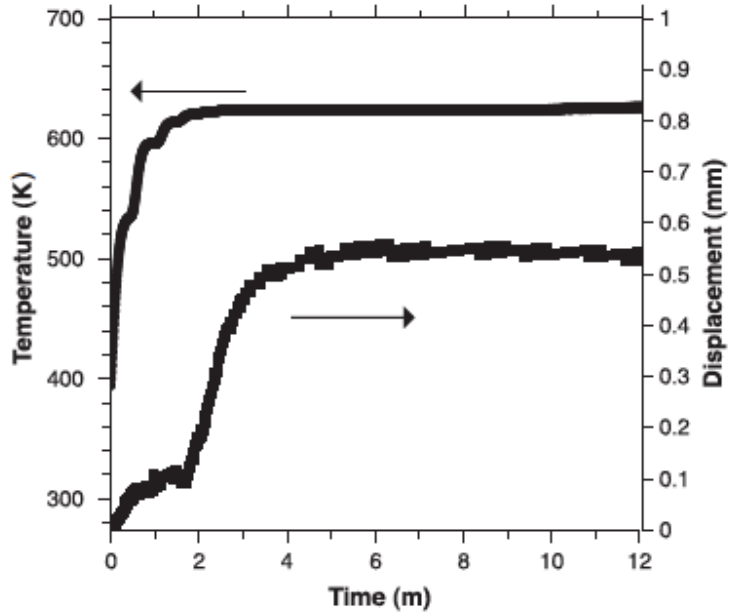


FIG. 2. Temperature vs ram displacement for consolidation of sample at 623 K for 10 min.

Radio Frequency (RF) Heating

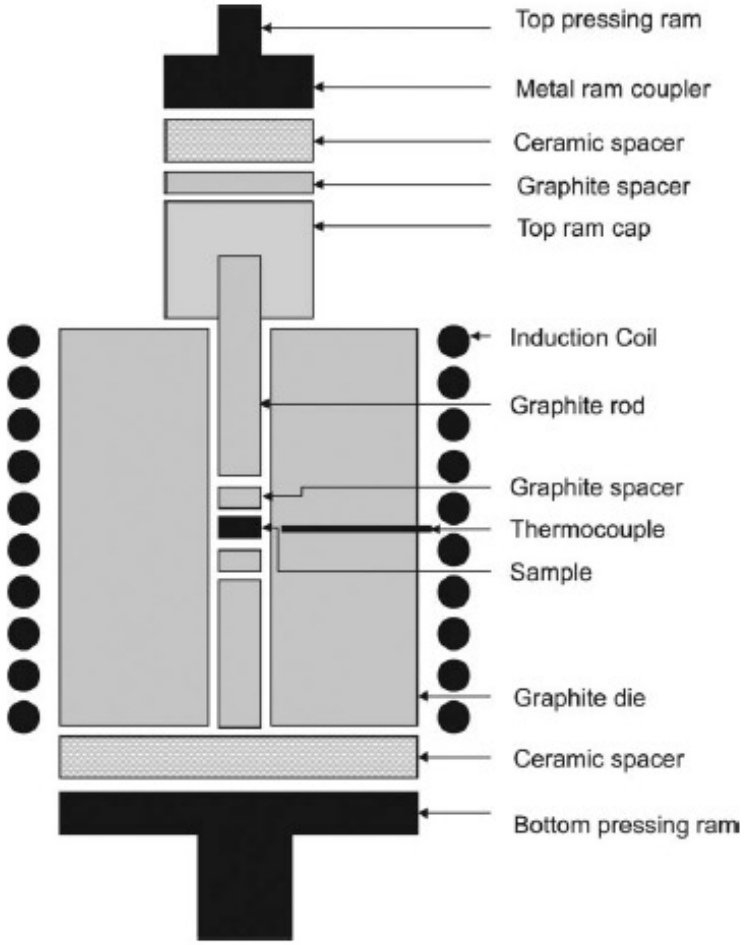
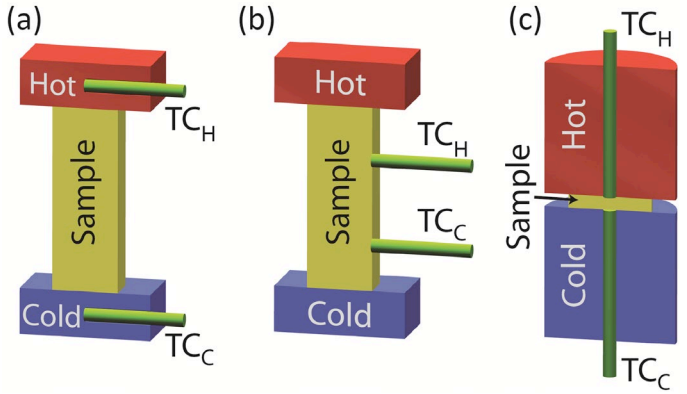


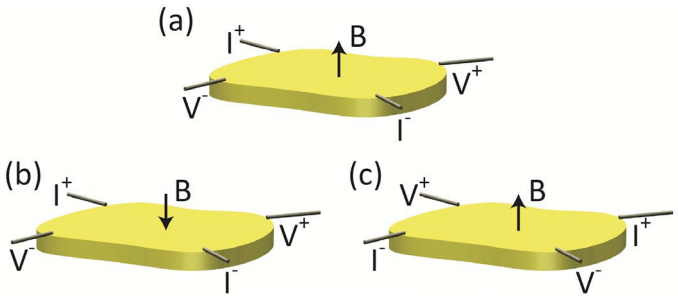
FIG. 1. Schematic of induction hot press setup.

Lalonde, Ikeda, Snyder *Rev. Sci Instruments*., ***82***, 025104 (2011)

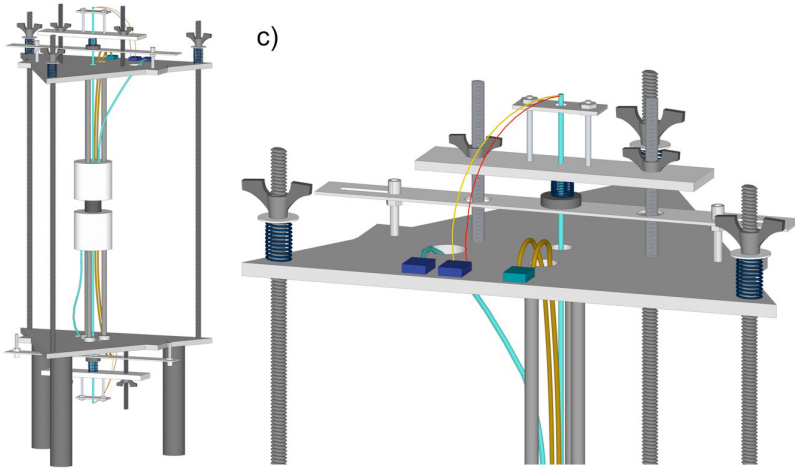
Measurement Techniques



Seebeck to avoid
Cold Finger Effect



Van der Pauw for Electrical
Conductivity and Hall Effect

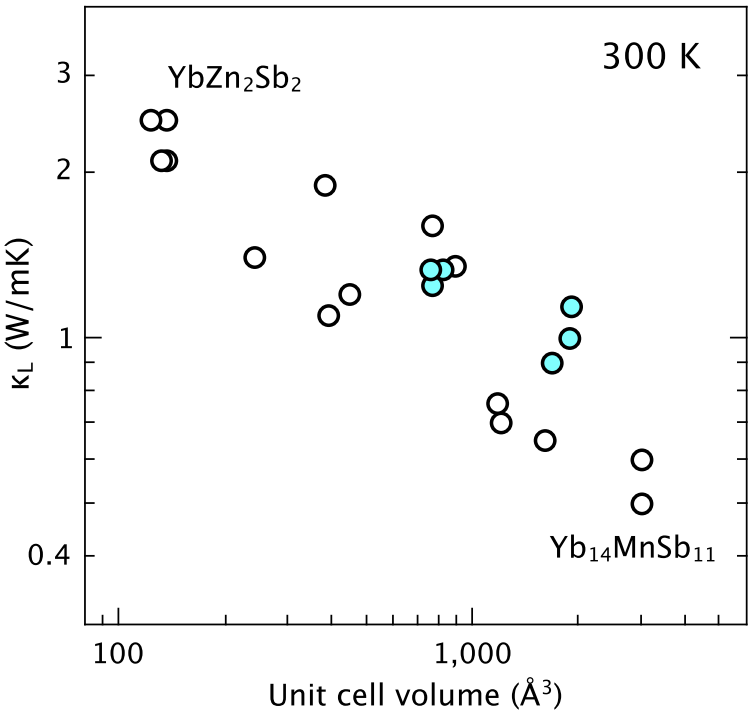


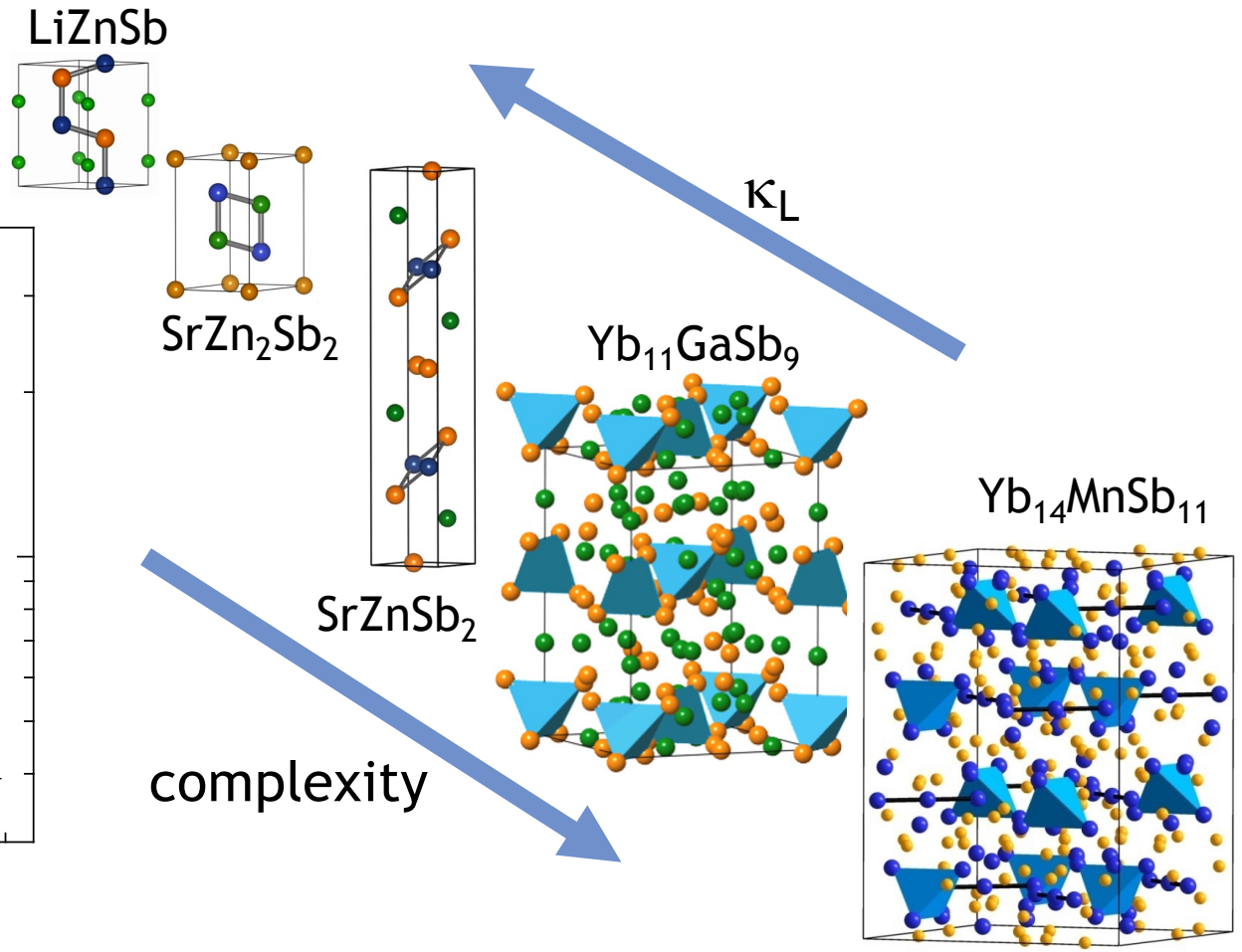
Borup, Snyder, et al., *Energy. Env. Sci.*, **8**, 423 (2015)
J. Martin, *Meas. Sci. Technol.*, 24, 085601 (2013)

Caltech 2006-2014

Thermoelectrics
Caltech Materials Science

Zintl Thermoelectrics





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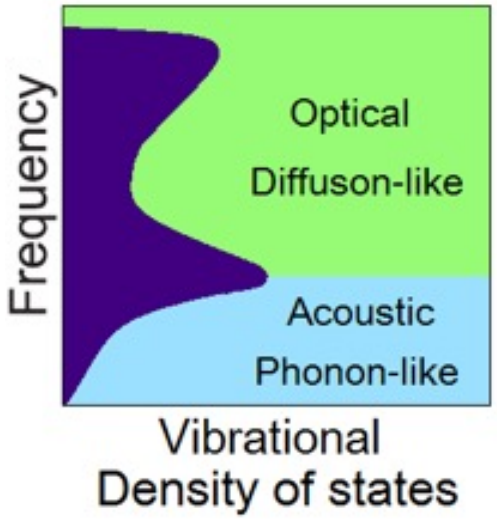
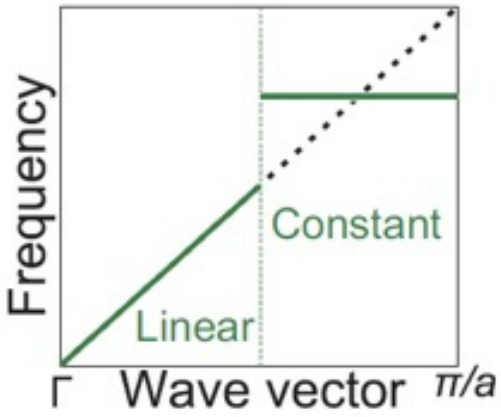
Toberer, May, Snyder *Chem. Mat.*, **22,** p. 624 (2010)

Thermal Conductivity model

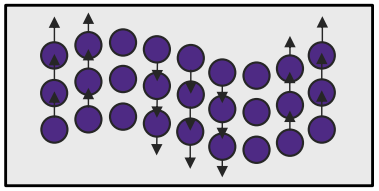
$$\kappa_L = \kappa_U + \kappa_{optic}$$
$$= \frac{A}{T} + B$$



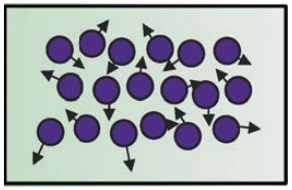


Acoustic phonons

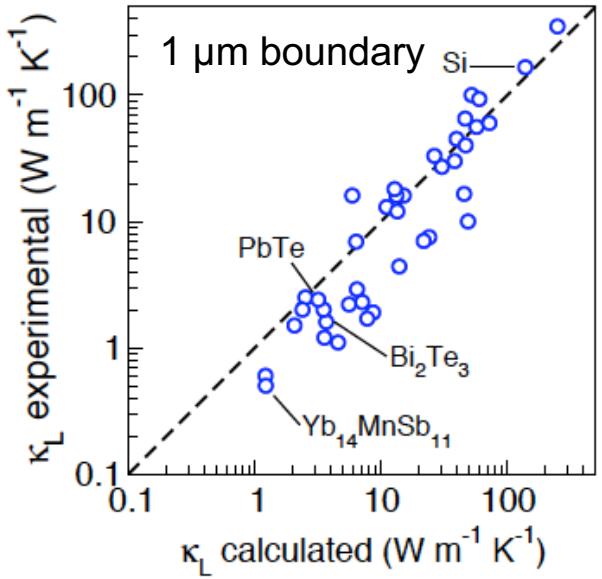
Umklapp Scattering



Diffusons at κ_{min}



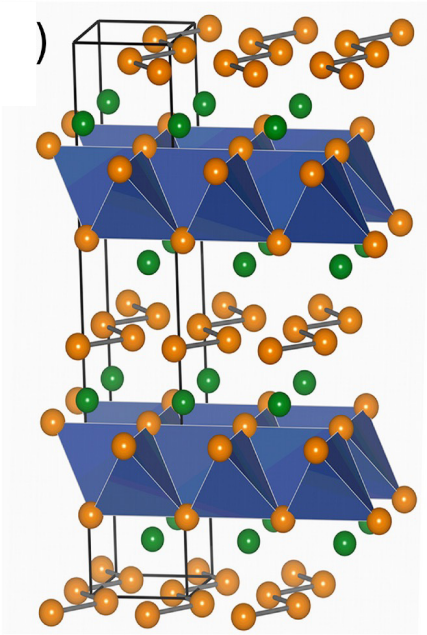
$$\kappa_{optic} \sim 0.76 \frac{k_B v_s}{V^{\frac{2}{3}}} \left(1 - N^{\frac{-2}{3}}\right)$$



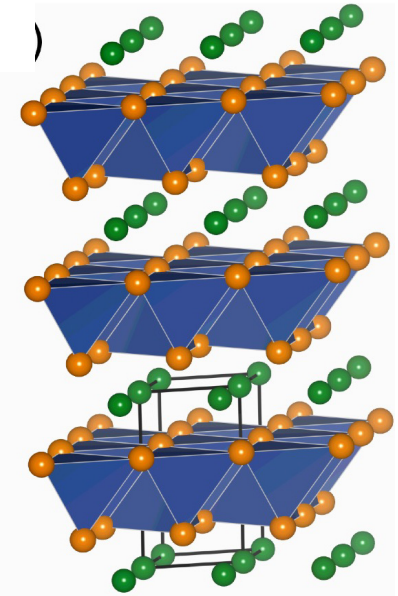
Agne, Snyder, *Energy. Eng. Sci,* 11 609 (2018); *National Sci. Rev.*, **6**, 380 (2019)

$SrZnSb_2$, $SrZn_2Sb_2$ and Mg_3Sb_2

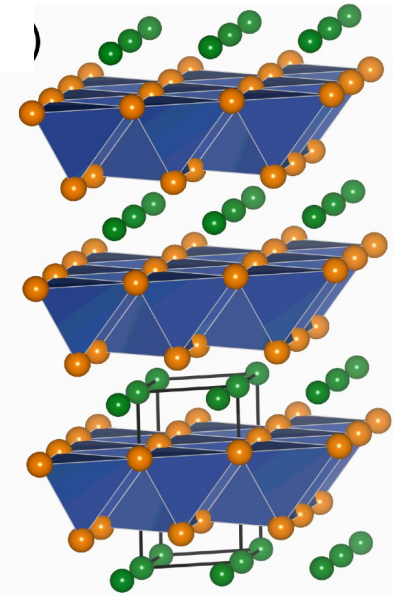
$SrZnSb_2$



$SrZn_2Sb_2$



Mg_3Sb_2



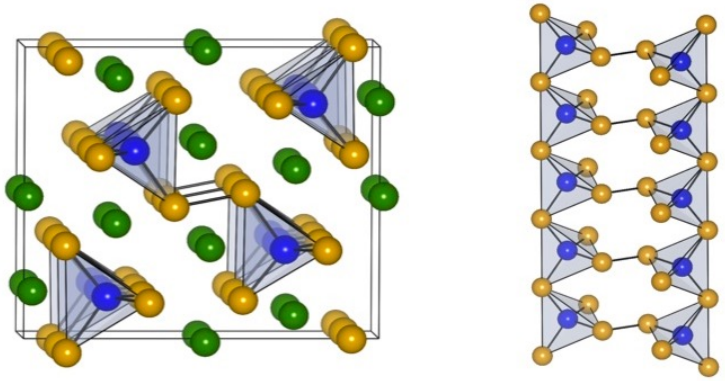
Toberer et. al. *Dalton Trans*., **39**, p. 1046, (2010)
Gascoin et. al. *Adv. Funct. Mat*., **15**, p. 1860, (2005)
Condron et al, J. Solid State Chemistry **179** 2252 (2006)

Some Zintl Chain Structures

$Ca_5M_2Sb_6$
M=Al, Ga, In

chains linked by Sb-Sb bonds to form "ladders"

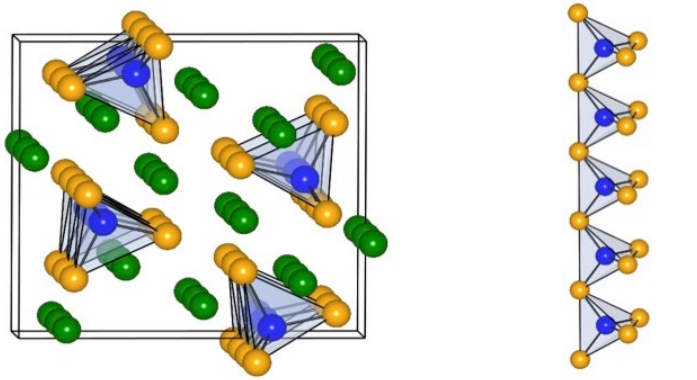
26 atoms per cell



Ca_3AlSb_3

simple corner sharing linear chains

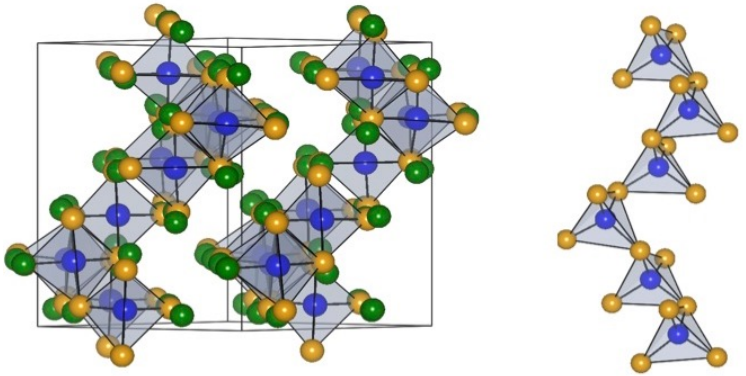
28 atoms per cell



Sr_3GaSb_3

non-linear corner sharing chains with 4-tetrahedra periodicity

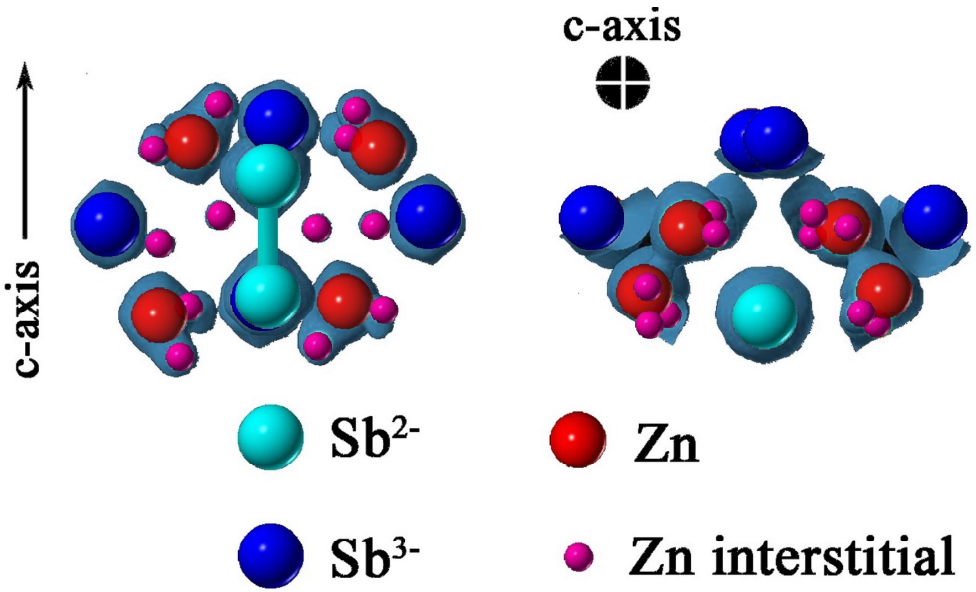
56 atoms per cell

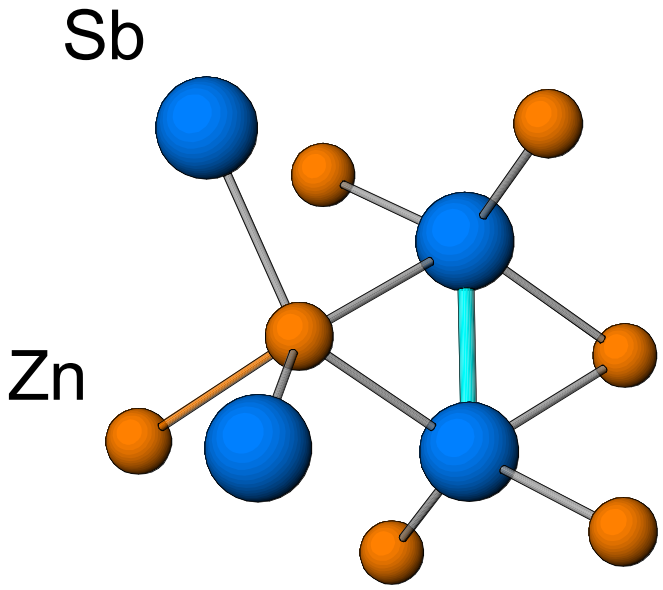


Zevalkink, GJS *Energy Environ. Sci.*, **5**, 9121 (2012)
Zevalkink, GJS *Chem. Mater.* **24**, 11, 2091 (2012)
Zevalkink, GJS J. Materials Chemistry 22(19), 9826 (2012)

Zn_4Sb_3 and ZnSb

$Zn_4Sb_3 = Zn_{3.9-x}Sb_3$ "Zintl"





Extra Zn found in interstitial sites

ZnSb: Sb^{-2}-Sb^{-2} dimers

Snyder et al, *Nature Materials* **3**, 458 (2004)
Böttger, Snyder, *Physics Status Solidi* **208**, 2753 (2011)

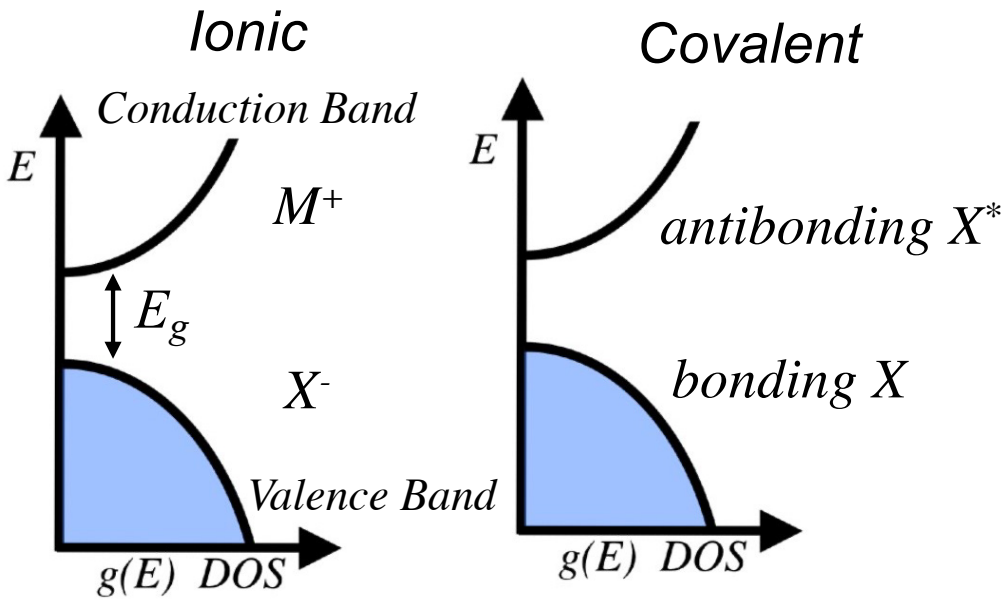
Zintl Valence Semiconductors

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

e valence electrons in atom

each bond b reduces |valence| by 1

Zintl Phase
Valence Balance
= Semiconductor



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

Zintl Valence Semiconductors

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

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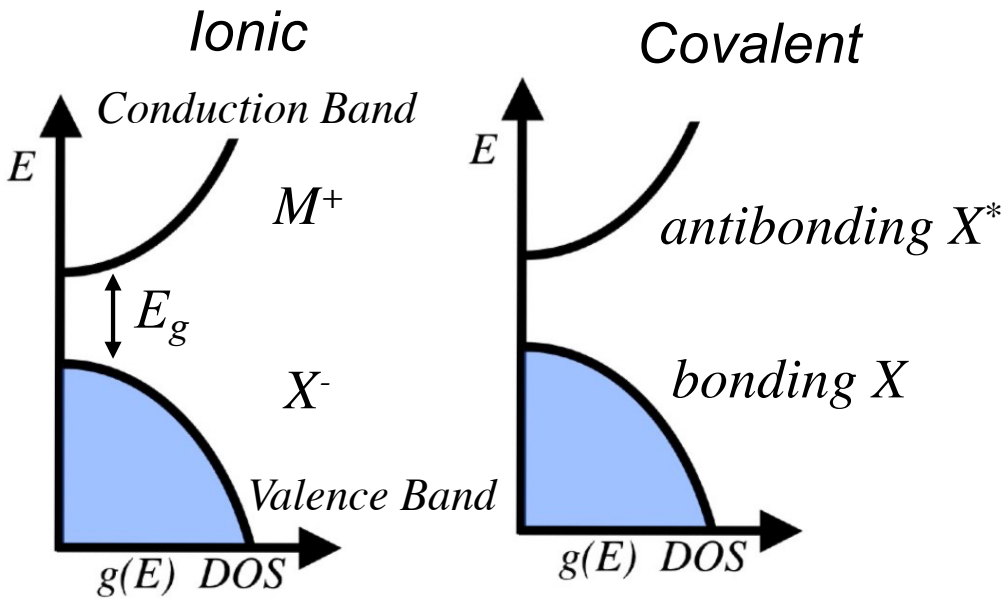
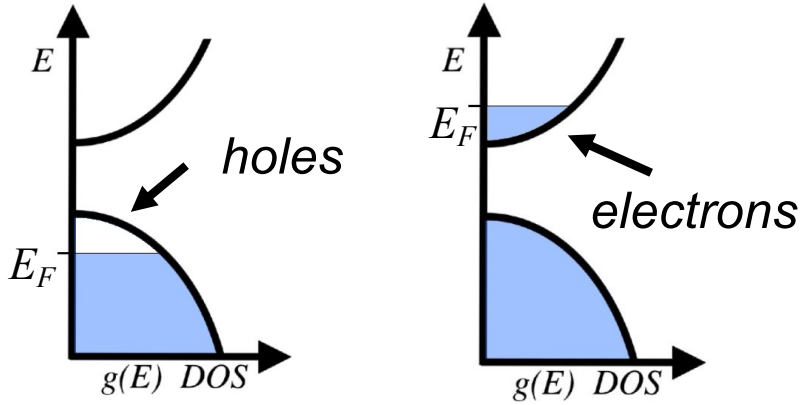
Valence Balance
= Semiconductor



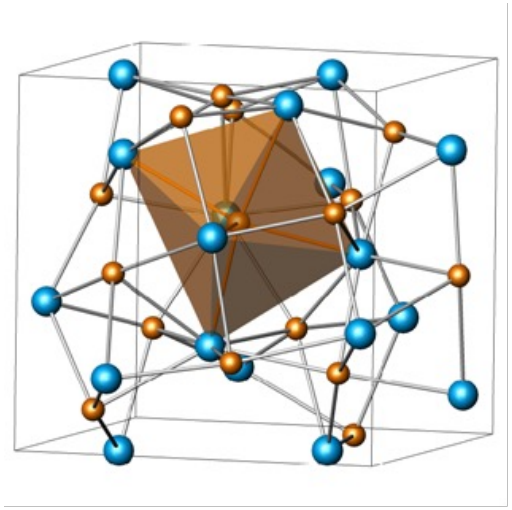
Zintl Metals
Valence ImBalance
= doped semiconductor

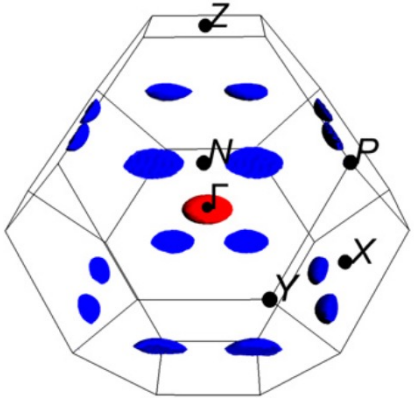


Toberer, May, Snyder *Chem. Mat.*, **22,** p. 624 (2010)

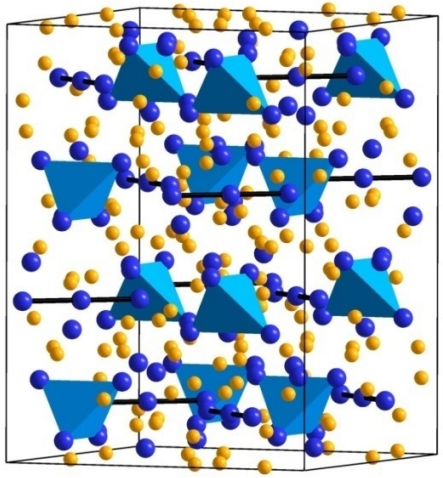
La_3Te_4 - $Yb_{14}MnSb_{11}$

Zintl Metals developed for NASA

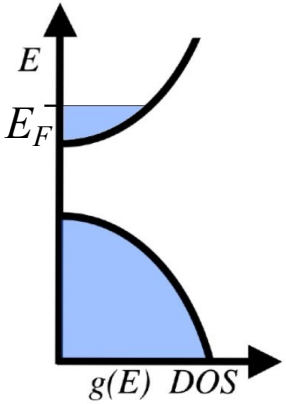


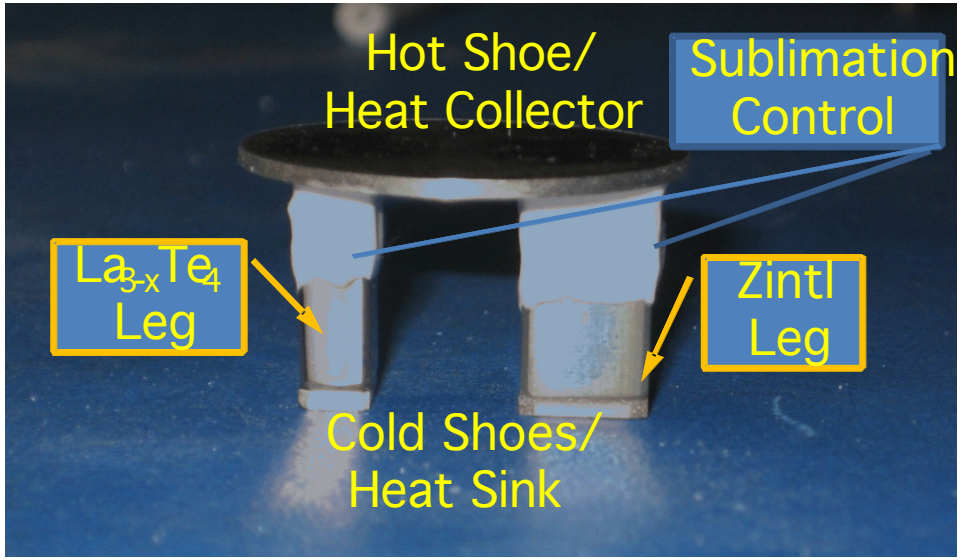


Fermi Surface

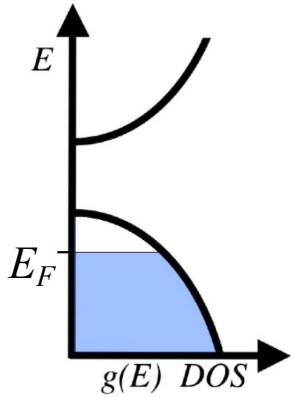


La_3Te_4
Exactly 1e⁻ extra





$Yb_{14}MnSb_{11}$
Exactly 1e⁻ less



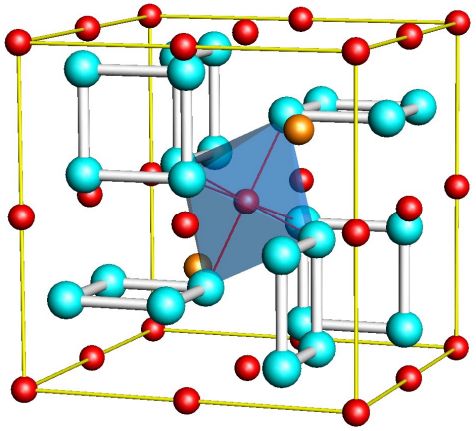
Jean-Pierre Fleurial (JPL)

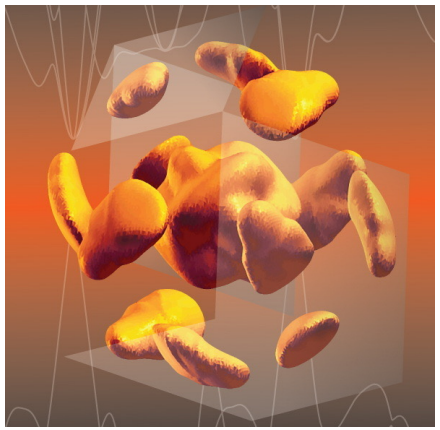
Perez, Wood Snyder *Science Advances,* **7,** 9439 (2021)
May, Snyder **Phys Rev B.** 79 (15), 153101 (2009)

Other Thermoelectric Zintl Metals

Filled Skutterudites

- Sb square rings 2b-Sb^{-1}
- $Co^{+3}Sb_3$ valence semicond.
- $La^{+3}Fe_4{}^{+2}Sb_{12}$ Zintl Metal
  - 1 hole/fu

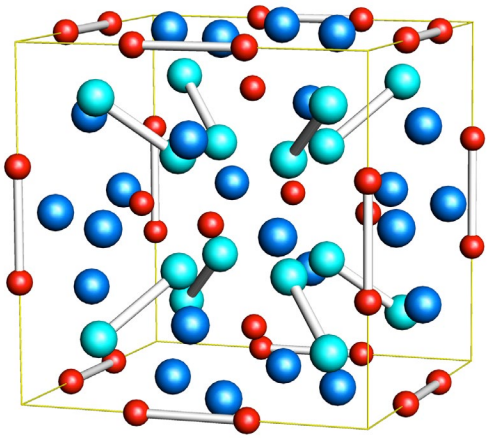




Fermi Surface (n-type)

Mo_3Sb_7

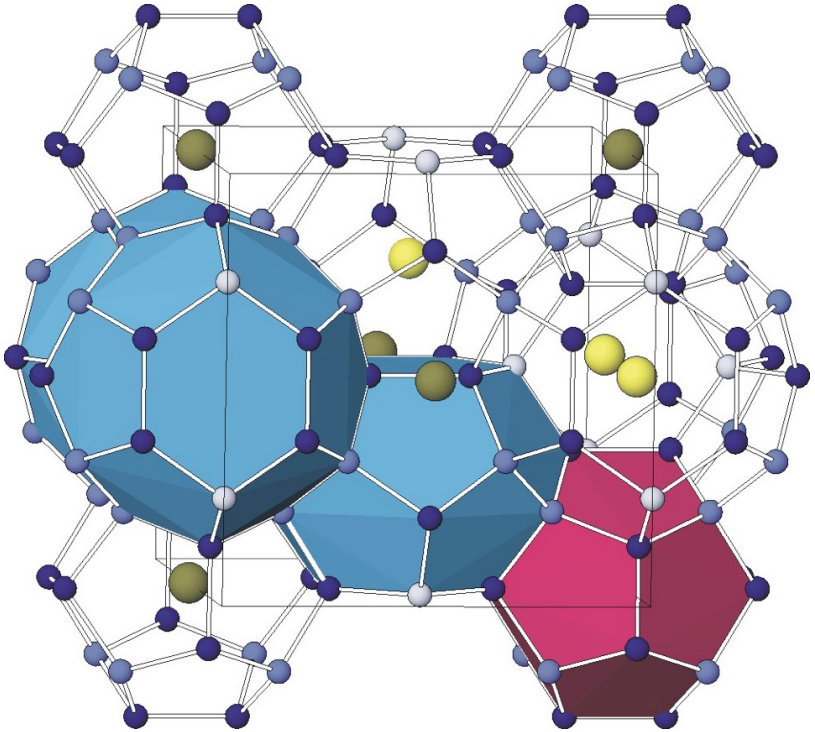
- 4x Sb dimers 1b-Sb^{-2}
- 3x Sb isolated 0b-Sb^{-3}
- Mo-Mo dimer 1b-Mo^{+5}
- 2 holes/FU = metal
  - $Mo_3Sb_5Te_2$ for SC

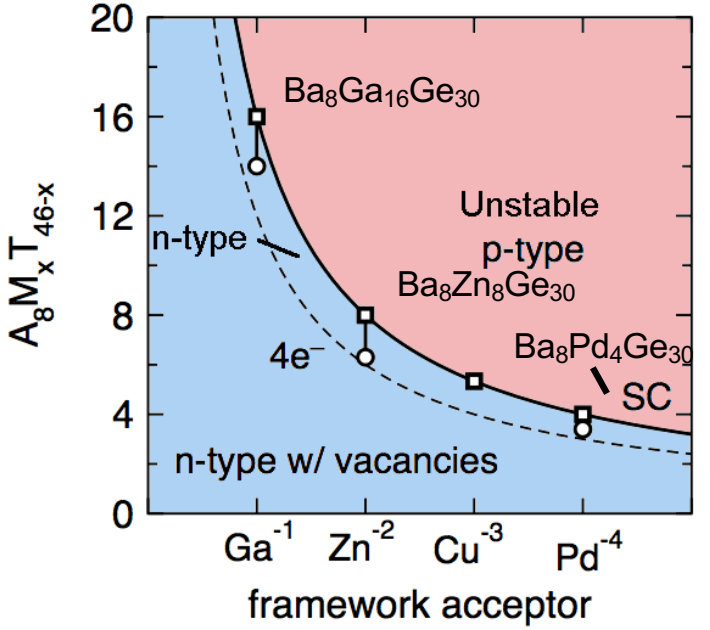


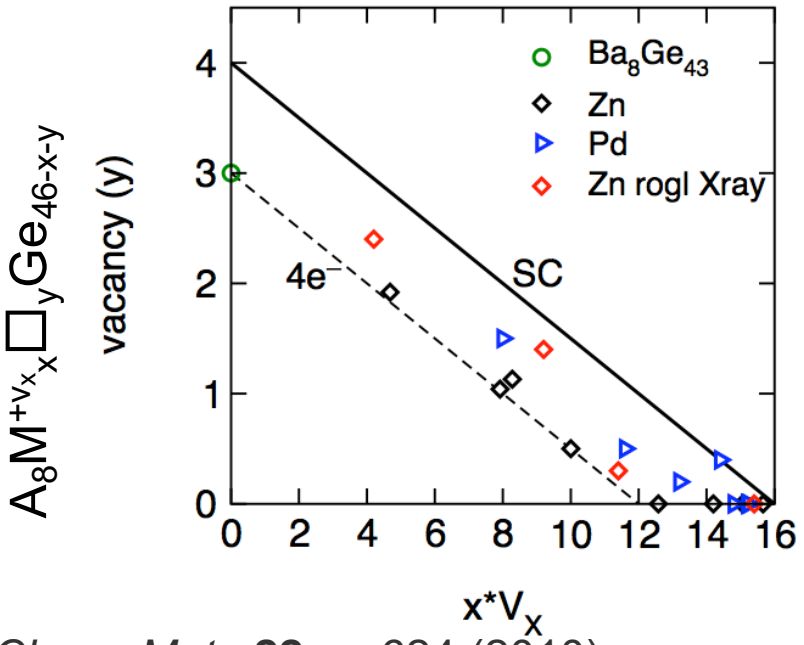
Y. Tang, Gibbs, Snyder, *et al* *Nature Materials* **14**, 1223 (2015)
Gascoin, et al *J. Alloys. Compounds* **427,** 324 (2007)
Kauzlarich, Snyder *et al, Dalton Trans.* p. 2099 (2007)

Clathrates

Most compositions near Zintl-valence balance







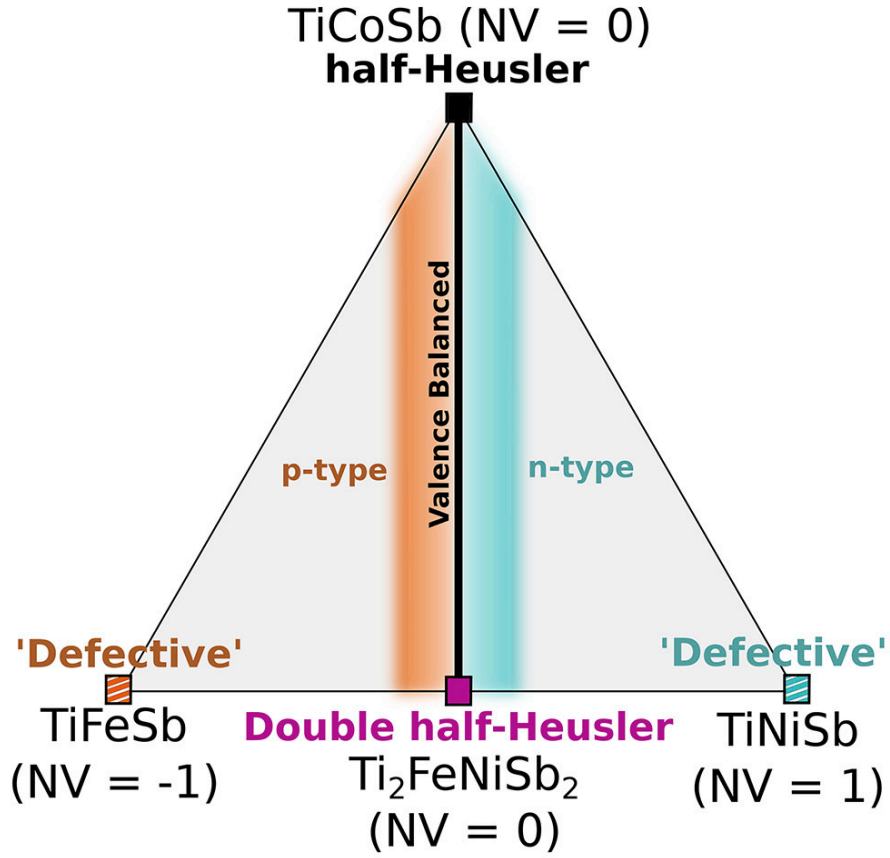
Thermoelectrics
Northwestern Materials Science and Engineering

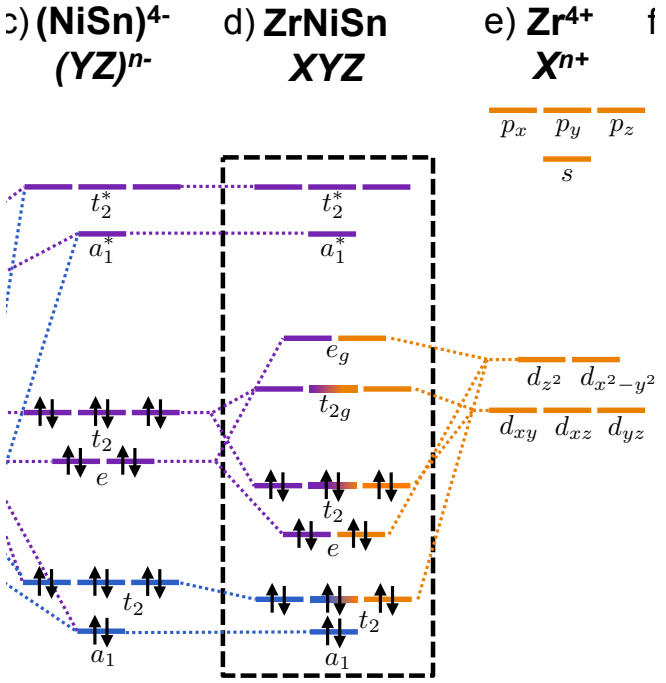
Toberer, May, Snyder *Chem. Mat.*, **22,** p. 624 (2010)

Half-Heuslers as Zintl

Zintl-valence balance = Semiconductor

Valence imbalance = doped semiconductor





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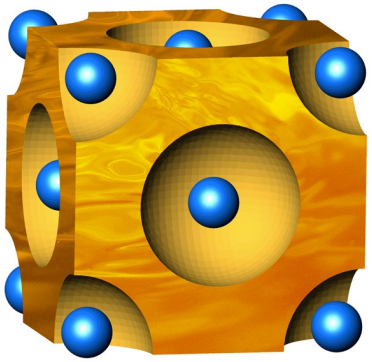
Northwestern Materials Science and Engineering

Zeier, Snyder *Nature Reviews Materials*, **1**, 16032 (2016)
Anand, Snyder *Joule* **3**, 1226 (2018)

Cu/Ag Chalcogenides

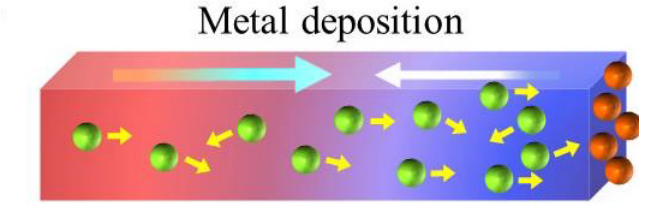
Superionic thermoelectrics

- glass-like thermal conductivity
- good thermoelectric properties



Copper deposition

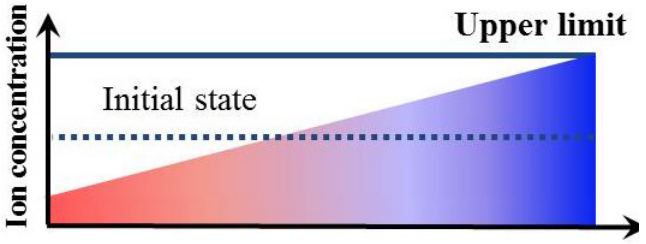
- considered ‘unstable’



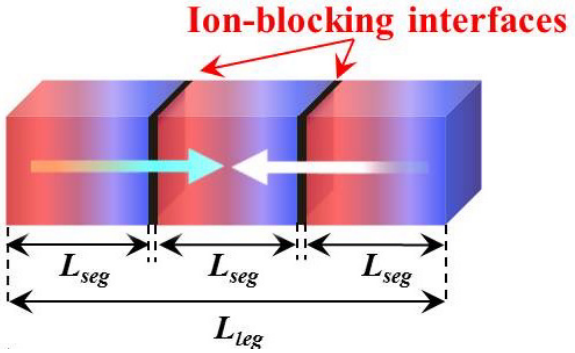
Thermodynamic Stability

- when below threshold potential

$$V_c = -\frac{1}{z_e F}\Delta\mu_{Cu}^{crit} - S^*\Delta T$$



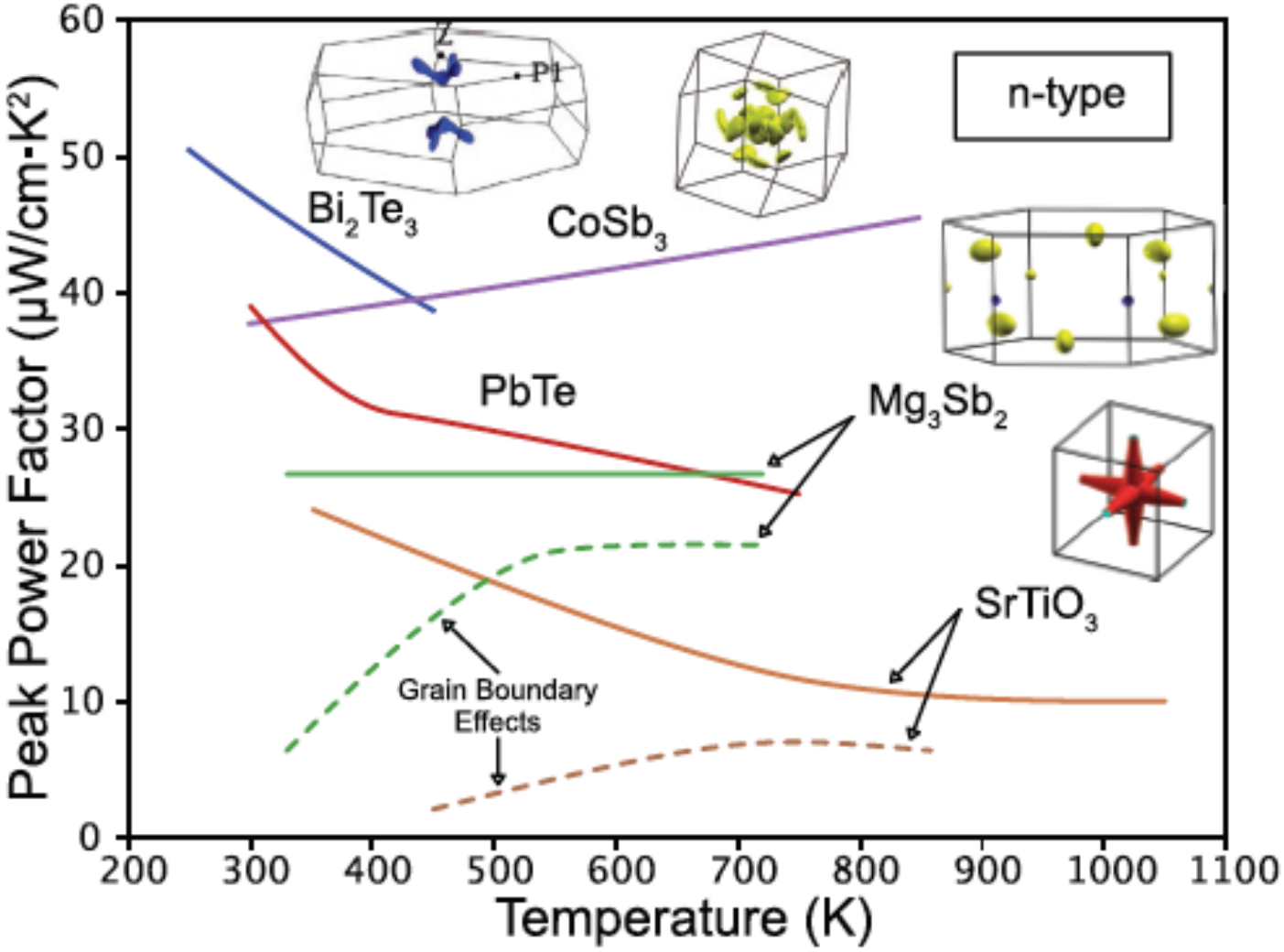
- leads to strategy of ion blocking interfaces



PF Qiu, Snyder *et al Nature Comm.* **9,** 2910 (2018)

Northwestern 2015-2024

TE with Complex Fermi Surfaces

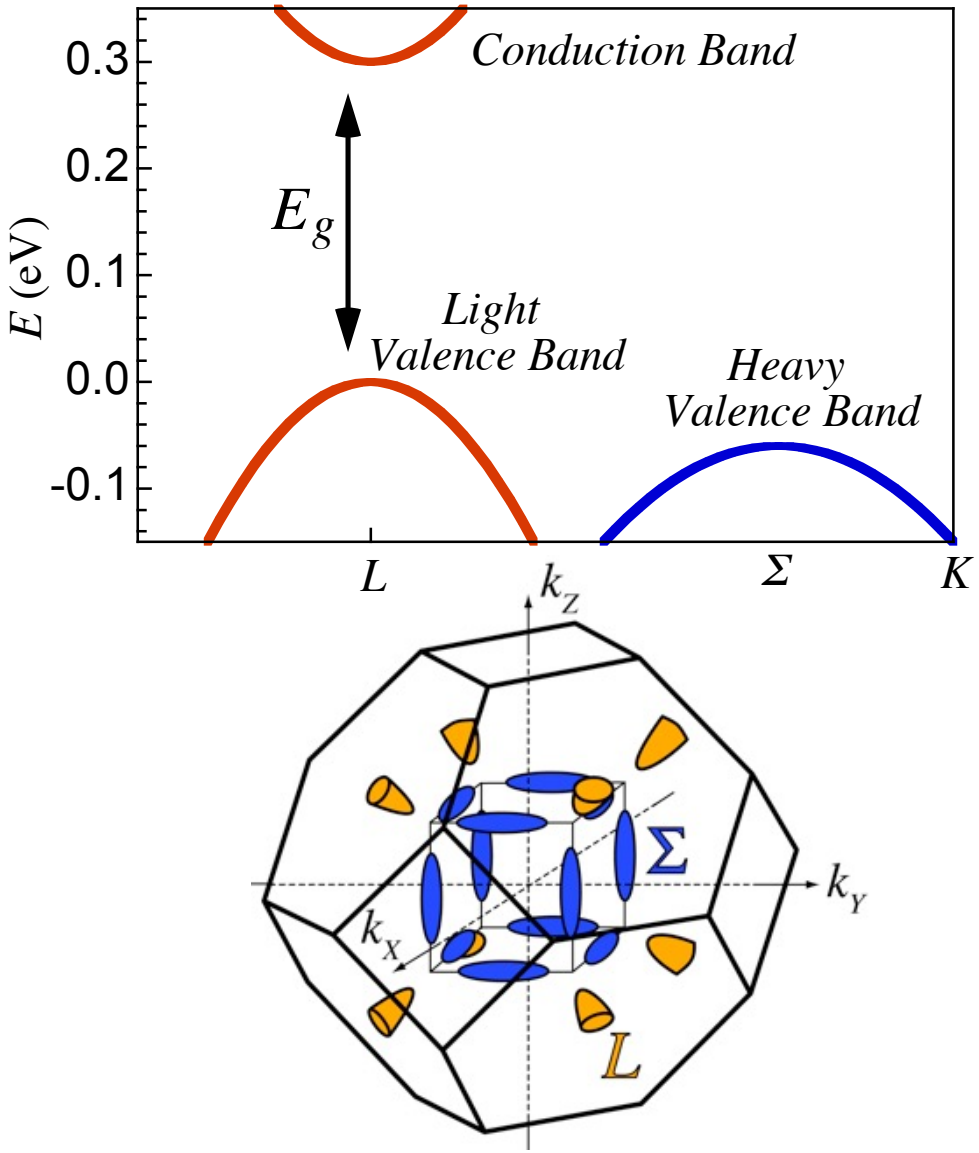


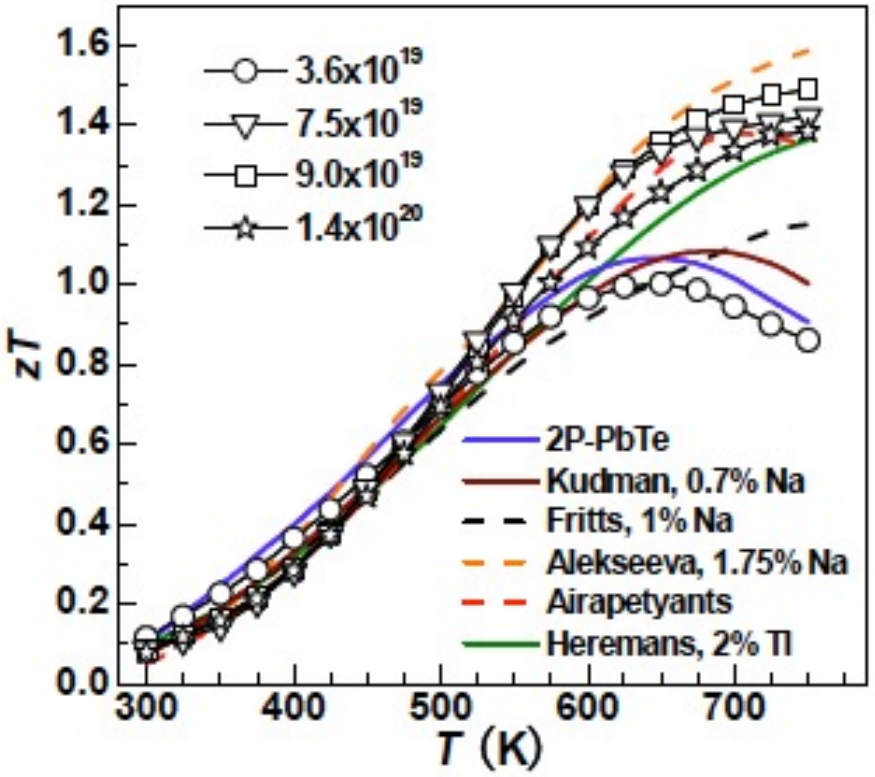
$$B \sim \frac{N_V}{m_I^* \kappa_L}$$

N_V = Fermi Surface complexity

Dylla Snyder *Adv. Materials Interfaces.* **6,** 1900222 (2019)

Heavy and Light holes in PbTe

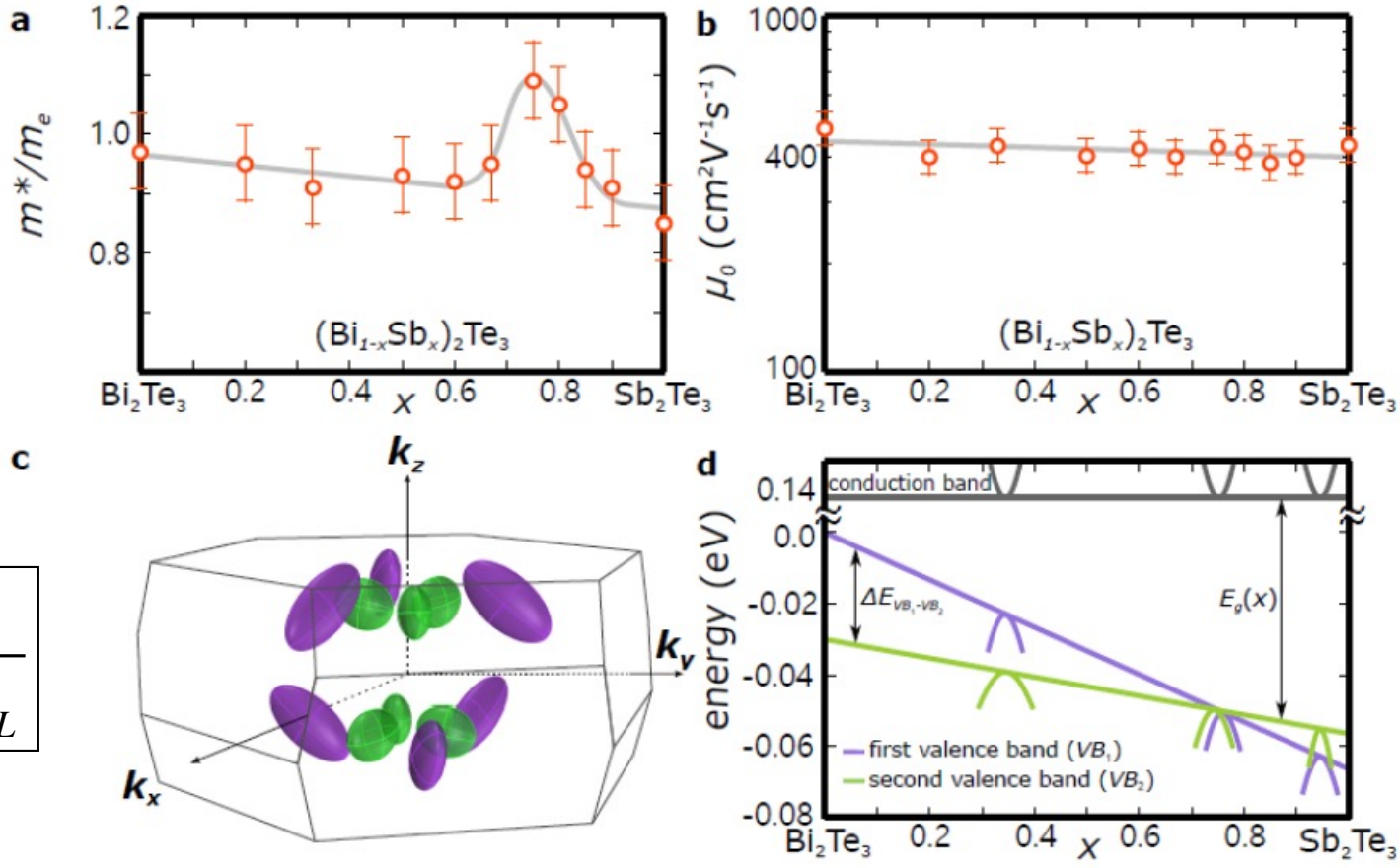




Pei, Snyder, et al.. *Energy Environ. Science* **4**, 2085 (2011)

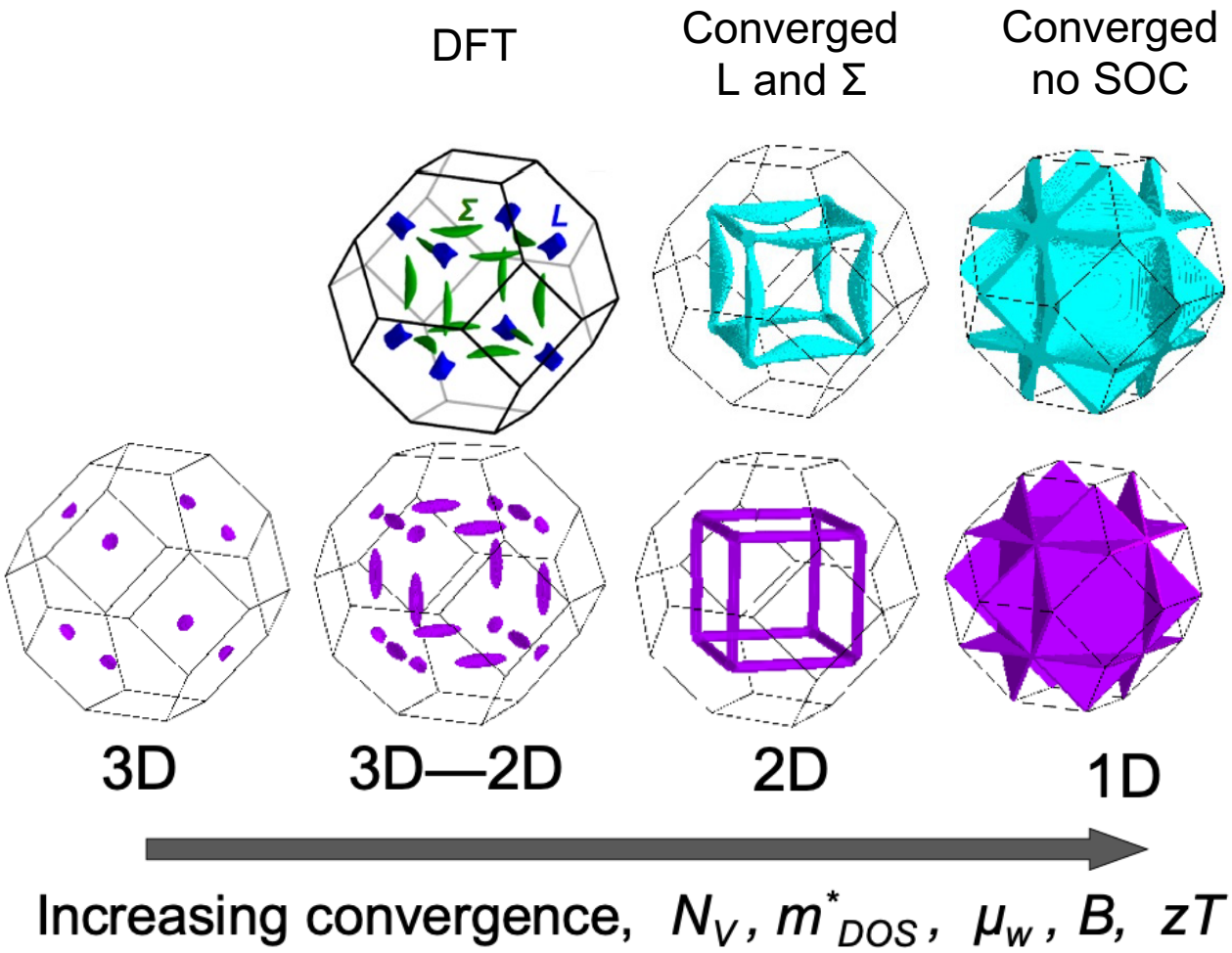
Band convergence in $(Bi,Sb)_2Te_3$

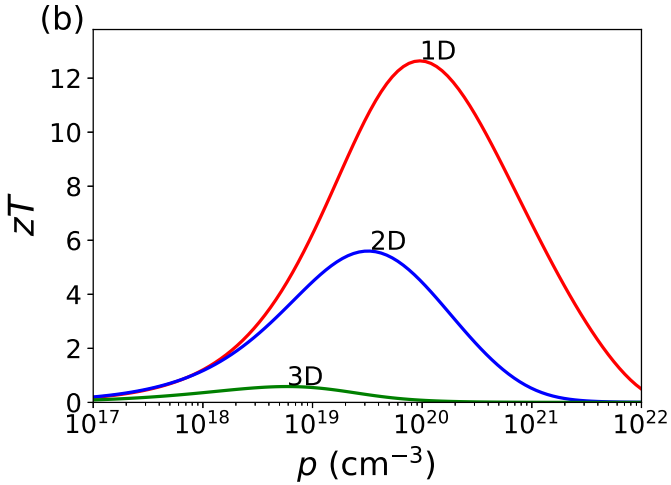
$$B \sim \frac{N_V}{m_I^* \kappa_L}$$



HS Kim, Snyder, *Materials Today,* **20**, 452 (2017)

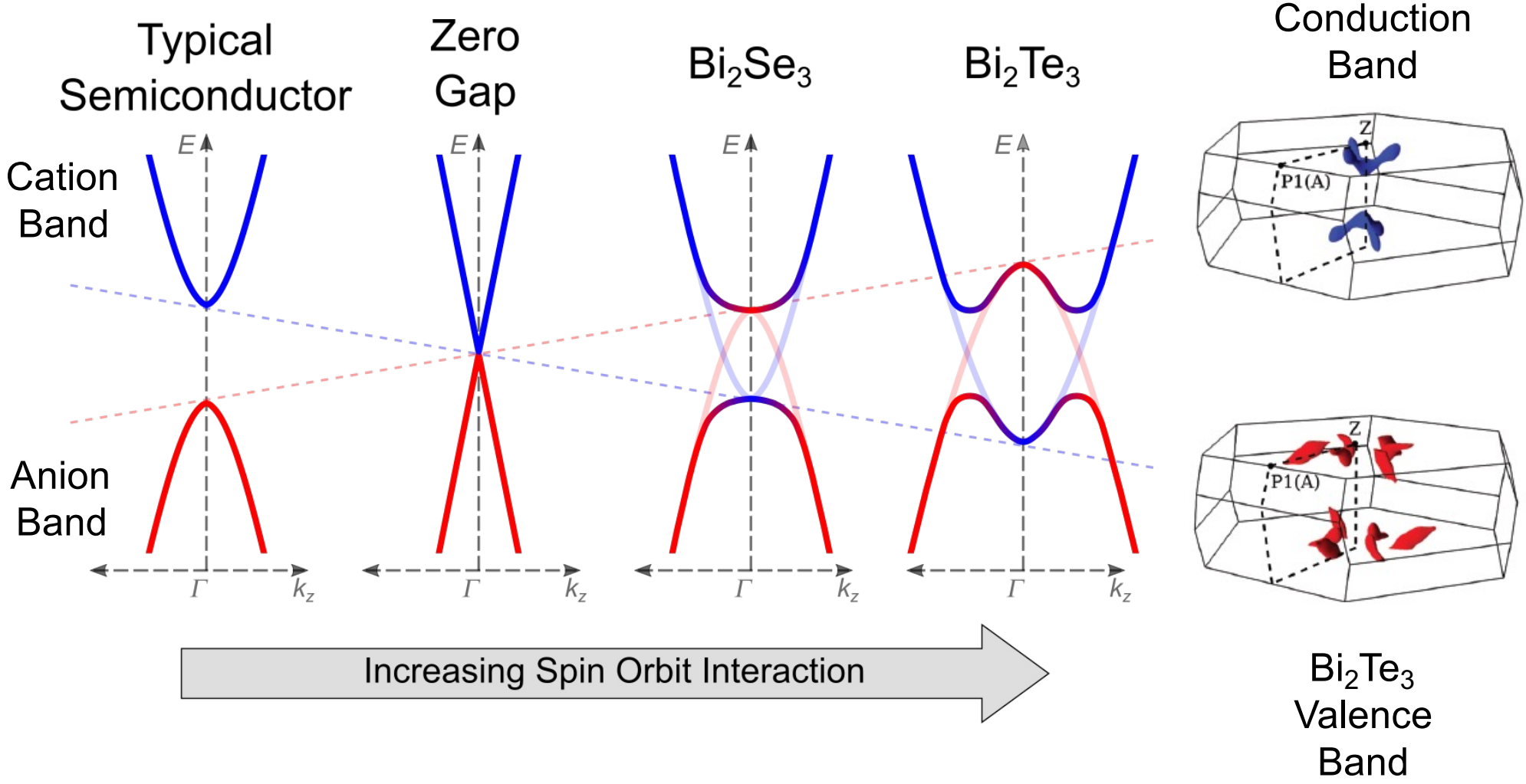
High *zT* predicted in low-D PbX





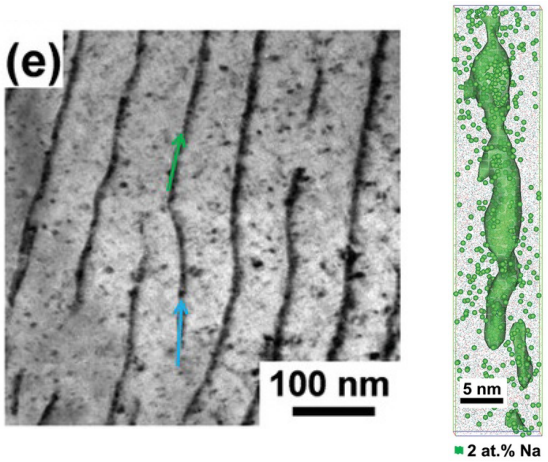
Brod, Snyder. et al *Chem. Mat.*, **32**, 9771 (2020)
Brod, Snyder. et al *J. Mater. Chem. A*, **9**, 12119 (2021)

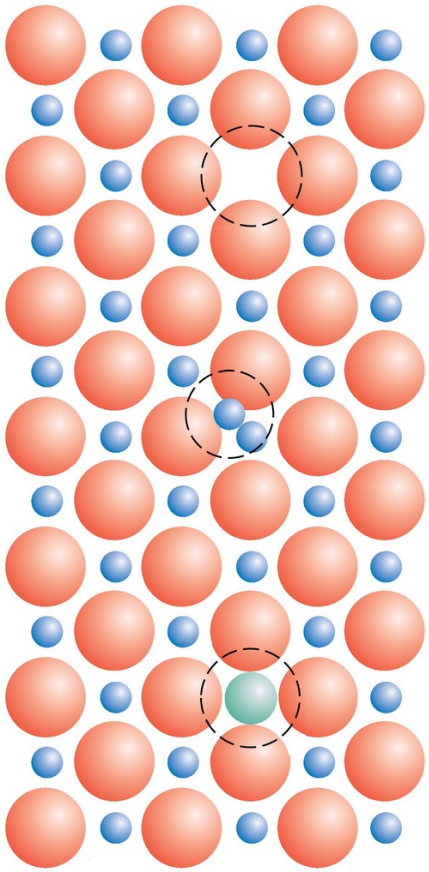
Why *some* TI are good TE

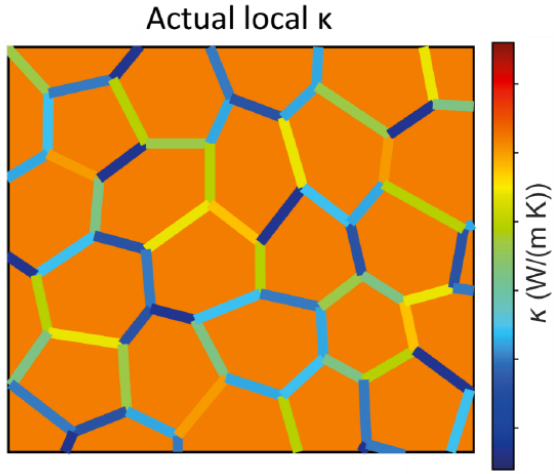


Witting, Snyder, et al *Research* 4361703 (2020)
Toriyama, Snyder *J. Mater. Chem. A*,10, 1588 (2022)

Defects



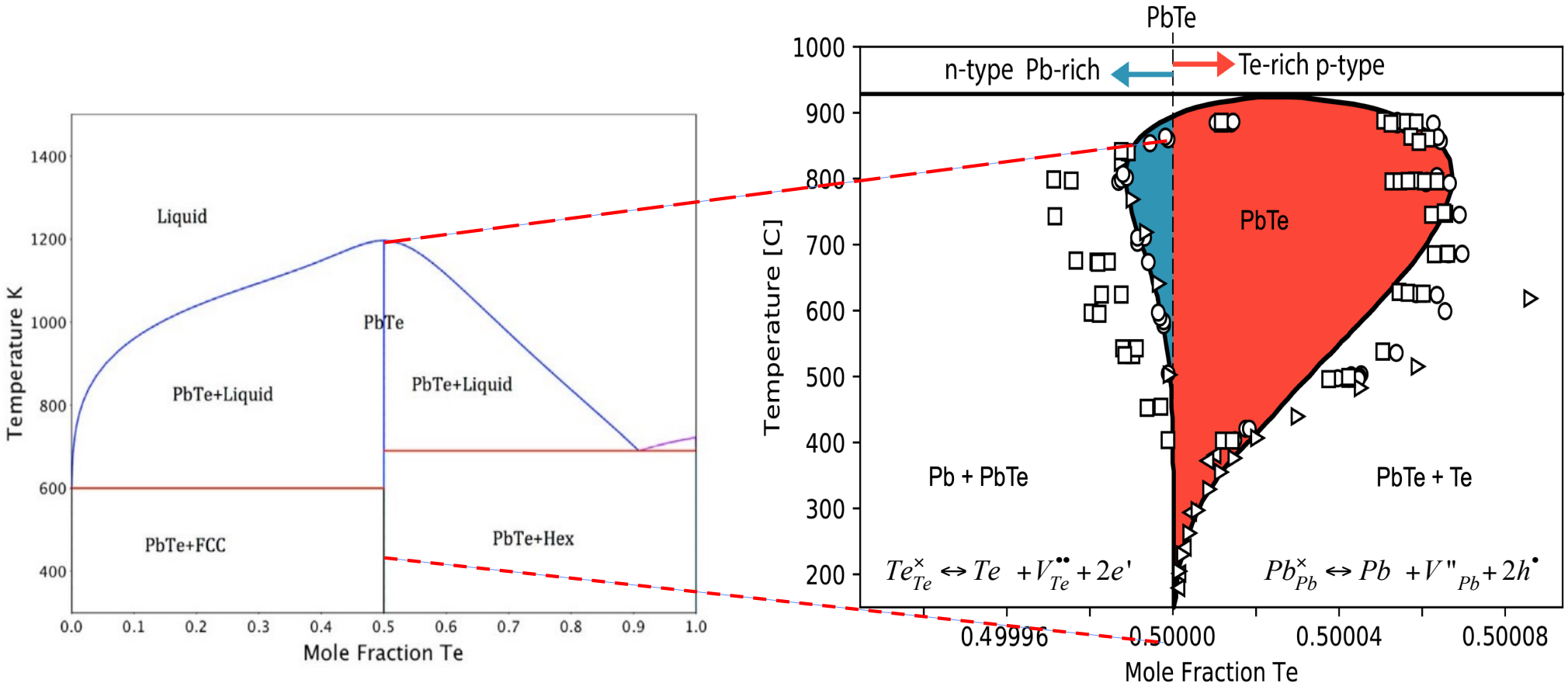




Two ‘flavors’ of PbTe

Pb-rich vs Te-rich defects change properties

Can now calculate phase diagram with DFT

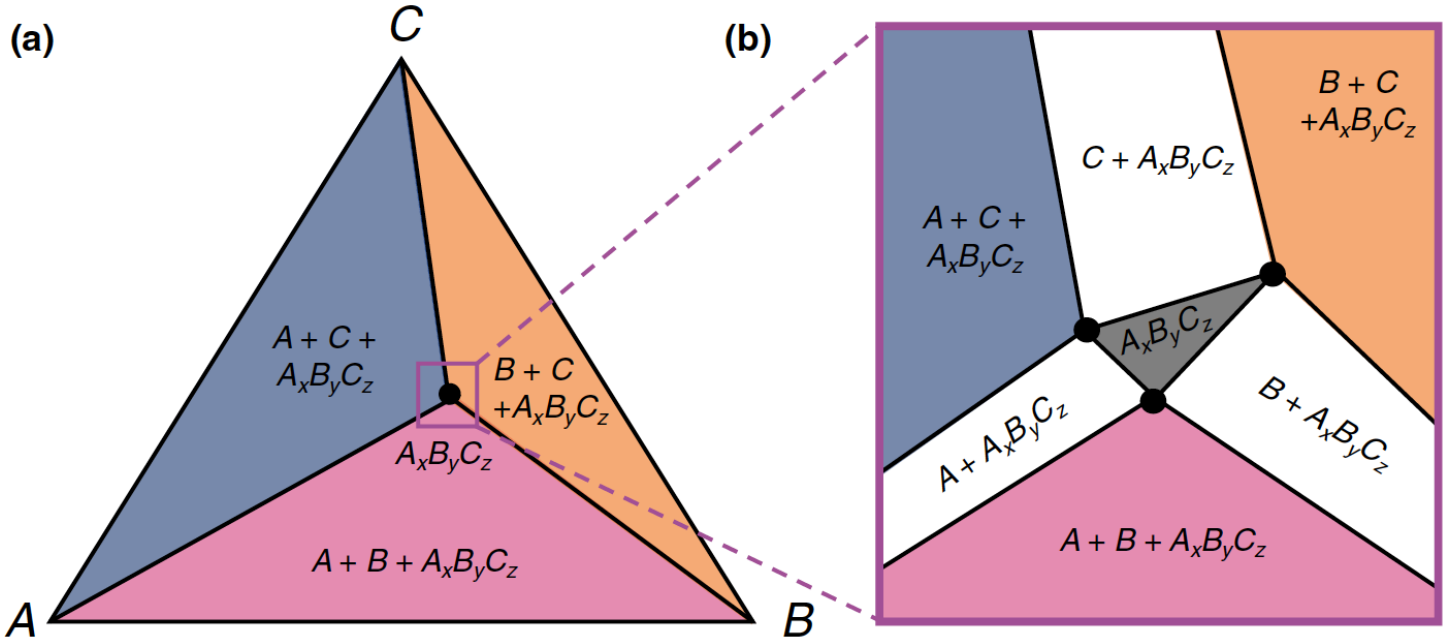


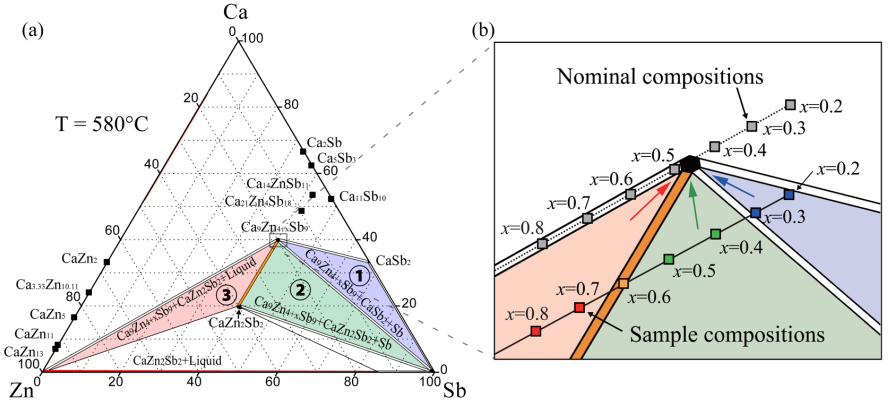
J. Male et. al. *Materials Horizons* **6**, 1444 (2019)

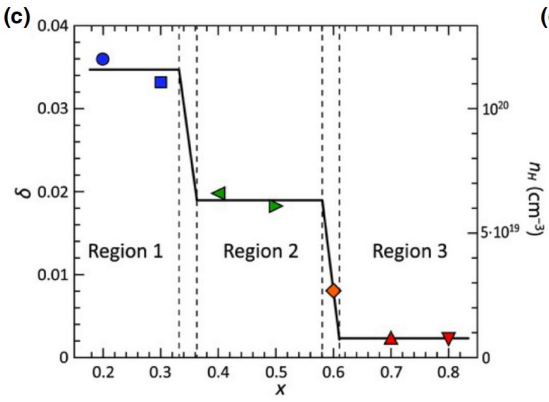
Anand, Snyder, *Acc. Mater. Res.* **3**, 685 (2022)

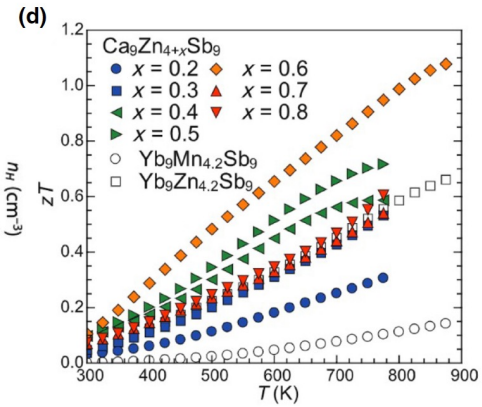
Adekoya, Snyder. *Advanced Functional Materials* 202403926 (2024)

Phase Boundary Mapping









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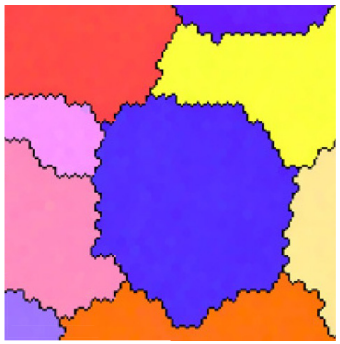
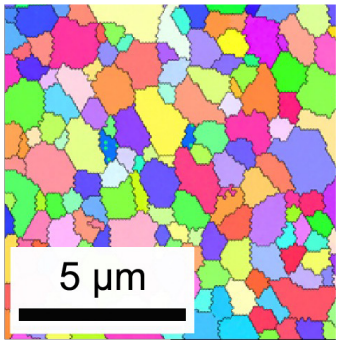
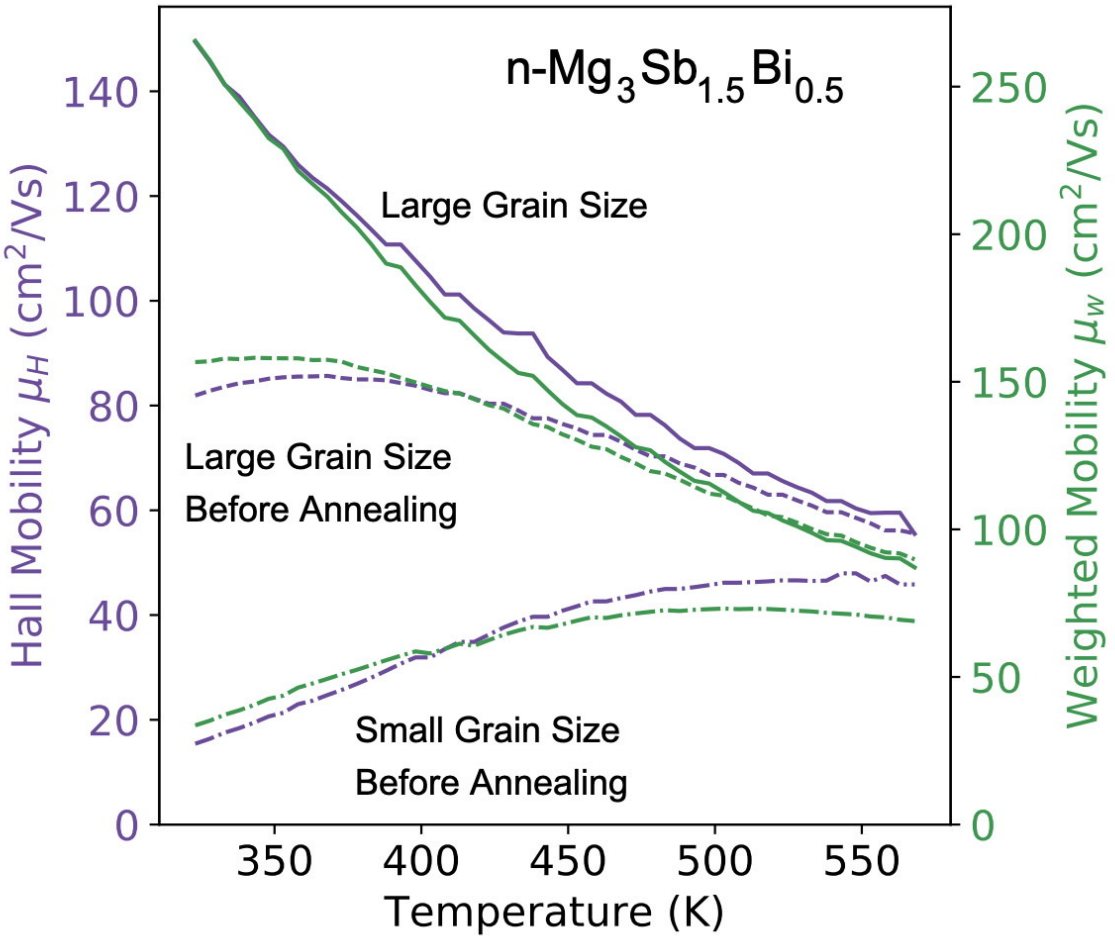
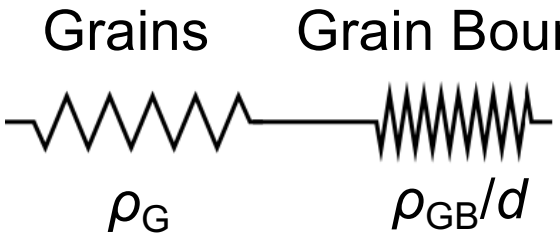
Borgsmiller, Snyder et al. *PRX Energy* **1**, 022001 (2022)
S. Ohno, Snyder, et al. *Adv. Funct. Mater.* **27**, 1606361, (2017)

Grain Boundary Electrical Resistance









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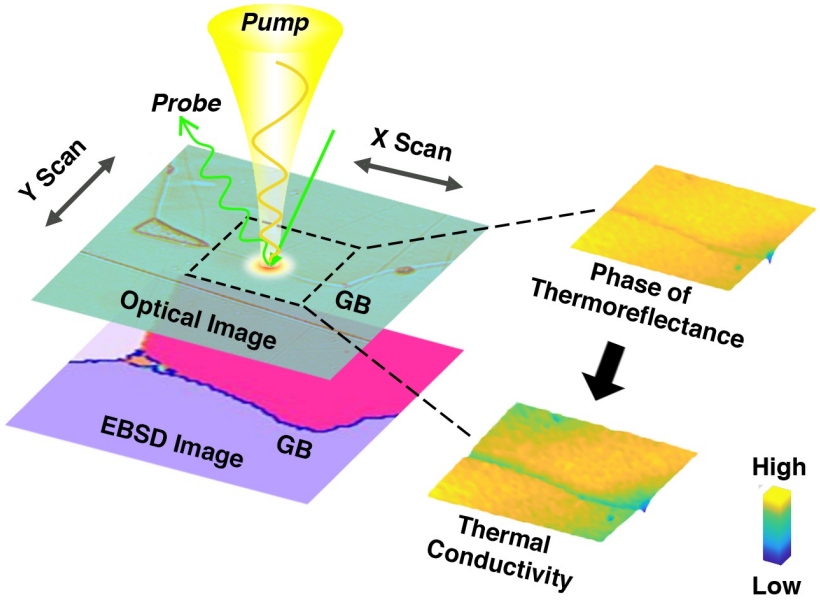
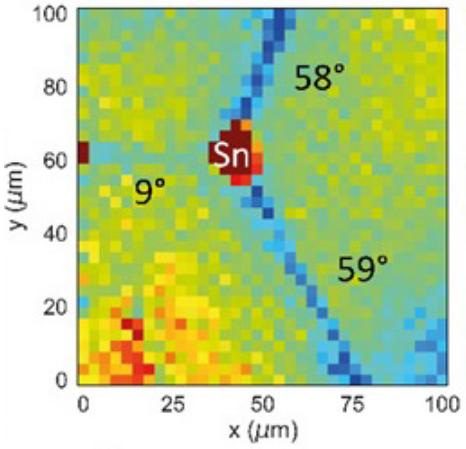
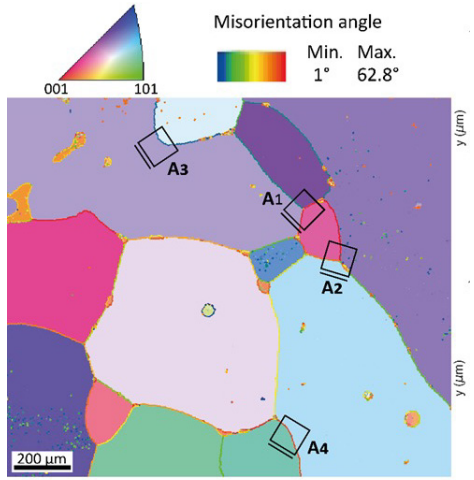
Kanno et. al., *Appl. Phys. Lett.* **112**, 033903 (2018)
J.J. Kuo, M. Wood, et al. *Energy Environ. Sci.* **13**, 1250 (2020)

Scanning Thermal Images

SnTe

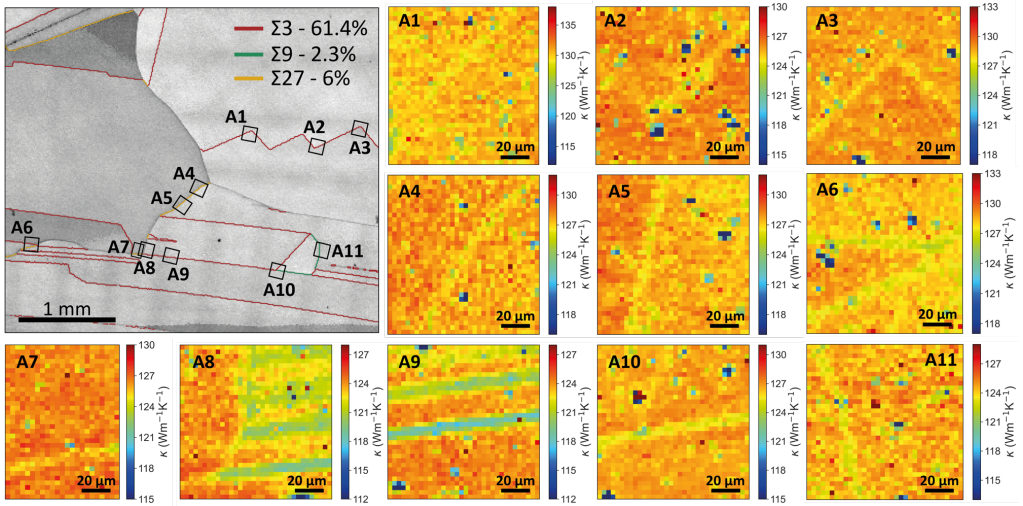






Si

Spatially-resolved frequency domain thermoreflectance (FDTR)



Isotta, GJS, et al, *Adv. Mater.* 2302777 (2023)
Isotta, GJS, et al, *Adv. Functional Mater.* 202405413 (2024)

Homogeneous Assumption

Homogeneous Models

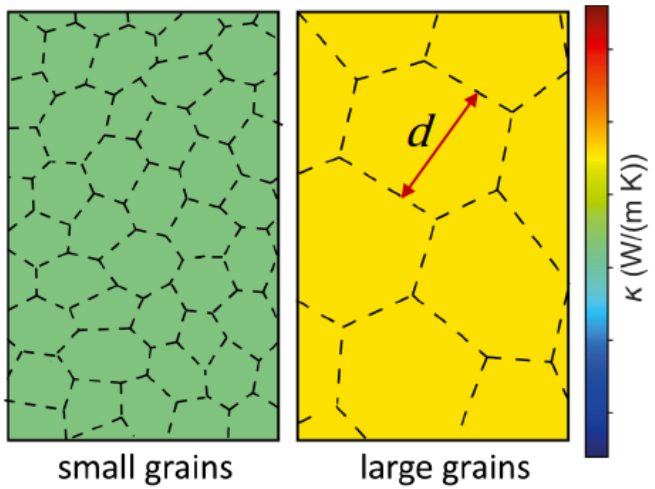
Klemens-Callaway

$$\kappa_l = \frac{1}{3}\int C_s(\omega) v_g^2(\omega)\tau(\omega)d\omega$$

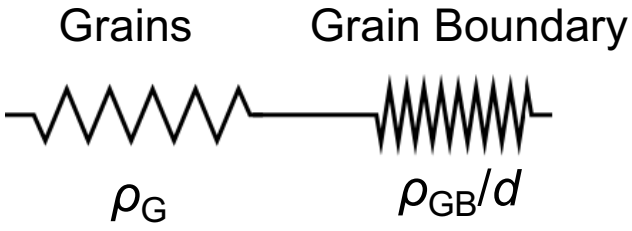
Lattice or Phonon thermal conductivity

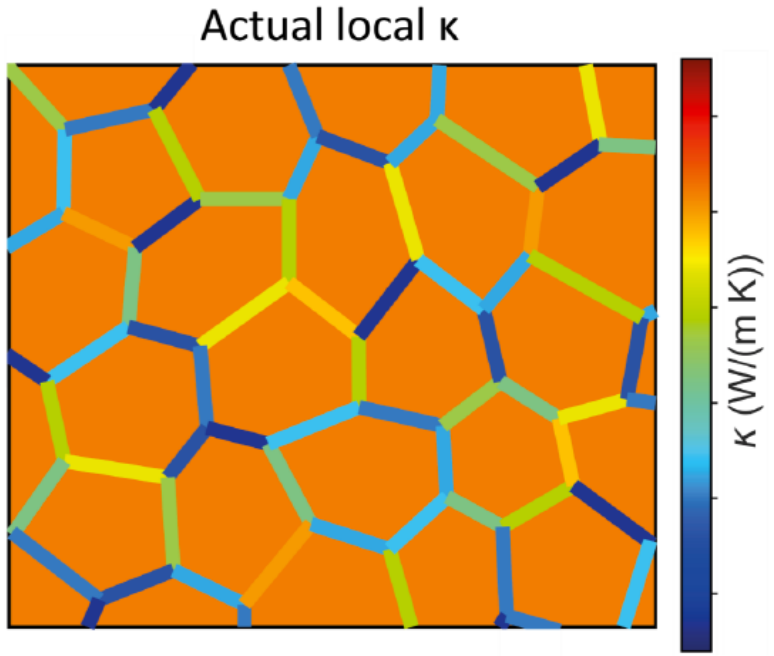
$$\tau^{-1} = \frac{v}{d} + C_{DS}N_D B_D^2\omega + C_U T\gamma^2\omega^2 + C_{PD}\omega^4$$

boundary — dislocation — Umklapp — point defect



InHomogeneous Model



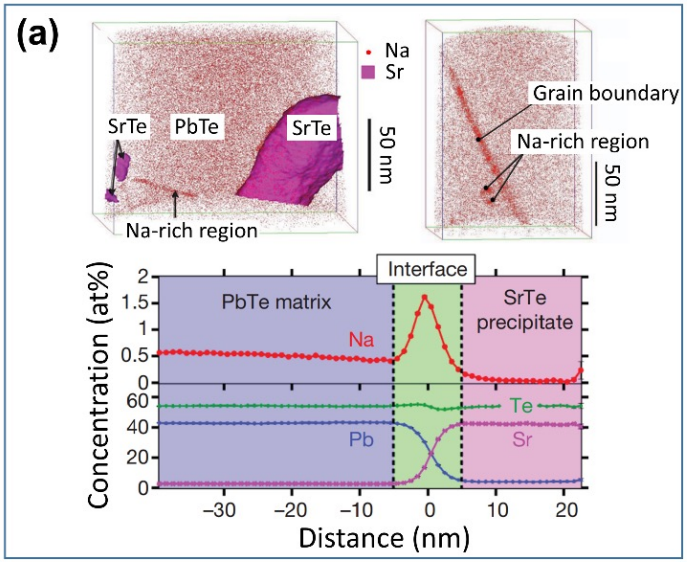


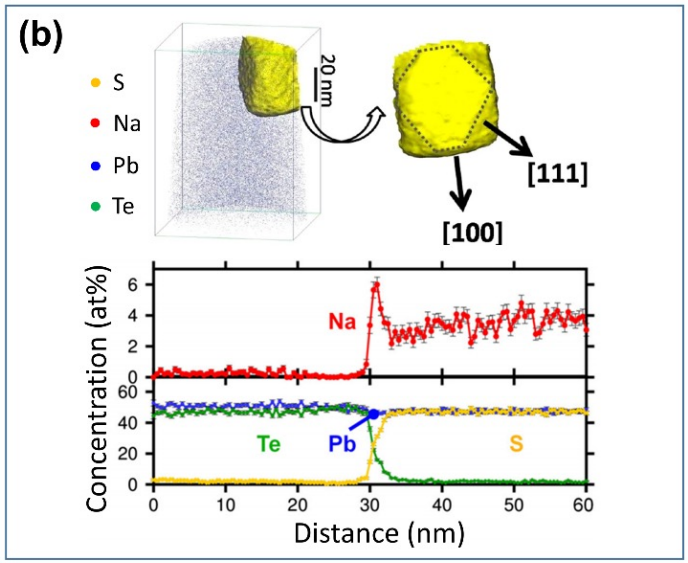
Isotta, GJS, et al, *Adv. Mater.* 2302777 (2023)
Isotta, GJS, et al, *Adv. Functional Mater.* 202405413 (2024)

Interface Complexion Chemistry

Atom Probe Tomography

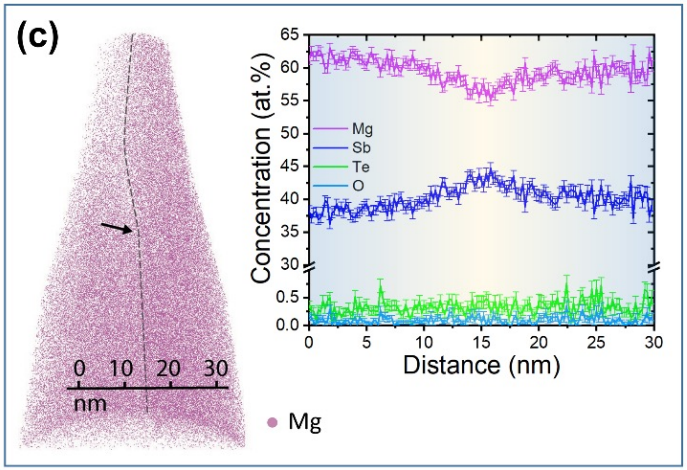
(Pb,Sr,Na)Te

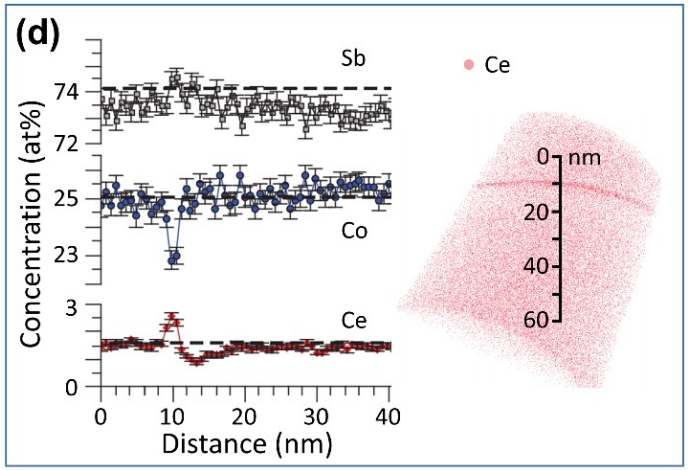




Pb(Te,S)

Mg_3Sb_2





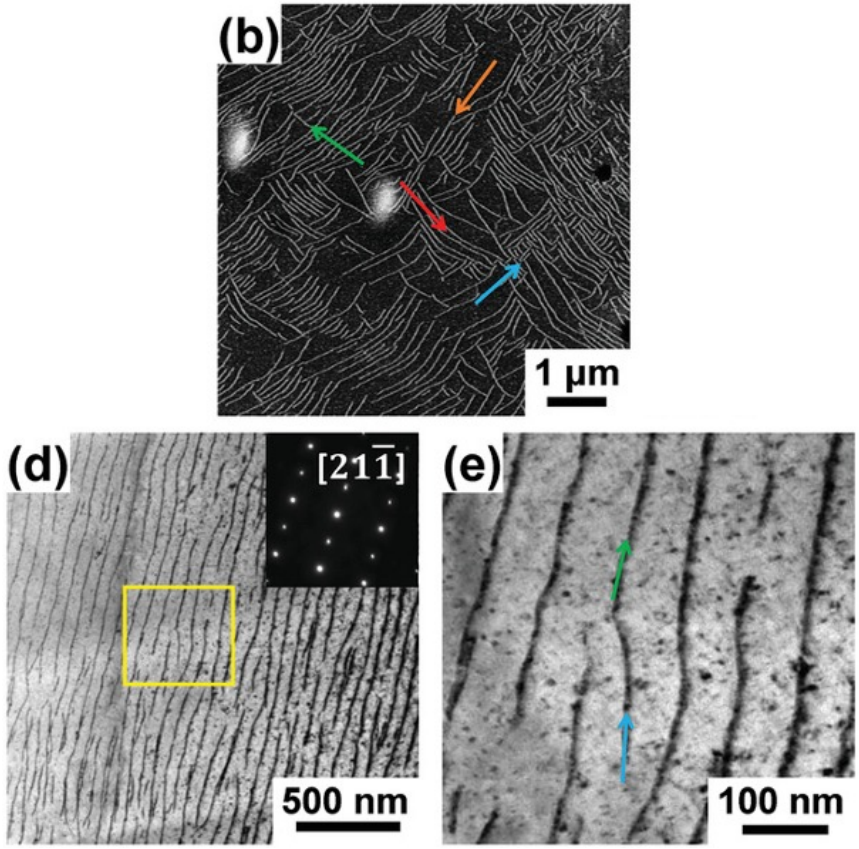
$CeCo_4Sb_{12}$

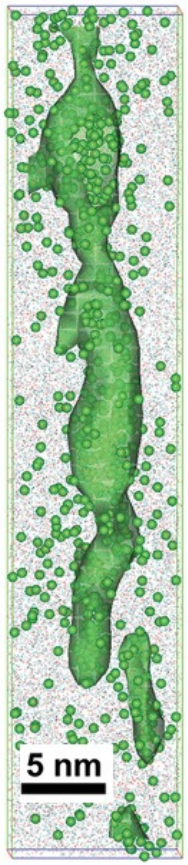
Yuan Yu, et. al., *Materials Today* **32**, 260 (2020)

Parallel Dislocation Networks

Parallel dislocation networks at nanometer scale

Dislocations collect impurity dopant atoms = Cottrell atmosphere





$Na_{0.025}Eu_{0.03}Pb_{0.945}Te$ with high zT

Lamya Abdellaoui et al., *Advanced Functional Materials* 2101214 (2021)

Acknowledgements

Many Projects

Beautiful science in Complexity

Physics, Chemistry, Materials Science, Engineering

Thank you All!

Mentors

Group Members

Collaborators

Thermoelectrics
Northwestern Materials Science and Engineering