Complex Thermoelectric Materials

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Device Engineering | Electron-Phonon Engr. | Interfaces

Compatibility | Complex Structures | Microstructures

Snyder, Toberer Nature Materials 7, 105 (2008)
JPL 1997-2006
Electrochemical MEMS MicroDevice

Snyder, Snyder,

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 reduced 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

\[ zT = \frac{S^2}{\rho K} \]

Efficiency comes from device \( ZT \)

Exact definition of \( ZT \)

Can be calculated from spreadsheet calculator easy!

\[ \eta = \frac{\Delta T}{T_h} \cdot \sqrt{\frac{1 + ZT}{1 + ZT^*}} - 1 \]

\[ \sqrt{\frac{1 + ZT}{1 + ZT^*} + \frac{T_c}{T_h}} \]

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

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

\[ \Theta_{TE} = \Theta_{Hx} \]

\[ \Theta_{TE} = \frac{l}{\kappa_{TE} A f} \]

- \( l \) = leg length
- \( f \) = TE fill factor
- \( A \) = area

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

Power Generation Design Space

$\Delta T$ (K) vs. $Q/A$ (W/cm$^2$)

- Bulk PbTe-TAGS
- Bulk Bi$_2$Te$_3$
- Thin Bulk Bi$_2$Te$_3$
- Thin Film

Thermopile
- L ~ 20 mm

Commercial Module
- L ~ 2 mm

Thin Film Device
- L ~ 0.02 mm

Thermoelectrics
Northwestern Materials Science and Engineering
ZT for maximum Power

not ‘power factor’: Proof by Contradiction

1) Suppose material or device design based on power not ZT (lower efficiency $\eta_P$)

\[ P = \alpha^2 \sigma \frac{A}{l} \Delta T^2 \frac{R_L / R_{TE}}{1 + R_L / R_{TE}} \]

\[ \Theta_{TE} = \Theta_{Hk} = \frac{l}{\kappa_{TE} AF} \]

2) Take same System Design: same heat flux $Q_h$ at same $\Delta T$,
   Use TE designed for efficiency (maximize ZT) $\eta_{ZT}$

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 $\mu_W$ (not $S$, $S^2\sigma$)

“Better Thermal Properties” = lower $\kappa_L$

Snyder et. al. *Advanced Materials*, **32**, 2001537 (2020)

Pei, Wang, Snyder *Advanced Materials* **24**, 6125 (2012)
$\mu_W$ for Disordered Materials

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

polyacetylene ($\star$); PBTTT (■□); P2TDC17-FT4 ($\star$)
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 $D$

Mechanical Alloying - Ball Milling
Reduce particle size $l$ to 10-100nm
speed reaction time at low temperature

Target Composition
Resultant microstructure from melt

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 |

Radio Frequency (RF) Heating

![Diagram](image)

**FIG. 1.** Schematic of induction hot press setup.

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

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
Zintl Thermoelectrics

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

\[ \kappa_L = \kappa_U + \kappa_{\text{optic}} \]

\[ = \frac{A}{T} + B \]

Acoustic phonons
Umklapp Scattering

Diffusons at \( \kappa_{\text{min}} \)

\[ \kappa_{\text{optic}} \approx 0.76 \frac{k_B v_s}{V^3} \left( 1 - N^{-2/3} \right) \]

Agne, Snyder, *Energy. Eng. Sci.*, 11 609 (2018); *National Sci. Rev.*, 6, 380 (2019)
SrZnSb$_2$, SrZn$_2$Sb$_2$ and Mg$_3$Sb$_2$

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

\[ \text{Ca}_5\text{M}_2\text{Sb}_6 \]
\[ \text{M=Al, Ga, In} \]
chains linked by Sb-Sb bonds to form “ladders”
26 atoms per cell

\[ \text{Ca}_3\text{AlSb}_3 \]
simple corner sharing
linear chains
28 atoms per cell

\[ \text{Sr}_3\text{GaSb}_3 \]
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$_4$Sb$_3$ and ZnSb

Zn$_4$Sb$_3$ = 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

\[ V_c = e_c - b_c \quad V_a = e_a + b_a - 8 \]

- \( e \) valence electrons in atom
- each bond \( b \) reduces \(|\text{valence}|\) by 1

Zintl Phase
Valence Balance
= Semiconductor

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

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Zintl Phase
Valence Balance  
= Semiconductor

Zintl Metals
Valence ImBalance  
= doped semiconductor

Toberer, May, Snyder Chem. Mat., 22, p. 624 (2010)
La$_3$Te$_4$ - Yb$_{14}$MnSb$_{11}$

Zintl Metals developed for NASA

La$_3$Te$_4$
Exactly 1e$^-$ extra

La$_{3-x}$Te$_4$
Zintl Leg

Hot Shoe/Heat Collector
Sublimation Control

Cold Shoes/Heat Sink

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

Mo\(_3\)Sb\(_7\)
4x Sb dimers 1b-Sb\(^{-2}\)
3x Sb isolated 0b-Sb\(^{-3}\)
Mo-Mo dimer 1b-Mo\(^{+5}\)
2 holes/FU = metal
  • Mo\(_3\)Sb\(_5\)Te\(_2\) 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

Toberer, May, Snyder *Chem. Mat.*, **22**, p. 624 (2010)
Half-Heuslers as Zintl

Zintl-valence balance = Semiconductor
Valence imbalance = doped semiconductor

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
  \[ V_c = -\frac{1}{Z_e F} \Delta \mu_{\text{Cu}}^{\text{crit}} - S^* \Delta T \]
  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 \((\text{Bi}, \text{Sb})_2\text{Te}_3\)

\[ B \sim \frac{N_V}{m^* \kappa_L} \]

HS Kim, Snyder, *Materials Today*, **20**, 452 (2017)
High $zT$ predicted in low-D PbX

Increasing convergence, $N_V$, $m^*_{DOS}$, $\mu_w$, $B$, $zT$

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

**Typical Semiconductor**

- **Cation Band**
- **Anion Band**

**Zero Gap**

**Bi$_2$Se$_3$**

**Bi$_2$Te$_3$**

**Increasing Spin Orbit Interaction**

**Bi$_2$Te$_3$ Conduction Band**

**Bi$_2$Te$_3$ Valence Band**

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

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

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

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

\[ \kappa_I = \frac{1}{3} \int C_s(\omega)v_g^2(\omega)\tau(\omega)d\omega \]

Lattice or Phonon thermal conductivity

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

InHomogeneous Model

Grains

Grain Boundary

\[ \rho_G \]

\[ \rho_{GB}/d \]

boundary dislocation Umklapp point defect

Actual local \( \kappa \)

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$_3$Sb$_2$

CeCo$_4$Sb$_{12}$

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)
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