Electronic Strategies for High Thermoelectric $zT$ in Bulk Materials

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Successful Strategies for TE

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

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

Conventional Thermoelectric Material

Desire High $zT$ Figure of Merit

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

“Electron Crystal - Phonon Glass”

- $\alpha$ Seebeck Coefficient
  - High in Crystalline Semiconductor
  - $\alpha = \frac{8\pi^2 k_B^2}{3e^2 h^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3}$

- $\sigma$ Electrical Conductivity
  - High in Crystalline Metal
  - $\sigma = ne\mu = \frac{ne^2 \tau}{m^*}$

- $\kappa$ Thermal Conductivity
  - Low for Glass
  - $\kappa \approx \kappa_i + L\sigma T$

See Eric Toberer 2:30
Carrier Concentration

Desire High $zT$ Figure of Merit

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

**Conflicting Materials Requirements**

$\alpha$ Seebeck Coefficient

- Need small $n$, large $m^*$
  - Semiconductor (Valence compound)

\[
\alpha = \frac{8\pi^2 k_B^2}{3\hbar^2} m^* T \left( \frac{\pi}{6n} \right)^{2/3}
\]

$\sigma$ Electrical Conductivity

- Need large $n$, high $\mu$, low $m^*$
  - Metal

\[
\sigma = ne\mu
\]

$\kappa$ Thermal Conductivity

- Desire small $\kappa$, small $n$

\[
\kappa \approx \kappa_l + LTne\mu
\]

Carrier Concentration Tuning using Zintl Chemistry
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 \(|\text{valence}|\) by 1

Valence Semiconductors
Stoichiometric balance of valences
- ionic \( \text{In}^{3+}\text{Sb}^{3-} \); covalent \( \text{In}^1\text{Sb}^{1+} \)

<table>
<thead>
<tr>
<th></th>
<th>Valence Band</th>
<th>Conduction Band</th>
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<tbody>
<tr>
<td>Ionic</td>
<td>anion states</td>
<td>cation states</td>
</tr>
<tr>
<td>Polar Covalent</td>
<td>Either/Both Interpretation</td>
<td></td>
</tr>
<tr>
<td>Covalent</td>
<td>bonding states</td>
<td>antibonding states</td>
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</tbody>
</table>

Ionic \( MX \)
\( \text{La}^{3+}_2\text{Te}^{2-}_3 \)

Polar SC \( MX \)
\( \text{InSb} \) \( E_g \sim 0.2 \text{ eV} \)

Semicond. \( X \)
\( \text{Ge}^0 \) \( E_g \sim 0.7 \text{ eV} \)

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$_4$Sb$_3$"

Semicond. $X$

Ge-clathrates

Zintl Phases for Low Cost Thermoelectrics
Ca<sub>5</sub>Al<sub>2</sub>Sb<sub>6</sub> valence balance

Zintl-Klemm valence counting gives valence balanced structure

Cation Valence = electron - bonds
Anion Valence = electrons + bonds - 8

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Al</th>
<th>Sb&lt;sup&gt;1,2&lt;/sup&gt;</th>
<th>Sb&lt;sup&gt;3&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>electrons</td>
<td>2</td>
<td>3</td>
<td>5</td>
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<tr>
<td>bonds</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>valence</td>
<td>2</td>
<td>3</td>
<td>-3</td>
<td>-2</td>
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<tr>
<td>total</td>
<td>10</td>
<td>6</td>
<td>-12</td>
<td>-4</td>
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</table>

Net Valence = 0
Ca$_5$Al$_2$Sb$_6$ cation doping

Replace with Na$^{1+}$ + hole$^+$
Induces free carriers
Heavily doped semiconductor: linear resistivity and Seebeck with T

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

\[
E_g = 2eT_{\text{max}} \alpha_{\text{max}}
\]
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$_x$Ca$_{5-x}$Al$_2$Sb$_6$ $zT$

$zT$ greater than 0.6 at 1000K for heavily doped sample

Input from $x=0.25$ sample: $m^*=1.9m_e$, $\mu_0 = 4.7 \text{ cm}^2/\text{Vs}$, $\kappa_l = 0.76 \text{ W/mK}$

$\text{Na}_x\text{Ca}_{3-x}\text{AlSb}_3$

Similar structure and chemistry to $\text{Ca}_5\text{Al}_2\text{Sb}_6$, except for no Sb-Sb bond

higher mobility, lower effective mass leads to higher $zT$

$\text{Ca}_3\text{Al}_1\text{Sb}_3$: $m^* = 0.8 \, m_e \quad \mu_o = 15 \, \text{cm}^2/\text{Vs} \quad \kappa_l = 0.78 \, \text{W/mK}$

$\text{Ca}_5\text{Al}_2\text{Sb}_6$: $m^* = 1.9 \, m_e \quad \mu_o = 4.7 \, \text{cm}^2/\text{Vs} \quad \kappa_l = 0.76 \, \text{W/mK}$

High Efficiency
from
Band Structure Engineering
Enhancing Thermopower

Seebeck

Typically described by \textit{effective} $m^*$

- Single Parabolic Band
  \[
  \alpha = \frac{8\pi^2 k_B^2}{3e\hbar^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3}
  \]
  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
   \[
   \sigma = n e \mu = \frac{n e^2 \tau}{m^*}
   \]

2. Greater band degeneracy $N_V$
   multiple parabolic bands
   \[
   m^* = m^*_{\text{band}} N_V^{2/3}
   \]

3. Scattering
   Energy dependence of $\tau$
Thermopower depends on carrier conc. \( n \) 
parabolic band metal \( \alpha \propto n^{-2/3} \)

\[ 
\alpha = \frac{8\pi^2 k_B^2}{3e^2 h^2} m^* T \left( \frac{\pi}{3n} \right)^{2/3} 
\]

\( m^* \) is the single Parabolic Band effective mass

PbTe:TI 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

Thermoelectric $\text{La}_{3-x}\text{Te}_4$

$\text{La}_{3-x}\text{Te}_4$ has high $zT$ at high $T$

Higher than SiGe used by NASA

Highest $zT$ for $\text{La}_{2.73}\text{Te}_4$

$E_F$ at edge of heavy band

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

$E_F$ deep inside light band

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


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$^3$
**$p$-PbTe $zT$**

Light band has peak $zT$ at low $n$
- $zT$ peak < 1
- “2P-PbTe” used by NASA in 1960’s
  - $n_H < 4 \times 10^{19}$ holes/cm$^3$

Heavy band requires high $n$
- $zT$ peak ~ 1.5
  - $n_H \geq 1 \times 10^{20}$ holes/cm$^3$

p-PbSe

Similar light-band heavy-band in PbSe
Leads to $zT > 1$
without expense of Te!

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$_x$Ca$_5$Al$_2$Sb$_6$ zT 0.6 at 1000K
- Na$_x$Ca$_3$Al$_1$Sb$_3$ 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
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**Thermoelectrics**
Actual band structure

Blue PbTe
Red Tl:PbTe (minus one band)
Supercell L is actually Gamma