Thermoelectric material ZnSb
--- its defects and impurity band conduction

For 17th Conference of Gettering and Defect Engineering in Semiconductor Technology (GADEST 2017) Oct 01-06, 2017
Lopota Resort, Georgia
Thermoelectric material ZnSb --- its defects and impurity band conduction
- What matters to thermoelectrics
- ZnSb and its defects
- Impurity band conduction and its impact on Thermoelectric performance
Phenomenological transport of thermoelectrics

**Seebeck effect**

Seebeck coefficient  \( \alpha = \frac{\Delta V}{\Delta T} \)
Phenomenological transport of thermoelectrics

Seebeck effect
Seebeck coefficient \( \alpha = \frac{\Delta V}{\Delta T} \)

Peltier effect
Peltier coefficient \( \Pi = \frac{J_Q}{J} \)
Performance of thermoelectric module and material

The coefficient of performance (COP) for a thermoelectric module

\[
\eta_{COP} = \left( \frac{T_H - T_C}{T_H} \right) \left( \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}} \right)
\]

Carnot limit

\( T_C \) -- Temperature at the cold reservoir
\( T_H \) -- Temperature at the hot reservoir
\( ZT \) -- Dimensionless thermoelectric figure of merit of module, including \((zT)_n\) and \((zT)_p\)

\( \alpha^2 \sigma \)

Power factor

\[ zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} \]

Thermal conductivity from electrons and phonons

- High Seebeck coefficient \( \alpha \)
- High electrical conductivity \( \sigma \)
- Low thermal conductivity \( \kappa \)

\( \mu \text{m} - \text{cm} \)

What matters to thermoelectrics

- Optimizing power factor

Seebeck coefficient

\[ \alpha = \frac{1}{qT} \frac{\int \tau v^2 (E - E_F)(-\frac{\partial f_0}{\partial E})d^3k}{\int \tau v^2 (-\frac{\partial f_0}{\partial E})d^3k} \]

Electrical conductivity

\[ \sigma = \frac{q^2}{4\pi^3} \int \tau v^2 (-\frac{\partial f_0}{\partial E})d^3k \]

\[ zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T \]
What matters to thermoelectrics

- Optimizing power factor

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

Electrical conductivity

\[ \sigma = q n \left( \frac{q \tau}{m^*} \right) \]

\[ zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T \]

- Optimize the interaction between transport coefficients
- Doping, defects scattering, energy filtering

\( E_F \)
\( \int d^3k \)
\( \sigma \)
\( \alpha \)
\( \frac{\partial f_0}{\partial E} \)
\( \text{DOS} \)

ZnSb and its defects
Impurity band conduction
What matters to thermoelectrics

- Optimizing power factor

![Graph showing the relationship between power factor, Seebeck coefficient, and electrical conductivity as a function of ln(n).]

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

- Electrical conductivity

\[ \sigma = qn \left( \frac{q\tau}{m^*} \right) \]

- Wiedemann-Franz law

\[ k_e = n q \mu \mathcal{L} T \]

- Optimize the interaction between transport coefficients
- Doping, defects scattering, energy filtering
What matters to thermoelectrics

• Reducing thermal conductivity

\[ zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T \]

Wiedemann-Franz law

\[ k_e = n q \mu \mathcal{L} T \]


• Phonon engineering.
• Nanostructuring, impurities.
# Choosing a material

<table>
<thead>
<tr>
<th>Expectation</th>
<th>ZnSb</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Non-toxic</td>
<td>• Safe compound</td>
</tr>
<tr>
<td>• Abundant</td>
<td>• Major industrial metals (Zn:13.7 MT; Sb 130 KT (2016))</td>
</tr>
<tr>
<td>• High price-performance</td>
<td>• Estimated cost &lt;10$/kg</td>
</tr>
<tr>
<td>• Relevant operation temperature</td>
<td>• 400K ~ 600K</td>
</tr>
<tr>
<td>• Narrow bandgap</td>
<td>• Optimal temperature can be further tuned</td>
</tr>
<tr>
<td>6 ~ 10 $k_B T$ (0.2~1 eV)</td>
<td>• Band gap ~ 0.5 eV</td>
</tr>
<tr>
<td>• “Complex” structures</td>
<td>• Deformed Zinc-blende</td>
</tr>
</tbody>
</table>

[Image: ZnSb and its defects - Impurity band conduction]
Choosing a material

Expectation

- Non-toxic
- Abundant
- High price-performance
- Relevant operation temperature
- Narrow bandgap $6 \sim 10 \ k_B T \ (0.2 \sim 1 \ eV)$
- "Complex" structures

ZnSb

Choosing a material

<table>
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<tr>
<th>Expectation</th>
<th>ZnSb</th>
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</thead>
<tbody>
<tr>
<td>• Non-toxic</td>
<td>Paper industry (ref.1)</td>
</tr>
<tr>
<td>• Abundant</td>
<td>Metal casting (ref.2)</td>
</tr>
<tr>
<td>• High price-performance</td>
<td>Cement industry (ref.2)</td>
</tr>
<tr>
<td>• Relevant operation temperature</td>
<td>Aluminium industry (ref.2)</td>
</tr>
<tr>
<td>• Narrow bandgap</td>
<td>Glass manufacturing (ref.2)</td>
</tr>
<tr>
<td>6 ~ 10 $k_B T$ (0.2~1 eV)</td>
<td>Steel industry (ref.2)</td>
</tr>
<tr>
<td>• “Complex” structures</td>
<td>Vehicle exhaust (ref.3)</td>
</tr>
<tr>
<td></td>
<td>Steam power plant (ref.4)</td>
</tr>
</tbody>
</table>

**ZnSb**

- $n$ - Bi$_2$Te$_3$ (ref.5)
- $n$ - PbTe (ref.5)
- $n$ - CoSb$_3$ (ref.5)
- $n$ - SiGe (ref.5)
- $p$ - Sb$_2$Te$_3$ (ref.5)
- $p$ - TAGS (ref.5)
- $p$ - PbTe (ref.5)
- $p$ - CeFe$_4$Sb$_12$ (ref.5)
- $p$ - Yb$_{14}$MnSb$_{11}$ (ref.5)
- $p$ - SiGe (ref.5)
- $p$ - Zn$_3$Sb$_3$ (ref.6)
- $p$ - ZnSb (ref.6)

**What matters to thermoelectrics**

**ZnSb and its defects**

- **Impurity band conduction**

**References**

(ref.1) *Thermal Science* 13, 165-174 (2009)
(ref.2) EERE Waste heat recovery, 2015
(ref.3) J. Electron. Mater., Vol. 44, No. 6, 2015
(ref.4) EPA, Waste Heat to Power, 2012
(ref.6) *Nature Materials* 7, 105 - 114 (2008)
Doping defects

Given by $E_g = 0.53 \text{ eV}$ and $m^* = 0.42$ for ZnSb,

The theoretical intrinsic charge carrier concentrations at:

- Room temperature $2.41 \times 10^{14} \text{ cm}^{-3}$;
- $300 ^\circ\text{C} : 8.42 \times 10^{16} \text{ cm}^{-3}$

Power factor peaks at $2 \times 10^{19} \text{ cm}^{-3}$ for ZnSb
Nano-oxide “defects”

Transmission electron microscopy image of nano oxide particles in ZnSb

Nano-oxide “defects”

Concept of energy filtering

\[ E \quad \int d^3 k \quad \alpha \quad \sigma \quad \frac{\partial f_0}{\partial E} \quad \text{DOS} \quad E_F \]

What matters to thermoelectrics

ZnSb and its defects

Impurity band conduction

Intrinsic defects

The theoretical intrinsic charge carrier concentrations at room temperature

\[ 2.41 \times 10^{14} \text{cm}^{-3} (E_g = 0.53 \text{ eV} \text{ and } m^* = 0.42) \]

However, most of reported on single crystal undoped ZnSb at RT: \(1 - 2 \times 10^{16} \text{cm}^{-3}\);
polycrystalline undoped ZnSb at RT: \(\sim 10^{18} \text{cm}^{-3}\).

\[ \begin{array}{cccccc}
V_{\text{Zn}} & V_{\text{Sb}} & Zn_{\text{Sb}} & \text{Sb}_{\text{Zn}} & Zn_i & \text{Sb}_i \\
\hline
q_d & V_{Zn} & V_{Sb} & \text{Sb}_{Zn} & Zn_{Sb} \\
-3 & 0.51 & 2.47 & 1.83 & 1.33 \\
-2 & 0.30 & 2.05 & 1.50 & 1.26 \\
-1 & 0.32 & 1.83 & 1.33 & 1.28 \\
0 & 0.52 & 1.79 & 1.34 & 1.41 \\
+1 & 0.88 & 1.70 & 1.39 & 1.67 \\
\end{array} \]


Occupancy of localized states associated with different charged \(V_{\text{Zn}}\) in ZnSb.

Intrinsic defects

\[ V_{\text{Zn}} : \quad \text{ZnSb}(s) \rightarrow \text{Zn}_{1-x}\text{Sb}(s) + x \cdot \text{Zn}(g) \]

Influence of annealing at 400 °C for 30 minutes on the electronic properties of ZnSb at room temperature. The carrier concentration increases significantly for both samples, leading to an increased conductivity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing</th>
<th>( p ) ( [10^{18}\text{ cm}^{-3}] )</th>
<th>( \sigma ) [\text{S cm}]</th>
<th>( \mu ) [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>Before</td>
<td>7.95</td>
<td>202</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>14.1</td>
<td>262</td>
<td>116</td>
</tr>
<tr>
<td># 2</td>
<td>Before</td>
<td>3.57</td>
<td>134</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>10.2</td>
<td>360</td>
<td>220</td>
</tr>
</tbody>
</table>

Impurity band conduction

(a) Low concentration  (b) Medium concentration  (c) High concentration

Impurity states

Impurity band

$E_C$

$E_V$

$N_i \sim 6 \times 10^{17}$ cm$^{-3}$ for ZnSb

Impurity band conduction

Classical semiconductor behavior in Si

In ZnSb

**Impurity band conduction**

- Two types of carriers with different effective mass and mobilities
- Common in thermoelectrics, Also see in ZnSe, PdTe and BiTe, Ge, etc.

\[ \text{CB, } E_C \text{ to } E_D \]

\[ \text{VB, } E_V \text{ to } E_{A1} \]

\[ \text{Fermi Level (eV)} \]

\[ \text{Carrier concentration (cm}^{-3} \text{)} \]

\[ \text{Mobilities (cm}^2/\text{Vs)} \]

\[ \text{Resistivity (Ω.cm)} \]
Impurity band conduction

Modelling of two carriers (VB carriers and IB carriers) conduction

Variables: \( E_{A1}, E_{A2}, N_{A1}, N_{A2}, N_D \)

\[
R_H = \frac{\rho_v \mu_v^2 + \rho_{im} \mu_{im}^2}{q(p_v \mu_v + p_{im} \mu_{im})^2}
\]

\[
\rho = \frac{1}{q(p_v \mu_v + p_{im} \mu_{im})}
\]

\( \rho_v, \mu_v \)
Carrier concentration, mobility in VB

\( \rho_{im}, \mu_{im} \)
Carrier concentration, mobility in IB

Fitting Hall coefficient, simulating resistivity

Fitting resistivity, simulating Hall coefficient

**Impurity band conduction**

- Magnetoresistance experimental prove of two carriers conduction:
  - (VB carriers and IB carriers)
- Bending down indicates contribution from IB

![Graph showing magnetoresistance vs magnetic field](attachment:image)

- How does it impact to thermoelectric performance?
- Can we manipulate impurity band?

---

Impurity band conduction

How does it impact to thermoelectric performance?

- Change shape of DOS

Seebeck coefficient

$$\alpha = \frac{1}{qT} \int \tau v^2 (E - E_F) \left(- \frac{\partial f_0}{\partial E}\right) d^3 k$$

Electrical conductivity

$$\sigma = \frac{q^2}{4\pi^3} \int \tau v^2 \left(- \frac{\partial f_0}{\partial E}\right) d^3 k$$

$$zT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_{ph}} T$$
Impurity band conduction

How does it impact to thermoelectric performance?

- Change shape of DOS
- Change position of Fermi level -- Seebeck coefficient

Seebeck coefficient

$$\alpha = \frac{1}{qT} \int \tau v^2 (E - E_F) (-\frac{\partial f_0}{\partial E}) d^3k$$

Position of Fermi level depends on

- Mass action law
- Charge neutrality

Fermi level goes between IB and VB at equilibrium
Impurity band conduction

Can we manipulate impurity band?

\[ \alpha = \frac{\alpha_{VB} \cdot p_{VB} + \alpha_{IB} \cdot p_{IB}}{p_{VB} + p_{IB}} \]

Impurity band at 0.065eV above VB with concentration \(2.5 \times 10^{18} \text{ cm}^{-3}\)

- Impurity band conduction in low concentration samples
- High concentration suppress impurity band conduction
Summary

- **What matters to thermoelectrics**
  - Maximum $zT$ at a particular carrier concentration
  - Optimising power factor
  - Reducing thermal transport

- **ZnSb and its defects**
  - Decent thermoelectric material around 300 °C
  - Doping defects – increase carrier concentration
  - Nano-oxide – energy filtering
  - Zn vacancies defects – intrinsic charge carriers

- **Impurity band conduction and its impact on thermoelectric performance**
  - Elevated carrier concentration at cryo-temperature
  - Two type of carriers with different effective mass and mobility
  - Change DOS shape and Fermi level -- power factor