Thermoelectricity: From Atoms to Systems

Week 5: Recent Advances in Thermoelectric Materials and Physics
Lecture 5.3: State-of-the-art thermoelectric materials, optimum bandgap

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Microscopic picture for thermoelectric effects (electrons)

- Energy
- DOS
- Fermi-Dirac
- Group velocity
- Scattering time (relaxation time)

\[ \sigma = \int \sigma(E) dE \]

\[ S = \frac{1}{eT} \frac{\int \sigma(E)(E - E_F) dE}{\int \sigma(E) dE} \propto <E - E_f> \]

\[ \sigma(E) \approx e^2 \tau(E) \bar{v_x}^2(E) \bar{n}(E) \left( -\frac{\partial f_{eq}}{\partial E} \right) \]

- \( \tau \) = relaxation time
- \( \bar{v_x} \) = average velocity
- \( \bar{n} \) = density-of-states
- \( f_{eq} \) = Fermi-Dirac distribution

Transport Function
Boltzmann Transport /nanoHUB simulation

n-PbTe, 300 K
Input e.g. $\tau = 0.1$ ps (const.)

$n$-PbTe has primary conduction and valence bands at the L valley in the Brillouin zone. There is a secondary valence band at the Sigma valley, of which the band edge is about 40 meV down below the first valence band edge at 300 K. The secondary conduction band is ignored. The band gap, the band offset between the two valence bands and their effective masses are all functions of temperature ($T$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Lead Telluride</th>
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<tbody>
<tr>
<td>Bands</td>
<td>3 Single Conduction Band - Double Valence Bands</td>
</tr>
</tbody>
</table>

$S = -95 \mu V/K$
$\sigma = 2.2e4 /\Omega cm$
for $E_F = 0.3$ eV

$S = -37 \mu V/K$
$\sigma = 4.6e3 /\Omega cm$
for $E_F = 0.1$ eV
Material Figure-of-Merit for Thermoelectrics

\[
Z = \frac{S^2 \sigma}{k}
\]

\[
Z = \frac{(\text{Seebeck})^2 (\text{electrical conductivity})}{(\text{thermal conductivity})}
\]

**Material Figure-of-Merit**

\[
\left( \frac{\mu m^{*1.5}}{k} \right) \cdot T_C^{2.5}
\]

Mobility \[\mu = \left( \frac{e \tau}{m^*} \right)\]

\(\tau\): scattering time
\(m^*\): effective mass

**Keyes’ Relation** (phonon-phonon scattering dominates \(k_{\text{lattice}}\) at high \(T\))

\[
k_{\text{latt}}T = \left( \frac{R^{3/2} T_m^{3/2} \rho^{2/3}}{3\gamma^2 \varepsilon^3 N_0^{1/3} A^{7/6}} \right)
\]

\(T_m\): melting temperature, \(A\): mean atomic weight, \(\gamma\): Gruneisen constant, \(\varepsilon\): fractional amplitude of interatomic thermal vibration, \(R\): ideal gas constant, \(N_0\): Avogadro’s number, \(\rho\): density

Chasmar and Stratton (J. Electron. Control 7, 52 (1959))

\[
B = T e \mu n(T)(k_B/e)^2/(4k_{\text{latt}})
\]

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

where \(e\) is the charge, \(\mu\) is the mobility, \(k_{\text{latt}}\) is the lattice thermal conductivity, \(m^*\) is the density of states mass of the band, and \(N\) is the degeneracy of the band because of different spin states, orbital states, and valley ellipsoids. Materials with the largest \(B\) have the largest \(Z\).
Material figure-of-merit for thermoelectrics


\[ \frac{\mu m^{*1.5}}{\kappa} \]

- \( \mu \) Mobility
- \( \kappa \) Thermal conductivity
- \( m^* \) Electron effective mass

AlSb, GaAs, GaN, GaP, GaSb, HgCdTe, InAs, InGaAs, InGaAsP, InN, InP, InSb, Ge (n), Ge (p), Si (n), Si (p), SiGe (n), SiGe (p), BiTe (n), BiTe (p)
Optimum bandgap for thermoelectric material

Indirect bandgap material

![Graph showing ZT vs \(\beta E_g = E_g / kT\)](image)

- \(\delta\) = scattering parameter \((r) + 3/2\)
- Phonon scattering: \(r = -1/2\)
- Impurity scattering: \(r = 3/2\)
- \(B\): Stratton material parameter

![Graph showing ZT vs \(E_g / kT\)](image)

- PO Phonon scatt. \(\sim m^*^{-1/2}\)
- Acoustic phonon scatt. \(\sim m^*^{-3/2}\)
- Ionized impurity scatt. \(\sim m^*^{+1/2}\)

**FIG. 1.** Maximum value of \(ZT\) as a function of the energy band gap \(E_g\) in units of thermal energy \(k_B T\), for parabolic bands and for nonparabolic bands with two different scattering mechanisms.

\[
m^* = \frac{3\hbar^2}{4P^2} E_g
\]

Optimum Bandgap

\(~6-10 k_B T\)


Best bandstructure for thermoelectrics

(1) What physical constraints should be placed on the Transport Distribution Function (TDF)?
The TDF(E) can be written as a product of the number of channel, M(E), and the mean-free-path, \( \lambda(E) \). Each of these two quantities is well-defined and directly relatable to the underlying electronic bandstructure. For a given dispersion, the maximum of M(E) is fixed not the area under M(E) vs. E.

(2) How does the Bandwidth (BW) of the TDF affect TE performance?
When the lattice thermal conductivity is zero, a \( \delta \)-function TDF produces an electronic efficiency at the Carnot limit, but no power can be delivered to a load. For a constant MFP (independent of BW), a narrow TDF maximizes the power delivered to a load—for both zero and finite lattice thermal conductivity. For a finite lattice thermal conductivity, it also maximizes the efficiency. The BW should match the width of the Fermi window. A \( \delta \)-function TDF produces an ZT at the Mahan-Sofo limit, ZT =\( k_0/k_{ph} \), but this upper limit itself depends on the BW, so higher ZTs result for higher BWs where operation is below the Mahan-Sofo limit.

(3) How does scattering affect optimum bandstructure?
Scattering profoundly changes these conclusions. If, instead of a constant MFP, we assume that the scattering rate is proportional to the density-of-states, we conclude that a very broad band is better than a narrow band.

(4) How should the improved performance of materials with a high valley degeneracy or with a resonant energy levels that distort the density-of-states be understood?
It is best to achieve a high density of states through valley degeneracy with a number of light mass valleys, as opposed to a single heavy mass valley because the higher velocity of the light mass valley increases both M(E) and \( \lambda(E) \). Offsetting the valleys in energy can enhance the Seebeck coefficient, but it degrades the conductivity. With a higher upper valley effective mass and the appropriate energy offset, TE performance can be enhanced, but the results are sensitive to the specifics of scattering.

(5) Is there a best bandstructure for TE performance?
Although there is no simple answer, the general considerations are clear. Assuming that scattering rate is proportional to density-of-states, high average velocities in the Fermi window produce the best results, so materials with a small density-of-states are best. The small \( D(E) \) helps to increase scattering times. The large velocity times this \( D(E) \) gives a significant number of channels for conduction, and the large velocity also increases the MFP.

Modification of Lorenz Number

Theory short period superlattice

InGaAs/InGaAlAs 6nm/3nm (200meV)

\[ Z = \frac{S^2 \sigma}{\kappa_{\text{lattice}} + \kappa_{\text{electronic}}} \]

\[ \frac{\kappa_{\text{electronic}}}{\sigma} \sim L \]

\[ L = \frac{\kappa_e}{\sigma T} \left( \frac{q}{k_B} \right)^2 \]


Doping concentration (cm\(^{-3}\))
Classical thermoelectric materials

Current thermoelectric technology based on the above materials.
Bi$_2$Te$_3$/Sb$_2$Te$_3$: highly anisotropic ($Z_\parallel>Z_\perp$), Te-Te van der Waals bond, solid solution to improve ZT (Ioffe)

PbTe: rock-salt, high dielectric constant, High temperature (loss of Te)

TAGS: (GeTe)$_{1-x}$(AgSbTe$_2$)$_x$, Rosi et al. 1961, ZT$_{(p\text{-type})}$~1.5 at 650-750K (stability issues at high-T)

Si$_{0.7}$Ge$_{0.3}$: high $T_m$↔high $T_{\text{Debye}}$↔high $k_{\text{lattice}}$; exceptional low $k_{\text{lattice}}$ upon alloying (Abeles et al. ’62), Klemens theory can explain $k_{\text{lattice}}$
Combine alkali metal, Bi$_2$Te$_3$ and PbTe: Kanatzidis (MSU, Northwestern)

CsBi$_4$Te$_6$: ZT=0.8 (@225K)


Kanatzidis (Northwestern)

**LAST-18:** $\text{Ag}_{1-x}\text{Pb}_{18}\text{SbTe}_{20}$ cubic compounds (phase segregation at nanometer scale) n-type, $\text{ZT} \sim 1.6$ @ 700K

Nanosize region (Pb-poor) sits endotaxially in the surrounding matrix.

Record $ZT \sim 2.2$ (Sept. 2012)

Spark-plasma-sintered Na(2%)-doped PbTe: SrTe(4%)

[Biswas et al. (Kanatzidis group), *Nature* 489, 414 (2012)]

Na-doped PbTe  Na-doped SrTe: PbTe  SPS
Boltzmann transport modeling of bulk PbTe

- Temperature-dependent bandgap
- Non-parabolic bands
- Acoustic phonon / Polar optical phonon / Impurity scattering

Transport Function (diff. conductivity)

\[
\sigma_d(E) = e^2 \tau(E) n_x^2(E) \rho_{DOS}(E) \left( - \frac{\partial f_0(E)}{\partial E} \right)
\]

\[
\sigma = \sum \int \sigma_d(E) dE \quad S = \sum \left( \frac{k_B}{q} \right) \int \left[ \frac{(E - E_F)}{k_B T} \right] \frac{\sigma_d(E)}{\sigma} dE
\]

\[m_e = 0.079m_0\]
\[m_{h,L} = 0.084m_0\]
\[m_{h,\Sigma} = 0.368m_0\]

Analysis of recent $ZT \sim 2.2$ paper

[Biswas et al. (Kanatzidis group), *Nature* 489, 414 (2012)]

Pure PbTe at 300 K:
- $p = 9 \times 10^{19}$ cm$^{-3}$ (measured by authors)
- $S = 77$ $\mu$V/K ($S_{\text{exp}} = 75$)
- $\sigma = 5500$ (\Ohm\text{cm})$^{-1}$ ($\sigma_{\text{exp}} = 1500$)

Mobility suppression by boundaries

Pure PbTe at 800 K:
- $p = 1.5 \times 10^{20}$ cm$^{-3}$ (estimated by us)
- $S = 250$ $\mu$V/K ($S_{\text{exp}} = 250$)
- $\sigma = 500$ (\Ohm\text{cm})$^{-1}$ ($\sigma_{\text{exp}} = 450$)

Smaller mobility suppression at higher $T$
Analysis of recent ZT~2.2 paper

[Biswas et al. (Kanatzidis group), Nature 489, 414 (2012)]

Total thermal conductivity

- **$\kappa_{total} = 1.0$**

Lattice thermal conductivity

- **$\kappa_{lat} = 0.5$**

J.-H Bahk calculation

- **$\kappa_e \approx 0.5$ W/mK**

$$K_{lat} = K_{total} - K_e$$
Week 5: Lecture 3 Summary

- Optimum band structure for thermoelectrics
  - Optimum bandgap, low Lorentz number
- Classical thermoelectric materials
  - Bi$_2$Te$_3$, PbTe, TAGS, SiGe
- Complex Chalcogenides CsBi$_4$Te$_6$: ZT=0.8 (@225K)
- Spark plasma sintered Na(2%)-doped PbTe:SrTe(4%) ZT~2.2 at 900K
  - Boltzmann modeling for electron transport
  - Different length scales nm-µm for phonon scattering