Thermoelectricity: From Atoms to Systems

Week 5: Recent Advances in Thermoelectric Materials and Physics
Lecture 5.6: Overview of Week 5, Recent reviews

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Thermionic (TI) vs. Thermoelectric (TE)

Thermionic: ballistic, non-linear transport

Superlattice: Linear transport: “effective” Seebeck coefficient

Embedded ErAs nanoparticles in InGaAs matrix

ZT~1.3-1.5 @800K

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 \( T \))

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

\( T_m \): 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
Boltzmann Transport /nanoHUB simulation

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

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

$S = -37 \ \mu V/K$
$\sigma = 4.6e3 /\Omega cm$
for $E_F = 0.1$ eV
Optimum band structure for thermoelectrics

\[ \kappa_{ph} = 0 \text{ W/mK} \]

\[ ZT \]

\[ PF \]

\[ \sigma \]

\[ \kappa_{el} \]

\[ S \]

\[ m^* = \frac{3h^2}{4P^2} E_G \]

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.


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

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

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

Na-doped PbTe  Na-doped SrTe: PbTe  SPS
**Oxide Thermoelectrics**

Potential cause of high power factor:
- Large entropy of mixed Co\(^{3+}/\)Co\(^{4+}\) state with low spin (Koshibae et al.)
- There are correlation effects, geometric frustration (B.S. Shastry)
- Potential explanation of high Seebeck using standard band theory (D. Singh)

Difficult to control Na content (evaporates at high T) and decomposition at 1100 K.


Maximum Spin Seebeck at 2.7T of the cold Pt bar.
PbTe: Tl doubles zT

Single Level Thermoelectrics


Nakpathomkun et al., *Phys. Rev. B* 82, 235428, 2010
Phase transition; Coupling between charge and energy transports

\[ \xi = \frac{Z^* T}{1 + Z^* T} \]

- \( \xi \): coupling factor between charge and energy density
- \( Z^* \): high frequency limit of figure of merit

- B. S. Shastry, *Rep, Prog, Phys* 72, 016501, (2009)

C. Vining, MRS Spring 1997 (Vol. 478, p.3)

Fig. 4: Specific heat ratios, \( \gamma_{PV} \) for a PV system (Freon 12) and thermal conductivity ratios, \( \gamma_{EI} = 1 + ZT \), for selected \( n \)-type semiconductor alloys as a function of temperature.
SiGe/Si superlattice thermal conductivity

S. Huxtable, A. Majumdar, E. Croke, et al.

A. Shakouri, Annual Review of Materials Research, July 2011
Ali Shakouri and John E. Bowers, "Heterostructure integrated thermionic refrigeration", *International Conference on Thermoelectrics*, Dresden, Germany, August 1997
New and Old Concepts in Thermoelectric Materials

Joseph R. Sootsman, Duck Young Chung, and Mercouri G. Kanatzidis*
Hot-pressed pellets showed electrical conductivity of 185 $\Omega\text{cm}$ and Seebeck coefficient of 180 $\mu$V/K at 1200 K. The low thermal conductivity 0.7–0.9 W/mK in temperatures between 200–1275 K gives rise to the remarkable ZT of $\sim$1.0 at 1200 K.

The low thermal conductivity is primarily attributed to the large lattice constant, the structural complexity, and to the ionic character bonding in the lattice.

It is possible that Yb$_{14}$MnSb$_{11}$ and its alloys may replace p-type Si-Ge alloys in future space missions.


**Nano-enhanced** (e.g. using Spark Plasma Sintering to create nanoparticle composites)


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**Figure 2** Complex crystal structures that yield low lattice thermal conductivity. **a**, Extremely low thermal conductivities are found in the recently identified complex material systems (such as $\text{Yb}_3\text{MnSb}_{11}$, ref. 45; $\text{CeFe}_3\text{CoSb}_{12}$, ref. 34; $\text{Ba}_5\text{Ga}_{14}\text{Ge}_{20}$, ref. 79; and $\text{Zn}_4\text{Sb}_3$, ref. 80; $\text{Ag}_3\text{TiTe}_5$, ref. 40; and $\text{La}_3\text{Te}_4$, Caltech unpublished data) compared with most state-of-the-art thermoelectric alloys ($\text{Bi}_2\text{Te}_3$, Caltech unpublished data; $\text{PbTe}$, ref. 81; $\text{TAGS}$, ref. 69; $\text{SiGe}$, ref. 82 or the half-Heusler alloy $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}$, ref. 83). **b**, The high thermal conductivity of $\text{CoSb}_3$ is lowered when the electrical conductivity is optimized by doping (doped $\text{CoSb}_3$). The thermal conductivity is further lowered by alloying on the $\text{Co}$ ($\text{Ru}_3\text{Pd}_{12}\text{Sb}_3$) or $\text{Sb}$ ($\text{FeSb}_2\text{Te}$) sites or by filling the void spaces ($\text{CeFe}_3\text{CoSb}_{12}$) (ref. 34). **c**, The skutterudite structure is composed of tilted octahedra of $\text{CoSb}_3$ creating large void spaces shown in blue. **d**, The room-temperature structure of $\text{Zn}_4\text{Sb}_3$ has a crystalline Sb sublattice (blue) and highly disordered Zn sublattice containing a variety of interstitial sites (in polyhedra) along with the primary sites (purple). **e**, The complexity of the $\text{Yb}_3\text{MnSb}_{11}$ unit cell is illustrated, with $[\text{Sb}]^{1−}$ trinmers, $[\text{MnSb}]^{1+}$ tetrahedra, and isolated Sb anions. The Zintl formalism describes these units as covalently bound with electrons donated from the ionic $\text{Yb}^{2+}$ sublattice (yellow).
Week 5: Recent Advances

5.1 • TE vs. TI: non-linear, lateral momentum conservation

5.2 • ErAs embedded nanoparticles in InGaAs
   • Reduce $k_{lattice}$ by mid/long phonon scattering, doping the matrix, energy dependent scattering

5.3 • Optimum band structure
   • Classical TE materials: Bi$_2$Te$_3$, PbTe, TAGS, SiGe
   • Chalcogenides: SPS Na(2%)-PbTe:SrTe(4%) ZT~2.2 at 900K

5.4 • Skutterudites, Clathrates, Half Heuslers, Oxides, Zintl phase, nano-composites
   • Spin Seebeck • Resonant state

5.5 • Carnot vs. Curzon-Ahlborn
   • Single level thermoelectrics
   • Some open questions (phase transition, coupled charge/energy transport, superlattice thermal conductivity, opto thermo electric devices)
Thermoelectricity: Atoms to Systems

Generic thermoelectric device

\[ \mu_1, T_1, \mu_2, T_2 \]

- **Systems**
  - Energy balance and module models
  - Weeks 4-5

- **Nano and macro characterization**
  - Experimental methods
  - Week 3

- **Terminal characteristics of device**
  - Transport models
  - Weeks 1-2

- **Atoms**