From Heat to Electricity: How “nano” Saved Thermoelectrics

Mercouri Kanatzidis, Northwestern University

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Wednesday, October 24, 2007
Hotel Orrington, Evanston, IL
Collaborating Team interactions

Kanatzidis group
Chemistry
Materials design, discovery and optimization

Hogan group
E. Engineering
Module design and optimization

Tellurex Corp
Industry

Mahanti group
Physics (theory)
Fundamental understanding
Electronic structure, Property prediction

Case group
Materials Science
Powder processing
Mechanical properties

Schock group
M. Engineering
Materials scale-up and optimization, design/testing

Bruce Cook
TEM, transport

Uher group
Physics
TE Measurements
Outline

- Introduction
- Materials under investigation
- Synthesis (successes and challenges)
- TEM characterization and nanostructuring
- Structure property relationships- Nanostructures reduce the lattice thermal conductivity
- Materials scale up and optimization
- Module Fabrication Progress, low resistance contacts
- Making brittle materials strong
- Conclusions
Heat to Electrical Energy Directly

Up to 20% conversion efficiency with right materials

TE devices have no moving parts, no noise, reliable
Thermoelectric applications

- Waste heat recovery
  - Automobiles
  - Over the road trucks
  - Utilities
  - Chemical plants

- Space power
- Remote Power Generation
- Solar energy
- Geothermal power generation
- Direct nuclear to electrical
Given that ~60% of energy becomes waste heat, even a 10% capture and conversion to useful forms can have huge impact on overall energy utilization.
Figure of Merit

\[ ZT = \frac{\sigma \cdot S^2}{\kappa_{total} \cdot T} \]

\[ \eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + T_c / T_h} \]

Carnot efficiency

\[ \delta = \frac{R_c}{R} \]

For \( T_h = 800K \)
\[ T_c = 300K \]
Today’s situation

- The most efficient materials today for power generation:
  - PbTe: $ZT \approx 0.8$ at 800 K (n-type)
  - TAGS: $ZT \approx 1.2$ 700 K (p-type)
  - $\text{Bi}_2\text{Te}_3-x\text{Se}_x$: $ZT \approx 1$ at 300 K
- Further improvements are needed.
- New materials emerging

Quantum Dot Layers in thin MBE-grown PbSe/PbTe superlattices (Harman et al, ZT~3)


Recent Developments in Bulk Thermoelectric Materials

George S. Nolas, Joe Poon, and Mercouri Kanatzidis

Abstract

Good thermoelectric materials possess low thermal conductivity while maximizing electric carrier transport. This article looks at various classes of materials to understand their behavior and determine methods to modify or “tune” them to optimize their thermoelectric properties. Whether it is the use of “rattlers” in cage structures such as skutterudites, or mixed-lattice atoms such as the complex half-Heusler alloys, the ability to manipulate the thermal conductivity of a material is essential in optimizing its properties for thermoelectric applications.

Keywords: alloy, compound, thermal conductivity, thermoelectricity.

March 2006 issue of MRS Bulletin
**ZT and Electronic Structure**

**Isotropic structure**

\[ Z_{\text{max}} \propto \gamma \]

\[ T^{3/2} \tau \sqrt{m_x m_y m_z} e^{(r+1/2)} \]

\[ \kappa_{\text{latt}} \]

- \( m \): effective mass
- \( \tau \): scattering time
- \( r \): scattering parameter
- \( \kappa_{\text{latt}} \): lattice thermal conductivity
- \( T \): temperature
- \( \gamma \): band degeneracy

Large \( \gamma \) comes with
- (a) high symmetry e.g. rhombohedral, cubic
- (b) off-center band extrema

**Anisotropic structure**

For acoustic phonon scattering \( r = -1/2 \)

**Complex electronic structure**
Selection criteria for candidate materials

- Narrow band-gap semiconductors
- Heavy elements
  - High $\mu$, low $\kappa$
- Large unit cell, complex structure
  - low $\kappa$
- Highly anisotropic or highly symmetric...
- Complex compositions
  - low $\kappa$, complex electronic structure
Investigating the A/Bi/Q system

\[ A_2Q + PbQ + M_2Q_3 \rightarrow (A_2Q)_n(PbQ)_m(M_2Q_3)_p \]

Map generates target compounds

Cubic materials

\[ A_mB_nM_mQ_{2m+n} \]

Phases shown are promising new TE materials

A=Ag, K, Rb, Cs
M=Sb, Bi
Q=Se, Te
Compounds discovered

- $\text{K}_2\text{Bi}_8\text{Se}_{13}$, $\text{KPbBi}_9\text{Se}_{13}$, $\text{KPb}_4\text{Sb}_7\text{Se}_{15}$
- $\text{Cs}_{1-x}\text{Pb}_{5-x}\text{Bi}_{10+x}\text{Se}_{21}$
- $\text{CsPbBi}_3\text{Te}_6$, $\text{CsPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPbBi}_3\text{Te}_6$, $\text{RbPb}_2\text{Bi}_3\text{Te}_7$, $\text{RbPb}_3\text{Bi}_3\text{Te}_8$,
- $\text{KPbBiSe}_3$, $\text{K}_2\text{PbBi}_2\text{Se}_5$
- $\text{AgPb}_1\text{SbTe}_{12}$, $\text{NaPb}_{20}\text{SbTe}_{22}$
AgPb$_m$SbTe$_{2+m}$ (LAST-$m$)
NaPb$_m$SbTe$_{2+m}$ (SALT-$m$)

- No phase transitions to melting point
Synthesis

Ingot properties very sensitive to cooling profile

Gravity induced inhomogeneity


R. G. Maier Z. Metallkunde 1963, 311
Large scale LAST-18 (n-type)

Strong composition grading along ingot

\[ m = 8 \]
\[ m = 14 \]
\[ m = 18 \]
\[ m = 25 \]
\[ m = 40 \]

Deviations from the \( \text{AgPb}_{18}\text{SbTe}_{20} \) composition
Best samples are Te-deficient

**Ag<sub>0.86</sub>Pb<sub>19</sub>SbTe<sub>20</sub>**

**EDS analysis**

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LAST-18: Synthesis with Slow Cooling

-2 deg/hr

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1000 °C, 4 h, 700 °C, 7 d, 12 h, 50 °C

ETN125

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<th>σ (S/cm)</th>
<th>S (μV/K)</th>
<th>PF (μW/cm·K²)</th>
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fast cooled sample

slow cooled sample
Properties of $\text{Ag}_{1-x}\text{Pb}_{18}\text{SbTe}_{20}$
TEM investigation on nanostructuring: LAST-18 (Cook)

MSU DY-92062 quenched and annealed (450°C 2 days)
Ag_{0.63}Pb_{18}Sb_{1.2}Te_{20}

Sample was thinned, dimpled, ion-milled, and carbon coated (~10 nm/side) prior to examination.

Near edge of foil – note semi-coherent feature (dark contrast) and high density of fully-coherent regions (light contrast).

Semi-coherent phase near edge of foil:

Example of coherent phase
Note: strain field surrounds the region

Annealing may promote nucleation and growth of nanoscale phases. Coherent features appear to be intrinsic, not a result of sample preparation.
Nanostructures reduce the lattice thermal conductivity

Lattice thermal conductivity

Clemens-Drabble theory

0.35 W/mK (Harman PbTe/PbSe superlattice)
Recent Report for Sintered Pellet $\text{Ag}_{0.8}\text{Pb}_{22}\text{SbTe}_{20}$, $\text{ZT} \sim 1.4$ at 680 K

APPLIED PHYSICS LETTERS 88, 092104 (2006)

High-performance $\text{Ag}_{0.8}\text{Pb}_{18+x}\text{SbTe}_{20}$ thermoelectric bulk materials fabricated by mechanical alloying and spark plasma sintering

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(Received 7 December 2005; accepted 7 February 2006; published online 28 February 2006)

FIG. 4. $\text{ZT}$ value and thermal conductivity (upper left corner) of $\text{Ag}_{0.8}\text{Pb}_{22}\text{SbTe}_{20}$ sample at different temperatures.
P-type materials, LASTT

- (LASTT-m) $\text{Ag}(\text{Pb}_{1-x}\text{Sn}_x)\text{mSbTe}_{2+m}$
- Sn atoms act as acceptors
- Ag atoms act as acceptors
- Sb atoms act as donors
- e.g. $\text{AgPb}_{10}\text{Sn}_8\text{SbTe}_{20}$, $\text{Ag}_x\text{Pb}_7\text{Sn}_3\text{Sb}_y\text{Te}_{12}$, $\text{Ag}_{1-x}\text{SnSb}_{1+x}\text{Te}_3$, etc
- Very low lattice thermal conductivity
- Good homogeneity
LASTT: Very low lattice thermal conductivity

LASTT-16: AgPb$_{14}$Sn$_{4}$Sb$_{0.4}$Te$_{20}$
LASTT-10: AgPb$_{10}$Sn$_{10}$Sb$_{0.7}$Te$_{22}$

J. Androulakis, K. F. Hsu, R. Pcionek, H. Kong, C. Uher, J. J. D'Angelo,
Why do the LAST materials nanostructure?

Driving force for segregation $\text{Ag}^+$/Sb$^{3+}$ pair: thermodynamics

Dissociated state..unstable

Associated state..stable

Any $+1/+3$ pair
Figure of Merit LASTT (p-type)

Na-based materials (SALT-m)

New high ZT p-type material $\text{Na}_{1-x}\text{Pb}_m\text{SbTe}_{2+m}$

$\sim 19-21$
What is nanostructuring worth?

Matrix Encapsulation as a Route to Nanostructured PbTe

$\text{PbTe} + X$

$X = \text{Sb}$

$X = \text{Bi}$

$X = \text{InSb}$

20 nm

100 nm

2 nm

100 nm
Nanocrystals of Sb in PbTe

• An optimum concentration of nanoscale second phase is necessary
• Mass fluctuations play a role in thermal conductivity reduction
• Lattice thermal conductivity reduced, however ZT low due to small Seebeck
Phonons
Electrons
Completed and Processed Ingot

Composition: $\text{Ag}_{0.43}\text{Pb}_{18}\text{Sb}_{1.2}\text{Te}_{20}$  Weight: 200 grams

Temperature cyclability
Cool from 1020°C to 700, 800, 825, 850, 875, 900°C typically from one – two hours

Ag\textsubscript{0.43}Pb\textsubscript{18}Sb\textsubscript{1.2}Te\textsubscript{20}

ETN61
1020°C to 700°C @ 120°C/hr

ETN64
1020°C to 825°C @ 97.5°C/hr

ETN65
1020°C to 875°C @ 72.5°C/hr

ETN68
1020°C to 900°C @ 120°C/hr
Module Fabrication

1.78mΩ total → 16.0µΩ·cm²

- Hot side diffusion contacts, and cold side solder contacts with <10 µW·cm² have been achieved.
Scanning Probe Results

Ni electrode on LASTT

Ag\textsubscript{0.9}Pb\textsubscript{9}Sn\textsubscript{9}Sb\textsubscript{0.6}Te\textsubscript{20}

Jarrod Short

I = 100mA
Slope = 26 (μV/mm)
4.7mm x 4.7mm
σ = 1740 (S/cm)
Making brittle materials strong

For brittle materials in general, the fracture strength is a function of the reciprocal square root of grain size.

- In region 1 (large grains), grain size dominates the fracture behavior.
- In region 2 (smaller grains), grain size and surface defects contribute to fracture.

Hot pressing
Ingot LAST/T materials have a large mean grain size (~500 to 700 μm), resulting in poor mechanical properties.

We utilize planetary ball milling to generate micron-scale powders from LAST/T ingots.

To date, we have achieved equiaxed powders with a mean particle size of ~5 μm via dry milling.

Wet milling studies demonstrate further size reduction with a mean grain sizes of ~2 to 3 μm.

To improve mechanical integrity, smaller grain size is needed.
Hot Press Billets

HPMSU-01

1 inch

HPMSU-02

Schock, Case
Best ZT Materials

![Graph showing ZT values for various materials against temperature (K). The materials include LAST, LASTT, Na$_{0.95}$Pb$_{20}$Sb$_{22}$Te, TAGS, Tl$_{1}BiTe$_{6},$ PbTe, Ce$_{0.9}Fe$_{3}CoSb$_{12},$ and SiGe. Each material is represented by a different marker and color on the graph. The ZT values range from 0 to 2, and the temperature range is from 0 to 1400 K.]
Conclusions

- LAST, LASTT and SALT: promising thermoelectric materials for next generation power generation modules. (expected device efficiency ~14%)
- Nanostructures strongly reduce thermal conductivity.
- Nanostructures are closely linked to high ZT.
- Scaleup successful in producing large quantities but material is brittle and contains microcracks.
- Hot pressing and powder processing yield 3x improvement in strength.
- Higher average ZT (>2) needed to reach 20% efficiency.
Students and postdocs

Graduate Students
- Joe Sootsman, Chemistry
- Huijun Kong, Physics, U. of Michigan
- Adam Downey, Electrical Engineering
- Jarrod Short, Electrical Engineering
- Jonathan D’Angelo, Electrical Engineering
- Fei Ren, Chem. Engineering and Materials Science
- Chris Malliakas, Chemistry
- Khang Hoang, Physics
- Ahmed Salameh, Physics
- Mayank Mittal, Mech. Engineering
- Aurelie Guegen, Chemistry

Postdocs and Research Associates
- Ferdinand Poudre, Chemistry
- Ed Timm, Mechanical Engineering
- Robert Pcionek, Chemistry
- Chun-I Wu, E. Engineering
- Jim Salvador, Chemistry
- Chia-Her Lin, Chemistry
- Xun Shi, Physics U of Michigan

Undergraduates
- Adam Pilchak, Materials Science
- Teresa Rhodes, Chemistry
- Jason Johnson, Materials Science

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