Lattice Thermal Conductivity and Stability of “TE Nano-Composites”

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Motivation for Low Dimensional TE Materials:

- Quantum Enhancement
  - Increase Seebeck
  - Interface Scattering
  - Large Kapitza Resistance
  - Reduce $\kappa_L$

Hicks & Dresselhaus, PRB 1993
Dresselhaus, Plenary Talk - ICT 05, Adv. Mats 07
Relative Importance of $\alpha^2/\rho$ and $\kappa$

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Venkatasubramanian et al., Nature 413, 597, 2001

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Relative Importance of $\alpha^2/\rho$ and $\kappa$

### Bi$_2$Te$_3$/Sb$_2$Te$_3$ Superlattice

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### PbTe/PbSeTe Quantum Dots

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PbSe$_x$Te$_{1-x}$ quantum dots in PbTe layers
TE Enhancement of Roughened Si Nanowires

Jan 2008 -- LBNL & Berkeley Groups

Surface Roughness Above
Leads to Reduction in Thermal Conductivity (Left)
Embedding Nanoparticles in Crystalline Semiconductors

ErAs nanoparticles in In$_{0.53}$Ga$_{0.47}$As matrix
Epitaxial growth
Goal to “Beat the Alloy Limit”
Uncorrelated Phonon Scattering

- Reduction in $\kappa_L$ (“nano-phonon effect”)
  Depends on ML thickness (ErAs nano)*
- Power Factor about same
  but ErAs can act as a dopant
- ZT significantly enhanced
- Theoretical analysis showed that
  - ErAs nanoparticles scatter mid to long $\lambda$ phonons*
  - While atomic scale defects scatter short $\lambda$ phonons.

W. Kim et al., PRL, 96-045901 (2006)
Santa Cruz & Berkeley Groups

\[ \text{normalized} \]

$\kappa_L$ reduced a factor of 2 below the alloy limit!
ZT enhanced a factor of 2!
TE Nanomaterials Growth, TE Nanocomposites & Grain Boundary Engineering

But First, Discussion on TE Measurements!
Resistivity and Seebeck Measurement Description:

\[ V_{Total} = V_{IR} + V_{TE} \]

\[ V_{IR} = \frac{[V(I^+) + V_{TE}^*] - [V(I^-) + V_{TE}^*]}{2} \]

\[ \alpha_{AB} = \frac{\Delta V}{\Delta T} = \frac{(V_H - V_L)}{(T_H - T_L)} \]

Important to measure \( \Delta T \) Correctly where \( \Delta V_{TE} \) is measured.

Measure all Properties on Same Sample!
Crycooler Head for R & α Measurements System (3 Systems):

Typical Size: 2 x 2 x 8 mm³
6-10K < T < 320 K

Measures two samples simultaneously
6 K < T < 320 K

IC Chip receptacle

**Thermal Conductivity - Bulk Samples**

- Phosphor Bronze wire
- Strain Gauge
- #38 Cu wire with stycast
- Stable T base

**Low Temp Thermal Conductivity:**

**Steady State Method**

(6K to 320 K)

P vs. $\Delta T$ Sweeps @ Constant T

\[
P_{\text{Sam}} = \kappa_{\text{Tot}} \frac{A}{L_s} \Delta T
\]

- PSam = $\kappa_{\text{Tot}} \frac{A}{L_s} \Delta T$

- Sample Width $\approx 3\text{mm}$

**Equation:**

\[
\kappa = \frac{P_s L}{A \Delta T}; P_s = I^2 R - P_{\text{loss}}
\]

*Pope et.al* Cryogenics, 41, 725 (2001)
Thermal Conductivity - Bulk Samples

Absolute steady state technique
Two samples may be mounted simultaneous
Dismountable puck
The puck socket attached on a Cryocooler
Three Separate Systems
Thermal conductivity measured from 6 K to 300 K

A. L. Pope, B. M. Zawilski and Terry M. Tritt
Cryogenics, 41, 725 (2001)
High Temp Thermal Conductivity:

High Temperature DSC
Measure $C_p$ To 1500°C
Thermal Stability & Heat Capacity

NETZSCH LFA 457
Thermal Diffusivity ($d$)
Or Conductivity ($\kappa$)
Temp Range: RT to 1100°C

$$\kappa = d \rho_D C_V$$
\[ \kappa = d \rho_D C_V \]

\( \kappa \) = thermal conductivity  
\( d \) = thermal diffusivity  
\( \rho_D \) = density  
\( C_V \) = Heat Capacity
Temperature increase for various experimental conditions

\[ d = 0.1388 \left( \frac{L^2}{t_{1/2}} \right) \]

\( t_{1/2} = \) Rise half time
\( d = \) thermal diffusivity
\( L = \) sample thickness

assumes ideal conditions of adiabatic sample and instantaneous pulse heating

\[ \kappa = d \rho D C_V \]

High Temp DSC in conjunction with Laser Flash --- Shows Thermal Stability of Half Heusler Alloys to 900°C

UVA & Clemson Results

Total Thermal Conductivity (Wm⁻¹K⁻¹)

Temperature (K)

Sample: CG-5-111
(Hf₀.₇₅Zr₀.₂₅NiSn₀.₉₇₅Sb₀.₀₂₅)
Instrument: DSC 404 C
Sample Mass: 280.05 mg
Crucible: Pt+Al₂O₃-liner
Atmosphere: Argon


Derived Thermal Conductivity Half Heusler Alloys to 900°C
Ti$_{1-x-y}$Zr$_x$Hf$_y$Ni Sn$_{0.975}$Sb$_{0.025}$

Good Agreement From the Two Systems

Very Different Techniques

Two Carrier Heat Conduction
Acquisition of Commercial High Temperature R & α System

Commercial High Temperature R & α System

25°C to 800°C

Automated

Enhanced Through put

Less Down Time
ULVAC (ZEM-2)
Commercial high temp. R & S system

- Temp. range: -30 to 800°C
- Sample size: 2mm x 2mm x 7mm min.
- Both rod & bar samples can be mounted
- R & S data collected simultaneously
- Completely automated system
- Design allows rapid data collection

See also: V. Ponnalbalam et. al., Rev. Sci Instrum., 2006
R & S data of $\text{TiNiSn}_{0.99}\text{Sb}_{0.01}$ nano-composites

Data collected using both low temp. setup and ULVAC (ZEM-2) high temp. system
Data matched well at RT
**Elementary Error Propagation**

\[ Q = Q(a, b, c) \]

\[
\delta Q = \frac{\partial Q}{\partial a} \delta a + \frac{\partial Q}{\partial b} \delta b + \frac{\partial Q}{\partial c} \delta c
\]

\[
\frac{\delta Q}{Q} = \frac{\delta a}{a} + \frac{\delta b}{b} + \frac{\delta c}{c}
\]

\[
ZT = \frac{\alpha^2 \sigma_T}{\kappa} = \frac{\alpha^2 \sigma_T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho \kappa}
\]

\[
\frac{\delta ZT}{ZT} = 2 \frac{\delta \alpha}{\alpha} + \frac{\delta T}{T} + \frac{\delta \rho}{\rho} + \frac{\delta \kappa}{\kappa}
\]

\[
\kappa = K \frac{L_{TC}}{A}
\]

\[
\rho = R \frac{A}{L_v}
\]

\[
\frac{\delta \rho}{\rho} = \frac{\delta R}{R} + \frac{\delta w}{w} + \frac{\delta t}{t} + \frac{\delta L_v}{L_v}
\]
High Temp Measurements
\( d - (\kappa) \) by Laser Flash & DSC (\( C_p \))

\[ \kappa = d \rho_D C_V \]

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho \kappa} \]

Measure all on One Sample

Low Temp Measurements
\( K - (\kappa) \) by Steady State

\[ P = K \Delta T = I^2 R - P_{Loss} \]

\[ \kappa = K \frac{L_{TC}}{A} \]

\[ \rho = R \frac{A}{L_V} \]
High Temp Measurements 
\( d - (\kappa) \) by Laser Flash & DSC \((C_p)\)

\[ \kappa = d \rho_D C_v \]

Low Temp Measurements 
\( K - (\kappa) \) by Steady State

\[ P = K \Delta T = I^2 R - P_{Loss} \]

\[ ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 \sigma T}{\kappa_E + \kappa_L} = \frac{\alpha^2 T}{\rho \kappa} \]

\[ ZT = \frac{\alpha^2 T}{\rho \kappa} = \frac{\alpha^2 T}{R \left( \frac{A}{L_v} \right) K \left( \frac{L_{TC}}{A} \right)} \]

\[ \kappa = K \frac{L_{TC}}{A} \]

\[ \rho = R \frac{A}{L_v} \]

At best \( \approx 5-7\% \) uncertainly on ZT!

Same Sample -- A cancels
TE Nanomaterials Growth,
TE Nanocomposites &
Grain Boundary Engineering

Summary Slide Highlights

Expanded Version at End
Various TE Materials Research @ Clemson:

**Skutterudites:**
*Double-filled In$_x$Yb$_y$Co$_4$Sb$_{12}$ Skutterudites;* J. Peng et.al.
Jour. of Appl. Phys., **105**, 084907 (2009);

*La$_{0.9}$CoFe$_3$Sb$_{12}$-CoSb$_3$ Skutterudite Nanocomposites,* P. Alboni, et.al.

**Half Heusler Alloys:**
*(Zr,Hf)Co(Sb,Sn) half-Heusler phases as p-type thermoelectric materials*

*Boundary scattering on the thermal conductivity of TiNiSn-based HH alloys,*

**Oxide TE Mats:**
*In-plane thermal conductivity of Na$_x$Co$_2$O$_4$ single crystals*
Nanocomposites fabricated by Hydrothermal/solvothermal nano-planting/coating

- Nanoparticles are easy to form aggregates.
- In TE nanocomposites, inhomogeneity may debase the TE performance.

Mechanical mixing

Solvothermal nano-coating

Nanoparticle-clusters

Better homogenous distribution of Nanostructures

Relatively-homogeneous nanocomposite

Hot press
An alkali metal hydrothermal treatment technique

Bulk TE raw powder

Various alkali metal (Na, K) compounds solution

Hydrothermally treat

Remove powder, wash & dry

150°C for 36 hr

alkali metal hydrothermal treatment process, an admixture of 6 mmol NaOH (KOH), 2 mmol NaF (KF), 3 mmol NaBH₄ (KBH₄), 35 ml distilled water, and ~ 2.5 g Pb₀.₇₅Sn₀.₂₅Te bulk reference powder were loaded into a 45 ml Teflon-lined autoclave

Hot press

pellet

CLEMSON UNIVERSITY
Hydrothermal Treatment of Pb$_{0.75}$Sn$_{0.25}$Te


Hydrothermal Treat with NaOH

Observe 20-50 nm Clusters On Surface of Pb$_{0.75}$Sn$_{0.25}$Te Hot Pressed to T > 400°C (Te rich interface)
Hydrothermal Treatment of Pb$_{0.75}$Sn$_{0.25}$Te


Figure 5 (online colour at: www.pss-a.com) Resulting enhancement of thermoelectric figure of merit at 420 K. Thermal conductivity, power factor, and thermoelectric figures of merit $Z$ and $ZT$ of Na solution hydrothermally treated Pb$_{0.75}$Sn$_{0.25}$Te are normalized by the corresponding values of the bulk reference Pb$_{0.75}$Sn$_{0.25}$Te. The dash-dotted line shows where the bulk reference is. It is clear that the increases of $Z$ and $ZT$ are due to

Normalized Properties

Dashed Line -- Bulk reference

Enhancements in ZT Due to Reduction in $\kappa_L$!
Novel Nanostructures and High ZT in Melt Spun p-type Bi$_{0.52}$Sb$_{1.48}$Te$_3$

Collaboration with Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
W.Xie et.al, Applied Phys Letters, 94, 102111-09
Also Jour. Appl. Phys., 2009

Supported by China Scholarship Program,
973 Programs and China NSF
US Dept. of Energy EPSCoR
Novel Nanostructures in Melt Spun p-type $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$

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Wuhan Univ. of Tech:
Novel Nanostructures in Melt Spun $p$-type $\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$

Spark Plasma Sintering Conditions

300-400 °C
For several minutes
Force $\approx$ 3-5 KN

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
Novel Nanostructures in Melt Spun p-type Bi\textsubscript{0.52}Sb\textsubscript{1.48}Te\textsubscript{3}

Contact Surface

Free Surface

Amorphous Microstructure near Contact surface

5-15 nm Nanocrystalline Regions or grains near CS

Large dendritic regions near free surface

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
Spark Plasma Sintering System: 1500 Amps

Sample In Mold
TE Properties of Melt Spun p-type Bi$_{0.52}$Sb$_{1.48}$Te$_3$

But the MS-SPS Sample Exhibited lower $\kappa_L$ and thus Higher ZT ($\approx 1.5$) Than other samples

Collaboration w. Prof. X. Tang and student Wenjie Xie
Wuhan Univ. of Tech:
Low Temperature (T < 300K) Properties of MS-SPS -- Bi$_2$Te$_3$

Low Temperature (κ) by Steady State Technique
(see Cryogenics- Pope et.al 2000)
High Temp. Using (κ) Laser Flash and DSC
Concluding Remarks

- Increased Demands for Alternative Energy Systems
- Significant Progress in TE’s in Last 10 Years
- Thermoelectrics: (Shift to Waste Heat Recovery)
  Efficiency & Stability is a Materials Issue.
- Thermoelectric Materials Research:
  “Designer Materials” Approach
  Complex Structures & Transport Properties
  Challenges in Theory, Synthesis & Characterization
- Low Dimensional TE Materials - - High ZT
  Due primarily to reductions in lattice thermal conductivity
- Many Opportunities in Nanocomposites, “Grain Surface Engineering” or Nanoscaled Bulk TE Materials
  or Nanocomposites (Future-Spark Plasma Sintering)
- More Theoretical Modeling & Insight Needed

ZT ≈ 1.4
Acknowledgements:

Dept. of Energy: DOE EPSCoR Implementation Grant (DOE #: DE: FG02-04ER-46139)

SC EPSCoR & Clemson University

DARPA & ONR for Previous Support

Jeff Sharp, Marlow Inds.

Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/RXLMD)