Nanostructures
Thermoelectrics. The New paradigm

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Sponsored by the Department of Energy
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The nanostructure...

**Endotaxy**: lattice matched placement of one material inside another

Controlling nanostructuring

- New means of introducing nanostructures in bulk materials
  - Spinodal decomposition
  - Nucleation and growth
  - Liquid encapsulation
electronic band structure of PbTe

Valence band is multiple peaks

\[ a \approx 6.45 \text{ Å (300K)} \]

\[ m^*_\Sigma (\sim 2m_0) \gg m^*_L (\sim 0.2m_0) \]
Introducing strain into PbTe

- SrTe: rock salt structure Fm-3m
- $a = 6.660 \text{ Å}$
- PbTe: $a = 6.460 \text{ Å}$

Solubility of SrTe unknown

MgTe, CaTe, BaTe
Indexed based on PbTe structure (space group $Fm\overline{3}m$)
No SrTe or other phase observed

TGA up to 900 K under N$_2$ atmosphere: Samples are stable without weight loss
Electrical conductivity

\[ \sigma \approx T^{-\delta} \]

<table>
<thead>
<tr>
<th>% of SrTe</th>
<th>( T ) (300-800 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-2.8</td>
</tr>
<tr>
<td>1</td>
<td>-2.7</td>
</tr>
<tr>
<td>2</td>
<td>-2.4</td>
</tr>
</tbody>
</table>

Hall measurement

Two valance band: p-type PbTe

Light (h1) and heavy hole (h2)
Effective mass: \( m_{h2} = 1.5m_{h1} \)

\[ \mu = \frac{\sigma}{Ne} \]

\( \mu \), mobility
\( \sigma \), electrical conductivity
\( N \), Carrier concentration

\( N = \frac{1}{eR_H} \)
\( N \), carrier concentration
\( E \), is the electronic charge
\( R_H \) is the Hall coefficient

Assuming parabolic band and single band conduction

Seebeck coefficient and Power factor

\[ S = \frac{S_{h1}\sigma_{h1} + S_{h2}\sigma_{h2}}{\sigma} \]

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

\[ m_{h2} = 1.5m_{h1} \]

Valence bands of PbTe...

Rising temperature
**Thermal conductivity**

\[ k_{\text{total}} = k_{\text{lattice}} + k_{\text{electronic}} \]

\[ \kappa_e = L \cdot \sigma \cdot T \]

\[ L_o = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2} \]

All samples are ingots

Transmission electron microscopy (TEM)

PbTe matrix and SrTe nanocrystals have similar symmetry, structure and lattice parameters, and corresponding crystallographic planes and directions are completely aligned in 3-D.

Nanoparticle Density $\approx 1.5 \times 10^{12} / \text{cm}^2$

SrTe nanocrystals are endotaxially placed in the PbTe matrix

Nanocrystal density is greater in PbTe-SrTe(2%) than in PbTe-SrTe (1%)
Optimizing charge transport

Comparable mobilities

$\mu_{\text{pristine}} \sim \mu_{\text{nanostructure}}$

Pristine matrix

$K_{\text{pristine}} \gg K_{\text{nanostructure}}$

nanostructured

matrix

$E_g$

CB

VB

Eg

Band alignment
Figure of merit, $ZT$

- $\text{PbTe - SrTe (0.5 \%)}$
- $\text{PbTe - SrTe (1 \%)}$
- $\text{PbTe - SrTe (2 \%)}$
- $\text{p-type PbTe}$

All samples are ingots

CaTe in PbTe

MgTe $ZT \approx 1.6$
BaTe $ZT \approx 1.3$

![Graph showing ZT vs. T for different CaTe concentrations and MgTe, BaTe reference values.](graph.png)

*All samples are ingots*
Earth abundant materials: Recent exciting results: thermal conductivity reduction
thermal conductivity reduction below alloy limit

\[ K_l (\text{W/mK}) \]

**KD theory**

**Experimental data**

\[ x \]

**PbSe-PbS x\%**

Density of precipitates increases with increasing \( x \).
PbSe-x\% PbS : doped with 0.3\% of In

\( x = 0, 4, 8, \text{ and } 16 \)

- 0\% of PbS/0.3\% of In : \( 3.04 \times 10^{19} \) cm\(^{-3} \)
- 4\% of PbS/0.3\% of In : \( 3.68 \times 10^{19} \) cm\(^{-3} \)
- 8\% of PbS/0.3\% of In : \( 5.58 \times 10^{19} \) cm\(^{-3} \)
- 12\% of PbS/0.3\% of In : \( 4.67 \times 10^{19} \) cm\(^{-3} \)
- 8\% of PbS/0.3\% of Pb\(^*\) : \( 2.6 \times 10^{19} \) cm\(^{-3} \)
- 8\% of PbS/0.3\% of PbCl\(_2\)\(^*\) : \( 2.8 \times 10^{19} \) cm\(^{-3} \)
- 12\% of PbS/0.3\% of PbCl\(_2\)\(^*\) : \( 2.4 \times 10^{19} \) cm\(^{-3} \)
- 16\% of PbS/0.3\% of PbCl\(_2\)\(^*\) : \( 2.2 \times 10^{19} \) cm\(^{-3} \)
- 12\% of PbS/0.3\% of Bi\(^*\) : \( 3.2 \times 10^{19} \) cm\(^{-3} \)

PbSe-PbS system: high ZT at 900K

Dopant plays strong role in the resulting ZT.
Thermoelectric Properties of n-type PbS
Binary phase diagram of PbS-Bi$_2$S$_3$ (Sb$_2$S$_3$)
The solubility limit of PbCl$_2$ in PbS ranges between 1.0 and 2.0 mol %.

n-type PbS
n-type PbS with second phases

PbS with second phases without doping

Second phases: Bi$_2$S$_3$, Sb$_2$S$_3$
$\sigma$ (Scm$^{-1}$) vs Temperature (K)

$S(\mu V K^{-1})$ vs Temperature (K)

$PF$ (µWcm$^{-1}$K$^{-2}$) vs Temperature (K)

$\kappa_L$ (Wm$^{-1}$K$^{-1}$) vs Temperature (K)

$ZT$ vs Temperature (K)

n-type PbS with second phases

Seebeck independent on second phases

Significantly reduce

PbS with Sb$_2$S$_3$ $\sim$ 0.78 @ 723 K

$\sim$ 0.80 @ 723 K
TEM: nanostructured PbS

PbS+1.0 at. % Bi$_2$S$_3$+1.0 at. % PbCl$_2$

PbS + 1.0 at. % Sb$_2$S$_3$ + 1.0 at. % PbCl$_2$
Nanostructures n-type PbS, $ZT=1.1$

$ZT \sim 1.1 \text{ @ } 923 \text{ K}$

Good repeatability!

$ZT \sim 1.06 \text{ @ } 923 \text{ K}$

M: normal melting
B: Bridgman
S: SPS
BN coating
Panoscopic view of thermoelectrics

Hierarchical Length-scale Architecture:

Implications for “Nanostructured” Thermoelectrics

- Interactions along varied length-scales
- Identification of individual microstructure elements in electronic and phonon transport
- Tailoring and design of “microstructure”
Conclusions

• Strain at interfaces increases phonon scattering
• Small nanostructured (1-10 nm) are more likely to create strain
• Superior properties in p-type PbTe-SrTe achieved through endotaxial placement of nanoprecipitates
  – Nanostructures do not reduce the power factor and function exclusively as phonon scatterers
• Large power factor enhancements are need for continued ZT increases
• PbSe-PbS is nanostructured!
• PbSe-PbS n-type ZT~1.3 at 900K.
• High performance in PbS (ZT>1)