Improving the thermoelectric properties of Half Heusler compounds

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March 31th, 2011
Outlines

• Introduction of thermoelectrics and applications

• TE properties improvement via:
  • Seebeck coefficient
  • Thermal conductivity

• Bulk Half Heusler with nano-inclusions

• Nanostructured HH and Predictions
Seebeck Effect

- Temperature gradient deducing Voltage gradient or vice versa

\[ S = -\frac{\Delta V}{\Delta T} \]

- Thermal conductivity: \( \kappa \)

- Dimensionless figure of Merit:

\[ ZT = \frac{S^2T}{\rho \kappa} \]

- Efficiency- the higher ZT is, the closer the efficiency of TE circuit getting to Carnot Engine.

\[ \eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}} \]
Semiconductor is the best TE material

- $\alpha =$ Seebeck coefficient
- $\sigma =$ Electrical Conductivity
- $\lambda =$ Thermal Conductivity

- Power factor combined with thermal conductivity shows semiconductor is the best choice for TE materials

$$ZT = \frac{\alpha^2 \sigma T}{\lambda}$$
Thermoelectrics Applications

Waste Heat Recovery

Thermoelectric Generator

Thermoelectric Cooler
State of the Art TE materials (n-type)
State of the Art TE materials (p-type)
Half Heusler alloys

Ti and Sn atoms form a rock salt structure and Ni atoms fill half of the hollows at the center of Ti-Sn cubic.

Pros: Easy preparation, multiple doping options, non-toxic, high electrical conductivity
Cons: comparably high thermal conductivity

How can we improve the properties of Thermoelectric materials

\[ ZT = \frac{S^2 T}{\rho \kappa} = \frac{S^2}{L_e + \frac{\kappa_L \rho}{T}} \]

- \( L_e \) – electrical Lorentz number
- \( \kappa_L \) – Lattice thermal conductivity
- \( \rho \) – electrical resistivity

\( K_e = L * \sigma * T \)
resonant states

Mahan-Sofo Theory

Mott Expression

\[
S = \frac{\pi^2 k_B}{3} \frac{k_B T}{q} \left\{ \frac{d[\ln(\sigma(E))]}{dE} \right\}_{E=E_F} = \frac{\pi^2 k_B}{3} \frac{k_B T}{q} \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F}
\]

\[n(E) = g(E) \times f(E)\]

Band Structure Engineering

Doping iso-valent atoms with higher/lower electronegativity to resonate with corresponding conduction (n-type)/valence band edge of the majority component.

J.P. Heremans; V. Jovovic, E.S. Toberer, A. Saramat, K.Kurosaki, A.Charoenphakdee, S. Yamanaka, G.J. Snyder, Science, v321, July 2008
Energy Filtering

Carriers which have lower energy than $\varepsilon_b$ are greatly scattered

Calculated normalized seebeck distribution vs electron energy for heavily doped bulk n-type Si$_{80}$Ge$_{20}$ at RT. Low energy electrons contribute negatively to the Seebeck coefficient. This is also one of the motivation of our nano-inclusions bulk materials.

Thermal conductivity

The thermal conductivity $\kappa$ can be expressed as the sum of contributions from different sources:

$$\kappa_T = \kappa_C + \kappa_e + \kappa_p$$

- Photon contribution $\kappa_p$ is negligible.
- Electronic contribution $\kappa_e$ is exactly what we are working on.

**Wiedemann–Franz law**

$$\kappa_e = L \sigma T$$

where $L$ is the Lorentz number $L = 2.44 \times 10^{-8} \text{W} \Omega \text{K}^{-2}$.

Lattice contribution $\kappa_C$ is exactly what we are working on.
Lattice TC model

Callaway’s Lattice TC relaxation time

where:

Impurity scattering

Umklapp scattering

Boundary scattering

\[ \kappa_C = \frac{k_B}{2\pi^2 v} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{8/T} \tau_C(x, T) \frac{x^4 e^x}{(e^x - 1)^2} dx \]

\[ \tau_C^{-1} = \tau_I^{-1} + \tau_U^{-1} + \tau_B^{-1} \]

\[ x = \frac{\hbar \omega}{k_B T} \]

\[ \tau_I^{-1} = A \omega^4 \]

\[ \tau_U^{-1} = B \omega^2 T^3 \]

\[ \tau_B^{-1} = \frac{v}{L} \]

J. Callaway, Physics Review, v113, n4, 1959
This is TC of various silicide nanoparticles (0.8% volume fraction) into Si$_{50}$Ge$_{50}$ main matrix at T=300K:
1) TC decrease greatly even with small fraction of nanoinclusions.
2) It is not necessary to make accurate nanoparticle size control.

Mingo developed the grain boundary term to deal with bulk materials involving nanoparticles:

\[
\tau_{\text{np}}^{-1} = \nu(\sigma_s^{-1} + \sigma_l^{-1})^{-1} \rho
\]

\[
\sigma_s = 2\pi R^2
\]

\[
\sigma_l = \pi R^2 \left(\frac{(\Delta D)}{D}\right)^2 (\omega R^2 \nu)^4
\]

\[\rho\] is the volume density of the nano-inclusions.

Preparing bulk HH with nano-inclusions

2% ZrO₂ nanoparticles dispersed Hf_{0.3}Zr_{0.7}CoSn_{0.3}Sb_{0.7}
Seebeck

Electrical Resistivity

Thermal Conductivity

ZT

25%
X-Ray Pattern as proof of existence of ZrO2
**SEM and TEM in process....**

**SEM and EDS**

*SEM* is used to determine the gain size of the main matrix as well as existence of ZrO$_2$ nano-inclusions. 
*EDS* is used to determine HH compound’s uniform distribution as well as rough chemical composition.

**SEM**

Providing accurate proof for nano-inclusions existence as well as information of their grain size and position in main matrix
Higher nanoparticles dispersion level will further decrease TC
Nano-structure instead of nano-inclusions?

How about ball milling the main matrix over hours?

grinding the main matrix to nano-scale?

<table>
<thead>
<tr>
<th></th>
<th>Main matrix grains</th>
<th>Inclusion grains</th>
<th>Ball milling time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-inclusions</td>
<td>Micron scale</td>
<td>Nano scale</td>
<td>&lt;5 mins</td>
</tr>
<tr>
<td>Nano-structure</td>
<td>Nano scale</td>
<td>Nano scale</td>
<td>hours</td>
</tr>
</tbody>
</table>

Investigation in process.....

1) Prevent oxidization while ball milling

2) Prevent contamination from the vial itself
Further decreasing in thermal conductivity shows nano-structure bulk more promising than nano-inclusions bulk.
Further predictions..........

$k/k_h$ - Lattice TC of nano-structured Half Heusler alloy normalized to the reference regular bulk alloy

w - the size range of the particles
What ZT can we expect from this theoretical model?

\[
ZT = \frac{S^2 T}{\rho \kappa} = \frac{S^2}{L_e + \frac{\kappa L \rho}{T}}
\]

For N-type HH Hf\textsubscript{0.6}Zr\textsubscript{0.4}NiSn\textsubscript{0.995}Sb\textsubscript{0.005} at 900K

<table>
<thead>
<tr>
<th>Grain size</th>
<th>Lattice TC</th>
<th>ZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 to 100μm (bulk)</td>
<td>1.10</td>
<td>0.91</td>
</tr>
<tr>
<td>100 to 200 nm</td>
<td>0.99</td>
<td>0.93</td>
</tr>
<tr>
<td>20 to 60 nm</td>
<td>0.704</td>
<td>0.99</td>
</tr>
<tr>
<td>5 to 25 nm</td>
<td>0.418</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Acknowledgement

• Many thanks to Dr. Poon for his work on lattice TC prediction for nanostructured Half Heusler

• Appreciate the help of Thermal conductivity measurement and SPS from Clemson University

Thanks for your attendance!