Overview of Recent Progress in Half-Heusler Alloys for High Temperature Application

Han-Byul Kang, Myung-Eun Song, Wenjie Li and Shashank Priya
60% of energy loss occurred by waste heat

Utilize this huge loss by thermoelectrics

* From Lawrence Livermore National Laboratory and U.S. Department of Energy.
Background: TE Application

Thermoelectric Applications

*Thermoelectric generator (TEG) for automobile & NASA’s Mars Rover, Curiosity

- The 1.5 ZT thermoelectric efficiency would translate into 10% increase in the fuel economy of cars and trucks. (ZT=3.0, Increase 15% of fuel economy) – MIT Technology Review
Background: TEG

Thermal Energy → Seebeck Effect → Electrical Energy

Higher Efficiency

Mechanical Design
Conversion Efficiency (%)

Modeling & System Design

Material Development
Figure of Merit (ZT)

Nanostructuring, Band tuning & New composition
Background: TE Materials

Materials Development

- There are temperature peaks of ZT for each TE materials
- Maximizing material ZT over a broad temperature range
- Dividing temperature range into three parts
  → Developing three types of TE materials
  → Cascade Device

✓ Materials in Different Temp Region
  - Low Temp: Skutterudite
  - Intermediate Temp: PbTe
  - High Temp: Half-Heusler

**Background: Challenges**

- **Conflicting Parameters**
  
  \[ ZT = \alpha^2 \sigma T / \kappa \]

  \[ \alpha = 8\pi^2 k B^2 / 3 e h^2 \]

  \[ m^* T (\pi / 3 n)^{12/3} \]

  \[ \sigma = n e \mu \] (\( \approx 1 / m^* \))

  \[ \kappa = \kappa_{\perp e} + \kappa_{\perp l} \]

  \[ \kappa_{\perp e} = L\sigma T = n e \mu LT \]

- **Stability at High Temperature**

**Oxidation Problem**

*TE – Metal Electrodes*

→ Mech. & Thermal stable materials

→ Special protection coating
Half-Heusler Alloys

**XAB solids**

- **A,B site**: Transition or rare earth elements
  - **X site**: Main group element
- Three interpenetrating *face-centered cubic* sublattice structure
- Heusler with a vacancy in one of the two doubly degenerate sublattices
- Bandgap (0.1 eV ~ 3.7 eV)
  - 8 VEC per unit cell: ~3.7 eV (ex. LiMgP)
  - 18 VEC per unit cell: 0.1~1.1 eV (ex. MNiSn, M=Ti,Zr,Hf)
- **High power factor** ($\alpha^2\sigma$)
- **High Thermal conductivity** (6.7 - 20 Wm$^{-1}$K$^{-1}$)

> Good thermal and mechanical stability at high temperature

> All of position can be doped to change the electrical configuration
### The State of the Art

- **Reported Thermoelectric data in HH alloys**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Type</th>
<th>( ZT_{\text{max}} ) @( T ) (K)</th>
<th>( ZT_{\text{ave}} ) @( T_{\text{range}} ) (K)</th>
<th>( \kappa ) (W/mK) @( T ) (K)</th>
<th>Synthesis Technique</th>
<th>Main Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNb(<em>{0.88})Hf(</em>{0.12})Sb</td>
<td>p</td>
<td>1.5@1200</td>
<td>0.2-1.5 @300-1100</td>
<td>8-4.5 @300-1200</td>
<td>SPS</td>
<td>Heavier Hf doping</td>
</tr>
<tr>
<td>Zr(<em>{0.5})Hf(</em>{0.5})CoSb(<em>{0.8})Sn(</em>{0.2})</td>
<td>p</td>
<td>0.8@973</td>
<td>0.2-0.8 @300-973</td>
<td>3.5-3.4 @400-1073</td>
<td>HP</td>
<td>Nanostructuring</td>
</tr>
<tr>
<td>Ti(<em>{0.25})Hf(</em>{0.75})CoSb(<em>{0.85})Sn(</em>{0.15})</td>
<td>p</td>
<td>1.2@993</td>
<td>0.3-1.2 @400-993</td>
<td>4.2-2.9 @400-993</td>
<td>SPS</td>
<td>Fine doping &amp; Post Annealing</td>
</tr>
<tr>
<td>Zr(<em>{0.25})Hf(</em>{0.75})NiSn+2%FH</td>
<td>n</td>
<td>0.7@773</td>
<td>0.1-0.7 @323-773</td>
<td>4.0-3.3 @323-773</td>
<td>SPS</td>
<td>Nanoinclusion</td>
</tr>
<tr>
<td>Hf(<em>{0.75})Zr(</em>{0.25})NiSn(<em>{0.99})Sb(</em>{0.01})</td>
<td>n</td>
<td>1.0@873</td>
<td>0.25-1.0 @373-973</td>
<td>4.0-5.0 @373-973</td>
<td>HP</td>
<td>Nanostructuring</td>
</tr>
<tr>
<td>ZrNiSn(<em>{0.99})Sb(</em>{0.01})</td>
<td>n</td>
<td>0.8@875</td>
<td>0.1-0.9 @325-875</td>
<td>7.5-5.8 @325-875</td>
<td>SPS</td>
<td>Sb doping</td>
</tr>
<tr>
<td>Hf(<em>{0.6})Zr(</em>{0.4})NiSn(<em>{0.995})Sb(</em>{0.005})</td>
<td>n</td>
<td>1.2@873</td>
<td>0.1-1.2 @300-1173</td>
<td>5.4-2.2 @300-1173</td>
<td>SPS</td>
<td>Post Annealing</td>
</tr>
</tbody>
</table>
**Experimental Procedures**

- **RF inductive melting**
- **Arc melting**
- **Mechanical milling**
- **Spark Plasma Sintering**
- **Cutting & Shaping**

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- **Metal precursor (> 99.99%)**
- **HH Alloy Ingot**
- **HH Alloy Nanopowder**
- **HH Alloy Pellet/Sample**

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- **Single phase synthesis**
- **Size reduction**
- **Shaping disk/bar type**

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- **Dopant Engineering Nanoprecipitates**
- **Nanostructuring & Nanoinclusion**
- **Microstructure Nanostructuring Disorder controls**
Dopant/Band Engineering

✔ All three position can be doped in HH alloys

XAB

Band gap, Carrier concentration
Carrier mobility, Point defect

Fig. Carrier concentration (red squares), mobility (green circles), and absolute value of Seebeck coefficient (blue triangles) vs V at% in (Hf_{0.75}Zr_{0.25})_{1-x}V_xNiSn

Theoretical Evaluation

Based on theoretical modeling and simulation, promising compounds and optimized doping level can be predicted.

Electrical transport properties by Boltzmann equation & Band structure

Thermal conductivity by high-throughput computational prescreening

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{\text{anh}} (\text{Wm}^{-1}\text{K}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiBaK</td>
<td>1.24</td>
</tr>
<tr>
<td>CoHfSb</td>
<td>21.9</td>
</tr>
<tr>
<td>FeNbSb</td>
<td>29.1</td>
</tr>
<tr>
<td>CoNbSn</td>
<td>20.7</td>
</tr>
<tr>
<td>NiSnZr</td>
<td>17.5</td>
</tr>
</tbody>
</table>

Dopant/Band Engineering

- Disorder parameters - mass fluctuation scattering and strain field effect

- Larger mass and radius differences between host and doping atoms

- Point-defect scattering of phonons → Lower $\kappa_L$

- Heavy band structure could be an effective strategy.

Comparison of transport character of light- and heavy-band TE materials.

- Heavy-band materials (2 m_e - 10 m_e) have 2-3 times higher power factor than that of light-band PbTe.

Nanostructuring

- Reduce thermal conductivity by increasing phonon scattering

- Unit cell expansion $\rightarrow$ Orbital overlap ↓ $\rightarrow$ Narrowing of bands in the vicinity of $E_F$

  $\Rightarrow$ **Seebeck coefficient** $\alpha \uparrow$

- Small grain $\rightarrow$ Grain boundary scattering $\uparrow$

  $\Rightarrow$ **Thermal conductivity** $\kappa \downarrow$
Phonon Scattering

Calculation:

\[ \beta = \frac{1}{3} \frac{c \rho v l}{m_f} \]

\( \beta \): percentage of heat carried by phonons with a mean free path shorter than \( L_\beta \).

Phonon scattering on

- Grain boundary
- Precipitates

\( \kappa_{latt} \): phonon scattering coefficient.
Nanoinclusions

- Reduce thermal conductivity with remaining high mobility

Nanoinclusion in matrix act as **scattering center**

- Phonon scattering : $\kappa_{\text{lattice}}$ decrease $\rightarrow$ $ZT\uparrow$
- Carrier charge : mobility drop $\rightarrow$ $ZT\downarrow$

**Compensated effect for ZT**

**Coherent phase boundary**

- Low energy electron filtering $\rightarrow$ mobility $\uparrow$
- Same structure, similar lattice constant

(ex. HH-FH nanoinclusion, HH-SiC nanoinclusion)

Coherent Nanoinclusions

Incoherent Nanoinclusion
Disturb the carrier transports

Coherent Nanoinclusion
Maintain high mobility of carriers

Similar lattice constant, Same crystal structure, Electrical properties
Candidates for coherent nanoinclusions in HH alloys

Structure: Face-centered cubic (Space group: F43m)

Lattice parameter:
- \( a_{\text{ZrNiSn}} = 0.6113 \) nm, \( a_{\text{HfNiSn}} = 0.6083 \) nm
- \( a_{\text{ZrCoSb}} = 0.6069 \) nm, \( a_{\text{HfCoSb}} = 0.6039 \) nm

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{InSb}<em>{0.33}\text{Te}</em>{0.67} )</td>
<td>0.6122</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Ti}_2\text{CoGa} )</td>
<td>0.6120</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Ni}_2\text{CrIn} )</td>
<td>0.6100</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{AlSb} )</td>
<td>0.6090</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Zr}<em>{1.14}\text{Co}</em>{0.86}\text{Sb} )</td>
<td>0.6066</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Sc}<em>{0.5}\text{Nb}</em>{0.5}\text{NiSn} )</td>
<td>0.6042</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{TiSn} )</td>
<td>0.6030</td>
<td>F43m</td>
</tr>
<tr>
<td>( \text{Fe}_2\text{TiIn} )</td>
<td>0.6020</td>
<td>F43m</td>
</tr>
</tbody>
</table>
Antisite Disorder Control

Perfectly ordered  Antisite disorder

✓ HH phases are prone to antisite disorder

- Post annealing process → Structural ordering
  - Reduce lattice strain
  - Mobility increase with decreasing carrier concentration
  - Influence the PF and $zT$

Antisite Disorder Control

✓ zT improvement from antisite disorder control by applying post annealing near to melting point

The thermoelectric energy harvesting has been gaining interest as a promising mechanism for power generation from waste heat.

Half-Heusler Alloy is one of the promising materials for high temperature application due to its excellent electrical properties and thermal/mechanical stability at high temperature.

Thermoelectric properties are sensitive to the doping process that can change the band structure, charge carrier configuration, and point defect.

Nano engineering has a key role in reducing thermal conductivity.

Post annealing process is beneficial to control antisite disorder of alloys.
Thank you for your attention
Question?
Background: Thermoelectric Effect

✔ Seebeck Effect

- The conversion of heat directly into electricity by temperature difference
- Temp. gradient → Electrical current

✔ Thermoelectric Generator

- \( p-n \) thermoelectric materials coupling
- Electrically series, thermally parallel

Seebeck Effect, \( V = \alpha \Delta T \)

\[ \text{Charge carrier diffusion} \]

\[ E \]

Nature 508, 327-328 (2014)
**ZrNiSn Compound (n-Type)**

- \((\text{Zr}_{0.4}\text{Hf}_{0.6})\text{NiSb}_{0.95}\text{Sn}_{0.05}\) alloy was successfully synthesized by RF induction heating.
- Tungsten crucible with graphite cover.
- Optimized melting time: 5 min (3 times).
- Complete cooling under Ar protection to prevent secondary phase forming.

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**Graph:**

- **2θ (degree):** 20, 30, 40, 50, 60, 70, 80
- **Intensity (a.u.):**
  - (111)
  - (200)
  - (311)
  - (222)
  - (400)
  - (331)
  - (420)
  - (422)

**ZrNiSn Ingot:**

10% weight loss during pulverization process (Product: 10~12g/1cycle).
• Taking same condition with ZrNiSn alloy (5 min melting time)
• \((\text{Zr}_{0.5}\text{Hf}_{0.5})\text{CoSb}_{0.8}\text{Sn}_{0.2}\) alloy was successfully synthesized by RF induction heating
• Both of n-type and p-type HH alloy was reproduced without secondary phase
Grinding Test w/o Liquid

- Size Reduction by Increasing Milling Time

- No ground (Sieving by 250 μm)

- Crystal Size by X-ray line broadening
  - Significant particle size reduction (SEM)
  - Particle agglomeration
  - Saturated with increasing operation time (X-ray line broadening)
Grinding with Liquid Agent

- Secondary phase formation was efficiently suppressed by adding liquid agents in grinding process
- Amount of liquid affects to size reduction (Large volume $\rightarrow$ inefficient grinding)
  - Optimized volume : 2-3 ml/10 g powders
Grinding with Liquid Agent

- Microstructure and Crystal size by X-ray line broadening

- By increasing grinding time, crystal size is successfully decreased to 20 nm
- Size reduction is lower than w/o liquid agent sample
Spark Plasma Sintering

- **SPS Samples**

  - **Sample Type:** $\text{Hf}_{0.6}\text{Zr}_{0.4}\text{NiSn}_{0.95}\text{Sb}_{0.05}$ (n-type)
    
    $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ (p-type)

  - Ground 1 hr
  - Temperature: $1050^\circ \text{C}$
  - Pressure: 60 MPa
  - Time: 15 min

- **Relative density and microstructures of SPS sample**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp($^\circ \text{C}$)</th>
<th>Relative Density(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Hf}<em>{0.6}\text{Zr}</em>{0.4}\text{NiSn}<em>{0.95}\text{Sb}</em>{0.05}$ (n-type)</td>
<td>1050</td>
<td>97.26</td>
</tr>
<tr>
<td>$\text{Hf}<em>{0.5}\text{Zr}</em>{0.5}\text{CoSb}<em>{0.8}\text{Sn}</em>{0.2}$ (p-type)</td>
<td>1050</td>
<td>97.02</td>
</tr>
</tbody>
</table>

* Measured by Archimedes principle method
TE Properties (n-type HH)

**Seebeck coefficient (µV/K)**

- Reported Seebeck ~200 µV/K

**Resistivity (mΩ cm)**

**Thermal Conductivity (W/mK)**

- Reported thermal conductivity 4~5 W/mK

**ZT**

- Reported ZT ~ 1.0 (600°C)
TE Properties (p-type HH)

- **Seebeck coefficient** (µV/K)
  - Temperature (K) vs. Seebeck coefficient (µV/K)
  - Graph shows an increase in Seebeck coefficient with temperature.
  - Reported ZT ~ 0.8 (700°C)

- **Resistivity** (mΩ·cm)
  - Temperature (K) vs. Resistivity (mΩ·cm)
  - Resistivity increases with temperature.

- **Thermal Conductivity** (W/mK)
  - Temperature (K) vs. Thermal Conductivity (W/mK)
  - Conductivity shows a slight increase with temperature.

- **ZT**
  - Temperature (K) vs. ZT
  - ZT value is reported as 0.42.
• **Secondary phase** was observed in SPS samples

• These phase can act as the scattering centers in TE matrix

  → *Increasing thermal conductivity by scattering*