Enhancing the Figure-of-Merit in Half-Heuslers for Vehicle Waste Heat Recovery

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Outline

• Why Half-Heuslers for auto waste heat recovery?
• Status of Half-Heuslers before our work
• The effect of nanostructures on thermoelectric figure-of-merit
• The effect of larger differences in atomic mass and size on thermal conductivity and thermoelectric figure-of-merit

• Bonus: New promising materials with good ZT
## Why Half-Heuslers?

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bi$_2$Te$_3$</th>
<th>PbTe/PbSe</th>
<th>Skutterudites</th>
<th>Half-Heusler</th>
<th>SiGe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Working</strong></td>
<td>-100-200 °C</td>
<td>100-500 °C</td>
<td>100-500 °C</td>
<td>100-700 °C</td>
<td>100-1000 °C</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td><strong>Peak ZT</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>1.1</td>
<td>1.3</td>
<td>1.7</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>P</td>
<td>1.4</td>
<td>1.8</td>
<td>1.0</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Supply</strong></td>
<td>Te</td>
<td>Te</td>
<td>Rare-earth</td>
<td></td>
<td>Ge</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>moderate</td>
<td>moderate</td>
<td>low</td>
<td>moderate</td>
<td>high</td>
</tr>
<tr>
<td><strong>Toxicity</strong></td>
<td>low</td>
<td>high</td>
<td>low</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td><strong>Mechanical Strength</strong></td>
<td>moderate</td>
<td>poor</td>
<td>moderate</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Thermal Stability</strong></td>
<td>moderate</td>
<td>poor</td>
<td>poor</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td><strong>Contact</strong></td>
<td>easy</td>
<td>done</td>
<td>being studied</td>
<td>easy</td>
<td>done</td>
</tr>
</tbody>
</table>
Status of Half-Heuslers

N type, $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.975}\text{Sb}_{0.025}$

P type, $\text{Zr}_{0.5}\text{Hf}_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$

- Thermal conductivity too high!
- Nanocomposite approach: reduce thermal conductivity


Phonon Engineering nanostructure in n-type half-Heusler


Hf$_{0.75}$Zr$_{0.25}$NiSn$_{0.99}$Sb$_{0.01}$

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![Diagram of electrical conductivity vs. temperature](image1)

![Diagram of Seebeck coefficient vs. temperature](image2)

![Diagram of power factor vs. temperature](image3)

![Diagram of thermal conductivity vs. temperature](image4)

![TEM image](image5)

Scale bar: 200 nm
**Specific heat and thermal diffusivity**

\( \text{Hf}_{0.75}\text{Zr}_{0.25}\text{NiSn}_{0.99}\text{Sb}_{0.01} \)

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**Diagram a:** Specific heat capacity vs. temperature

**Diagram b:** Thermal diffusivity vs. temperature
ZT Improvement due to Lower Thermal Conductivity by Nanostructures in n-type


Hf$_{0.75}$Zr$_{0.25}$NiSn$_{0.99}$Sb$_{0.01}$

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Effect of Nanostructures on p-type
By comparison with the data on ingot samples previously reported, we found that the resistivity of our ingot sample is almost the same as the reported value, and the Seebeck coefficient is higher, which leads to a higher power factor. However, the thermal conductivity of our ingot sample is proportionally higher than the reported value, which leads to the same ZT of our ingot samples as the reported value. These small differences in individual properties may be due to some minor differences on sample preparation procedures, which is very reasonable and understandable.

Figure 3. Temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) lattice part of thermal conductivity, and (f) ZT of ball-milled and hot-pressed sample in comparison with that of the ingot.

Figure 4. Temperature-dependent specific heat (a) and thermal diffusivity (b) of ball-milled and hot-pressed sample in comparison with that of the ingot.

Specific heat and thermal diffusivity

Lattice thermal conductivity and nanostructures

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Improved ZT by Nanostructures in p-type Half-Heuslers


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Phonon Engineering larger differences in mass and size in half-Heuslers

Shiomi, Esfarjani, Chen, Phys. Rev. B 84, 104302 (2011)

Green Kubo Calculation (300 K)

$k (\text{Wm}^{-1}\text{K}^{-1})$

$Hf_xZr_{1-x}\text{CoSb}$
$Hf_{1-x}Ti_x\text{CoSb}$
$Zr_xTi_{1-x}\text{CoSb}$

Experiment
$Hf_{0.5}Zr_{0.5}\text{CoSb}_{0.8}\text{Sn}_{0.2}$
(Yan, Nano Lett, 2011)
How to Further Cut the Cost?

Need to reduce the usage of Hf as much as possible.

Source: U.S. Geological Survey

Need to reduce the usage of Hf as much as possible.
Summary for Half-Heuslers

![Graphs showing ZT vs Temperature for N-type and P-type materials.](image-url)
A New Potentially Interesting TE Material: Cu$_2$Se

Copper ion liquid-like thermoelectrics

Huili Liu$^{1,2}$, Xun Shi$^{1,3,\ast}$, Fangfang Xu$^3$, Linlin Zhang$^3$, Wenqing Zhang$^3$, Lidong Chen$^{1\ast}$, Qiang Li$^4$, Ctirad Uher$^5$, Tristan Day$^6$ and G. Jeffrey Snyder$^6$

NATURE MATERIALS DOI: 10.1038/NMAT3273

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Thermoelectric properties of copper selenide with ordered selenium layer and disordered copper layer

Bo Yu, Weishu Liu, Shuo Chen, Hui Wang, Hengzhi Wang, Gang Chen, Zhifeng Ren

Effect of pressing temp. on structure of Cu$_2$Se

Structure change observed by TEM


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Thermoelectric properties of Cu$_2$Se


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Temperature dependent thermoelectric properties of Cu$_2$Se bulk samples prepared with different hot pressing temperatures (400–700°C). (e) Total thermal conductivity (filled symbols) and lattice thermal conductivity (open symbols). (f) Figure-of-merit, ZT, as a function of temperature for Cu$_2$Se bulk samples.

Overall, ZT$_{avg}$, which is the average of ZT at 300–800°C, is around 0.5 W m$^{-1}$ K$^{-1}$ for all samples. As for ZT$_{max}$, which is the highest ZT value at around 140°C, the Cu$_2$Se sample shows not only the highest ZT$_{max}$ but also the highest ZT$_{max}$ value from the initial compositions (Figure 4). For all these samples, we also studied the composition effect on the thermoelectric properties. Copper selenide, Cu$_2$Se, is an interesting material for thermoelectric applications due to its high carrier concentration, but also the highest phonon thermal conductivity. Figure 4(d) shows the data of specific heat, Cp, for all the samples. The Cu$_2$Se$_{1.02}$ sample shows not only the highest phonon thermal conductivity, but also the highest phonon thermal conductivity at high temperatures according to Dulong–Petit law or slight increase with temperature due to the thermal expansion of the materials. On the other hand, the Zn$_4$Sb$_3$ sample shows the lowest phonon thermal conductivity, but also the lowest phonon thermal conductivity at high temperatures due to the thermal expansion of the materials.
Summary for Cu$_2$Se

• Good ZT may happen in non traditional thermoelectric materials

• Structure with ordered layer for charger carrier and disordered layer for phonon scattering is probably a good way to get high ZT

• Search of ZT higher than 2 should be in a lot of exotic materials
Acknowledgment

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• Prof. Gang Chen at MIT

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