Evaluation of Thermal to Electrical Energy Conversion of High Temperature Skutterudite-Based Thermoelectric Modules

James R. Salvador and Gregory P. Meisner
Chemical Sciences and Materials Systems Laboratory
General Motors Global Research and Development
Warren, MI

Jan König
Fraunhofer Institute for Thermoelectrics and Integrated Sensor Systems
Freiburg Germany

Joshua Moczygemba and Jeffrey Sharp
Marlow Industries
Dallas Texas
Acknowledgements

U.S. Department of Energy Grant # DE-FC26-04NT 42278
John Fairbanks (DOE), Carl Maronde (NETL)

U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies, as part of the Propulsion Materials Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC

GM R&D Thermoelectrics Team:

- Researchers:
  - Gregory P. Meisner
  - Jihui Yang
  - Mike Reynolds

- Postdocs:
  - Jung Cho
  - Zuxin Ye

- Engineering Operations:
  - Kevin Rober
  - John Manole

- Gov. Contracts:
  - Ed Gundlach
  - Amanda Demitrish
  - Rick Leach

- Management:
  - Jan Herbst
  - Mark Verbrugge

- GMPT Integration & Testing:
  - Jennifer Stanik
  - Joshua Cowgill

Collaborators/Subcontractors:

- Marlow Industries: Jeff Sharp, Jim Bierschenk, Josh Moczygemba, and Alan Thompson
- Oak Ridge National Laboratory: Hsin Wang, Andy Wereszczak
- University of Nevada,
- Future Tech: Francis Stabler
- Heat Technology, Inc
- Emcon (Faurecia)
- Shanghai Institute of Ceramics:
- University of Michigan:
- University of South Florida:
- Brookhaven National Laboratory:
- Michigan State University:
- General Electric Global Research:

Acknowledgements

University of Michigan: Francis Stabler, Rick Leach, John Manole, Jan Herbst, Mark Verbrugge.

University of South Florida: Hsin Wang, Andy Wereszczak, Jeff Sharp, Jim Bierschenk, Josh Moczygemba, Alan Thompson.

Shanghai Institute of Ceramics: Ed Gundlach, Amanda Demitrish.


Brookhaven National Laboratory: Michigan State University: General Electric Global Research.
Transitioning Lab Scale to Large Scale: Challenges

In the last two decades numerous University labs have demonstrated significant improvements in $ZT$, nearly doubling the value.

Despite this progress no new materials have transitioned to new products such as high temperature modules or power generation devices.
Transitioning Lab Scale to Large Scale: Challenges

ZT is only part of the story: Raw material cost and availability as well as mechanical strength and chemical stability need consideration.

For perspective in 2008, (mainly due to refining shortages) 1 kg of solar grade polycrystalline silicon $450.00. ²
Preparation of Skutterudites

Co(and Fe) and Sb shot were pre-melted by induction at 1400 °C in a ratio of 1:3 in BN crucible. Filler species and melt combined in BN crucible. Induction melted at 1200 °C 5 min. Followed by annealing at 700 °C for 1 week. Annealed pellets were reground, sieved and consolidated by SPS. Typical grain size ~3 μm. Resulting melt was ground, cold pressed and annealed for an additional week.

Compositions Targeted
N-type Yb_{0.05}Ba_{0.08}La_{0.05}Co_{4}Sb_{12}
P-type Mm_{0.28}Fe_{1.52}Co_{2.48}Sb_{12}

Ingot 98.5% or higher of theoretical density.
3.0 kg of n- and p-type Skutterudites Prepared

P-type material was grossly inhomogeneous

Refinement of skutterudite preparation will be required going forward.

N-type material was homogenous but contained significant amounts of Yb-oxide. It does not seem to affect transport. Its just wasteful.

3.0 cm puck

Significant difficulty in powder processing

Vacated Vein Post 473C Heat Treat, 67 hours
# Scaled up Synthesis and Skutterudite Module Fabrication

<table>
<thead>
<tr>
<th>Lot #</th>
<th>N-type</th>
<th>κ (W/m·K)</th>
<th>ρ (mΩ·cm)</th>
<th>S (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>0.45</td>
<td>-115</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>0.45</td>
<td>-112</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>0.40</td>
<td>-111</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3.5</td>
<td>0.35</td>
<td>-110</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.8</td>
<td>0.3</td>
<td>-100</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.8</td>
<td>0.33</td>
<td>-100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lot #</th>
<th>P-type</th>
<th>κ (W/m·K)</th>
<th>ρ (mΩ·cm)</th>
<th>S (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.77</td>
<td>1.13</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.70</td>
<td>1.18</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.75</td>
<td>1.27</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Peak ZT $\approx 1.0$ to 1.2
## Temperature Independent Characteristic Strength

Results are for large scale (1.0 kg batches and 3.0 cm (80 g billets)).

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp (°C)</th>
<th># of Tests</th>
<th>Characteristic Strength* (MPa)</th>
<th>Weibull Modulus* (MPa)</th>
<th>Gaussian Ave. Strength  (MPa)</th>
<th>Gaussian Dev. (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(n-type)</strong></td>
<td>25</td>
<td>25</td>
<td>160</td>
<td>10.6</td>
<td>154</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>14</td>
<td>156</td>
<td>6.7</td>
<td>148</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>15</td>
<td>154</td>
<td>9.6</td>
<td>147</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>15</td>
<td>139</td>
<td>6.4</td>
<td>130</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>15</td>
<td>143</td>
<td>8.8</td>
<td>135</td>
<td>17</td>
</tr>
<tr>
<td><strong>(p-type)</strong></td>
<td>25</td>
<td>20</td>
<td>135</td>
<td>24.2</td>
<td>132</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>14</td>
<td>133</td>
<td>10.8</td>
<td>127</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>15</td>
<td>133</td>
<td>15.0</td>
<td>129</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>15</td>
<td>138</td>
<td>28.4</td>
<td>136</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>15</td>
<td>147</td>
<td>13.4</td>
<td>142</td>
<td>12</td>
</tr>
</tbody>
</table>

* Values in parenthesis = ± 95% confidence interval
### Scaled up Synthesis and Skutterudite Module Fabrication

<table>
<thead>
<tr>
<th>Module #</th>
<th>Module Impedance (Ω)</th>
<th>Module Impedance (Ω)</th>
<th>Module Impedance (Ω)</th>
<th>Module Impedance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lot #1</td>
<td>Lot #2</td>
<td>Lot #3</td>
<td>Lot #4</td>
</tr>
<tr>
<td>1</td>
<td>0.143</td>
<td>0.146</td>
<td>0.146</td>
<td>0.232</td>
</tr>
<tr>
<td>2</td>
<td>0.142</td>
<td>0.151</td>
<td>0.148</td>
<td>0.186</td>
</tr>
<tr>
<td>3</td>
<td>0.143</td>
<td>0.148</td>
<td>0.150</td>
<td>0.224</td>
</tr>
<tr>
<td>4</td>
<td>0.142</td>
<td>0.153</td>
<td>0.148</td>
<td>0.223</td>
</tr>
<tr>
<td>5</td>
<td>0.142</td>
<td>0.150</td>
<td>0.146</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.143</td>
<td>0.148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.143</td>
<td>0.147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.143</td>
<td>0.148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.145</td>
<td>0.147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>0.156</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>0.145</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Module Performance: Governing Equations

\[ V_{OC} = n \int_{T_c}^{T_h} S(T) p \, dT - n \int_{T_c}^{T_h} S(T) n \, dT \]

\[ I = \frac{V_{OC}}{(R_{int} + R_{Load})} \]

\[ P_{out} = V_{OC}^2 \frac{R_{Load}}{(R_{Load} + R_{Int})^2} \]

\[ Q_H = \kappa_n l_n \frac{dT}{dx} + \kappa_p l_p \frac{dT}{dx} + IT_H S - I^2 R \]

\[ Q_c = \kappa_n l_n \frac{dT}{dx} + \kappa_p l_p \frac{dT}{dx} + IT_C S + I^2 R \]

Efficiency = \( \frac{P_{out}}{Q_H} \)
Module Performance Evaluation

A temperature gradient is applied using a heater at the top of the module and a circulating cooling bath at the bottom. Specific temperatures are thereby maintained for the hot and cold sides of the module.

Thermography indicates that the module temperature gradient is not uniform.
**Module Performance Evaluation**

The measurement: A temperature gradient is applied across the module by the establishment of a steady state heat flow \( Q \).

The open circuit voltage is measured then current is allowed to flow and a load resistance is adjusted to trace a \( V \) and current curve.

The maximum electrical power output is determined by this scanning.

Grafoil was used as a thermal interface material on the hot and cold side between the hot source, cold sink and the ceramic module headers.
Based on the resistivities of the materials comprising the modules and their temperature dependencies, we can estimate the contact resistance to range from 26 to 40 \( \mu \Omega \cdot \text{cm}^2 \) for low temperature and high temp., respectively.

We estimate nearly 100\(^\circ\)C temperature drop between the measurement position and the predicted hot side temperature at the top of the thermal elements. Likely a smaller temperature gap exists at the cold side. Very high thermal contact resistance reduces efficiency.

\[
V_{OC} = n \int_{T_{c}}^{T_{n}} S(T)_{p} dT - n \int_{T_{c}}^{T_{n}} S(T)_{n} dT
\]

\[
R_{\text{Int}} = R_{\text{TE}} + R_{\text{CH}} + R_{\text{CH}}
\]

Module resistance varies weakly with temp. Good for load matching.
Measured Power Output at a Given $\Delta T$

Power output is stable over the 3 thermal cycles performed.

Heated hot side to 500 °C (773K), while performing measurements at 50°C increments.

Cooled hot side while performing measurements.

Finally heated hot side again to 500 °C in 50 °C increments.
Performance with Higher Cold Side Temperatures

As the ZT values increase with temperature the power output is improved for a given $\Delta T$ at a higher cold side temperature.

These measurements were performed on the same module after the lower cold side temperature measurements were run.
Power Output with Corrected $\Delta T$

We know from the $V_{OC}$ measurements that there is a significant discrepancy between the temperatures measured at the for the hot and cold side and actual temperature of the hot and cold side of the legs.

For the sake of making a conservative estimate we assume the temperature discrepancy is all at the hot side. Based on this assumption and the $V_{OC}$ equation adjusted $\Delta T$ can be calculated.
Estimates of Thermal Efficiency

The theoretical conversion efficiency for the materials only is given by:

\[ \eta = \left( \frac{T_H - T_C}{T_C} \right) \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H} \]

Taking the ZT values we have for the materials, and the largest \( \Delta T \) for the study (\( T_H = 773 K \) and \( T_C = 305 K \))

The average ZT for both materials in this temperature range is \( ZT = 0.47 \)

\( \eta = 8\% \) for the materials.

If we use Fourier’s law for the average thermal conductivities, cross sections and number of legs for the projected \( \Delta T(468 K) = 179 W \) of heat passes through the legs and 14 W of electricity is produced \( \sim 7.8\% \) conversion. Excellent agreement.

Similar analysis can be done for the apparent \( \Delta T \) and the measured \( P_{out} \), lower average ZT value of 0.4 \( \eta = 6.1\% \) from the above relation and 6.0\% obtained by Fourier’s law.

But much more power is being delivered to the module (how much is difficult to estimate)
Results of Initial Durability Studies

Skutterudite materials show good stability with thermal cycling and soak.

Increase in resistance in soak likely due to sublimation and oxidation of junctions.
Modules will Need Protection From the Environment

Results of several measurements performed in a poor vacuum atmosphere

Products of oxidation:
- N-type
- CoSb₂
- Sb
- SbO₂
- La₂CoO₄
- Sb₂O₃
- Ce₂O₂Sb
- BaYb₂O₃
- P-type
- FeSb₂O₄
- Sb₂O₃
- Skutterudite
- Ce₂O₂
- Sb
- CeO₂

Graphs showing integrated intensity and 2-theta values for various compounds.
Summary and Conclusions

- While not terribly flattering, the results shown here are likely representative of actual operating conditions, without significant improvement in thermal contact resistance.

- Skutterudite modules presented have demonstrated reasonable durability. Certainly superior to comparable test modules based on PbTe.

- Both skutterudite and PbTe materials are highly susceptible to oxidation and measures will need to be taken in order to protect them while in service. Significant challenge with hot side temperatures around 500°C.

- Significant improvement can be made by getting p-type materials to state of the art levels. (ZT=1 at 750 K) would improve $P_{out}$ to 12 to 13 W under the same operating conditions.

- Thermal efficiencies are difficult to estimate as at this point. Thermal contact resistance is not well characterized in the test cell.