On Thermoelectric Properties of P-Type Skutterudites

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Outline

- Automotive Waste Heat Recovery

- N-type skutterudites (PRL 95, 185503, 2005; PRL 102, 175508, 2009; JACS 131, 5560, 2009; JACS. 133, 7837, 2011)
  - Multiple Frequency Resonant Phonon Scattering
  - $\kappa_{\text{min}}$ at elevated temperatures
  - $ZT_{\text{max}} \approx 1.7$

- P-type Skutterudites
  - Lattice thermal Conductivity – filler phonon mode coherence, bipolar effect
  - Carrier transport – electron-phonon interaction
  - $5d$ transition metal based p-type

- Conclusion
Today’s ICE-based vehicles: < 20% of fuel energy is used for propulsion
> 60% of gasoline energy (waste heat) is not utilized
E-REV Operation Modes

- **Park Mode**
  - Engine off = Charge Depletion

- **Electric Vehicle Mode**
  - Engine off = Charge Depletion

- **Extended Range Mode**
  - Engine-generator on (off) = Charge Sustaining

- **Charge Mode**
  - Electric on-board charger for (electric) grid power

*State of Charge (SOC)*
Compelling Concept: Thermoelectric Augmented E-REV

- Li ion battery pack
- Engine & Generator
- TE Generator & Heat Exchanger
- Fuel tank and fuel delivery system
- Electric Motor
- Transmission
- Differential
- Clutch
- DC to DC converter
- Power inverter (DC/AC)

- Not for the initial EREV production vehicle
- May improve fuel eco. (efficiency)
- Simplified system design
**Skutterudites 101**

- CoAs$_3$-based minerals found in region of Skutterud, Norway
- Compounds with the same crystal structure are known as “skutterudites”

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Prospective TE power generation materials for automotive waste heat recovery

- Both the n- and p-type exist – optimal for TE module construction
- The materials are mechanically strong

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Excellent Thermoelectric & Thermomechanical Property

1. Nolas et al., APL 77, 1855 (2000)
2. Dyck et al., JAP 91, 3698 (2002)
Localized modes at frequencies sufficiently different from one another would scatter a broader range of heat carrying lattice phonons, hence, achieving even lower $\kappa_L$.

**Hypothesis - Double-filled Skutterudites for Additional $\kappa_L$ Reduction?**

Quasi-localized modes due to void filling

$$Z = \frac{S^2}{\kappa_T \rho} = \frac{S^2}{(\kappa_L + \kappa_e) \rho}$$
### Phonon Resonant Frequencies

TABLE II. Spring constant $k$ and resonance frequency $\omega_0$ in the [111] and [100] directions of $R_{0.125}\text{Co}_4\text{Sb}_{12}$, where $R$ = La, Ce, Eu, Yb, Ba, Sr, Na, and K.

<table>
<thead>
<tr>
<th>$R$</th>
<th>Mass ($10^{-26}$ Kg)</th>
<th>$k$ (N/m)</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$k$ (N/m)</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>23.07</td>
<td>36.10</td>
<td>66</td>
<td>37.42</td>
<td>68</td>
</tr>
<tr>
<td>Ce</td>
<td>23.27</td>
<td>23.72</td>
<td>54</td>
<td>25.18</td>
<td>55</td>
</tr>
<tr>
<td>Eu</td>
<td>25.34</td>
<td>30.16</td>
<td>58</td>
<td>31.37</td>
<td>59</td>
</tr>
<tr>
<td>Yb</td>
<td>28.74</td>
<td>18.04</td>
<td>42</td>
<td>18.88</td>
<td>43</td>
</tr>
<tr>
<td>Ba</td>
<td>22.81</td>
<td>69.60</td>
<td>93</td>
<td>70.85</td>
<td>94</td>
</tr>
<tr>
<td>Sr</td>
<td>14.55</td>
<td>41.62</td>
<td>90</td>
<td>42.56</td>
<td>91</td>
</tr>
<tr>
<td>Na</td>
<td>3.819</td>
<td>16.87</td>
<td>112</td>
<td>17.18</td>
<td>113</td>
</tr>
<tr>
<td>K</td>
<td>6.495</td>
<td>46.04</td>
<td>141</td>
<td>46.70</td>
<td>142</td>
</tr>
</tbody>
</table>

Phonon DOS Measurement – Inelastic Neutron Scattering

![Graph showing phonon DOS measurement for Yb0.2Co4Sb12-Co4Sb12 at 2.35A and 10K. The graph plots intensity (arb. units) against energy (meV) with peaks indicating phonon modes for Yb, Eu, Ba, and La.]
Lattice Thermal Conductivity Reduction without Power Factor Deterioration

1. X. Shi, et al, JACS 133, 7837 (2011)
Multiple-filled Skutterudites – Much Improved ZT values

$ZT_{ave} = 1.2$

2. X. Shi, et al, JACS 133, 7837 (2011)
ZT Mismatch – Device Challenge

1. X. Shi, et al, JACS 133, 7837 (2011)
2. R. Liu, et al., Intermetallics 19, 1747 (2011)
Lattice Thermal Conductivity

- **n-type**
- **p-type**

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

- **Graph a:** Graph showing \( \kappa_L \) vs. temperature for different compositions of materials.
- **Graph b:** Graph showing \( \kappa_L \) vs. temperature for different compositions of materials, highlighting the bipolar effect.

1. X. Shi, et al, JACS 133, 7837 (2011)
2. R. Liu, et al., Intermetallics 19, 1747 (2011)
3. Qiu et al., JAP 111, 023705 (2012)

- p-type has higher \( \kappa_L \), especially at high temperatures (bipolar effect)
Phonon DOS Measurement – Inelastic Neutron Scattering

Yb_{0.2}Co_4Sb_{12}
The incoherent rattler modes in the n-type result in lower $\kappa_L$. 

2. Shi et al., unpublished
Bipolar Effect

\[ \kappa_e = \kappa_n + \kappa_p + \frac{b}{(1 + b)^2} \left( \frac{E_g}{k_B T} + 4 \right)^2 \left( \frac{k_B T}{e} \right)^2 \sigma T \]

\[ b = \frac{\mu_n}{\mu_p} \]

- Significant when the mobilities of the two charge carriers are similar
- This has been observed in Bi\textsubscript{2}Te\textsubscript{3} and Si/Ge
- Electronic band structures need to be altered to mitigate the bipolar effect

Glassbrenner et al., Phys. Rev. 134, A1058 (1964)
Electrical Transport Comparison

n-type \( \leq 1 \times 10^{21} \text{ cm}^{-3} \)

p-type \( 2-3 \times 10^{21} \text{ cm}^{-3} \)

1. X. Shi, et al, JACS 133, 7837 (2011)
2. R. Liu, et al., Intermetallics 19, 1747 (2011)

The electrical resistivity of the p-type is about a factor of two too high
Electron-Phonon Interaction

\[
\frac{1}{\tau} = \frac{\sqrt{2} \varepsilon_c^2 \left( m_p^* \right)^{3/2} k_B T \pi \hbar \rho c_l^2}{\varepsilon_1 E^{1/2}} \propto N(E)
\]

- For skutterudites, electron phonon interaction dominates charge carrier scattering at elevated temperatures
- The strength of e-ph interaction is proportional to the carrier density of states
5d Transition Metal-based P-Type Skutterudites

5d transition metal-based p-type skutterudites offers potential of reducing $\rho$, and hence power factor enhancement.
Conclusions

- Skutterudites are leading material candidates for automotive exhaust waste heat recovery
- Multiple frequency resonant phonon scattering lead to very high ZT for the n-type
- High values of $\kappa_L$ in the p-type arise from the coherent low energy phonon mode and the bipolar effect – ongoing topic
- Power factor in the p-type can be improved by 5-d transition metal substitution
- Current challenges with the p-type lie in their electron band structures
Thank You!