Solid Solutions Formation: Improving the Thermoelectric Properties of Skutterudites

A. Borsheevsk, J. Caillat, J.-F. Fleuriel
Jet Propulsion Laboratory/California Institute of Technology
4800 Oak Grove Drive, MS 217-207, Pasadena, CA 91109

Materials with skutterudite structure have been known for a long time. Some of them are semiconductors. Typical skutterudite is CoSb₃ and its thermoelectric properties were partially studied in the 1960’s. Recently, it has been discovered that many skutterudite compounds are thermoelectrics with promising future. To make these materials more technically attractive for energy conversion purposes, their thermal conductivity should be decreased. Solid solutions formation is a well-known way to reduce the thermal conductivity. Formation of solid solutions with skutterudite structure will be described. It will be shown that a substantial decrease of thermal conductivity can be achieved in some cases.
Solid Solutions Formation: Improving the Thermoelectric Properties of Skutterudies

A. Borshchevsky, T. Cahat, J.-P. Fleurial-
Jet Propulsion Laboratory/California Institute of Technology
Pasadena, California
USA
• Skutterudite chemical compounds are known as attractive thermoelectric materials
• Room temperature thermal conductivity of skutterudites is ~10 Wm⁻¹K⁻¹ (80% lattice contribution)
• To achieve maximum ZT values the lattice thermal conductivity needs to be lowered
• Solid solution formation is a well known way to lower lattice thermal conductivity
Skutterudite Quasibinary Systems

- With full range of solid solutions:
  
  \[
  \begin{align*}
  \text{CoP}_3-\text{CoAs}_3^* & \quad \text{IrSb}_3-\text{RuSb}_2\text{Te} \\
  \text{RhSb}_3-\text{IrSb}_3 & \quad \text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3-\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3
  \end{align*}
  \]

- With partial range of solid solubility:

  \[
  \begin{align*}
  \text{CoAs}_3-\text{CoSb}_3^* & \quad \text{IrAs}_3-\text{IrSb}_2 \\
  \text{CoAs}_3-\text{IrAs}_3 & \quad \text{IrSb}_3-\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3 \\
  \text{CoSb}_3-\text{IrSb}_3 & \quad \text{CoSb}_3-\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3 \\
  \text{CoSb}_3-\text{Fe}_{0.5}\text{Ni}_{0.5}\text{Sb}_3 & \quad \text{IrSb}_3-\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3 \\
  \text{CoSb}_3-\text{FeSb}_2\text{Te} & \quad \text{FeSb}_2\text{Te}-\text{RuSb}_2\text{Te} \\
  \text{IrSb}_3-\text{RuSb}_2\text{Te} & 
  \end{align*}
  \]

*literature data
range of solid solutions
Lattice thermal conductivity values for some skutterudite alloys

\[ 10^{-3} \text{ W cm}^{-1}\text{K}^{-1} \]

<table>
<thead>
<tr>
<th>Skutterudite Alloys</th>
<th>Alloy</th>
<th>1st member</th>
<th>2nd member</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSb(<em>{2}) (_0.3) (FeSb(</em>{2})) (_0.7)</td>
<td>45</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (FeSb(<em>{2})) (</em>{0.2})</td>
<td>22</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (GeSb(<em>{2})) (</em>{0.2})</td>
<td>29</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (CoSb(<em>2)) (</em>{0.2})</td>
<td>37</td>
<td>134-150</td>
<td>100</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (CoSb(<em>2)) (</em>{0.2})</td>
<td>25</td>
<td>100</td>
<td>134-150</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (MnSb(<em>2)) (</em>{0.2})</td>
<td>31</td>
<td>100</td>
<td>134-150</td>
</tr>
<tr>
<td>(CoSb(<em>2)) (</em>{0.8}) (FeSb(_2)Se(<em>2)) (</em>{0.2})</td>
<td>35</td>
<td>100</td>
<td>~30</td>
</tr>
<tr>
<td>(IrSb(<em>2)) (</em>{0.8}) (RuSb(<em>2)) (</em>{0.2})</td>
<td>42</td>
<td>100</td>
<td>32</td>
</tr>
<tr>
<td>(Ru(<em>{0.5})Pd(</em>{0.5})Sb(<em>3)) (</em>{0.5}) (FeSb(<em>{2})) (</em>{0.5})</td>
<td>24</td>
<td>14</td>
<td>~30</td>
</tr>
</tbody>
</table>
Effect of Alloy Scattering on the Room Temperature Thermal Conductivity of CoSb₃
Skutterudite Group of Minerals

All are solid solutions

(Compositions are idealized)
Conclusions

- There exist many solid solutions in skutterudite family of compounds
- 3 quasibinary systems have been studied at JPL: 4 with full range of solubility and 9 with partial range of solubility
- Significant reduction in thermal conductivity of compounds has been achieved by solid solution formation
- Theoretical calculation of thermal conductivity for different systems of skutterudite solid solutions, at room temperature, has been performed and the lowest possible thermal conductivity value of about $8 \times 10^{-3}$ Wcm$^{-1}$K$^{-1}$ was predicted for CoSb$_3$-IrP$_3$ system
- Much more solid solutions within skutterudite group of materials are available for their thermoelectric properties evaluation