Filled Nd$_z$Fe$_x$Co$_{4-x}$Sb$_{12-y}$Ge$_y$ skutterudites: processing and thermoelectric properties

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System Background

- Skutterudites are based on CoAs$_3$ mineral; first mined in Skutterud, Norway.
- Exhibit a high figure of merit for n-type systems (ZT=1.7).
- Relatively low cost system.
- Introduce a range of fillers (A) to scatter various phonon wavelengths.
- Introduce disorder on pnictogen ring sites (X).
  - Dominate heat carrying modes are associated with pnictogen vibration.
- Tune electronic properties (A,B,X) for optimal thermoelectric power factor.

Crystal Structure

Body-centered cubic space group *Im-3*

\[ A_\delta B_4 X_{12} \]

Skutterudite System Investigated

- Nd filled, Ge doped $\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12}$ skutterudite, $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$.
- Zhang et al. has previously investigated $\text{Nd}_{0.6}\text{Fe}_2\text{Co}_2\text{Sb}_{12-y}\text{Ge}_y$ system.
  - Reported peak p-type ZT 1.1 for $y=0.15$.
  - Reported formation of a nano-structured precipitate, reported to lower thermal conductivity and cause high ZT.
- Interested to expand the parameter space of Zhang’s work.
  - Nd level $z = \{0 - 0.8\}$
  - Fe level $x = \{1,2,3\}$
  - Ge level $y = \{0,0.15\}$


Objectives

- Focus on finding a p-type skutterudite with improved ZT.
- Study thermoelectric behavior of the skutterudite $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$.
- Study processing conditions.
- Study effect of composition on properties.
- Samples created from a melt/mill/hot press procedure.

Pellet

Filled $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ Skutterudites
Processing Conditions

- Ingots were fabricated by solidification.
  - 1100°C for 1 hour
  - 10°C/min cooling rate
  - Ingot dimensions 1” diameter, 2” height
  - He atmosphere
  - Carbon crucibles
- Ingots crushed in mortar and pestle then milled.
  - Planetary ball mill
  - WC milling jar and media
  - 500 rpm for 3-6 hours
- Powder was consolidated in a hot press.
  - 520-575°C with 62 MPa for ½ hour
  - 1.5°C/min cooling rate
  - ½” graphite die, lined with grafoil
- All compositions were processed with identical conditions.
**X-Ray Diffraction**

- Powder XRD of crushed pellets was evaluated with Rietveld refinement.
- Main phase is SKD structure, secondary phases include FeSb$_2$ and Sb.
- SKD phase purity decreases significantly for Nd<0.5 and Fe>2, no major impact from Ge.
- Filler occupancy increases with Nd level from 0 to 0.6 then levels off with maximum around 0.6.

<table>
<thead>
<tr>
<th>Nd Level (z)</th>
<th>Fe Level (x)</th>
<th>Ge Level (y)</th>
<th>SKD Phase (wt%)</th>
<th>Filler Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2</td>
<td>0.15</td>
<td>57</td>
<td>0.00</td>
</tr>
<tr>
<td>0.2</td>
<td>2</td>
<td>0.15</td>
<td>62</td>
<td>0.16</td>
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<tr>
<td>0.4</td>
<td>2</td>
<td>0.15</td>
<td>66</td>
<td>0.23</td>
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<tr>
<td>0.5</td>
<td>2</td>
<td>0.15</td>
<td>87</td>
<td>0.45</td>
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<tr>
<td>0.6</td>
<td>2</td>
<td>0.15</td>
<td>100</td>
<td>0.62</td>
</tr>
<tr>
<td>0.7</td>
<td>2</td>
<td>0.15</td>
<td>95</td>
<td>0.52</td>
</tr>
<tr>
<td>0.8</td>
<td>2</td>
<td>0.15</td>
<td>96</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Nominal Composition

\( \text{Filled Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y \) Skutterudites
Similar microstructures for all hot pressed samples, no clear trends for composition.

- Grain size is bimodal with majority of grains 1-2µm, and others as large as 15µm.
- All samples had similar density (>96%) except for the sample with Fe content of 3 (90%).
Seebeck and Resistivity

- Seebeck coefficient trends well with Nd content. Increases with increasing Nd content from 0 to 0.6 then decreases.
- Electrical resistivity does not trend well with Nd content. It trends more with SKD phase purity than Nd content, secondary phases are metallic.
- More phase pure samples (0.5<Nd<0.8) had higher electrical resistivity than the less phase pure samples.
Seebeck coefficient is maximum for Fe content of 2, slightly lower for 1 and significantly lower for Fe 3.

Electrical resistivity for Fe 1 is highest, with nearly identical resistivity for both Fe 2 and 3.

In summary, Power factor is maximum for Fe content of 2 and lower for 1 and 3.
Lattice thermal conductivity (open symbols) is calculated using a single parabolic band model.
Only select samples are shown to avoid crowding the data.
Lattice conductivity decreases with increasing Nd content up to 0.6.
Highest ZT is obtained for the Nd 0.6 sample as a result of the low thermal conductivity.
The same composition in Zhang’s paper reported ZT peak 1.1.
Nd_{0.6}Fe_{x}Co_{4-x}Sb_{11.85}Ge_{0.15}
Nd_{0.6}Fe_{2}Co_{2}Sb_{12-y}Ge_{y}

**Thermal Conductivity**

- Lattice thermal conductivity is minimized for Fe content of 2.
- Fe content of 1 and 3 have similar thermal conductivity.
  - Suggests phonon scattering from Fe-Co bond. Maximized for Fe content of 2.
- Ge reduces lattice component of thermal conductivity.
  - Stronger scattering effect from Ge-Sb bond as Ge content is much lower than Fe content.

Carrier density increases with Nd content up to 0.7, while hall mobility decreases.

Carrier density and hall mobility show strongest change as a result of Fe content.

- Hall mobility is minimized and carrier density maximized for Fe content of 2.
- Fe content of 1 produces the lowest carrier density and highest mobility.
- SPB modeling on the system shows optimal ZT around \(2 \times 10^{19} \text{ cm}^{-3}\).
Electrical properties were tested on slow repeating loops, to investigate phase stability.

Samples were measured from 25 to 600°C, on 18 hour loops.

No change observed after 6 cycles.

XRD of samples annealed at 650°C for 72 hours in N₂ atmosphere showed no change in phase content.
Conclusions

- Fe and Nd content are critical in phase purity of the skutterudite phase, while Ge plays a lesser role.
- Microstructures of hot pressed samples are composed primarily of 1-2 µm grains of SKD with FeSb$_2$ and Sb phases.
- Electrical and thermal properties are dependant on Nd, Fe, and Ge level.
  - Highest figure of merit was achieved for Nd$_{0.6}$Fe$_2$Co$_{2-x}$Sb$_{11.85}$Ge$_{0.15}$ peak ZT 0.6.
  - Published literature reported ZT 1.1 for the same composition.
  - 45% discrepancy may be partially attributed to experimental uncertainty, but not totally.
- Electrical properties and XRD phase are thermally stable.

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