Filled $\text{Nd}_x\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$ 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*

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

Filled Nd$_{2}$Fe$_{x}$Co$_{4-x}$Sb$_{12-y}$Sn$_y$ Skutterudites
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.

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 \( y =\{0,0.15\} \)

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 FeSb₂ 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>
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<tbody>
<tr>
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<td>2</td>
<td>0.15</td>
<td>57</td>
<td>0.00</td>
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<tr>
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<th>Ge Level (y)</th>
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<th>SKD Phase (wt%)</th>
<th>Filler Occupancy</th>
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<tbody>
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<td>0.43</td>
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<tr>
<td>0.6</td>
<td>2</td>
<td>0.15</td>
<td>100</td>
<td>0.62</td>
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</table>

Nominal Composition
• 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%).

Filled Nd$_z$Fe$_2$Co$_2$Sb$_{11.85}$Ge$_{0.15}$ Skutterudites
Filled Nd$_x$Fe$_{3-x}$Co$_1$Sb$_{11.85}$Ge$_{0.15}$

Nd$_{0.6}$Fe$_3$Co$_1$Sb$_{11.85}$Ge$_{0.15}$

Nd$_{0.6}$Fe$_2$Co$_2$Sb$_{12}$
• 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.
Nd$_2$Fe$_2$Co$_2$Sb$_{11.85}$Ge$_{0.15}$

**Thermal and Figure of Merit**

- 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.

Filled Nd$_x$Fe$_{4-x}$Co$_{4-x}$Sb$_{11.85}$Ge$_{0.15}$ Skutterudites
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.

\[ \text{Nd}_{0.6} \text{Fe}_x \text{Co}_{4-x} \text{Sb}_{11.85} \text{Ge}_{0.15} \]
\[ \text{Nd}_{0.6} \text{Fe}_2 \text{Co}_2 \text{Sb}_{12-y} \text{Ge}_y \]

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 $2 \times 10^{19} \text{ cm}^{-3}$. 

\[
\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{11.85}\text{Ge}_{0.15}
\]
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.

Filled Nd₀.₆Fe₂Co₂Sb₁₁.₈₅Ge₀.₁₅ Skutterudites
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 FeSb₂ and Sb phases.
• Electrical and thermal properties are dependant on Nd, Fe, and Ge level.
  • Highest figure of merit was achieved for Nd₀.₆Fe₂Co₂Sb₁₁.₈₅Ge₀.₁₅ 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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