Filled $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Ge}_y$ 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 $I\overline{m}$-3

$A_\delta B_4 X_{12}$

Filled Nd$_2$Fe$_x$Co$_{4-x}$Sb$_{12-y}$Sn$_y$ Skutterudites

Skutterudite System Investigated

- Nd filled, Ge doped Fe_{x}Co_{4-x}Sb_{12} skutterudite, Nd_{z}Fe_{x}Co_{4-x}Sb_{12-y}Ge_{y}.
- Zhang et al. has previously investigated Nd_{0.6}Fe_{2}Co_{2}Sb_{12-y}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 Nd_{z}Fe_{x}Co_{4-x}Sb_{12-y}Ge_{y}.
- Study processing conditions.
- Study effect of composition on properties.
- Samples created from a melt/mill/hot press procedure.
**Processing Conditions**

- Ingots were fabricated by solidification.
  - $1100^\circ$C for 1 hour
  - $10^\circ$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$^\circ$C with 62 MPa for ½ hour
  - $1.5^\circ$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>
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<tbody>
<tr>
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<td>0.15</td>
<td>57</td>
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<th>SKD Phase (wt%)</th>
<th>Filler Occupancy</th>
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<td>0.15</td>
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</tbody>
</table>

Nominal Composition

Filled Nd$_z$Fe$_x$Co$_{4-x}$Sb$_{12-y}$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%).
Filled $\text{Nd}_z\text{Fe}_x\text{Co}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ Skutterudites
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.
Nd₂Fe₂Co₂Sb₁₁.₈₅Ge₀.₁₅

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.
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.

Thermal Conductivity

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

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

Filled $\text{Nd}_z \text{Fe}_x \text{Co}_{4-x} \text{Sb}_{11.85} \text{Ge}_{0.15}$ Skutterudites
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$_2$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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