Filled $Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$ skutterudites: processing and thermoelectric properties

Jon Mackey

Materials Science and Engineering,
Case Western Reserve University

Alp Sehirlioglu

Materials Science and Engineering,
Case Western Reserve University

Fred Dynys

NASA Glenn Research Center

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System Background

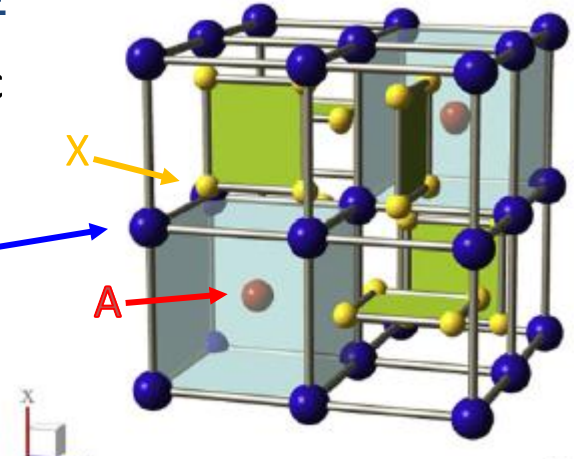
- Skutterudites are based on $CoAs_3$ mineral; first mined in Skutterud, Norway.
- Exhibit a high figure of merit for n-type systems (ZT=1.7).
- Relatively low cost system.
- Introduce a range of fillers (A) to scatter various phonon wavelengths.
- Introduce disorder on pnictogen ring sites (X).
  - Dominate heat carrying modes are associated with pnictogen vibration.
- Tune electronic properties (A,B,X) for optimal thermoelectric power factor .

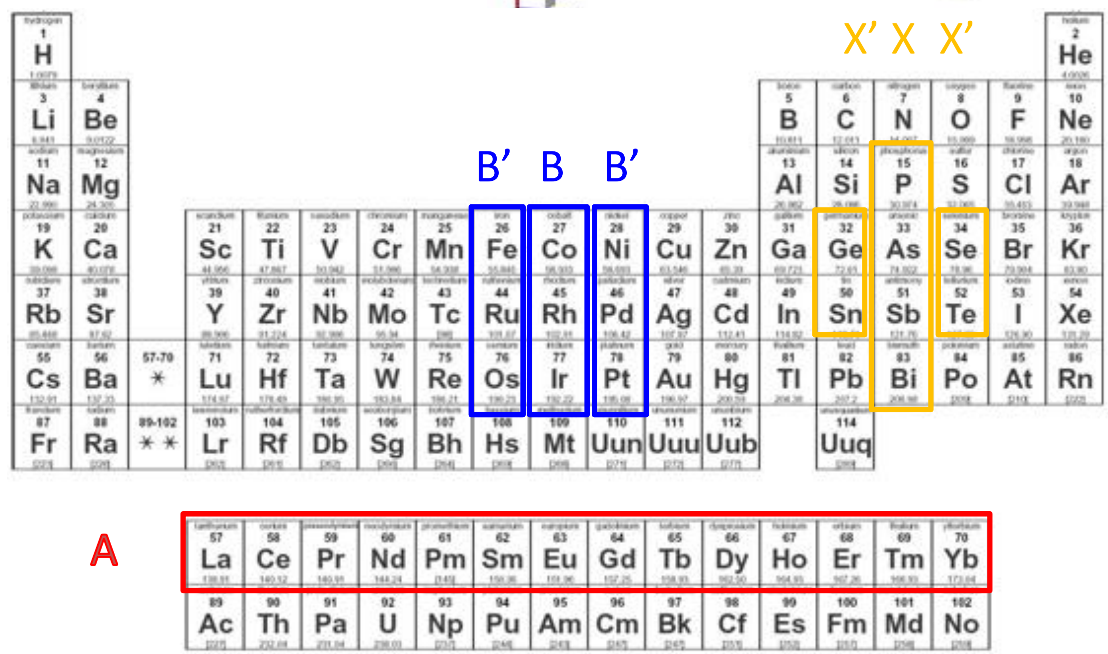
Crystal Structure

Eilertsen *et al.* Acta Mater. **60** (2012) 2178-2185.
Chi *et al.* Phys. Rev. B **86**: 195209 (2012).

Body-centered cubic space group *Im-3*

$A_{\delta} B_4 X_{12}$





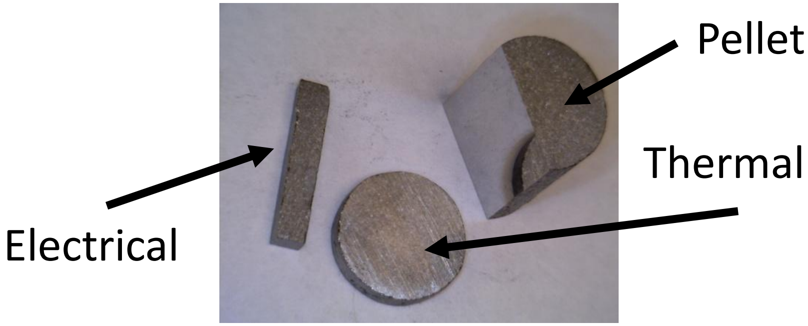
Skutterudite System Investigated

- Nd filled, Ge doped $Fe_xCo_{4-x}Sb_{12}$ skutterudite, $Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$.
- Zhang *et al.* has previously investigated $Nd_{0.6}Fe_2Co_2Sb_{12-y}Ge_y$ 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}

Zhang *et al.* J. Appl. Phys. **114** (2013).

Objectives

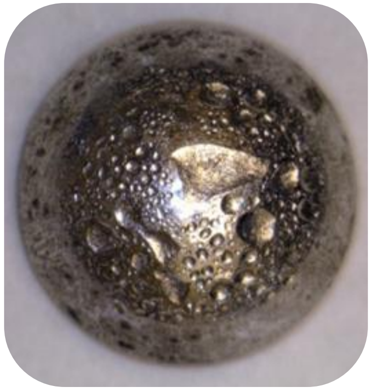
- Focus on finding a p-type skutterudite with improved ZT.
- Study thermoelectric behavior of the skutterudite $Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$.
- Study processing conditions.
- Study effect of composition on properties.
- Samples created from a melt/mill/hot press procedure.



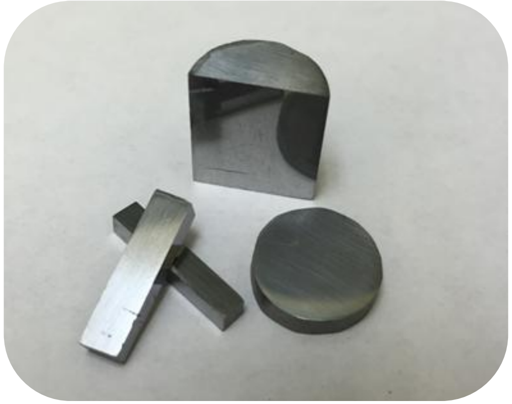
Processing Conditions

- Ingots were fabricated by solidification.
  - 1100°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.

Solidified Ingot



Hot Pressed Pellet



$Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$

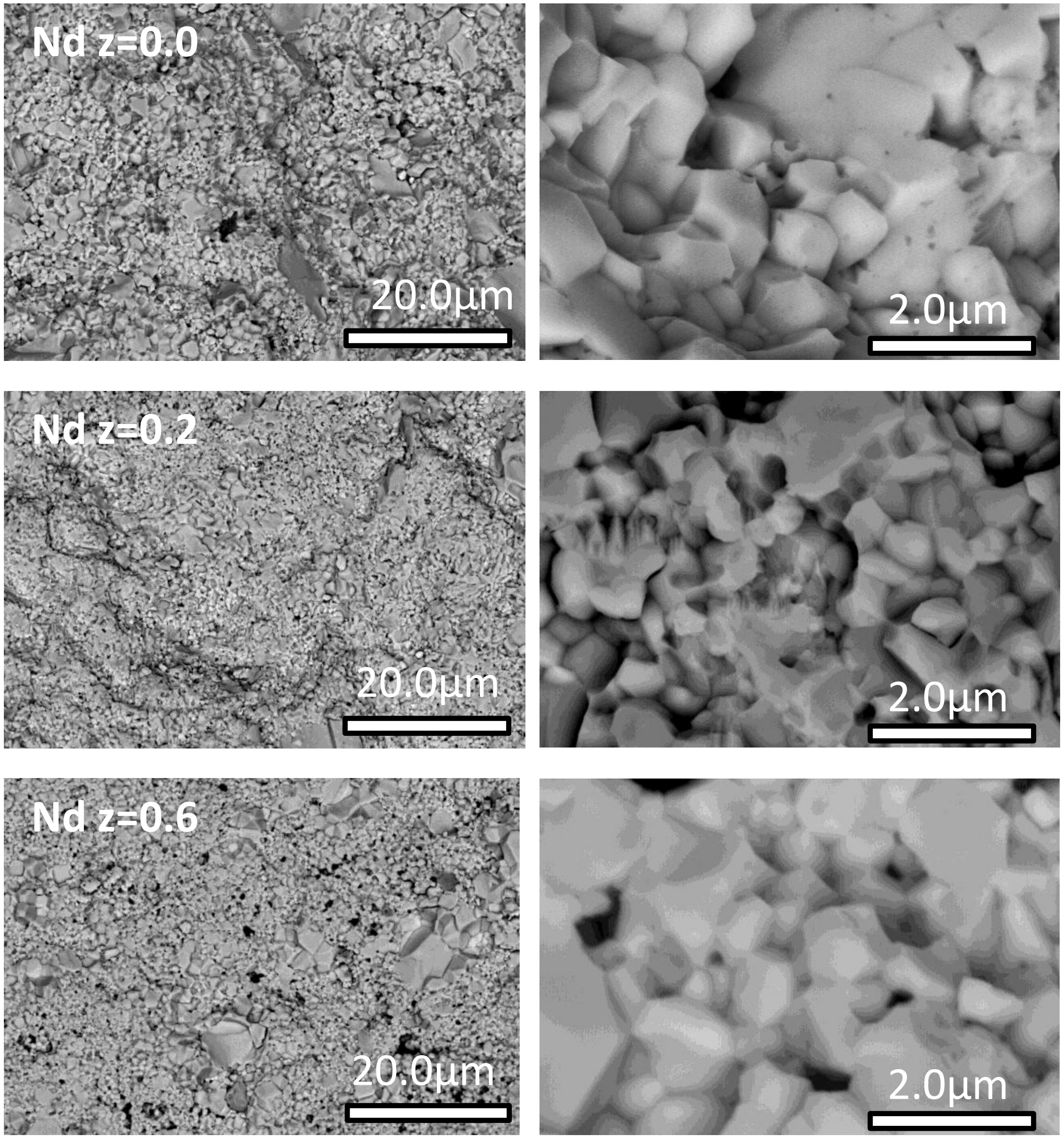
X-Ray Diffraction

- 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.

X-Ray Diffraction Summary

Nd Level (z)	Fe Level (x)	Ge Level (y)	SKD Phase (wt%)	Filler Occupancy
0.0	2	0.15	57	0.00
0.2	2	0.15	62	0.16
0.4	2	0.15	66	0.23
0.5	2	0.15	87	0.45
0.6	2	0.15	100	0.62
0.7	2	0.15	95	0.52
0.8	2	0.15	96	0.60
0.6	3	0.15	57	0.67
0.6	2	0.15	100	0.62
0.6	1	0.15	100	0.27
0.6	2	0.00	90	0.43
0.6	2	0.15	100	0.62

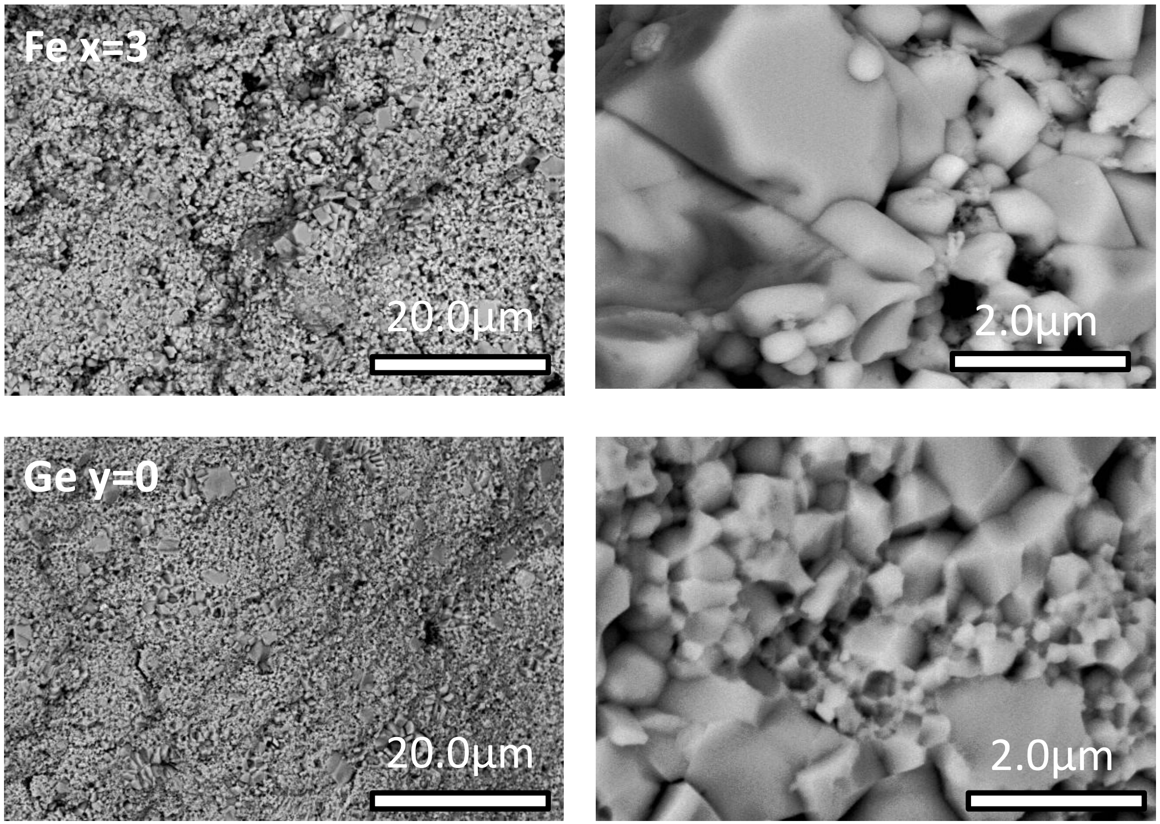
Nominal Composition (Nd Level, Fe Level, Ge Level)



$Nd_zFe_2Co_2Sb_{11.85}Ge_{0.15}$

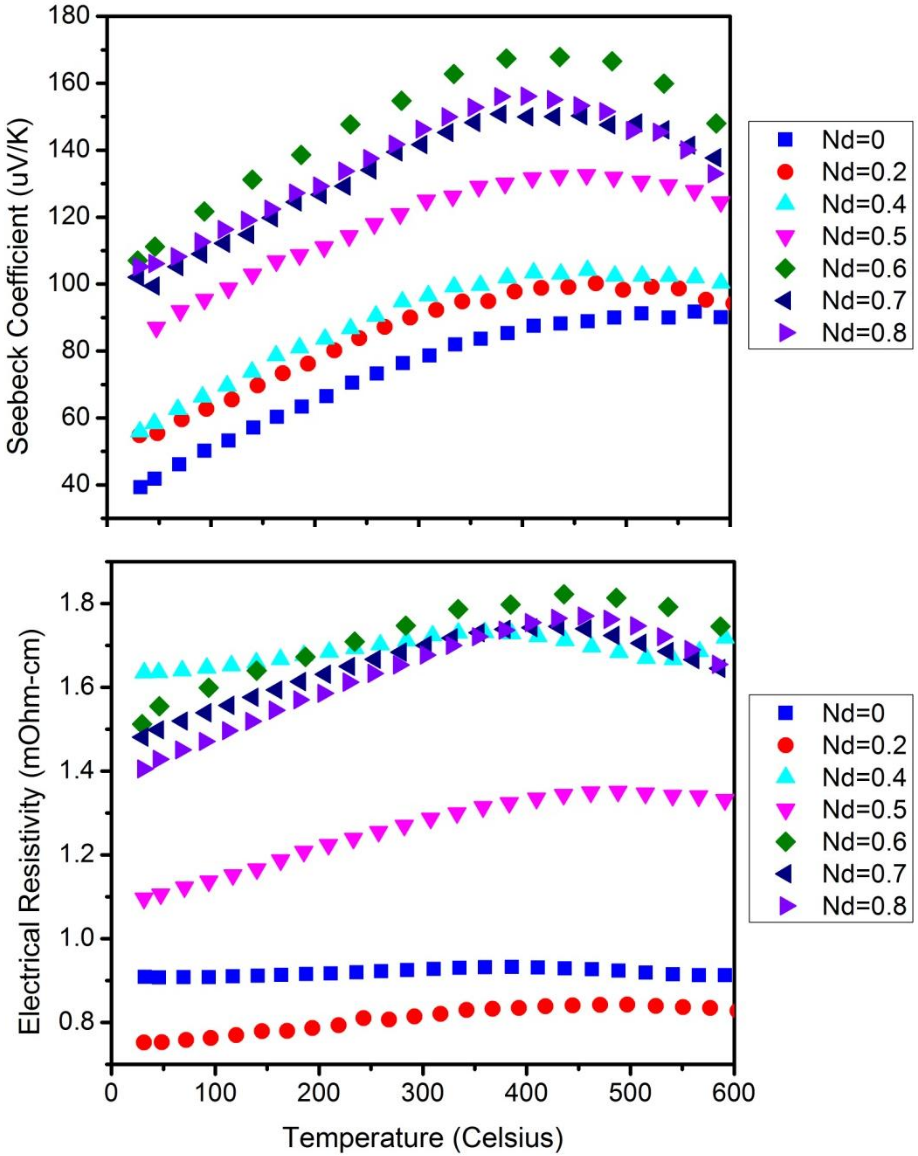
Microstructure

- 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%).



$Nd_{0.6}Fe_3Co_1Sb_{11.85}Ge_{0.15}$

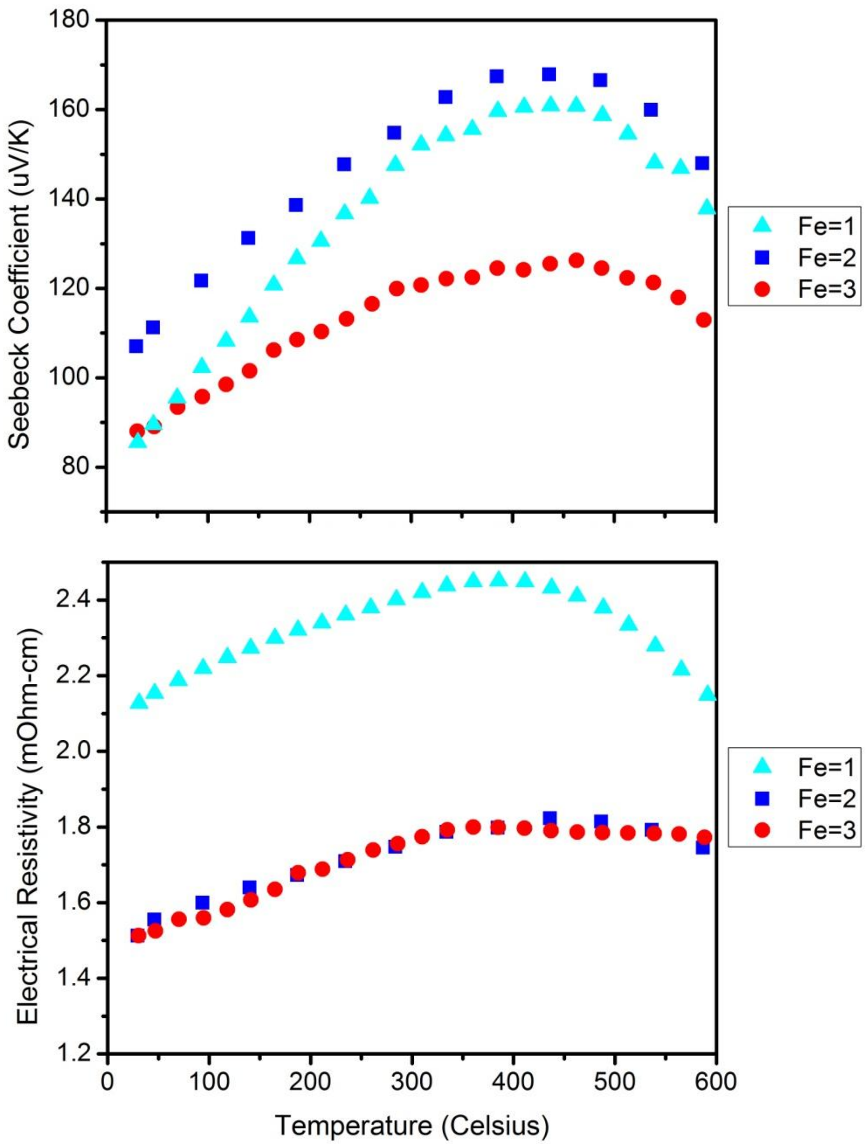
$Nd_{0.6}Fe_2Co_2Sb_{12}$



$Nd_zFe_2Co_2Sb_{11.85}Ge_{0.15}$

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.



$Nd_{0.6}Fe_xCo_{4-x}Sb_{11.85}Ge_{0.15}$

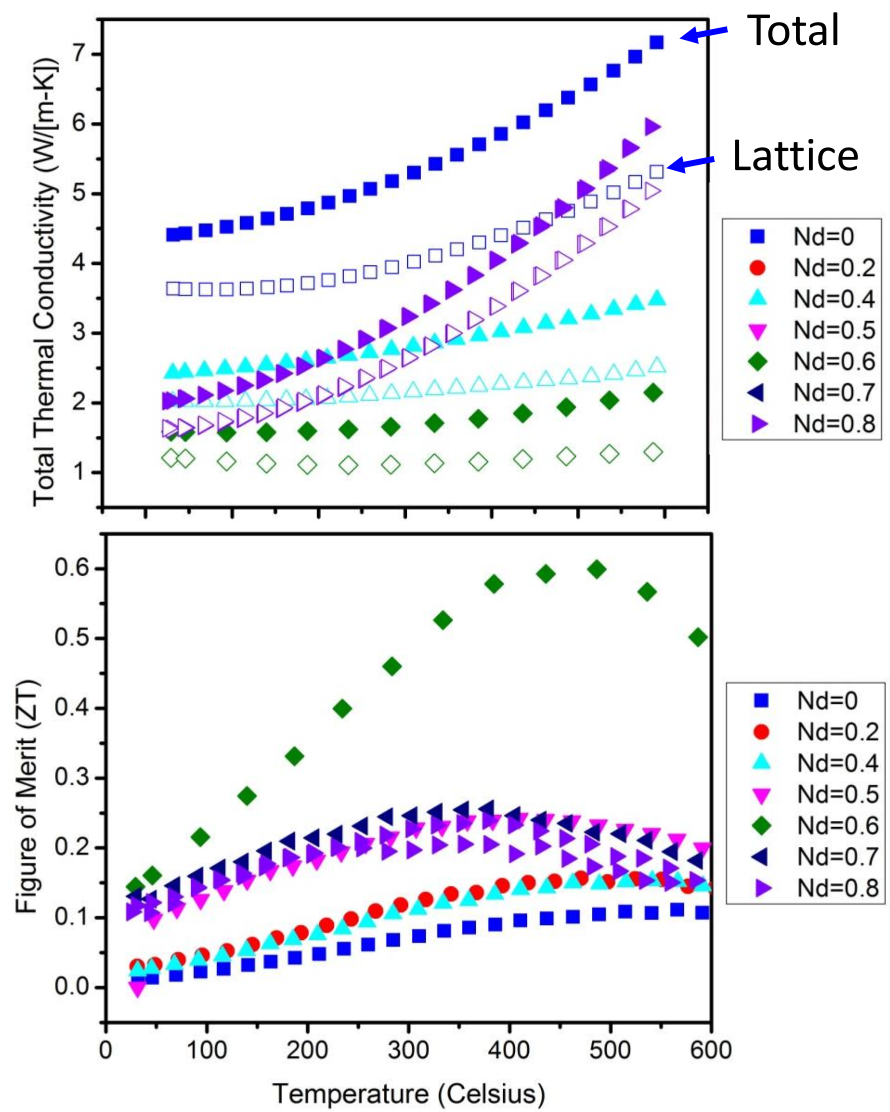
Seebeck and Resistivity

- 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.

$Nd_zFe_2Co_2Sb_{11.85}Ge_{0.15}$

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.



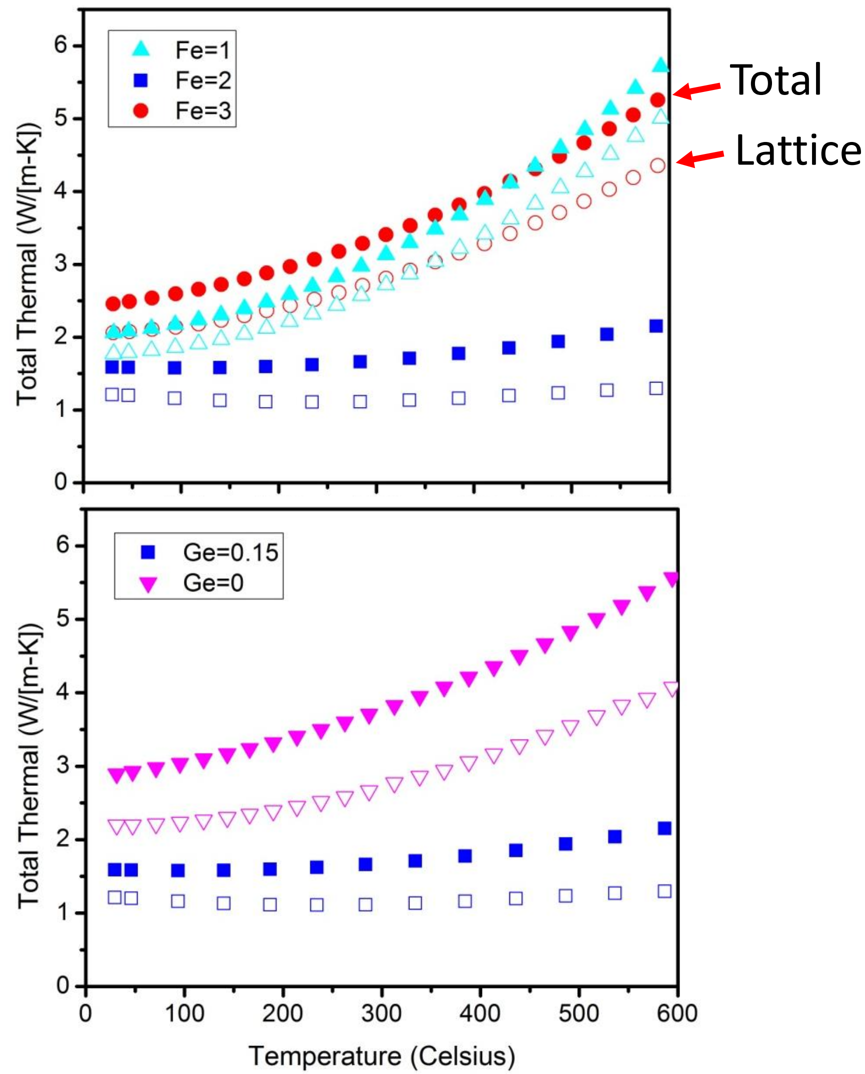
$Nd_{0.6}Fe_xCo_{4-x}Sb_{11.85}Ge_{0.15}$

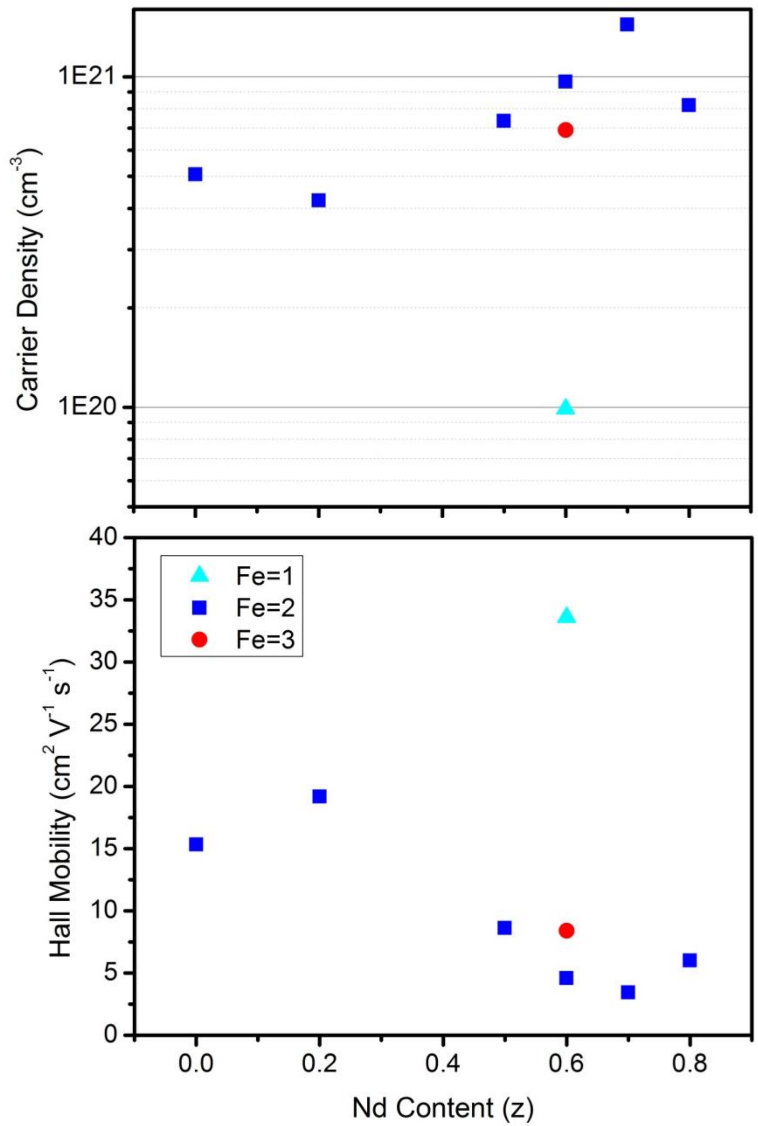
$Nd_{0.6}Fe_2Co_2Sb_{12-y}Ge_y$

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.

Chi *et al.* Phys. Rev. B **86**: 195209 (2012).





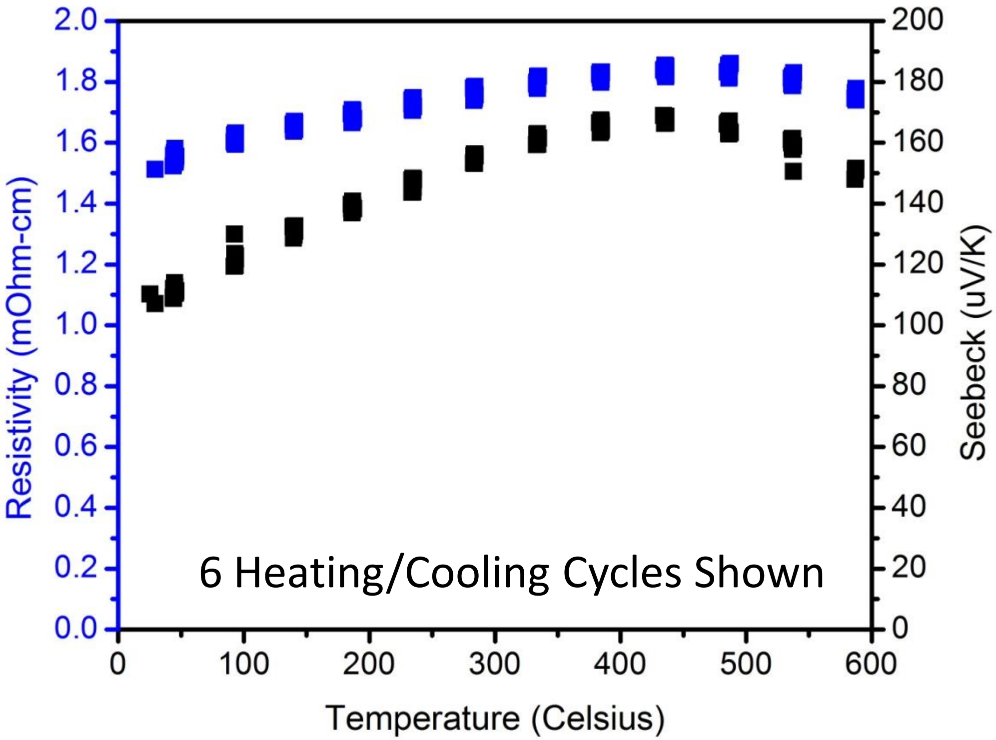
$Nd_zFe_xCo_{4-x}Sb_{11.85}Ge_{0.15}$

Room Temperature Hall

- 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 $2x10^{19}$ cm^{-3}.

Repeated Electrical Testing

$Nd_{0.6}Fe_2Co_2Sb_{11.85}Ge_{0.15}$



Property Stability

- 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 N_2 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 $Nd_{0.6}Fe_2Co_2Sb_{11.85}Ge_{0.15}$ 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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