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

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System Background

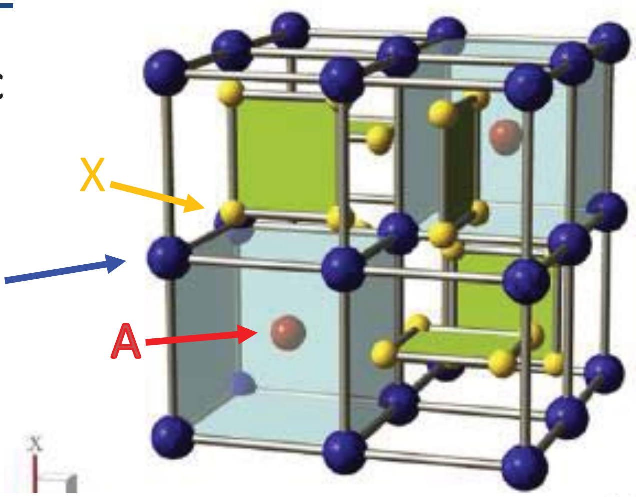
- Skutterudites are based on $CoAs_3$ mineral; first mined in Skotterud, Norway.
- Exhibit a high figure of merit for n-type systems (ZT=1.7).
- Relatively low cost system.
- Introduce disorder on pnictogen ring sites (X).
  - Dominate heat carrying modes are associated with pnictogen vibration.
- Introduce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

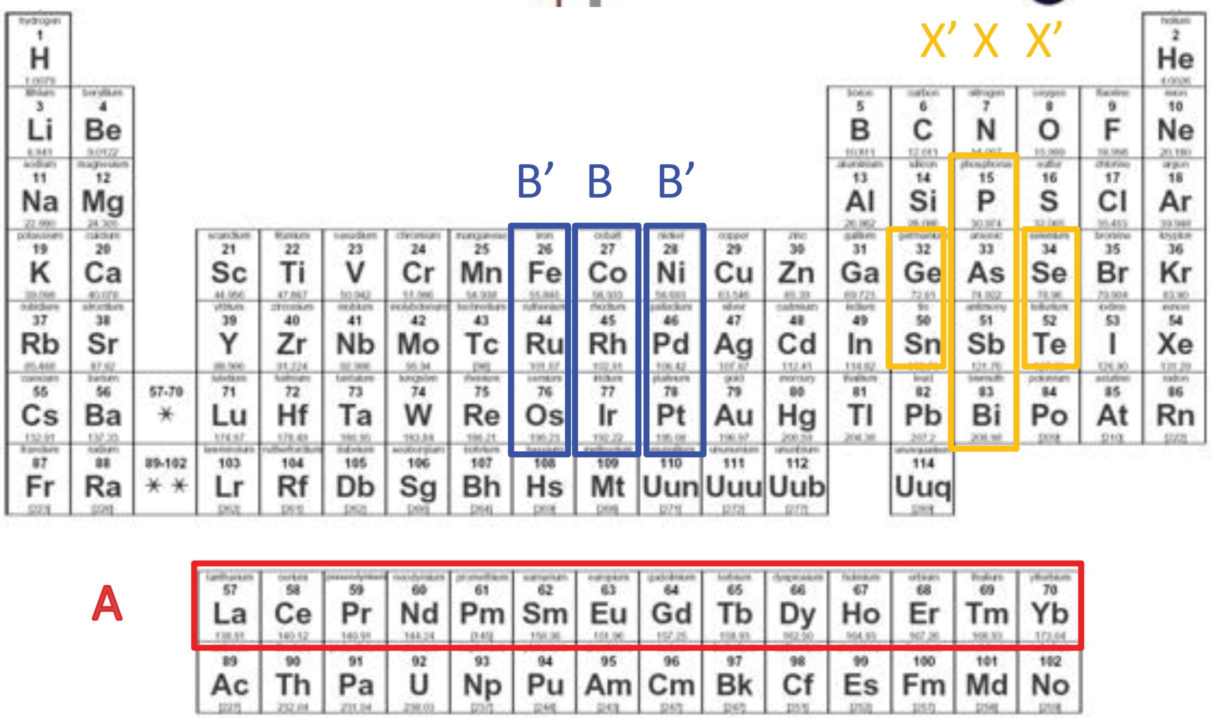
Crystal Structure

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

Body-centered cubic space group *Im3*

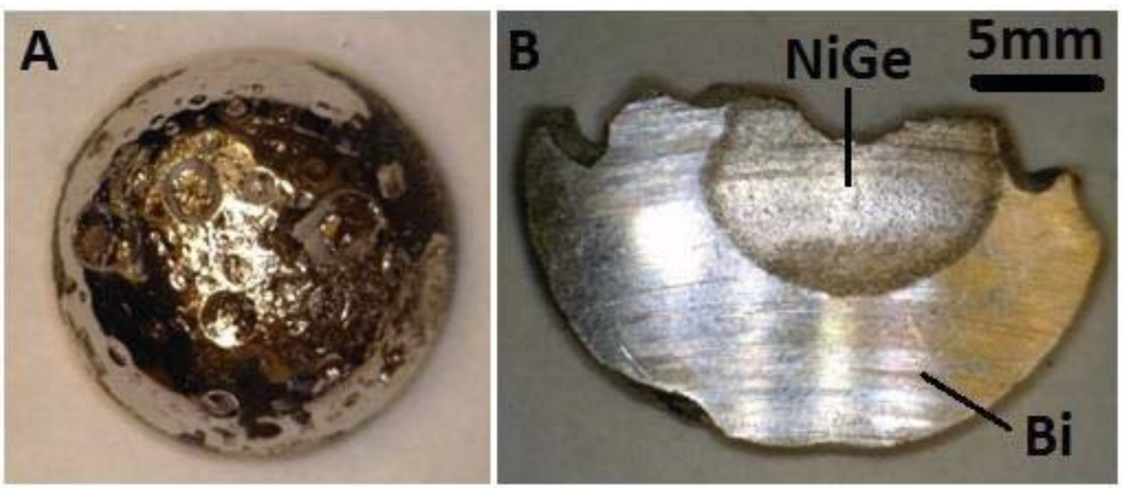
$A_{\delta} B_4 X_{12}$





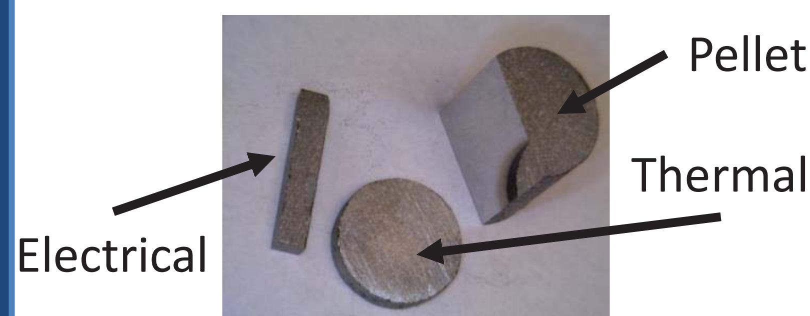
Systems Investigated

- Ternary systems studied with combination of solidification and powder processing techniques.
- $Ni_4Bi_8Ge_4$
  - Shown below, skutterudite phase not obtained.
- $Ni_4Sb_8Ge_4$
  - Skutterudite phase not obtained.
- $Ni_4Sb_8Sn_4$



Objectives

- Focus on finding a p-type skutterudite with improved ZT.
- Study behavior of the skutterudite $Co_xNi_{4-x}Sb_{12-y}Sn_y$.
  - Grytsiv et. al has reported a $Ni_4Sb_8Sn_4$ skutterudite system.
  - Parameters of study:
    - x= {0,0.5,1,1.5,2}
    - y={3,4,5}
- Samples created from a melt/mill/hot press procedure.



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- Ternary sy... of solidific... technique
- $Ni_4Bi_8Ge_4$
  - Show... obtai...
- $Ni_4Sb_8Ge_4$
  - Skutt...
- $Ni_4Sb_8Sn_4$

...on ...ot ...nm ...Bi

$Co_xNi_{4-x}Sb_{12-y}Sn_y$

Sample #	Co (x)	Sn (y)	Lattice Parameter (Å)
1	0.0	4.0	9.113
2	0.0	5.0	9.128
3	0.5	5.0	9.126
4	1.0	5.0	9.118
5	1.5	5.0	9.123
6	2.0	5.0	9.104
7	2.0	4.0	9.109
8	2.0	3.0	9.087

Objectives

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$A_zCo_2Ni_2Sb_8Sn_4$

Sample #	Filler A	Level (z)	Lattice Parameter (Å)
7	N/A	0.0	9.109
9	Ce	0.1	9.108
10	Dy	0.1	9.114
11	Yb	0.05	9.019
12	Yb	0.1	9.111
13	Yb	0.2	9.114

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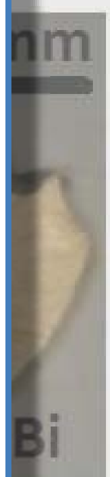

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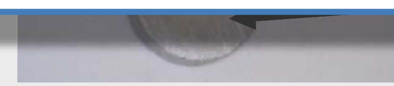

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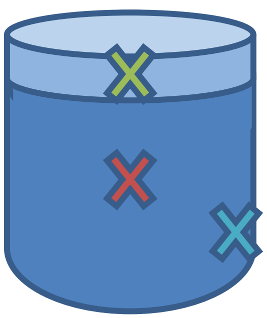
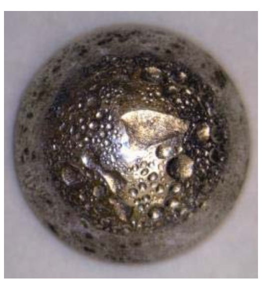
ICP analysis of an ingot

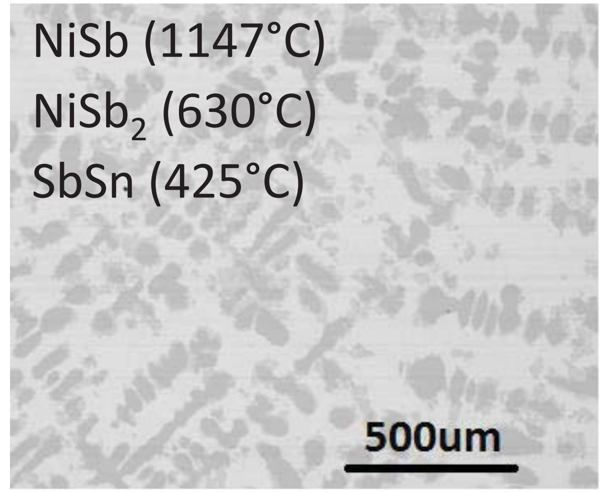
- 2 Hr @ 1100°C (+20,-10°C /min)
- Silica crucible in He atmosphere
- <1% wt loss

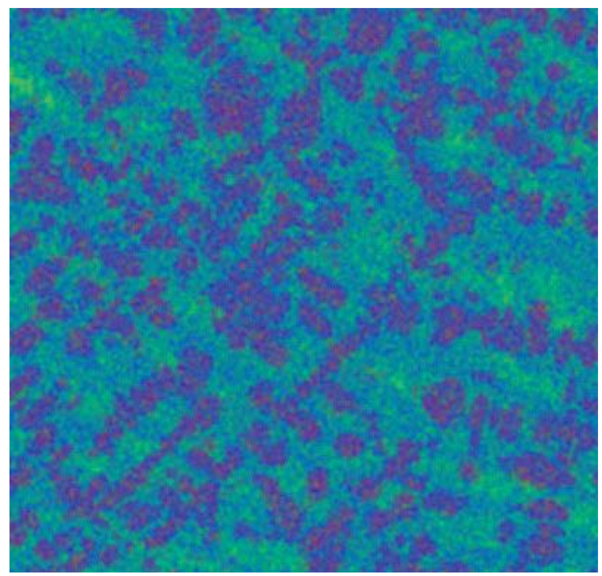


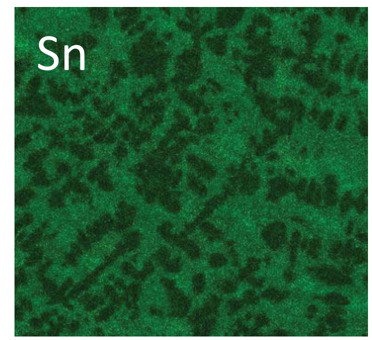


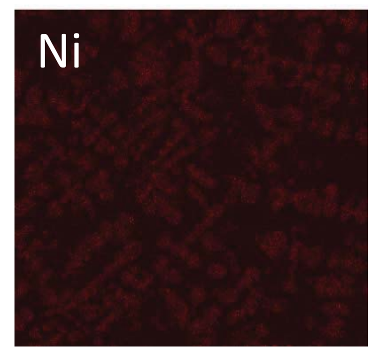
	Target	X	X	X
	at%	at%	at%	at%
Co	**9.4**	9.1	7.3	9.0
Ni	**15.6**	14.9	13.7	14.6
Sb	**43.7**	42.4	43.7	44.1
Sn	**31.2**	33.5	35.3	32.2
Ca	**0**	2e-4	7e-4	7e-4
Mg	**0**	1e-4	2e-4	2e-4
Na	**0**	3e-3	4e-3	4e-3

EDS map of an ingot



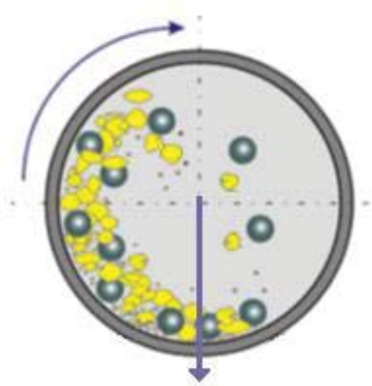




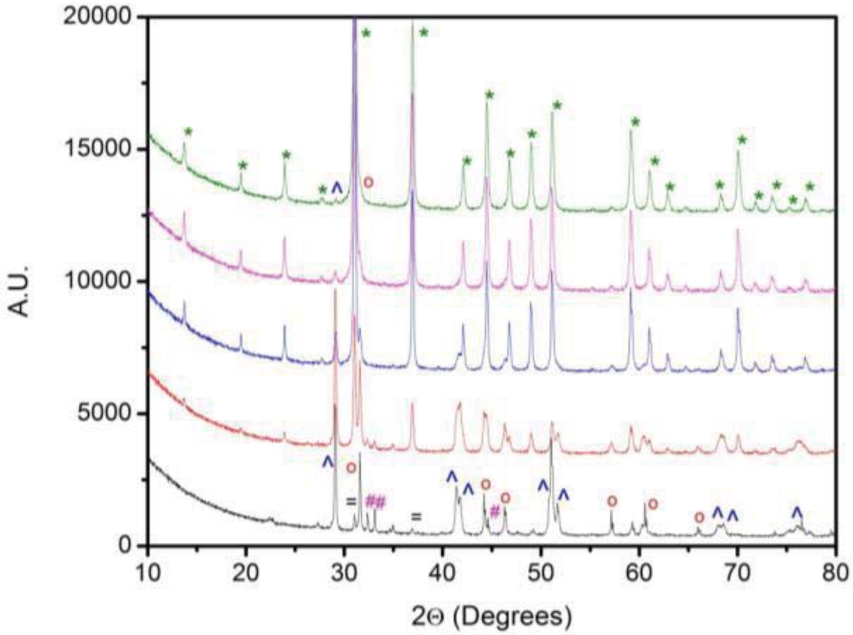


Milling Details

- Planetary mill
  - 550 rpm
  - Ball to powder weight ratio 3.8
  - Ar atmosphere

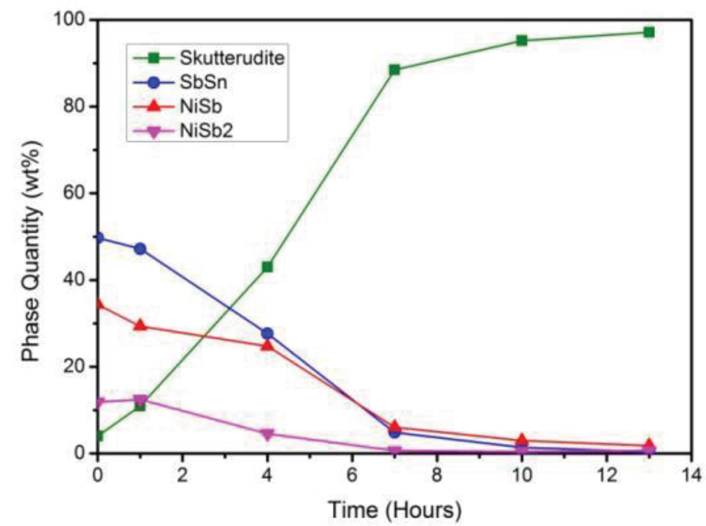


Milling XRD

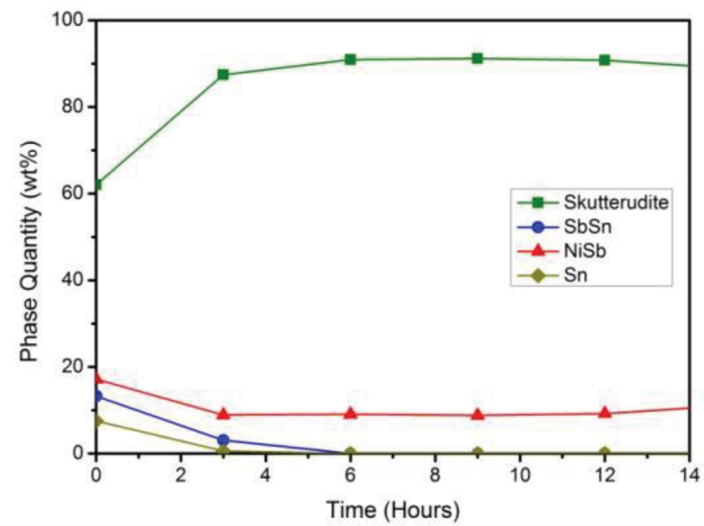


*SKD
^ SbSn
o NiSb
$NiSb_2$
= Sn_3Ni_4

Sample 1 $Ni_4Sb_8Sn_4$ Milling



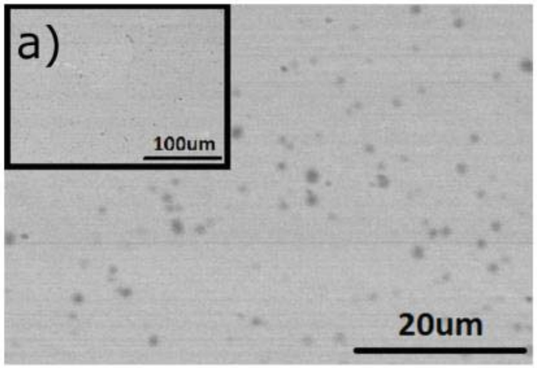
Sample 4 $Co_1Ni_3Sb_7Sn_5$ Milling



Hot Pressed SEM

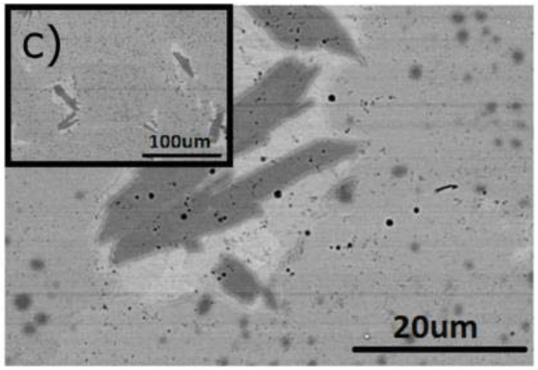
Sample 1 $Ni_4Sb_8Sn_4$

- NiSb (3.1wt%, 109nm cryst.) precip 1µm.
- SbSn (1.3wt%, 45 nm cryst.) precip 30 µm.



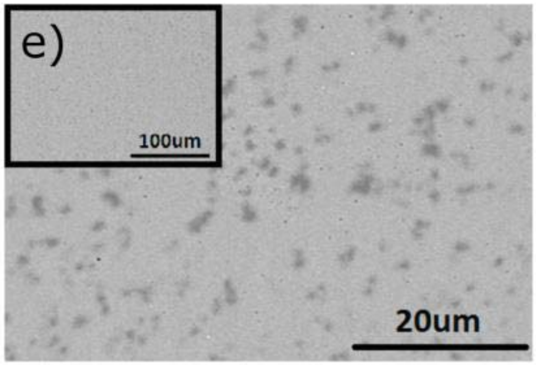
Sample 2 $Ni_4Sb_7Sn_5$

- NiSb (6.8wt%) precip 1µm.
- Ni_3Sn_4 (1.2wt%) precip 30 µm.
- SbSn (1.4wt%) surrounding Ni_3Sn_4.

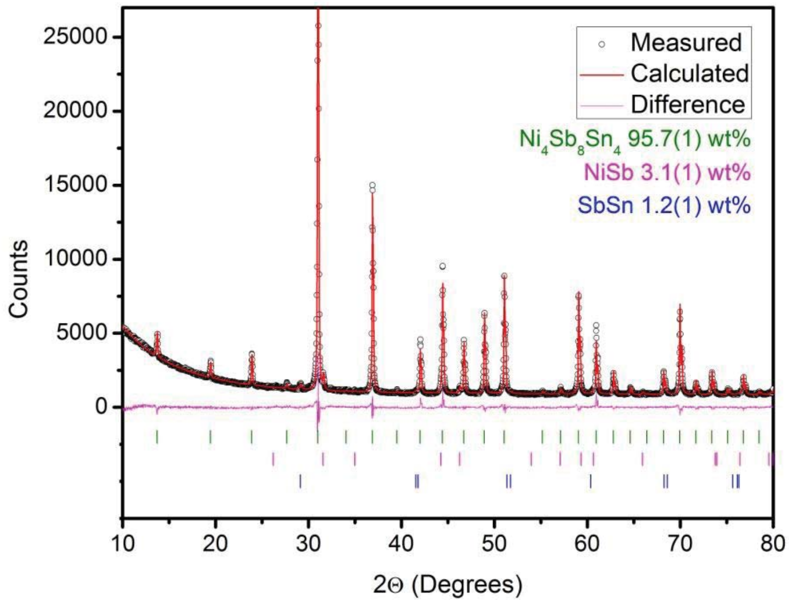


Sample 4 $Co_1Ni_3Sb_7Sn_5$

- NiSb (3.2wt%) precip 1µm.
- Ni_3Sn_4 (6.5wt%) precip 1µm.



Rietveld Refinement



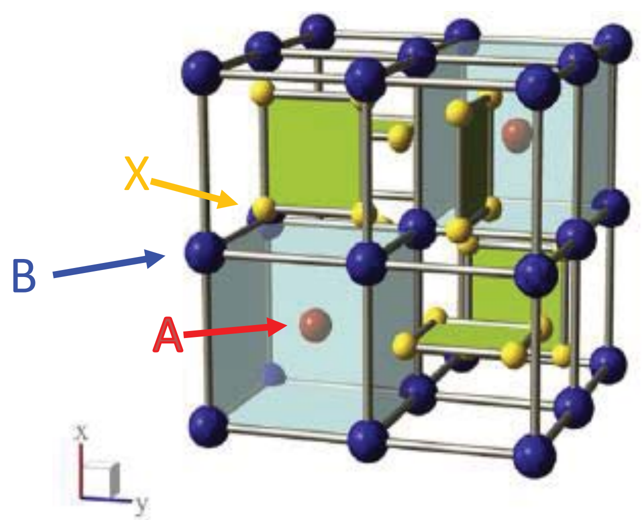


FIGURE: Eilertsen et al. Acta Mater. **60** (2012) 2178-2185.

Hot Pressed Structure Refinement

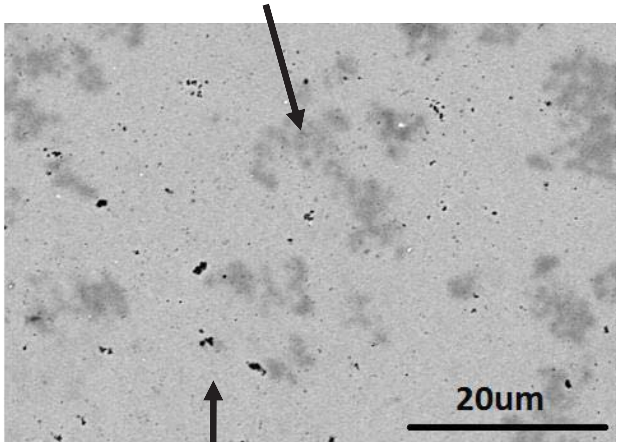
Sample #	Skutterudite $A_\delta B_x B'_{4-x} X_{12-y} X'_y$	Lattice (Å)	SKD (wt%)
1	$Sn_{0.2}Co_{0.0}Ni_{4.0}Sb_{8.5}Sn_{4.4}$	9.113	96.65
2	$Sn_{0.3}Co_{0.0}Ni_{4.0}Sb_{7.9}Sn_{5.1}$	9.128	87.38
3	$Sn_{0.3}Co_{0.6}Ni_{3.4}Sb_{7.2}Sn_{4.7}$	9.126	94.97
4	$Sn_{0.3}Co_{1.2}Ni_{2.8}Sb_{8.3}Sn_{5.4}$	9.118	89.25
5	$Sn_{0.3}Co_{1.5}Ni_{2.5}Sb_{7.0}Sn_{4.7}$	9.123	91.33
6	$Sn_{0.3}Co_{2.4}Ni_{1.6}Sb_{9.4}Sn_{5.8}$	9.104	80.08
7	$Sn_{0.3}Co_{2.1}Ni_{1.9}Sb_{9.1}Sn_{3.7}$	9.109	93.64
8	$Sn_{0.2}Co_{2.1}Ni_{1.9}Sb_{9.0}Sn_{2.6}$	9.087	98.20

Pressed $Co_2Ni_2Sb_7Sn_5$

Density 7.64 g/cm^3
99%

Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	82.6
Ni_3Sn_4	8.7
Sn	6.2

Ni_3Sn_4 (230°C)



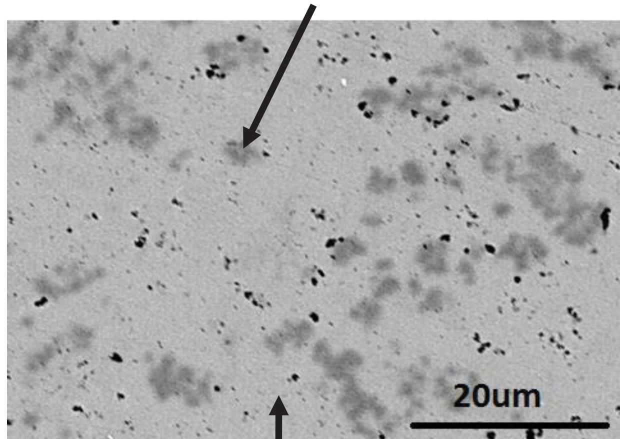
$Sn_{0.5}Co_{2.4}Ni_{1.6}Sb_{9.7}Sn_{5.7}$

200°C Anneal 72 Hrs

Density 7.25 g/cm^3
95%

Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	80.0
Ni_3Sn_4	11.9
Sn	7.6

Ni_3Sn_4 (230°C)



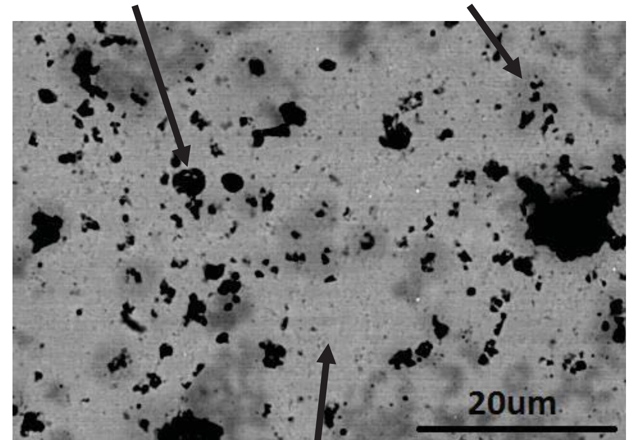
$Sn_{0.5}Co_{2.4}Ni_{1.6}Sb_{9.7}Sn_{5.7}$

400°C Anneal 72 Hrs

Density 6.75 g/cm^3
88%

Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	73.6
Ni_3Sn_4	14.7
Sn	10.0

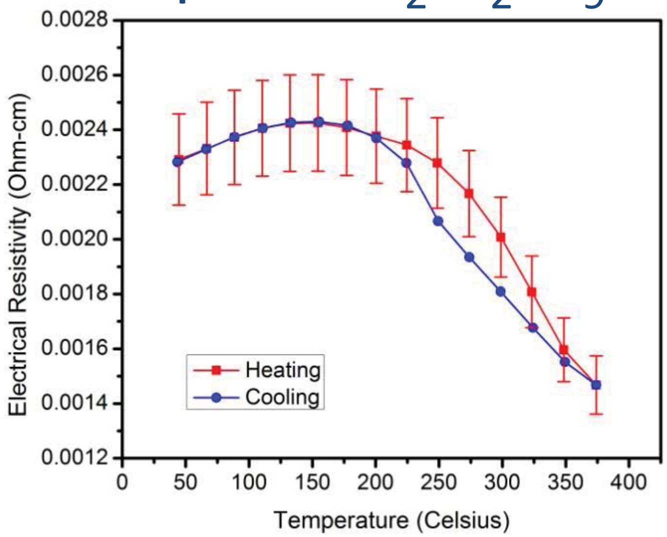
Porosity Ni_3Sn_4 (230°C)

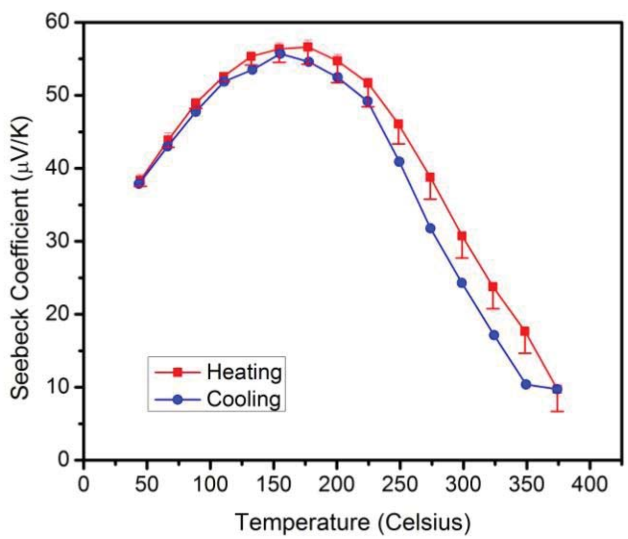


$Sn_{0.5}Co_{2.4}Ni_{1.6}Sb_{9.7}Sn_{5.7}$

Electrical Hysteresis

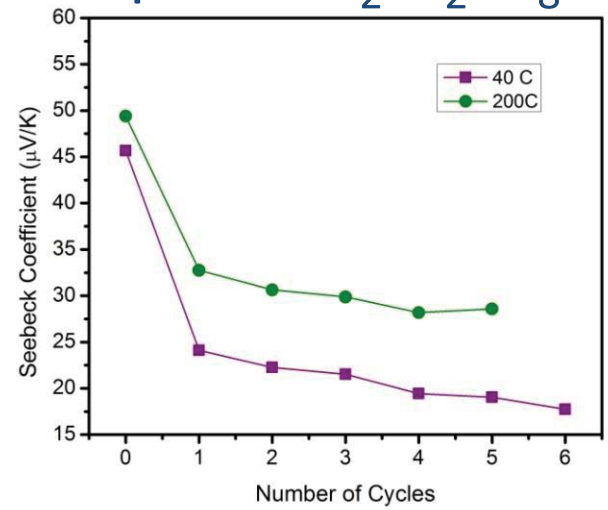
Sample 8 $Co_2Ni_2Sb_9Sn_3$





Sample Stability

Sample 7 $Co_2Ni_2Sb_8Sn_4$



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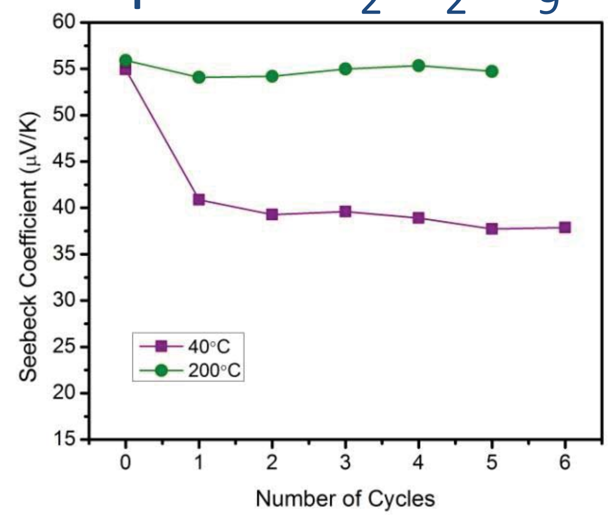
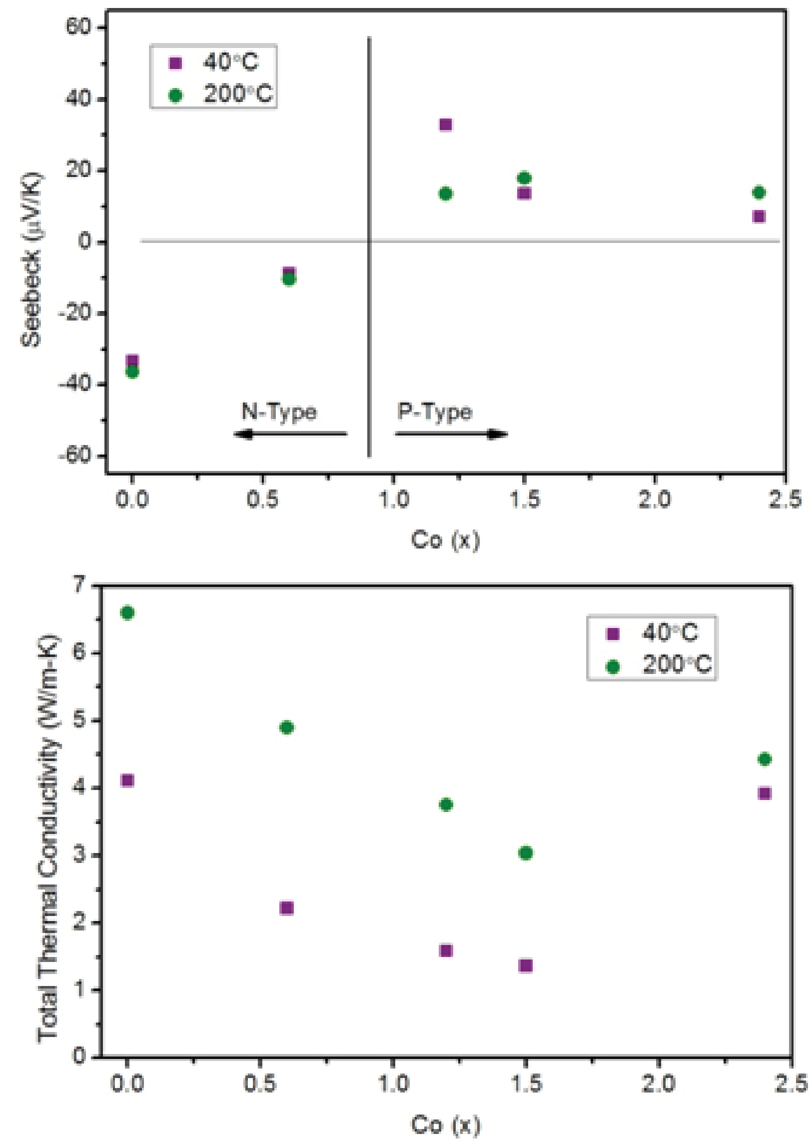


Transport Properties- Unfilled (40°C)

$Co_xNi_{4-x}Sb_{12-y}Sn_y$

Sample #	Co (x)	Sn (y)	Lattice Parameter (Å)	Seebeck Coefficient ($\mu V/K$)	Electrical Resistivity ($\mu Ohm - cm$)	Thermal Conductivity (W/m-K)
1	0.0	4.0	9.113	-40.7	233	4.7
2	0.0	5.0	9.128	-33.4	255	4.1
3	0.5	5.0	9.126	-8.7	560	2.2
4	1.0	5.0	9.118	32.9	784	1.6
5	1.5	5.0	9.123	13.7	449	1.4
6	2.0	5.0	9.104	7.1	233	3.9
7	2.0	4.0	9.109	17.7	540	2.5
8	2.0	3.0	9.087	37.9	2282	1.5

Co (x) Study



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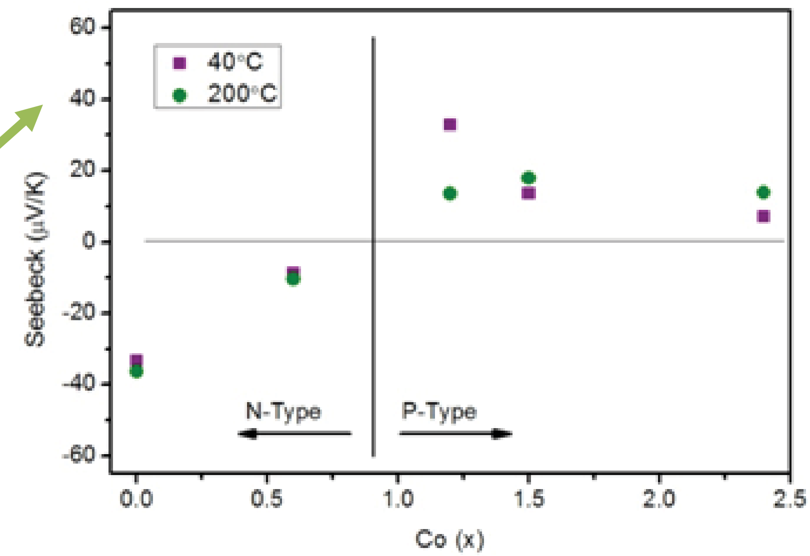

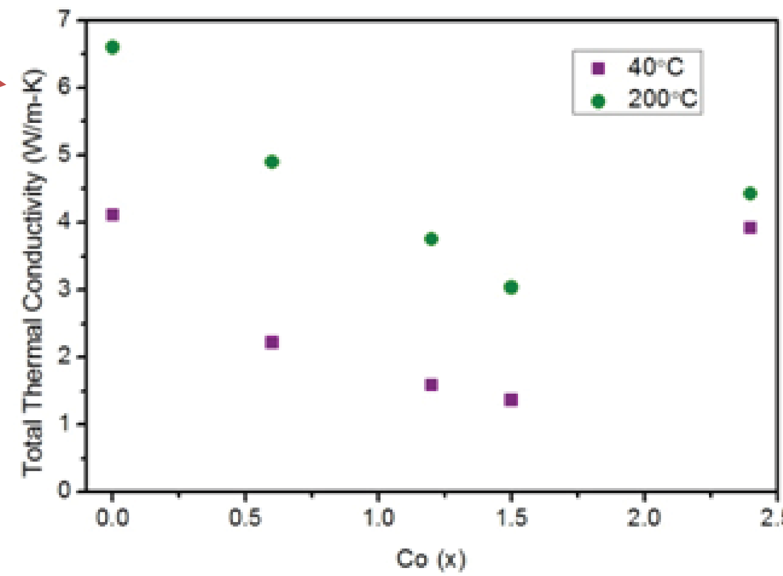

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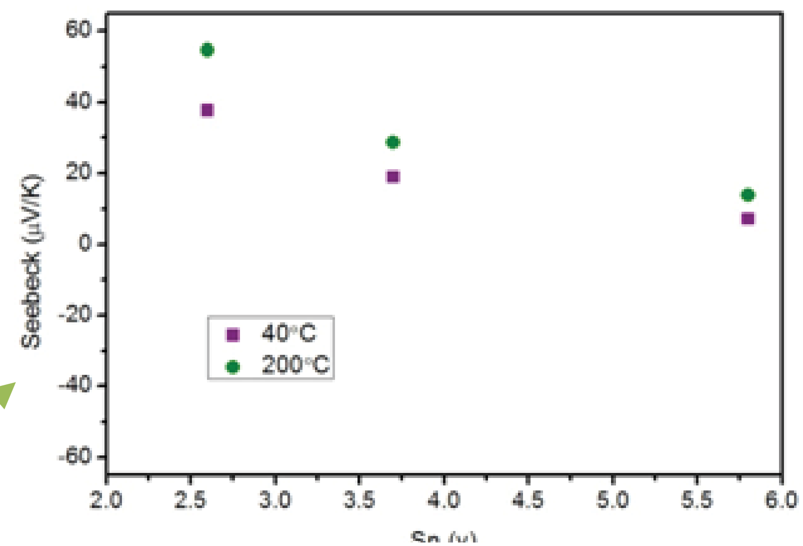
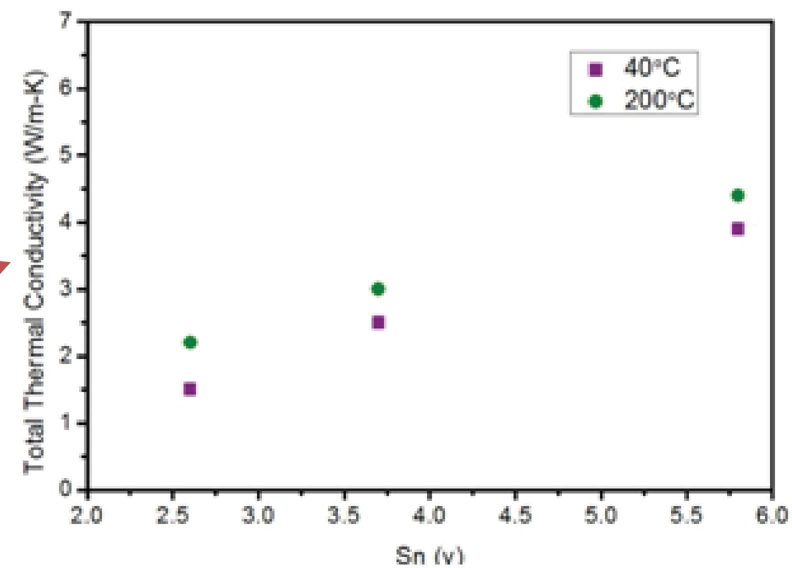
Sn (y) Study





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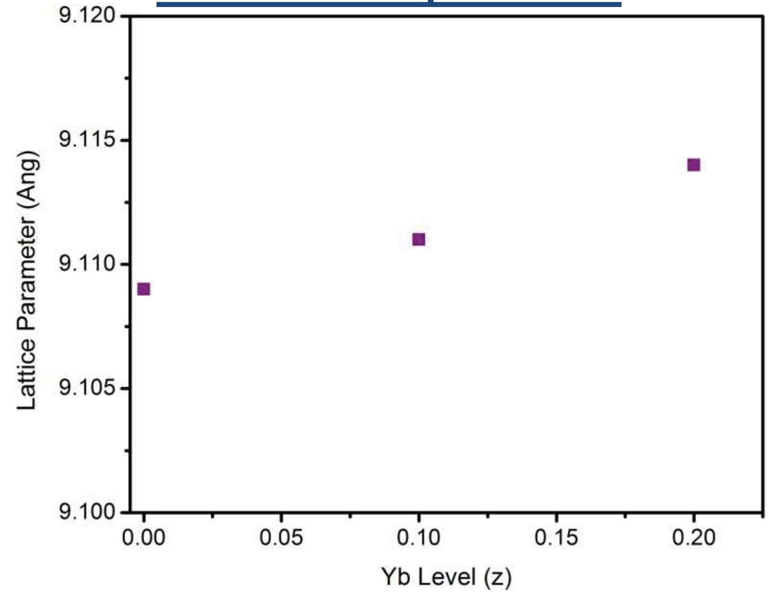
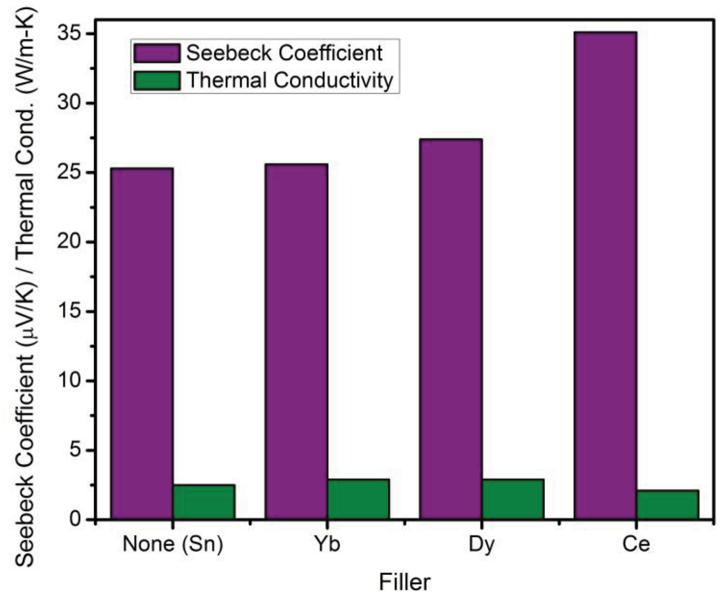
9	Ce	0.1	9.108	35.1	1036	2.1
10	Dy	0.1	9.114	27.4	681	2.9
11	Yb	0.05	9.019	23.3	618	2.6
12	Yb	0.1	9.111	25.6	592	2.9
13	Yb	0.2	9.114	-	-	-

Filled Properties





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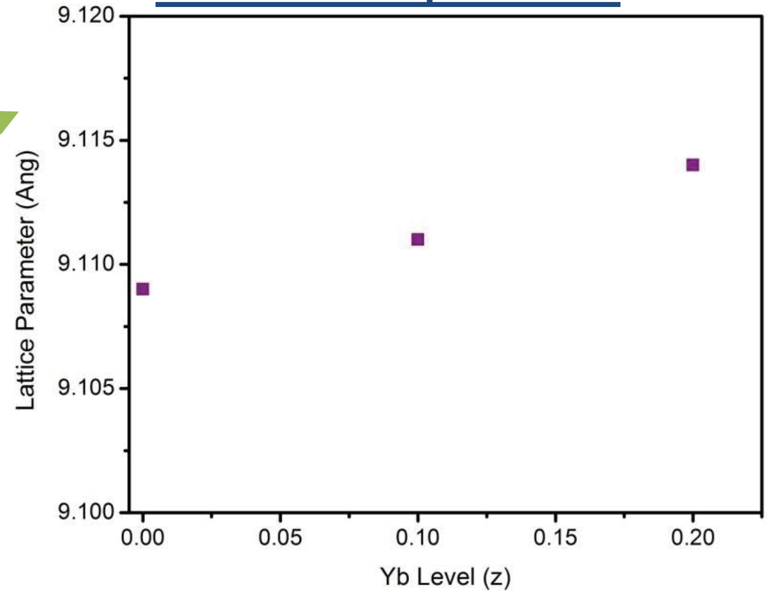
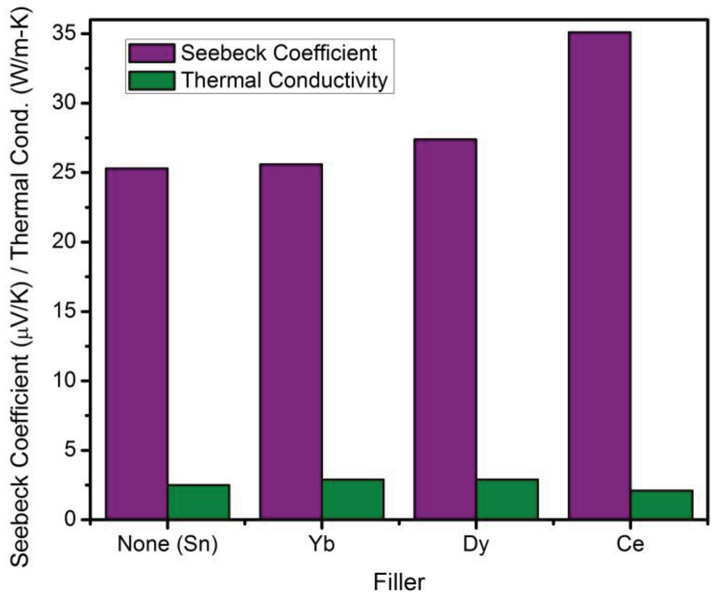
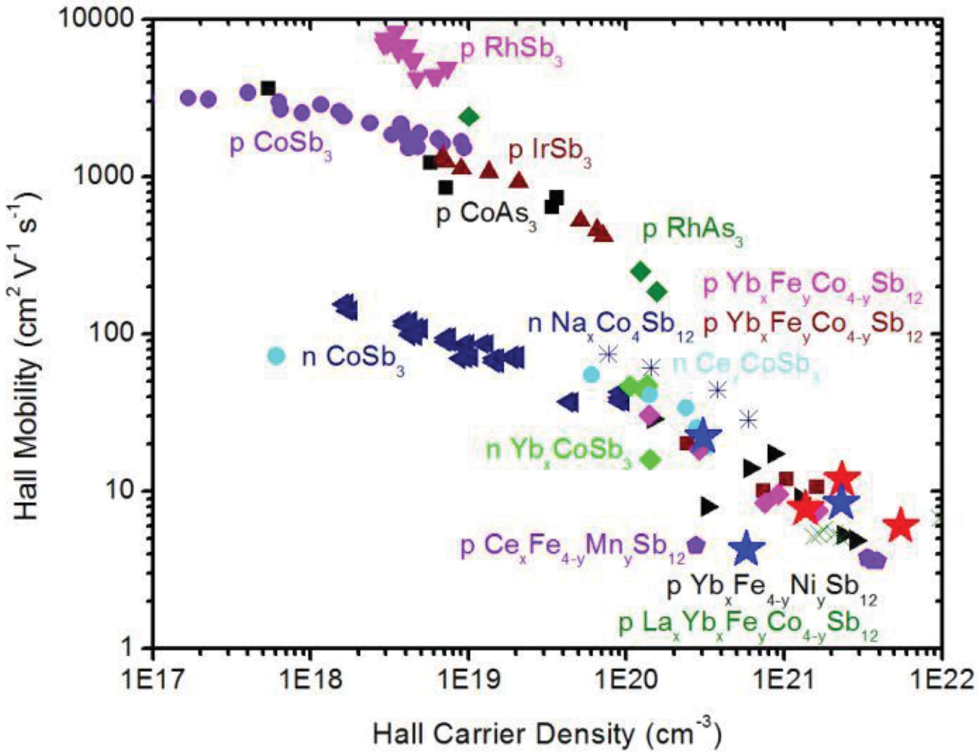
13	Yb	0.2	9.114	-	-	-

Filled Properties





Mobility and Carrier Comparison

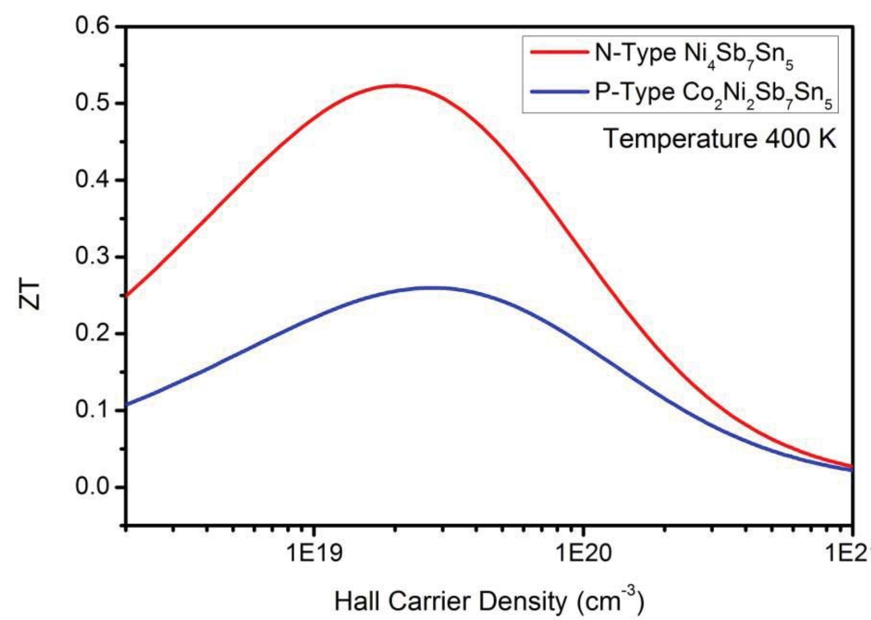


This Work

Yb_xCoSb_3: L. Fu et al. Intermetallics (2013)
Ce_xCoSb_3: D. Morelli et al. Phys. Rev. B (1997)
Others: J.-P. Fleurial et al. Proc. XVI ICT (1997)

S.P.B. Modeling

- Applied a single parabolic band model to the system
- Carrier mass (m/me)
  - N-Type: 5.48
  - P-Type: 1.48
- Optimal carrier density
  - N-Type: 2.1E19 cm^{-3}
  - P-Type: 2.7E19 cm^{-3}



Conclusion

- The $Co_xNi_{4-x}Sb_{12-y}Sn_y$ skutterudite can be synthesized from a melt/mill/hot press schedule.
- Both n- and p-type conduction can be achieved by Co doping.
- System exhibits low thermal conductivity, but also low Seebeck coefficient.
- Thermoelectric performance of the system is hindered by large carrier densities and low carrier mobilities.
- Fillers improve Seebeck coefficient, but do not reduce thermal conductivity.

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