

Filled $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ skutterudites: processing and thermoelectric properties

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NASA Cooperative Agreement: NNX08AB43A

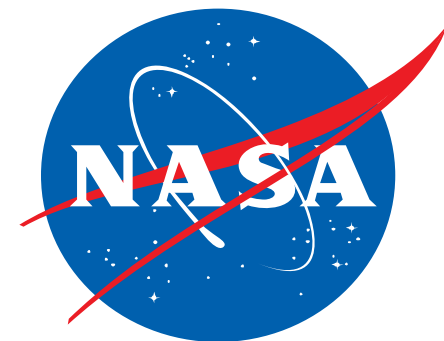
NASA/USRA Contract: 04555-004

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think beyond the possible

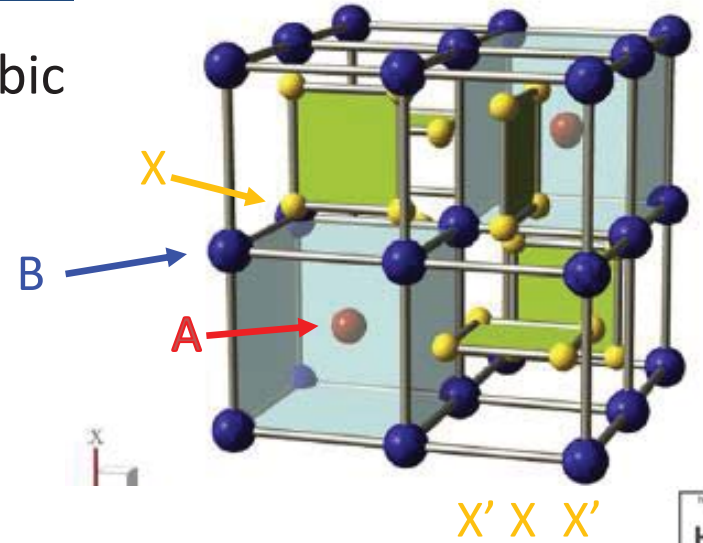


System Background

- 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

Body-centered cubic space group $Im\bar{3}$

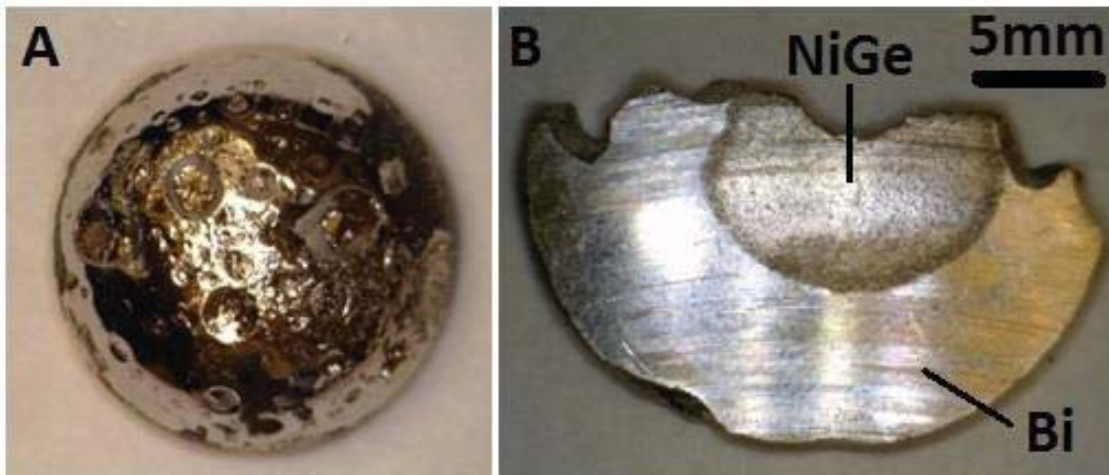


Eilertsen et al. Acta Mater. **60** (2012) 2178-2185.
Chi et al. Phys. Rev. B **86**: 195209 (2012).

Hydrogen 1 1.00794																	Helium 2 4.002602																												
Lithium 3 6.941	Beryllium 4 9.0122																	Boron 5 10.811	Carbon 6 12.011	Nitrogen 7 14.007	Oxygen 8 15.999	Fluorine 9 18.998	Neon 10 20.180																						
Sodium 11 22.990	Magnesium 12 24.305																	Aluminum 13 26.982	Silicon 14 28.086	Phosphorus 15 30.974	Sulfur 16 32.06	Chlorine 17 35.453	Argon 18 39.948																						
Potassium 19 39.098	Calcium 20 40.078	Scandium 21 44.956	Titanium 22 47.887	Vanadium 23 50.942	Chromium 24 51.996	Manganese 25 54.938	Iron 26 55.845	Cobalt 27 58.933	Nickel 28 58.693	Copper 29 63.546	Zinc 30 65.38	Gallium 31 69.723	Germanium 32 72.63	Arsenic 33 74.922	Selenium 34 78.96	Bromine 35 79.904	Krypton 36 83.80																												
Rubidium 37 85.468	Strontium 38 87.62	Yttrium 39 88.906	Zirconium 40 91.224	Niobium 41 92.906	Molybdenum 42 95.94	Technetium 43 98	Ruthenium 44 101.07	Rhodium 45 102.91	Palladium 46 106.42	Silver 47 107.87	Cadmium 48 112.41	Indium 49 114.82	Sn 50 118.71	Sb 51 121.76	Te 52 127.6	Iodine 53 126.905	Xenon 54 131.29																												
Cesium 55 132.91	Barium 56 137.33	* 57-70	Lanthanum 57 138.905	Hafnium 72 178.49	Tantalum 73 180.948	Tungsten 74 183.84	Rhenium 75 186.21	Osmium 76 190.23	Iridium 77 192.22	Pt 78 195.08	Au 79 196.97	Hg 80 200.59	Tl 81 204.38	Pb 82 207.2	Bi 83 208.98	Po 84	At 85	Rn 86																											
Francium 87 223	Radium 88 226	* * 89-102	Actinium 89 227	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uun 110	Uuu 111	Uub 112	Uuq 114																																
<table border="1"> <tr> <td>La 57 138.91</td> <td>Ce 58 140.12</td> <td>Pr 59 140.91</td> <td>Nd 60 144.24</td> <td>Pm 61 145</td> <td>Sm 62 150.36</td> <td>Eu 63 151.96</td> <td>Gd 64 157.25</td> <td>Tb 65 158.93</td> <td>Dy 66 162.50</td> <td>Ho 67 164.93</td> <td>Er 68 167.26</td> <td>Tm 69 168.93</td> <td>Yb 70 173.04</td> </tr> <tr> <td>Ac 89</td> <td>Th 90 232.04</td> <td>Pa 91 231.04</td> <td>U 92 238.03</td> <td>Np 93</td> <td>Pu 94 239</td> <td>Am 95 243</td> <td>Cm 96</td> <td>Bk 97</td> <td>Cf 98</td> <td>Es 99</td> <td>Fm 100</td> <td>Md 101</td> <td>No 102</td> </tr> </table>																		La 57 138.91	Ce 58 140.12	Pr 59 140.91	Nd 60 144.24	Pm 61 145	Sm 62 150.36	Eu 63 151.96	Gd 64 157.25	Tb 65 158.93	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.93	Yb 70 173.04	Ac 89	Th 90 232.04	Pa 91 231.04	U 92 238.03	Np 93	Pu 94 239	Am 95 243	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102
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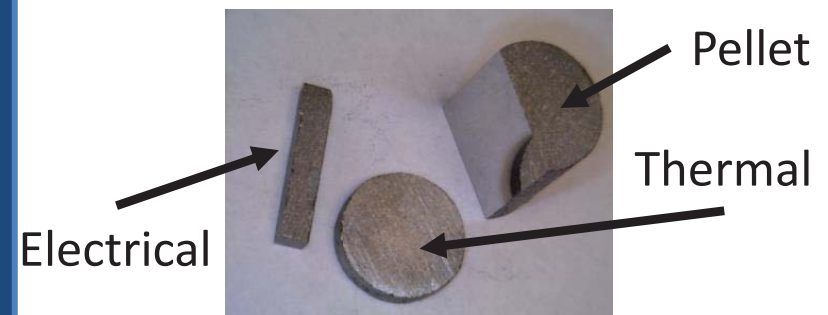
Systems Investigated

- Ternary systems studied with combination of solidification and powder processing techniques.
- $\text{Ni}_4\text{Bi}_8\text{Ge}_4$
 - Shown below, skutterudite phase not obtained.
- $\text{Ni}_4\text{Sb}_8\text{Ge}_4$
 - Skutterudite phase not obtained.
- $\text{Ni}_4\text{Sb}_8\text{Sn}_4$



Objectives

- Focus on finding a p-type skutterudite with improved ZT.
- Study behavior of the skutterudite $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$.
 - Grytsiv et. al has reported a $\text{Ni}_4\text{Sb}_8\text{Sn}_4$ 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.



S

- Ternary system of solidification technique

- $\text{Ni}_4\text{Bi}_8\text{Ge}_4$
 - Showed to be obtained

- $\text{Ni}_4\text{Sb}_8\text{Ge}_4$
 - Skutterudite

- $\text{Ni}_4\text{Sb}_8\text{Sn}_4$



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



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

S

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obtai

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System

- Ternary system of solidification technique
- $\text{Ni}_4\text{Bi}_8\text{Ge}_4$
 - Show
- $\text{Ni}_4\text{Sb}_8\text{Ge}_4$
 - Skutterudite
- $\text{Ni}_4\text{Sb}_8\text{Sn}_4$



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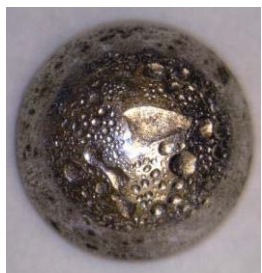
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ICP analysis of an ingot

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

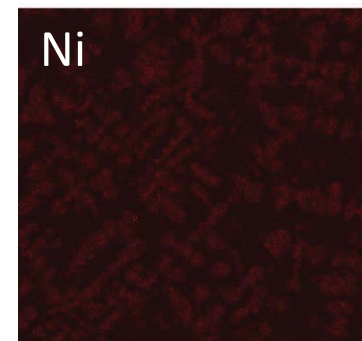
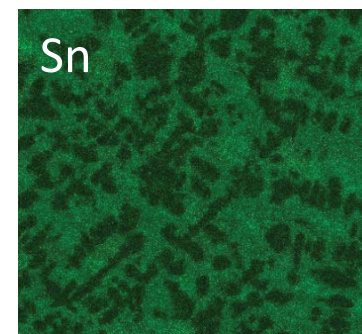
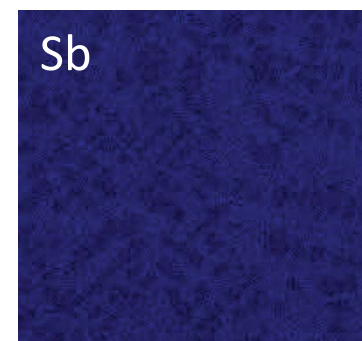
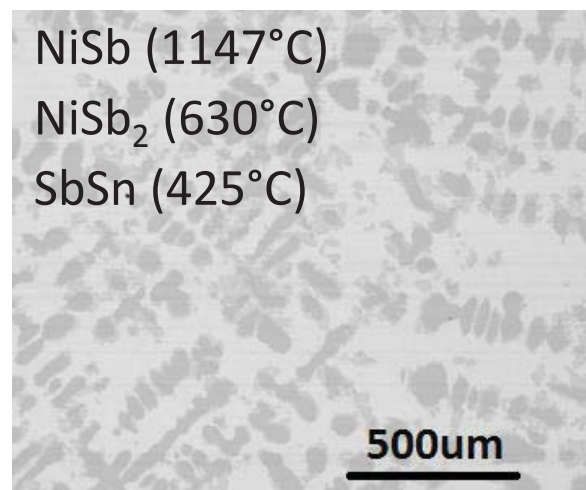


Target



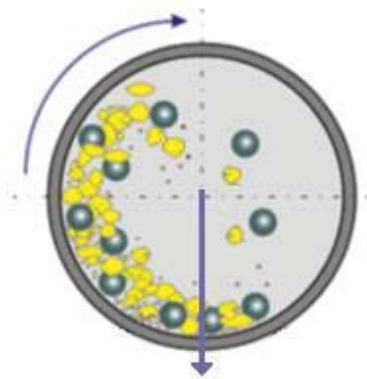
	at%	at%	at%	at%
Co	9.4	9.1	7.3	9.0
Ni	15.6	14.9	13.7	14.6
Sb	43.7	42.4	43.7	44.1
Sn	31.2	33.5	35.3	32.2
Ca	0	2e-4	7e-4	7e-4
Mg	0	1e-4	2e-4	2e-4
Na	0	3e-3	4e-3	4e-3

EDS map of an ingot

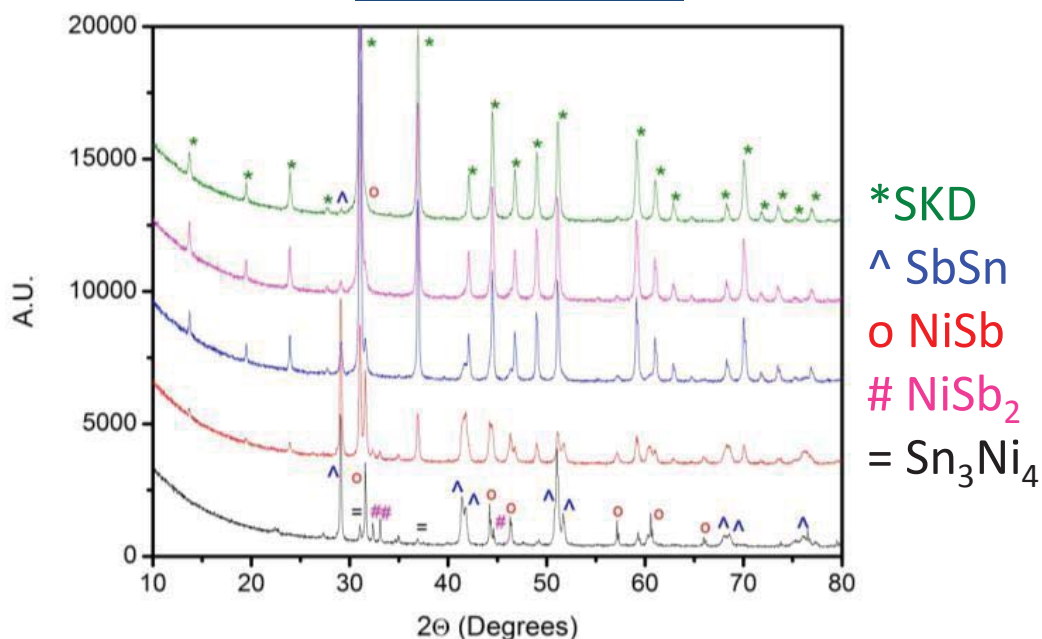


Milling Details

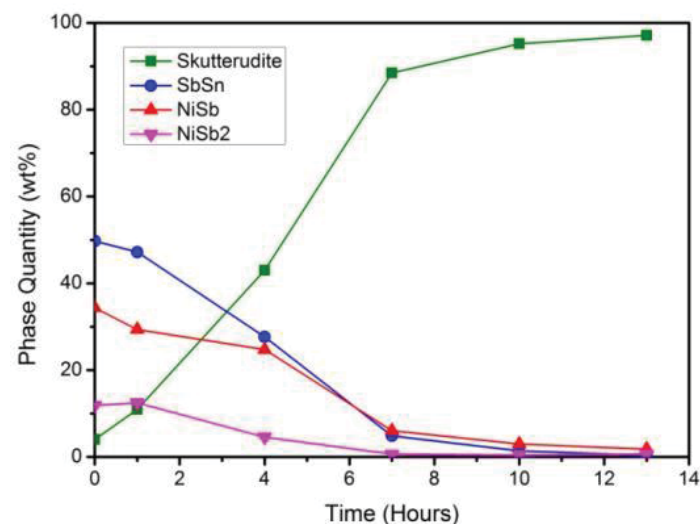
- Planetary mill
- 550 rpm
- Ball to powder weight ratio 3.8
- Ar atmosphere



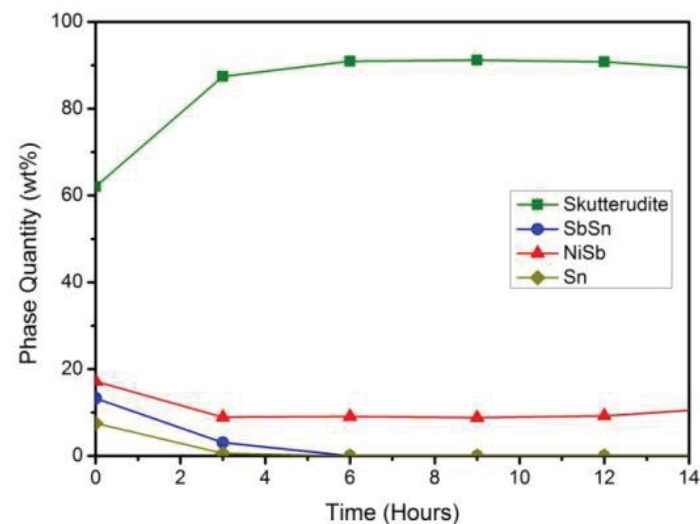
Milling XRD



Sample 1 Ni₄Sb₈Sn₄ Milling



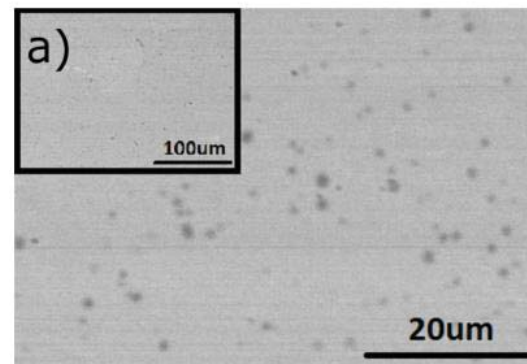
Sample 4 Co₁Ni₃Sb₇Sn₅ Milling



Hot Pressed SEM

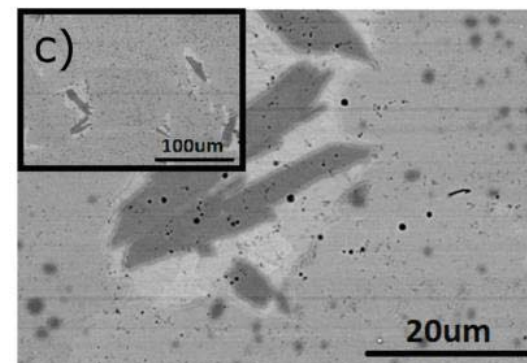
Sample 1 $\text{Ni}_4\text{Sb}_8\text{Sn}_4$

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



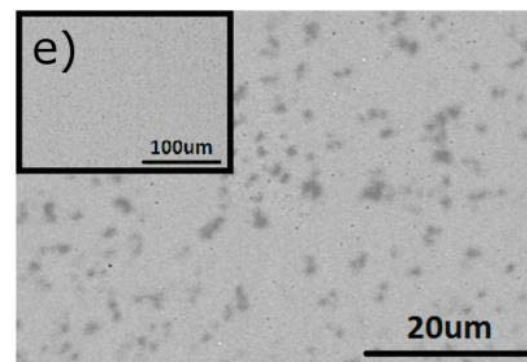
Sample 2 $\text{Ni}_4\text{Sb}_7\text{Sn}_5$

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



Sample 4 $\text{Co}_1\text{Ni}_3\text{Sb}_7\text{Sn}_5$

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



Rietveld Refinement

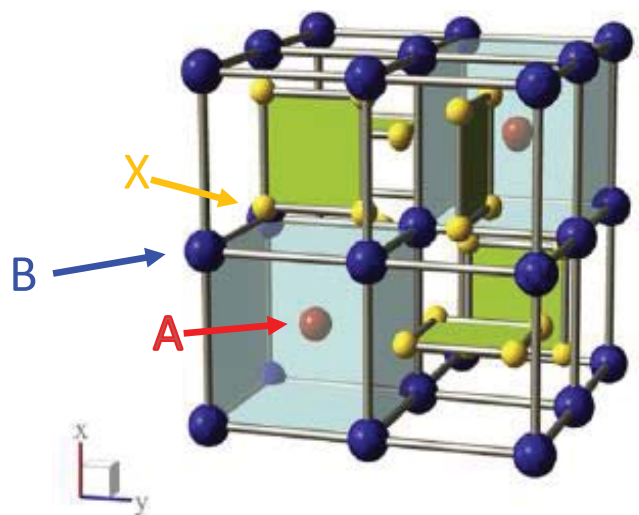
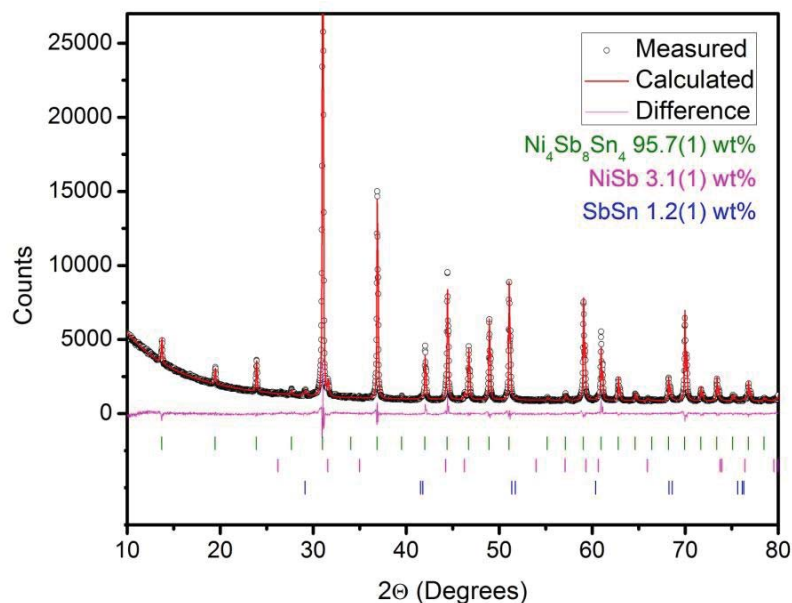


FIGURE: Eilertsen et al. Acta Mater. **60** (2012) 2178-2185.

Hot Pressed Structure Refinement

Sample #	Skutterudite	Lattice (Å)	SKD (wt%)
1	$\text{Sn}_{0.2}\text{Co}_{0.0}\text{Ni}_{4.0}\text{Sb}_{8.5}\text{Sn}_{4.4}$	9.113	96.65
2	$\text{Sn}_{0.3}\text{Co}_{0.0}\text{Ni}_{4.0}\text{Sb}_{7.9}\text{Sn}_{5.1}$	9.128	87.38
3	$\text{Sn}_{0.3}\text{Co}_{0.6}\text{Ni}_{3.4}\text{Sb}_{7.2}\text{Sn}_{4.7}$	9.126	94.97
4	$\text{Sn}_{0.3}\text{Co}_{1.2}\text{Ni}_{2.8}\text{Sb}_{8.3}\text{Sn}_{5.4}$	9.118	89.25
5	$\text{Sn}_{0.3}\text{Co}_{1.5}\text{Ni}_{2.5}\text{Sb}_{7.0}\text{Sn}_{4.7}$	9.123	91.33
6	$\text{Sn}_{0.3}\text{Co}_{2.4}\text{Ni}_{1.6}\text{Sb}_{9.4}\text{Sn}_{5.8}$	9.104	80.08
7	$\text{Sn}_{0.3}\text{Co}_{2.1}\text{Ni}_{1.9}\text{Sb}_{9.1}\text{Sn}_{3.7}$	9.109	93.64
8	$\text{Sn}_{0.2}\text{Co}_{2.1}\text{Ni}_{1.9}\text{Sb}_{9.0}\text{Sn}_{2.6}$	9.087	98.20

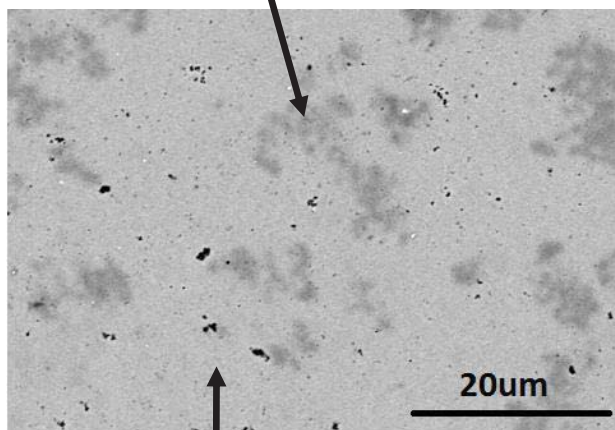
Introduction

Pressed $\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$

Density 7.64 g/cm^3
99%

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	82.6
Ni_3Sn_4	8.7
Sn	6.2

Ni_3Sn_4 (230°C)



$\text{Sn}_{0.5}\text{Co}_{2.4}\text{Ni}_{1.6}\text{Sb}_{9.7}\text{Sn}_{5.7}$

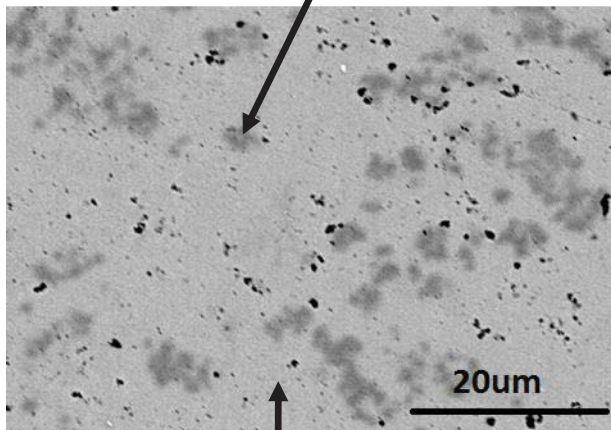
Processing

200°C Anneal 72 Hrs

Density 7.25 g/cm^3
95%

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	80.0
Ni_3Sn_4	11.9
Sn	7.6

Ni_3Sn_4 (230°C)



$\text{Sn}_{0.5}\text{Co}_{2.4}\text{Ni}_{1.6}\text{Sb}_{9.7}\text{Sn}_{5.7}$

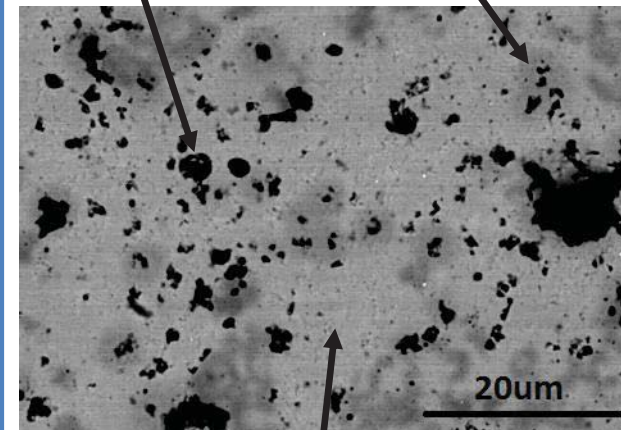
Properties

400°C Anneal 72 Hrs

Density 6.75 g/cm^3
88%

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	73.6
Ni_3Sn_4	14.7
Sn	10.0

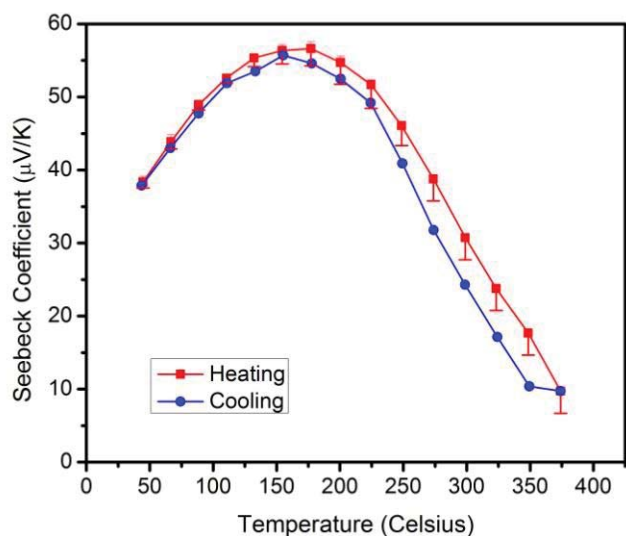
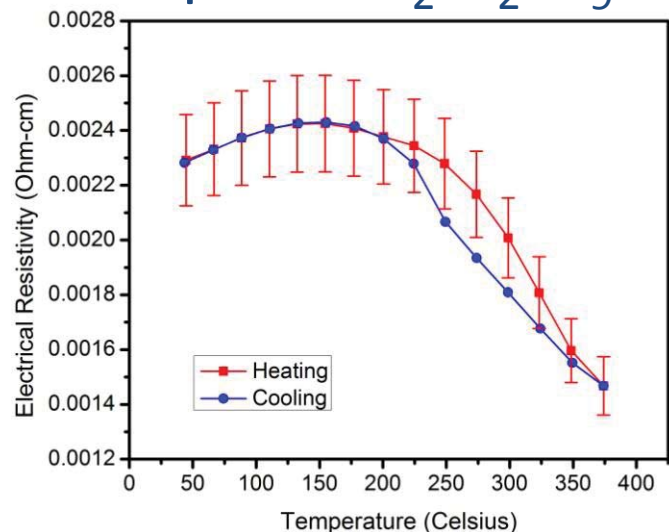
Porosity Ni_3Sn_4 (230°C)



$\text{Sn}_{0.5}\text{Co}_{2.4}\text{Ni}_{1.6}\text{Sb}_{9.7}\text{Sn}_{5.7}$

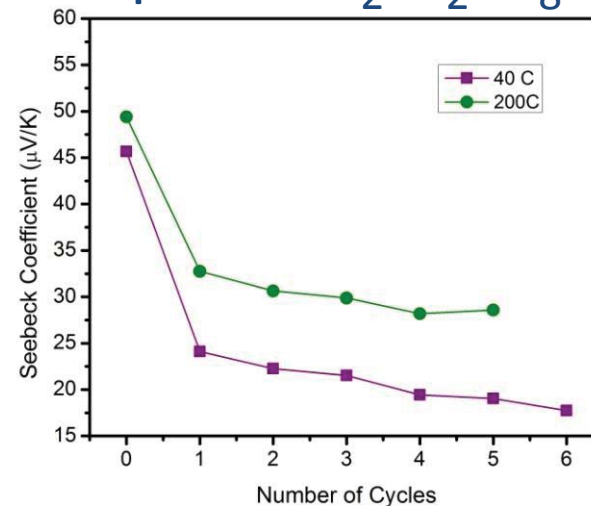
Electrical Hysteresis

Sample 8 $\text{Co}_2\text{Ni}_2\text{Sb}_9\text{Sn}_3$

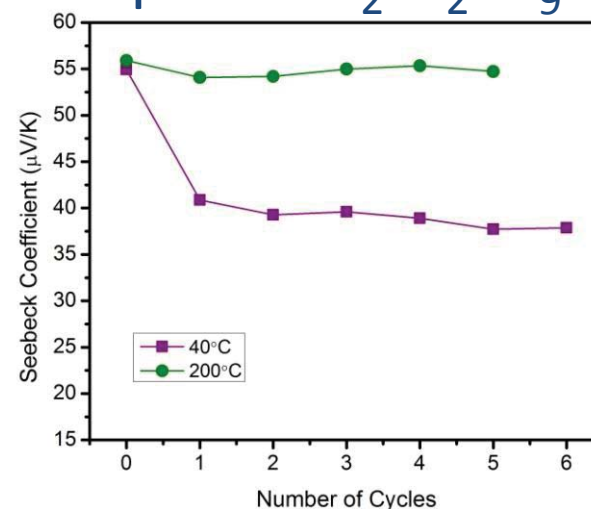


Sample Stability

Sample 7 $\text{Co}_2\text{Ni}_2\text{Sb}_8\text{Sn}_4$



Sample 8 $\text{Co}_2\text{Ni}_2\text{Sb}_9\text{Sn}_3$

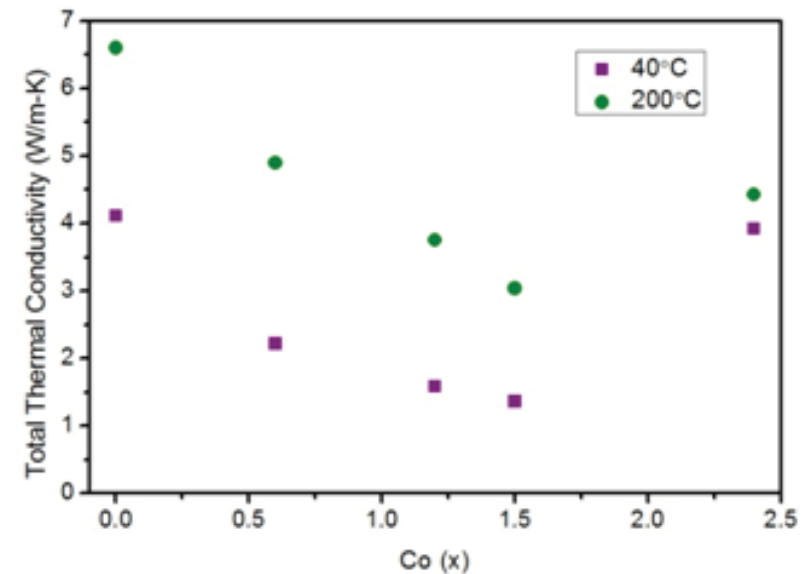
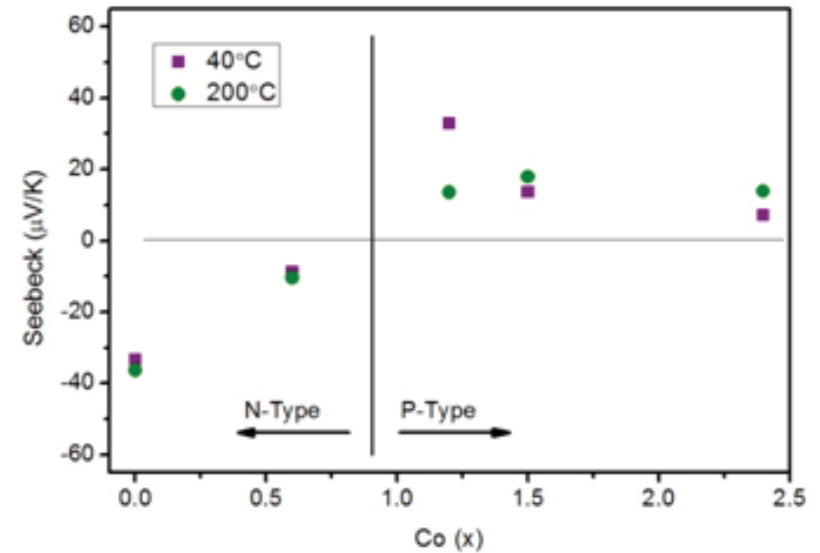


Transport Properties- Unfilled (40°C)



Sample #	Co (x)	Sn (y)	Lattice Parameter (Å)	Seebeck Coefficient ($\mu\text{V}/\text{K}$)	Electrical Resistivity ($\mu\text{Ohm} - \text{cm}$)	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

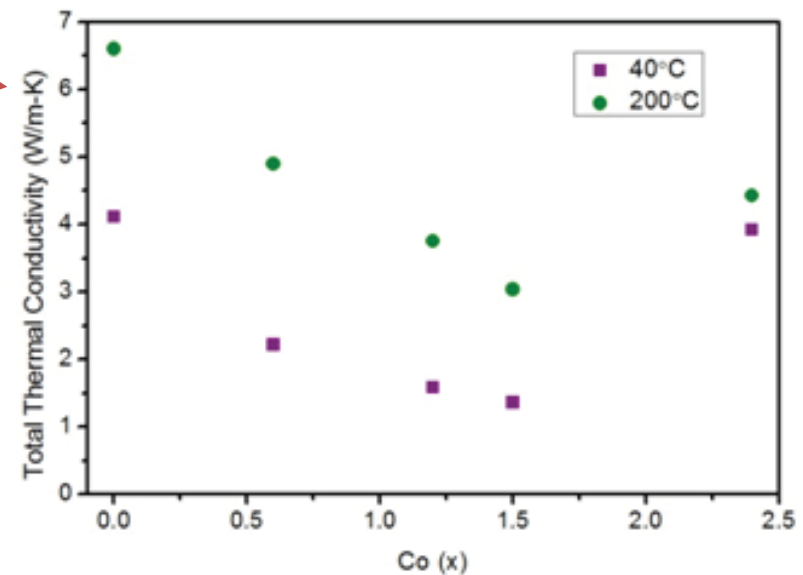
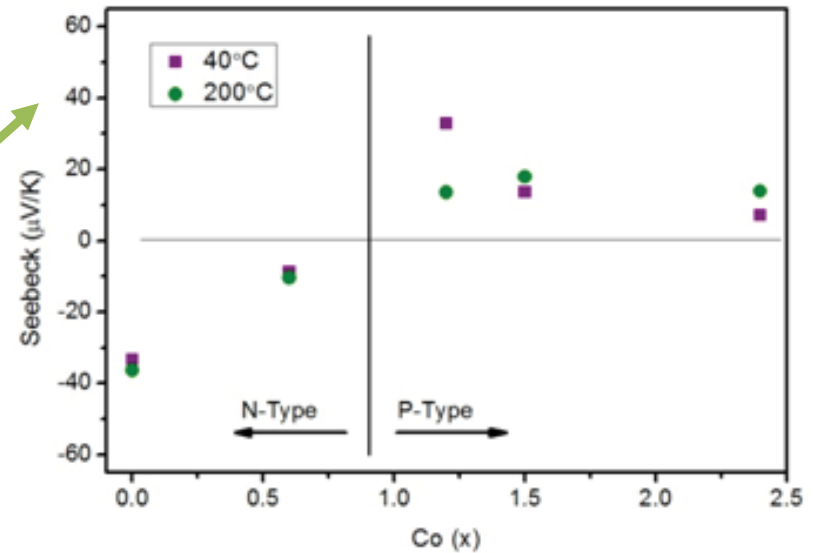


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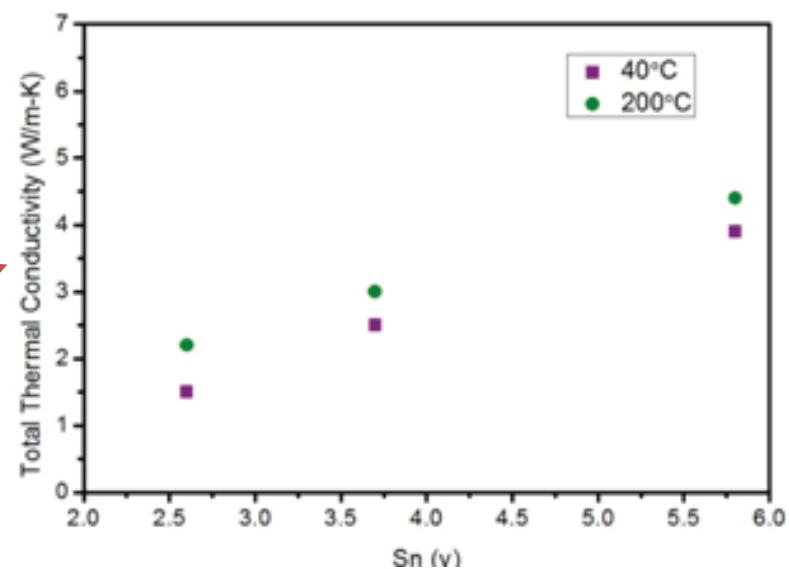
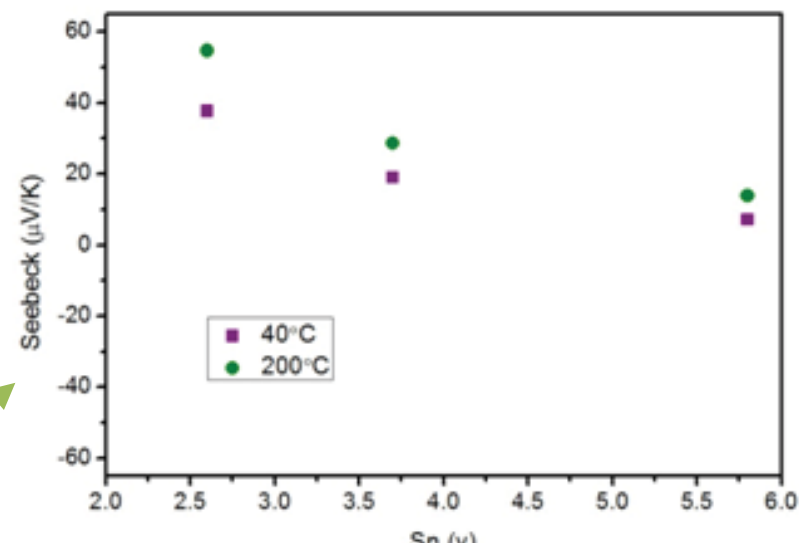


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Sn (y) Study

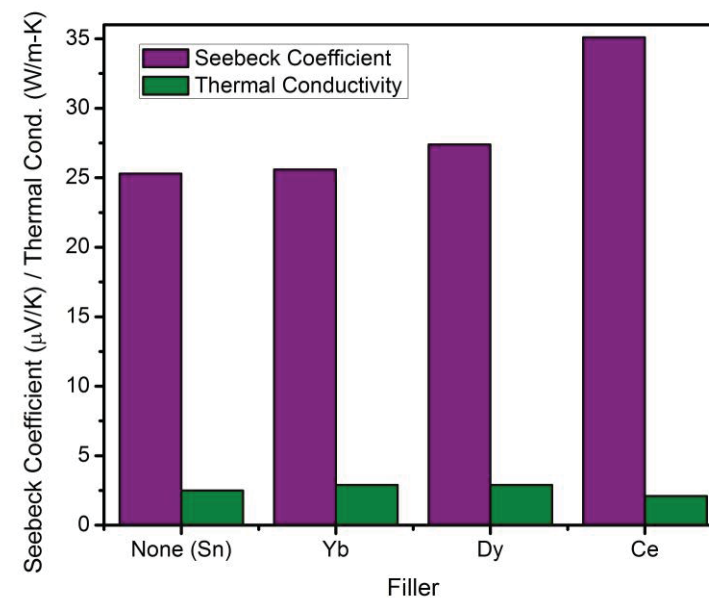
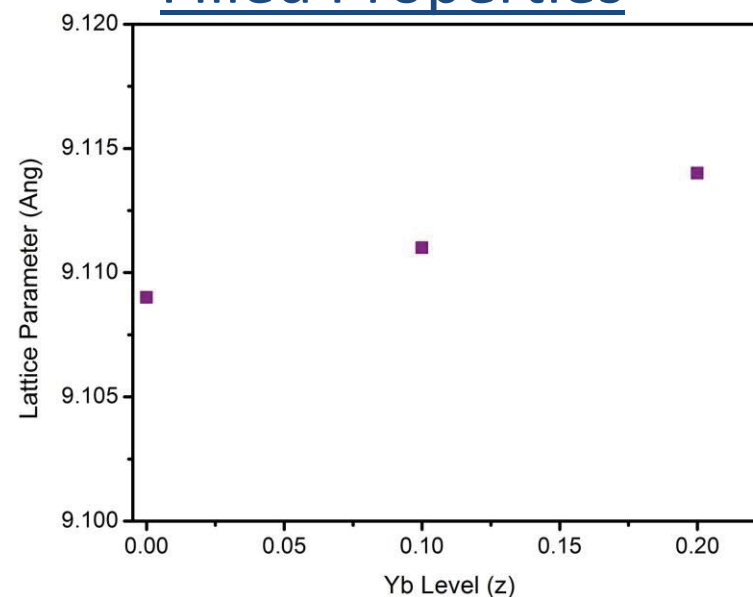


Transport Properties- Filled (40°C)



Sample #	Filler A	Level (z)	Lattice Parameter (Å)	Seebeck Coefficient ($\mu\text{V}/\text{K}$)	Electrical Resistivity ($\mu\text{Ohm} - \text{cm}$)	Thermal Conductivity (W/m-K)
7	N/A	0.0	9.109	25.3	659	2.5
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

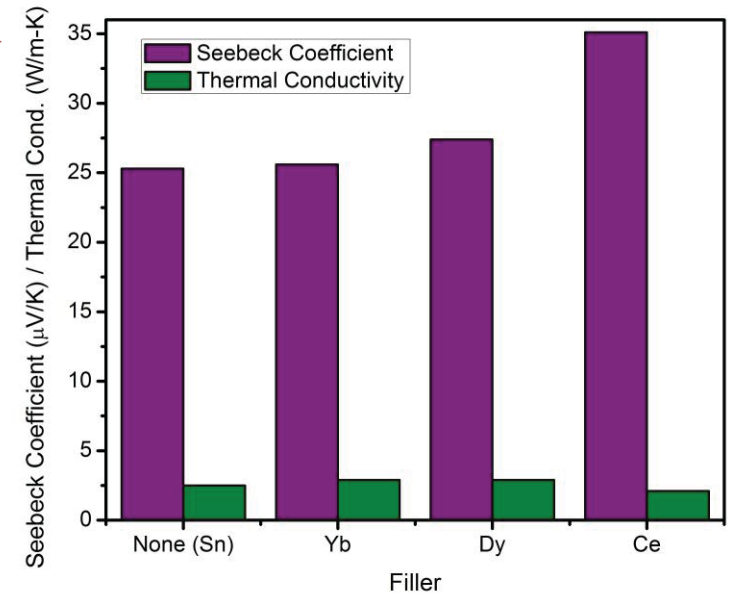
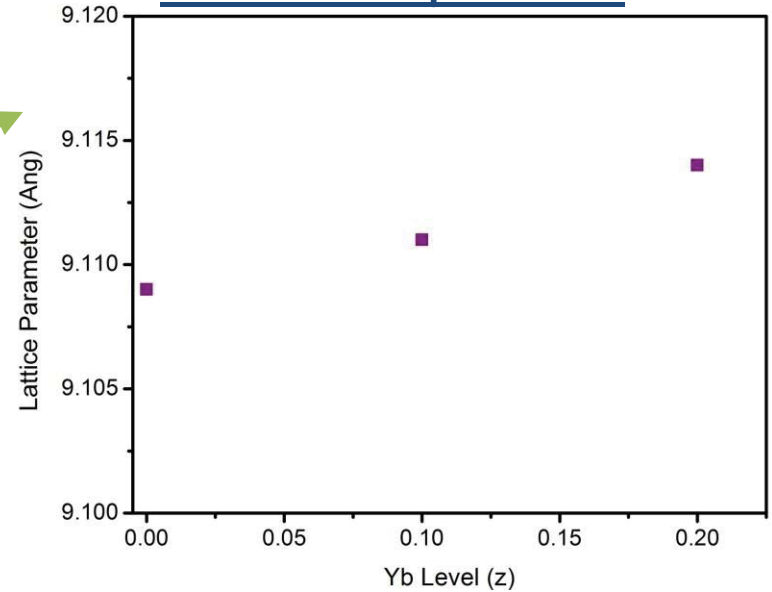


Transport Properties- Filled (40°C)

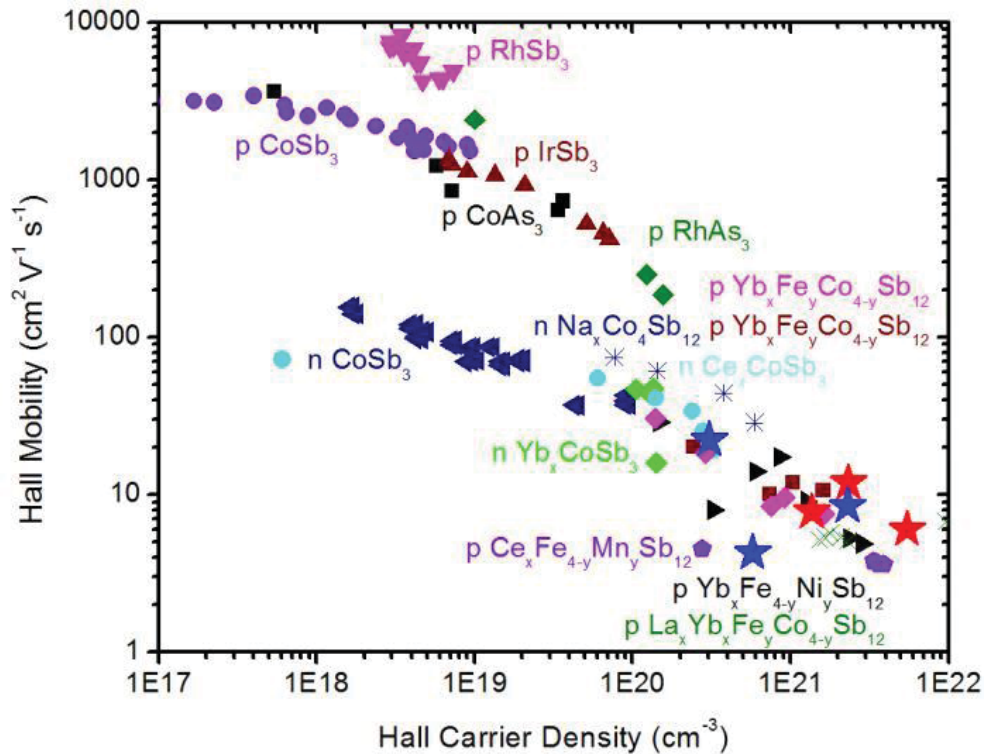


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Filled Properties



Mobility and Carrier Comparison



★ ★ This Work

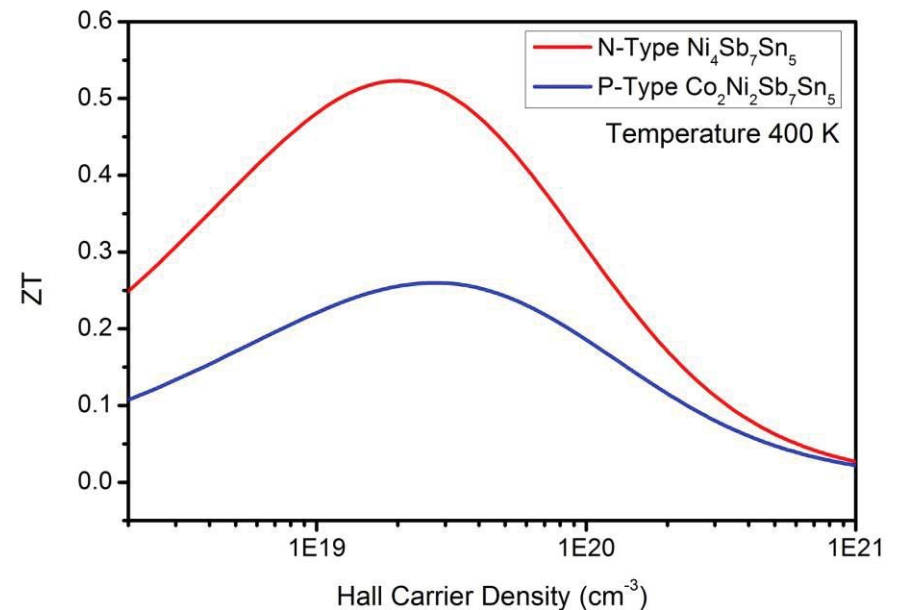
Yb_xCoSb_3 : L. Fu et al. Intermetallics (2013)

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/m_e)
 - N-Type: 5.48
 - P-Type: 1.48
- Optimal carrier density
 - N-Type: $2.1\text{E}19 \text{ cm}^{-3}$
 - P-Type: $2.7\text{E}19 \text{ cm}^{-3}$



Conclusion

- The $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ 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.

Acknowledgements

Tom Sabo, Ray Babuder, Ben Kowalski, Clayton Cross, Kerem Sayir

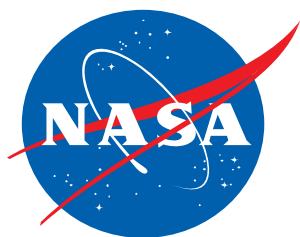
NASA Glenn Research Center

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