$Co_xNi_{4-x}Sb_{12-y}Sn_y$ Ternary Skutterudites: Processing and Thermoelectric Properties

Jon Mackey
Mechanical Engineering,
University of Akron

Alp Sehirlioglu
Materials Science and Engineering,
Case Western Reserve University

Fred Dynys
NASA Glenn Research Center

NASA Cooperative Agreement: NNX08AB43A
NASA/USRA Contract: 04555-004

Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p-type skutterudite with improved ZT
- Study behavior of the skutterudite $Co_xNi_{4-x}Sb_{12-y}Sn_y$

Ternary SKD Systems

AB_4X_{12}

$AB_4X_8X'_4$

A={La,Ce,Nb,Yb,Ca,…}

B={Fe,Co,Ni,Rh,Ir,…}

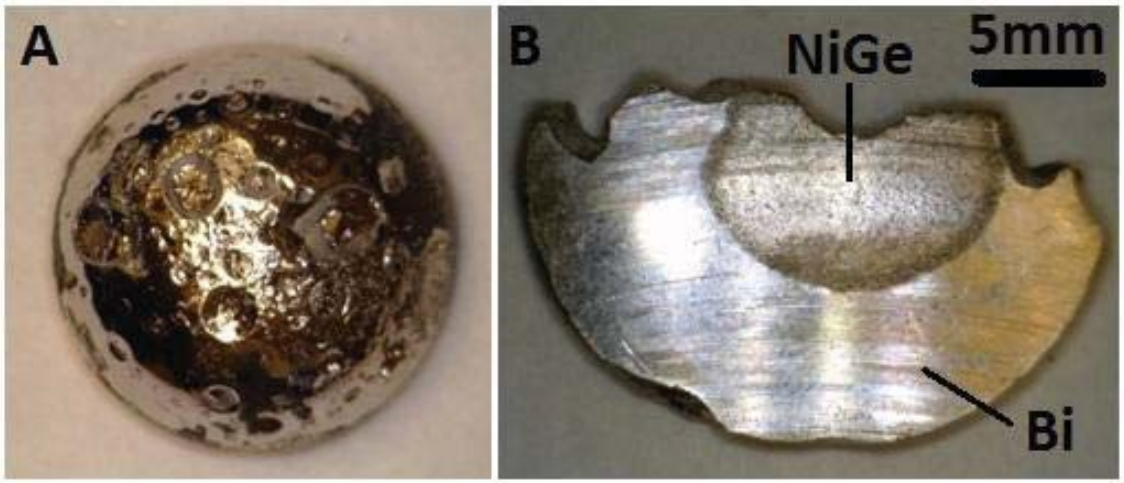
X={P,As,Sb,Bi}

X'={Ge,Sn}

Bauer et. al Acta Phys. Polon. B **34** (2003).

Systems Investigated

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



Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p
  skutterudite with im
- Study behavior of th
  skutterudite Co_xNi_{4-x}

Ternary SKD Sys

AB_4X_{12}

$AB_4X_8X'_4$

A={La,Ce,Nb,Yb,Ca

B={Fe,Co,Ni,Rh,Ir

X={P,As,Sb,Bi}

X'={Ge,Sn}

Bauer et. al Acta Phys. Polon. B **34** (2003).

Systems Investigated

- Ternary systems studied with combination of solidification and powder processing

utterudite phase was

se not obtained

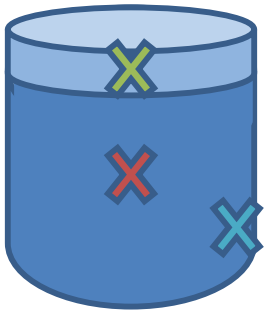
$Co_xNi_{4-x}Sb_{12-y}Sn_y$

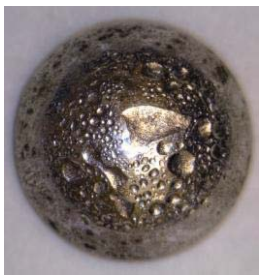
- Grytsiv et. al has reported a $Ni_4Sb_8Sn_4$ skutterudite system
- Interested in obtaining p-type behavior
- Parameters of study:
  - x= {0,0.5,1,1.5,2}
  - y={4,5}
- Samples created from a melt/mill/hot press procedure

Grytsiv et. al J. Phys.: Condens. Matter **14** (2002).

ICP analysis of an ingot

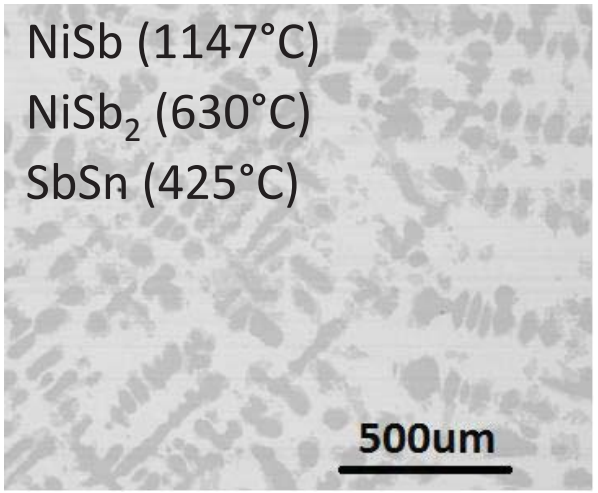
- 2 Hr @ 1100°C (+20,-10°C /min)
- Silica crucible in He atmosphere
- <1% wt loss

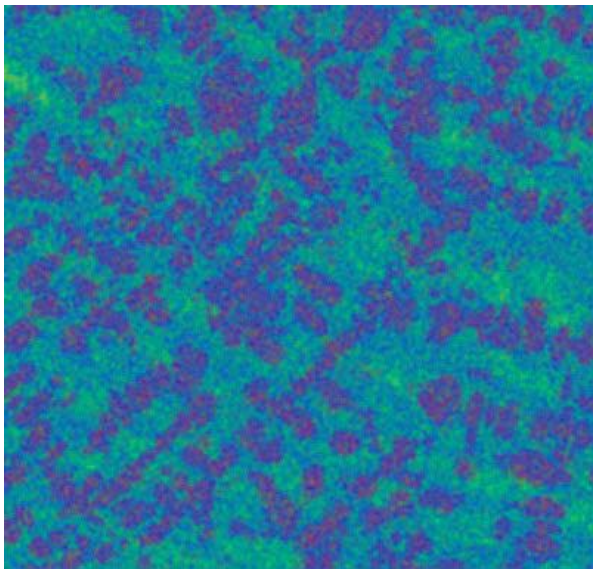


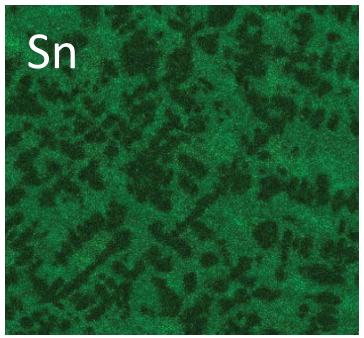


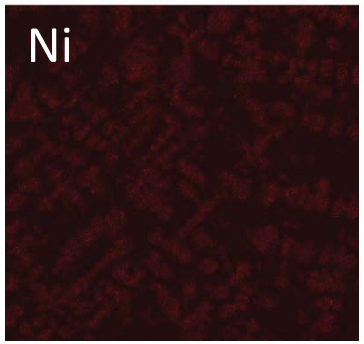
	at%	at%	at%	at%
Co	**9.4**	9.1	7.3	9.0
Ni	**15.6**	14.9	13.7	14.6
Sb	**43.7**	42.4	43.7	44.1
Sn	**31.2**	33.5	35.3	32.2
Ca	**0**	2e-4	7e-4	7e-4
Mg	**0**	1e-4	2e-4	2e-4
Na	**0**	3e-3	4e-3	4e-3

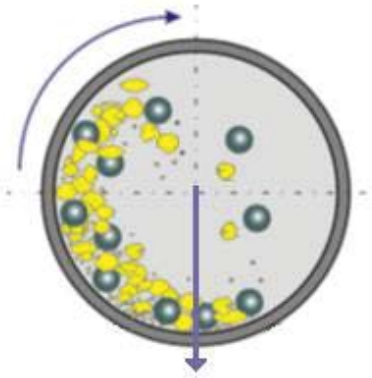
EDS map of an ingot







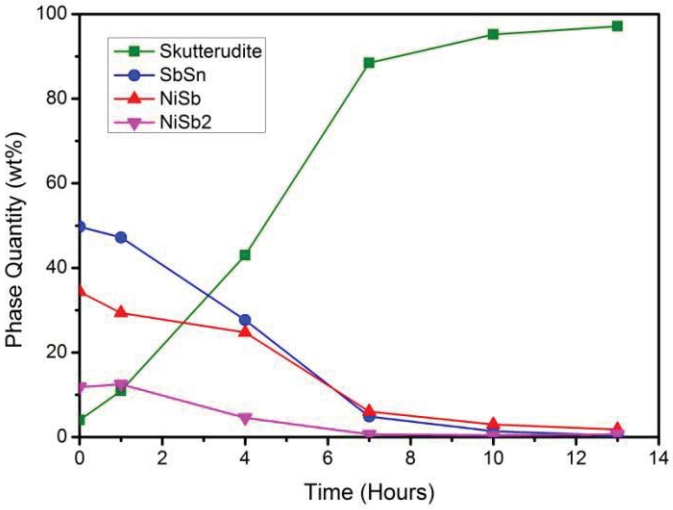


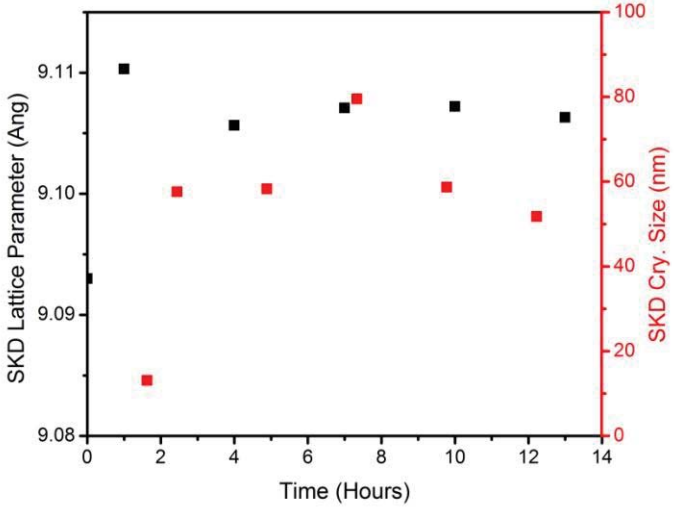


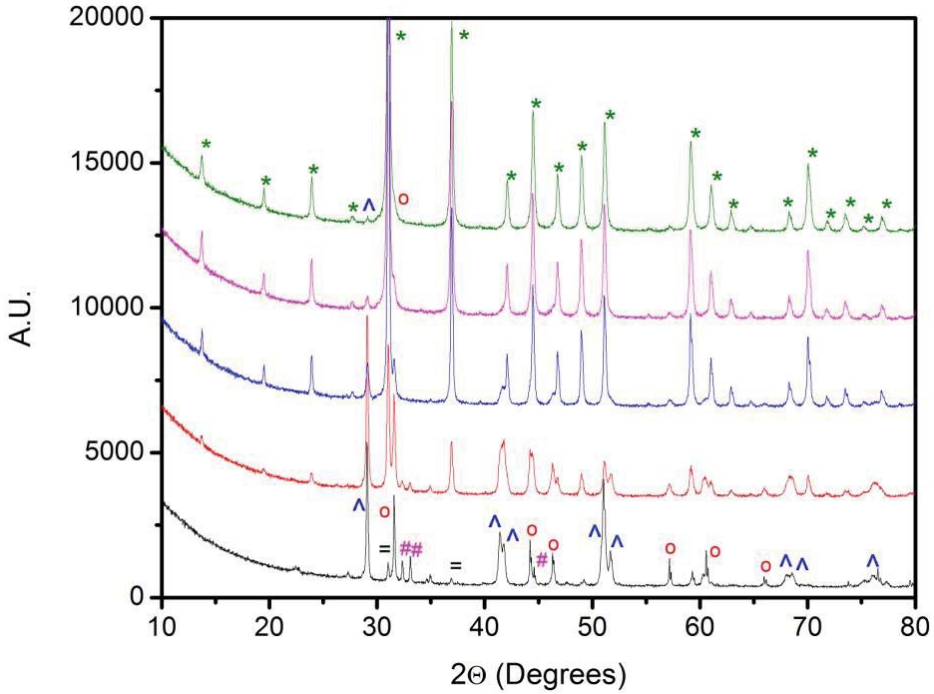
Milling Details

- Ingots crushed by hand
- Planetary mill
  - 550 rpm
  - Ball to powder weight ratio 3.8
  - Ar atmosphere

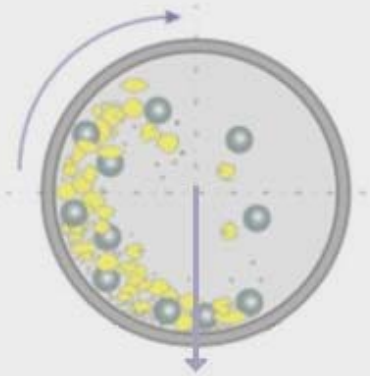
$Ni_4Sb_8Sn_4$ Milling

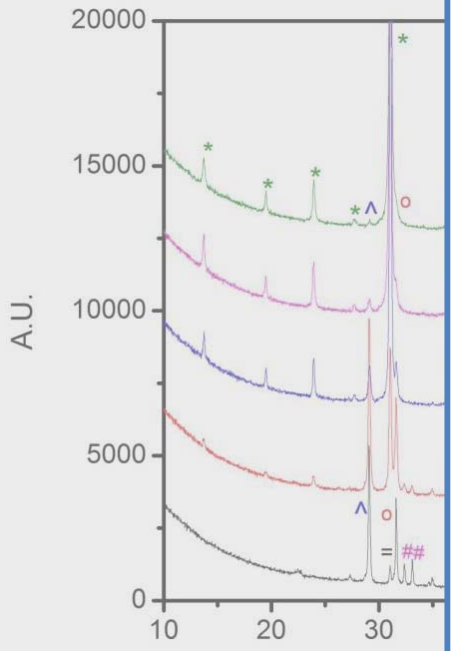




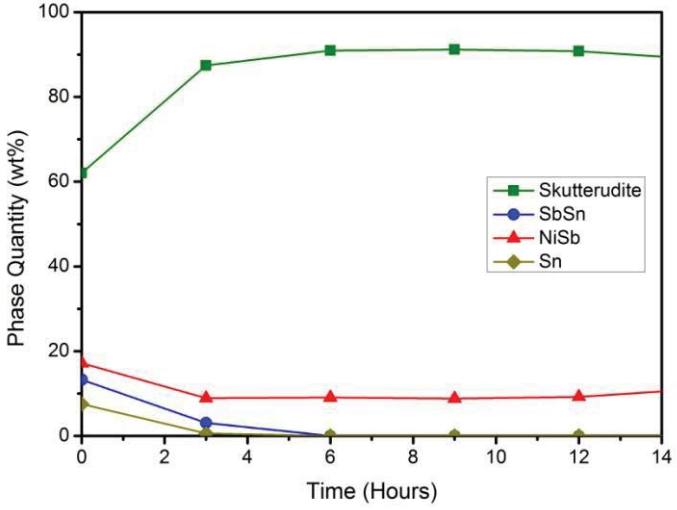


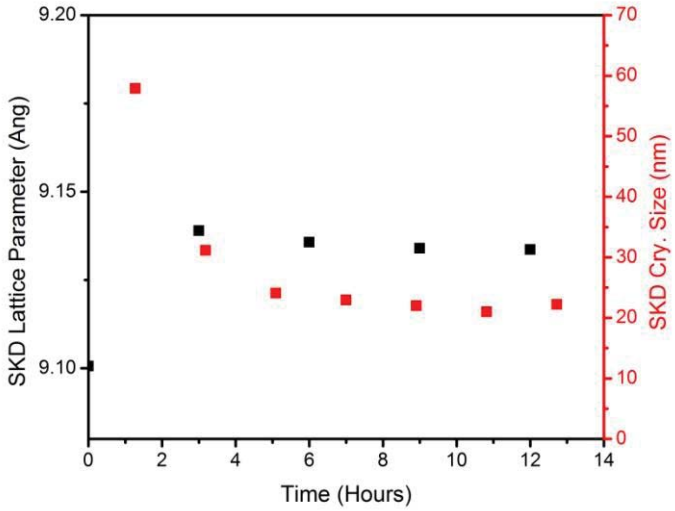
*SKD
^ SbSn
o NiSb
$NiSb_2$
= Sn_3Ni_4



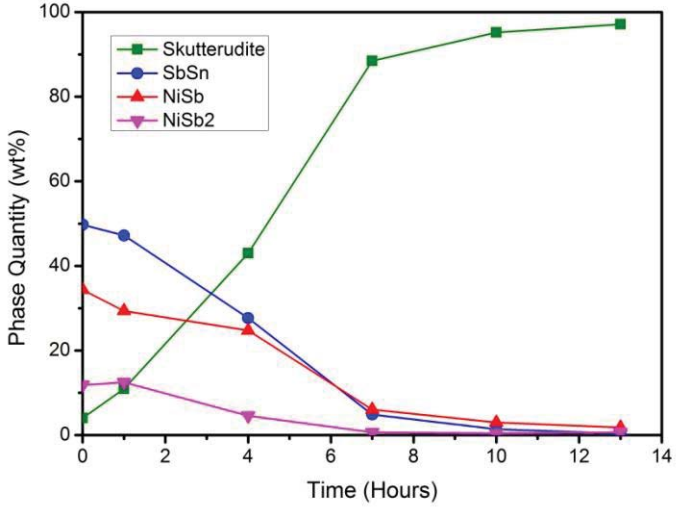


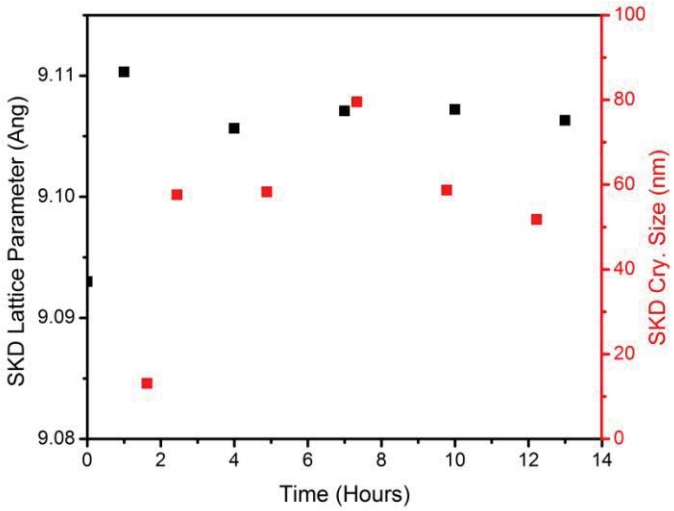
$Co_1Ni_3Sb_7Sn_5$ Milling





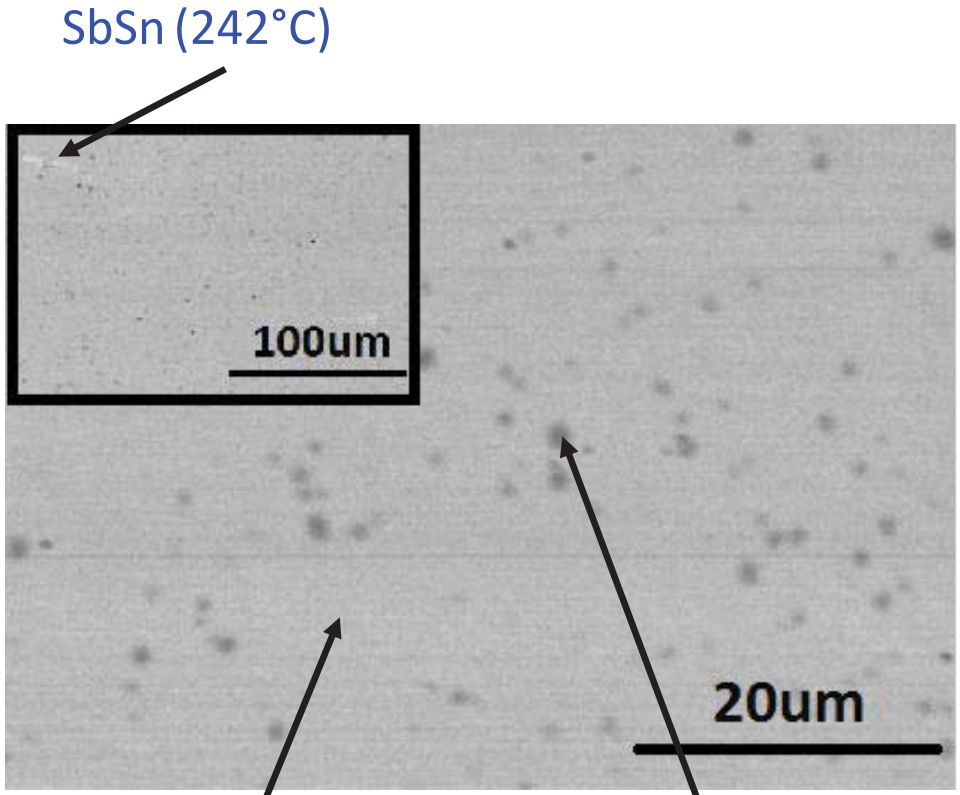
$Ni_4Sb_8Sn_4$ Milling



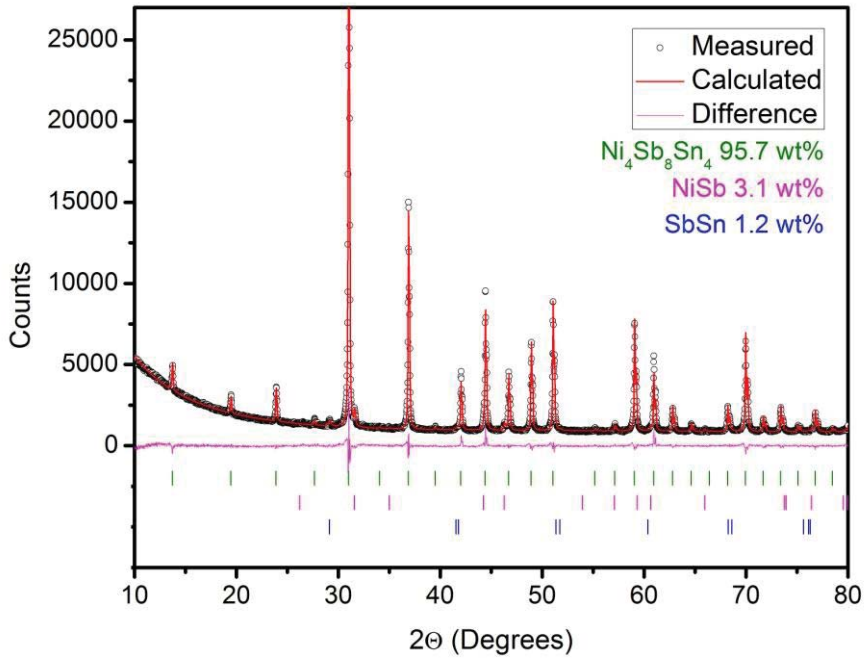


SEM/EPMA on Hot Pressed

Nominal Composition $Ni_4Sb_8Sn_4$

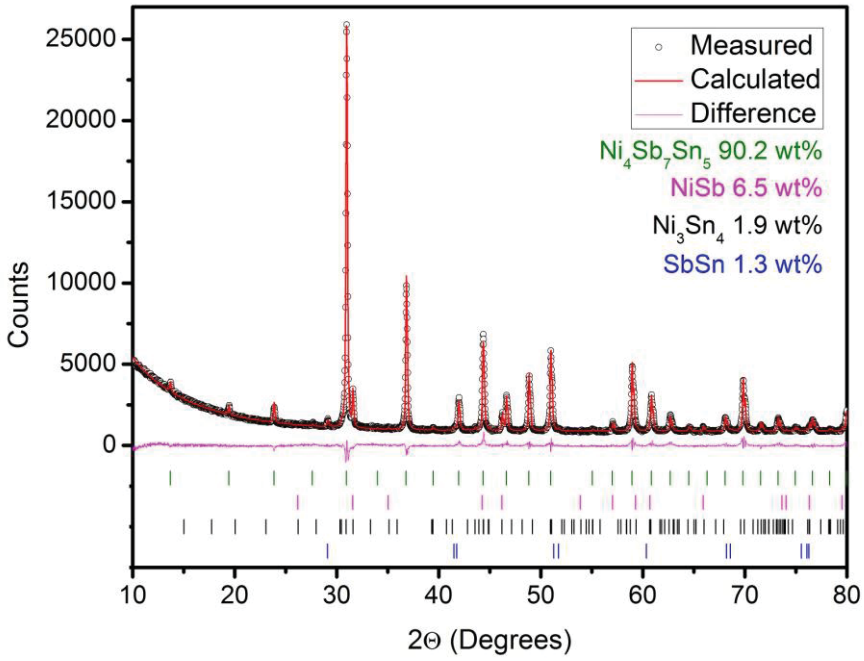


Rietveld on Hot Pressed



Parameter	Value
GOF	1.78
Lattice (Å)	9.115
Y	0.158
Z	0.336
2a Occ. (Sn)	0.27
24g Occ. (Sb+Sn)	0.99

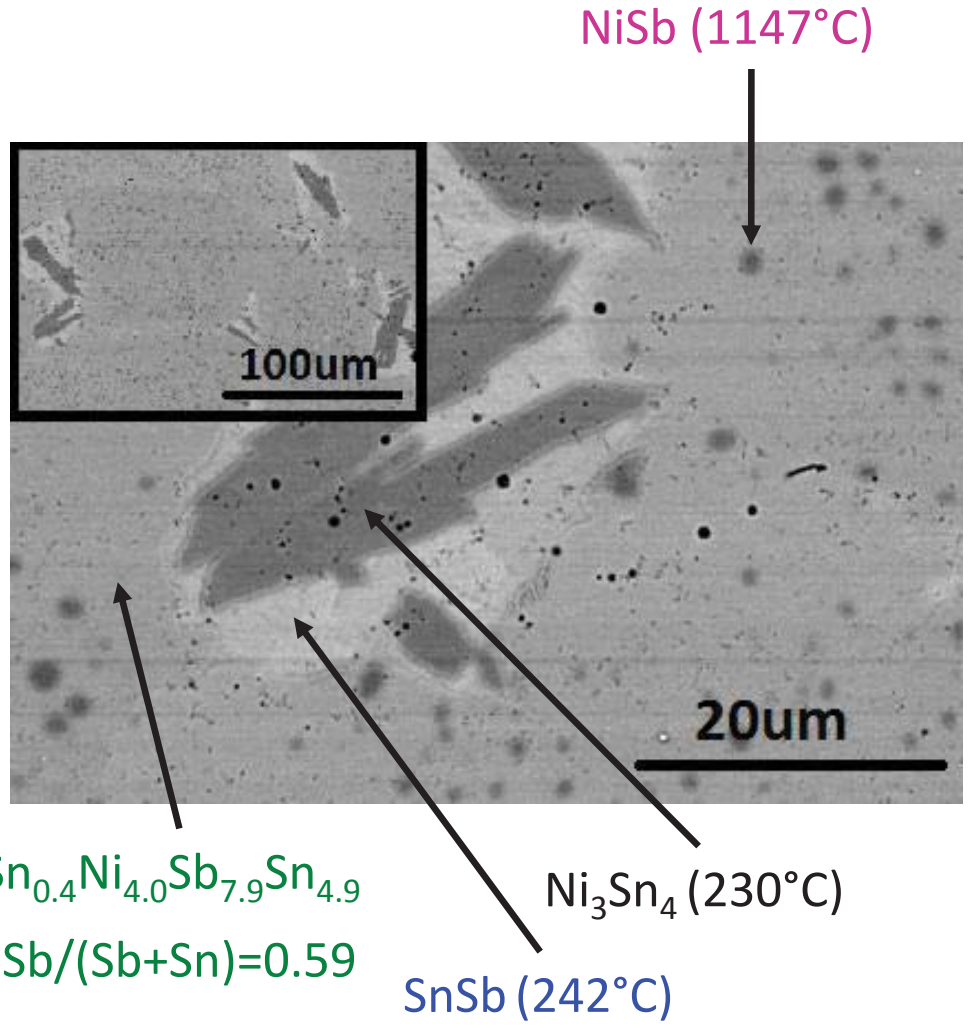
Rietveld on Hot Pressed



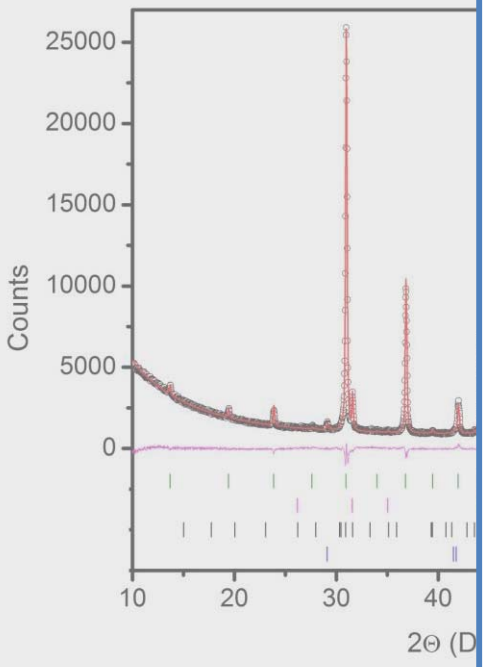
Parameter	$Ni_4Sb_7Sn_5$	$Ni_4Sb_8Sn_4$
GOF	1.67	1.78
Lattice (Å)	9.130	9.115
Y	0.159	0.158
Z	0.336	0.336
2a Occ. (Sn)	0.39	0.27
24g Occ. (Sb+Sn)	0.95	0.99

SEM/EPMA on Hot Pressed

Nominal Composition $Ni_4Sb_7Sn_5$

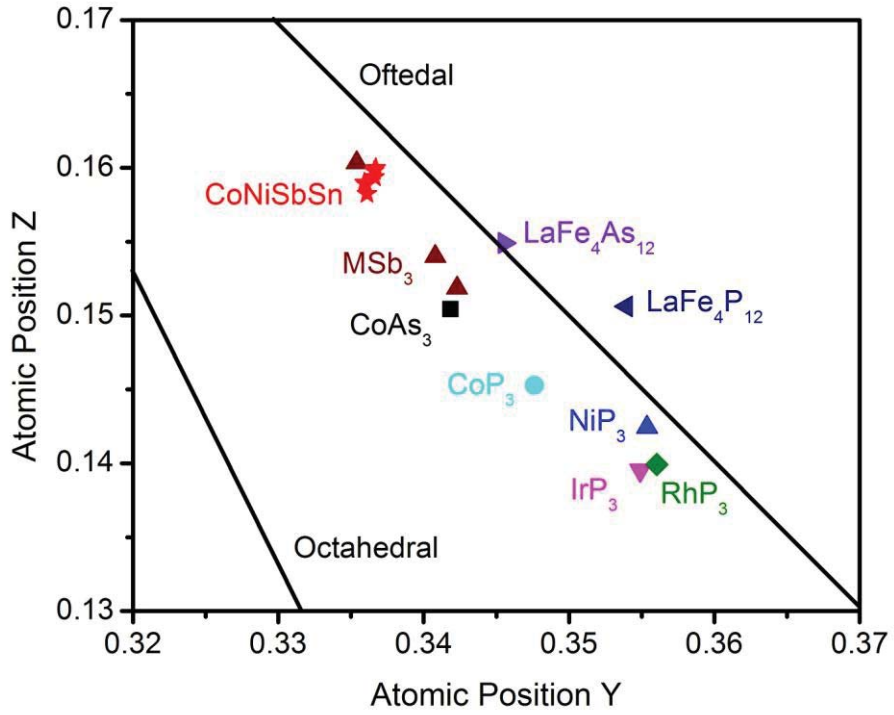


Rietveld on Hot Pressed



Parameter	Ni_4S	
GOF	1.	
Lattice (Å)	9.1	
Y	0.1	
Z	0.3	
2a Occ. (Sn)	0.	
24g Occ. (Sb+Sn)	0.95	0.99

Pnictogen Atomic Position



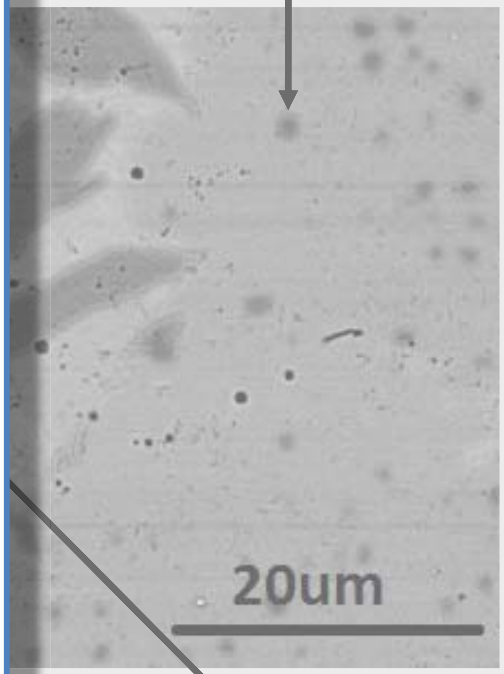
★ This Work

N. Mandel et al. Acta Cryst. (1971)
A. Kjekshus et al. Acta Chem. Scand. (1974)

SEM/EPMA on Hot Pressed

…sition $Ni_4Sb_7Sn_5$

NiSb (1147°C)



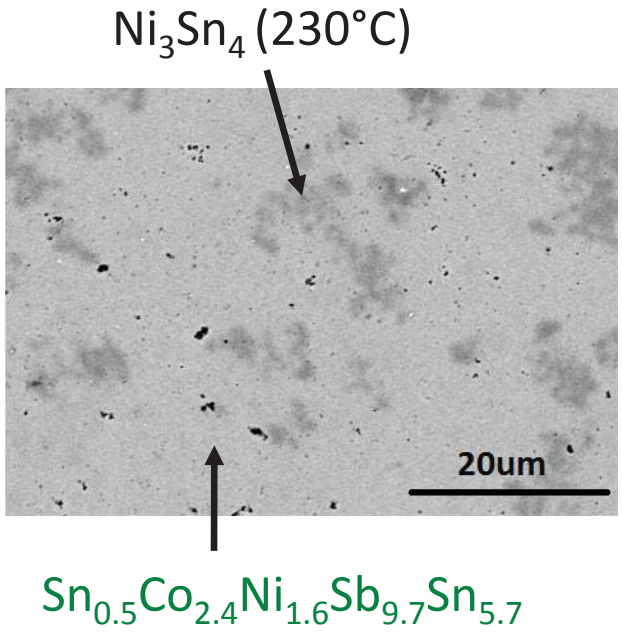
Ni_3Sn_4 (230°C)

SnSb (242°C)

Pressed $Co_2Ni_2Sb_7Sn_5$

Density 7.64 g/cm^3

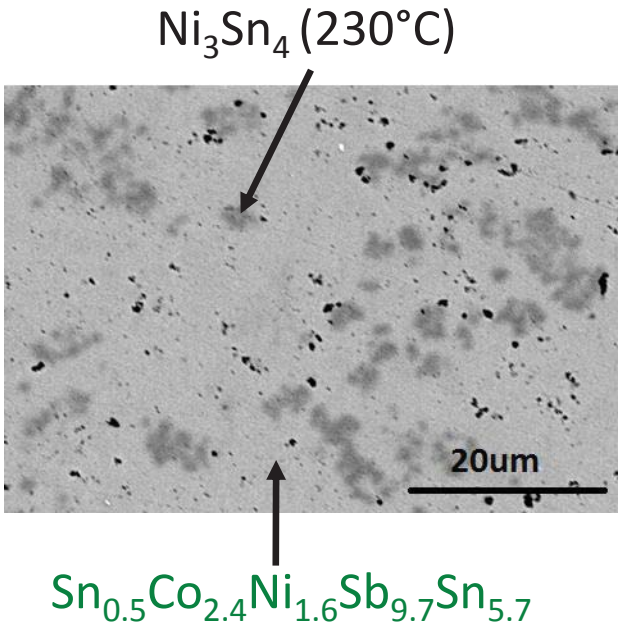
Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	82.6
Ni_3Sn_4	8.7
Sn	6.2



200°C Anneal 72 Hrs

Density 7.25 g/cm^3

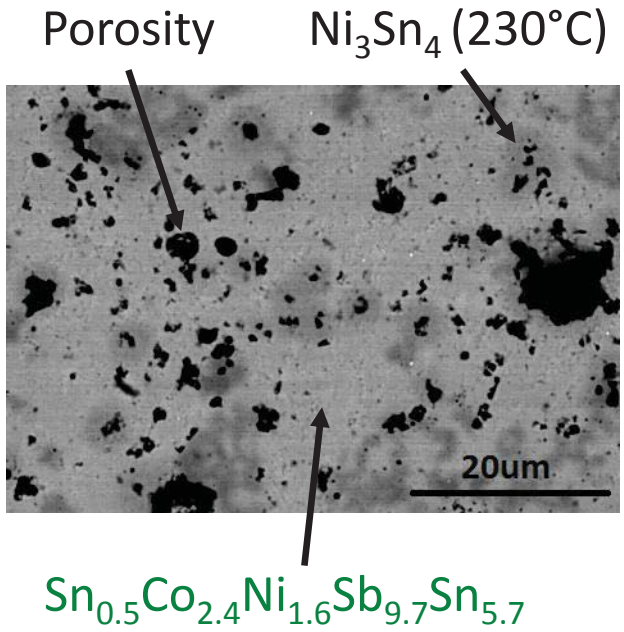
Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	80.0
Ni_3Sn_4	11.9
Sn	7.6

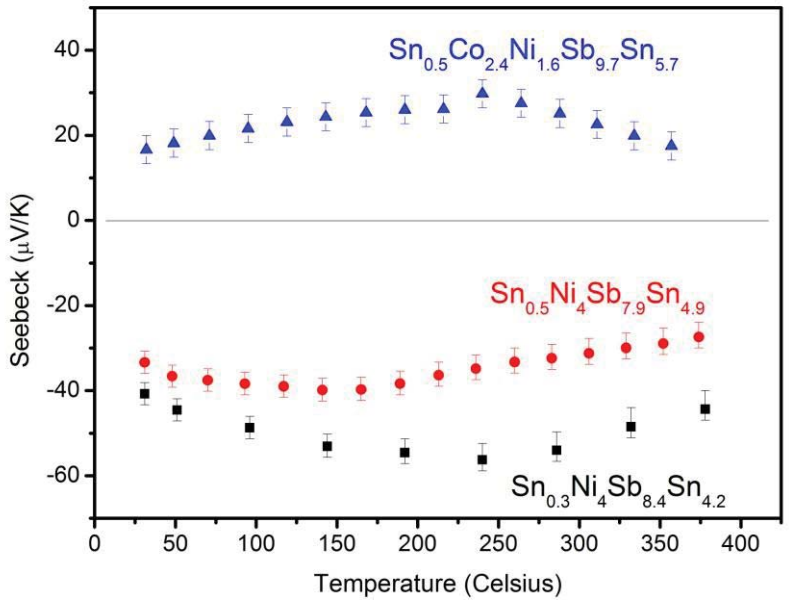


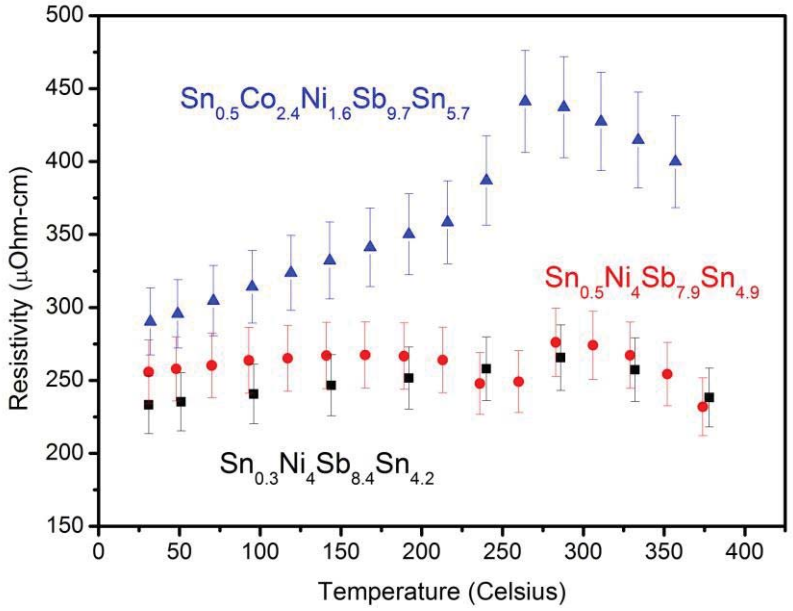
400°C Anneal 72 Hrs

Density 6.75 g/cm^3

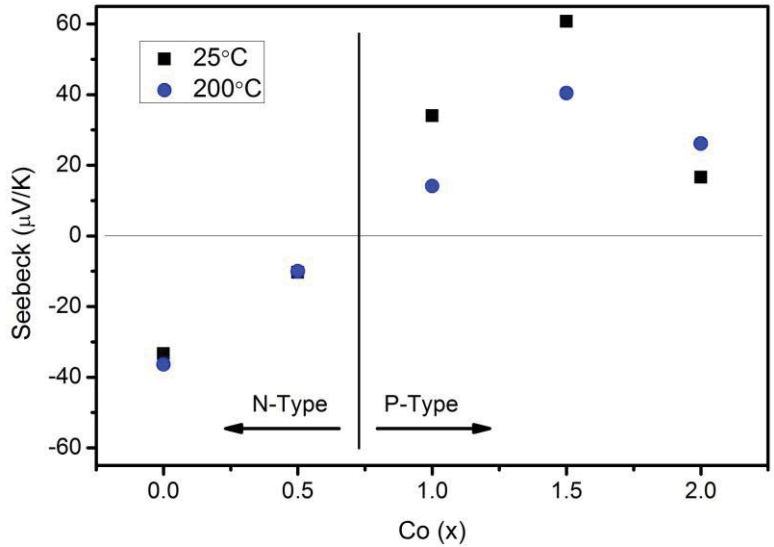
Phase	Wt%
$Co_2Ni_2Sb_7Sn_5$	73.6
Ni_3Sn_4	14.7
Sn	10.0

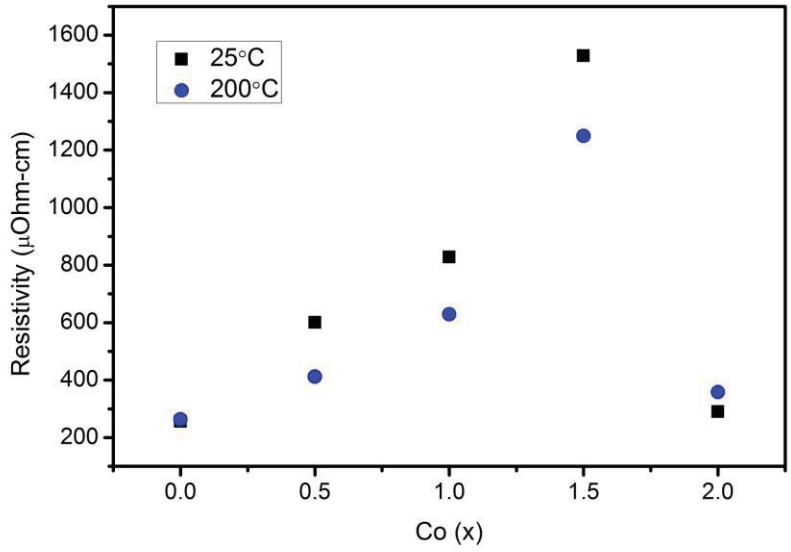


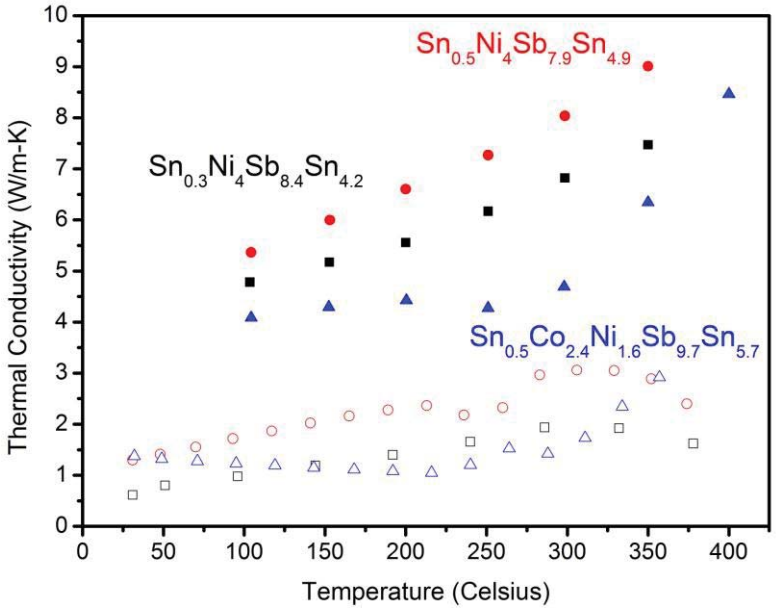


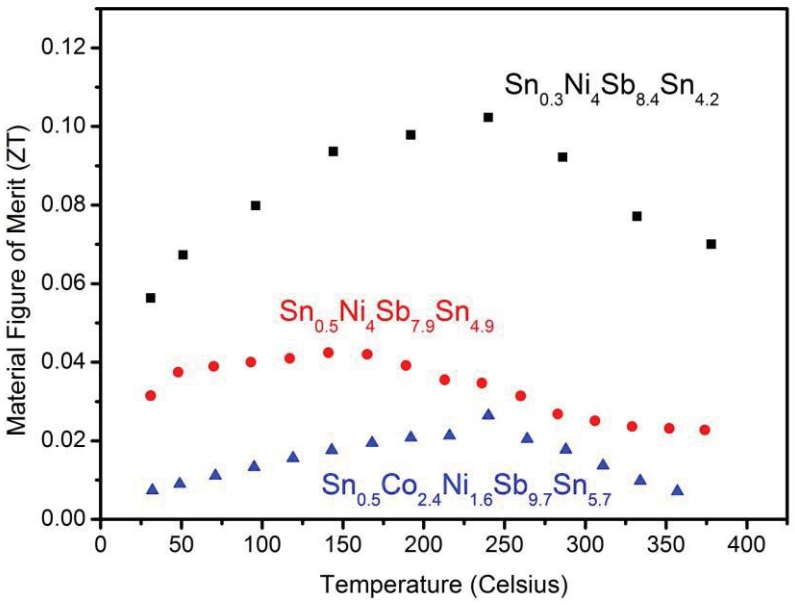


$Co_xNi_{4-x}Sb_7Sn_5$

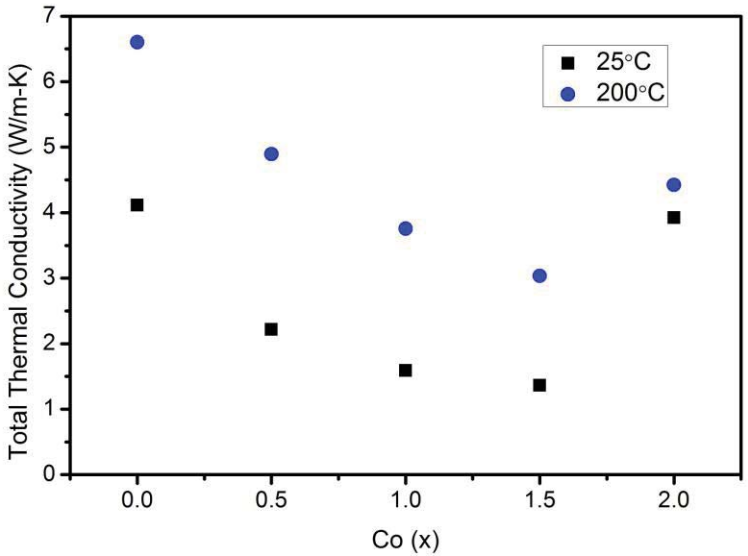


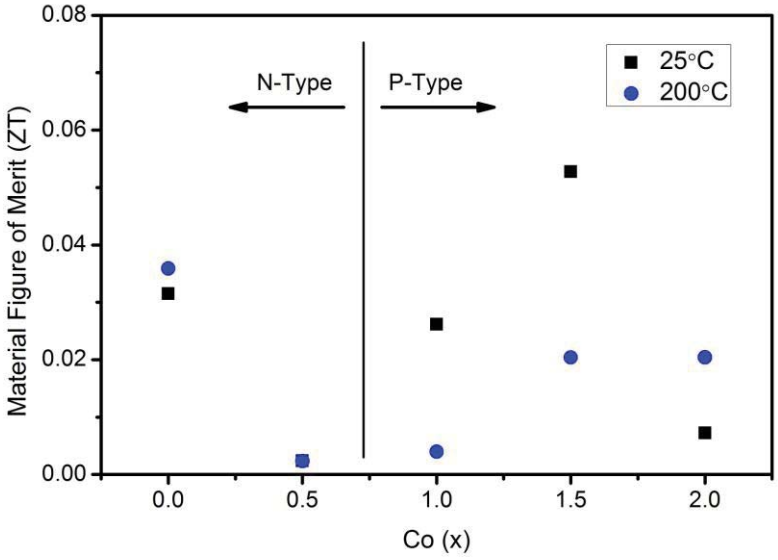




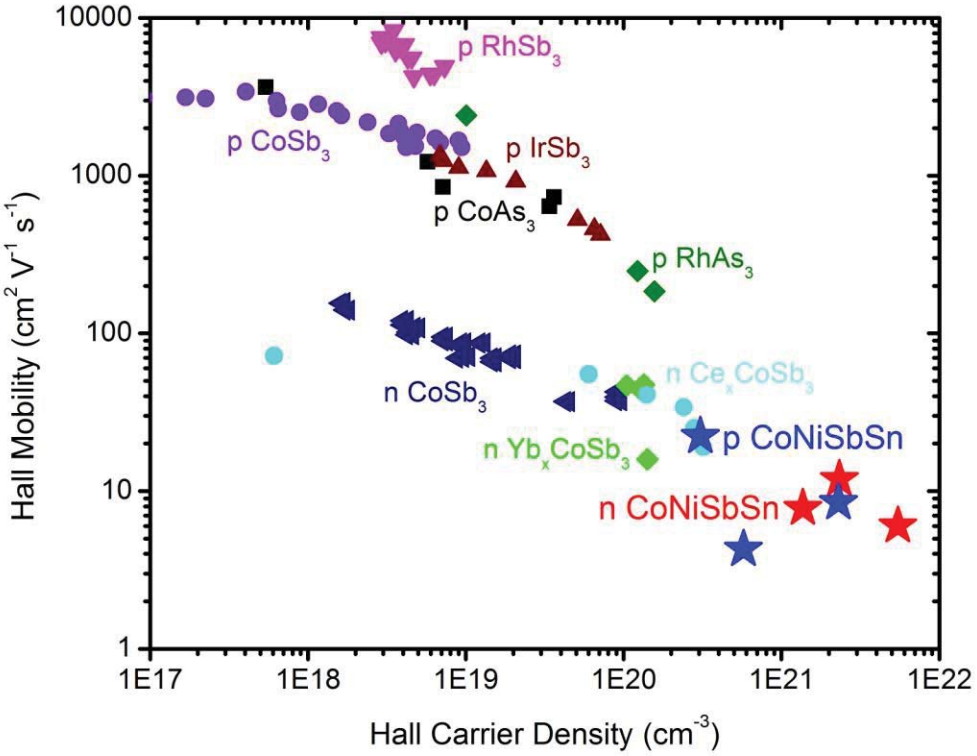


$Co_xNi_{4-x}Sb_7Sn_5$





Mobility and Carrier Comparison

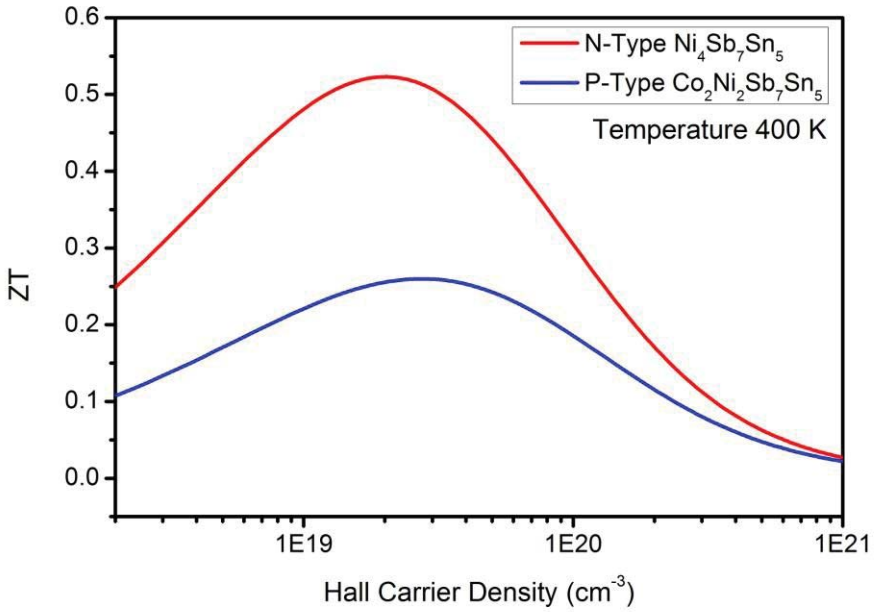


This Work

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

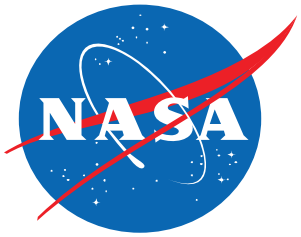
S.P.B. Modeling

- 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



The University of Akron

Acknowledgements

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

NASA Glenn Research Center

Dr. Sabah Bux, Dr. Jean-Pierre Fleurial

JPL

NASA Cooperative Agreement: NNX08AB43A

NASA/USRA Contract: 04555-004