

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

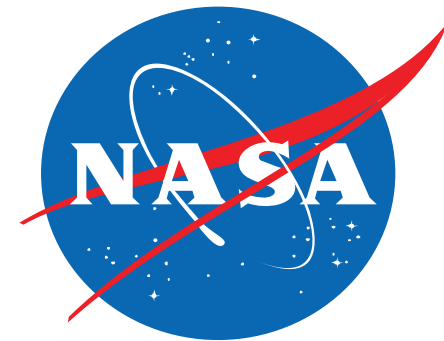
NASA/USRA Contract: 04555-004

The  
University  
of Akron



CASE WESTERN RESERVE  
UNIVERSITY EST. 1826

think beyond the possible™



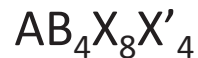
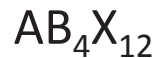
## Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p-type skutterudite with improved ZT
- Study behavior of the skutterudite  $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$

## 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 was not obtained
- $\text{Ni}_4\text{Sb}_8\text{Ge}_4$ 
  - Skutterudite phase not obtained
- $\text{Ni}_4\text{Sb}_8\text{Sn}_4$

## Ternary SKD Systems



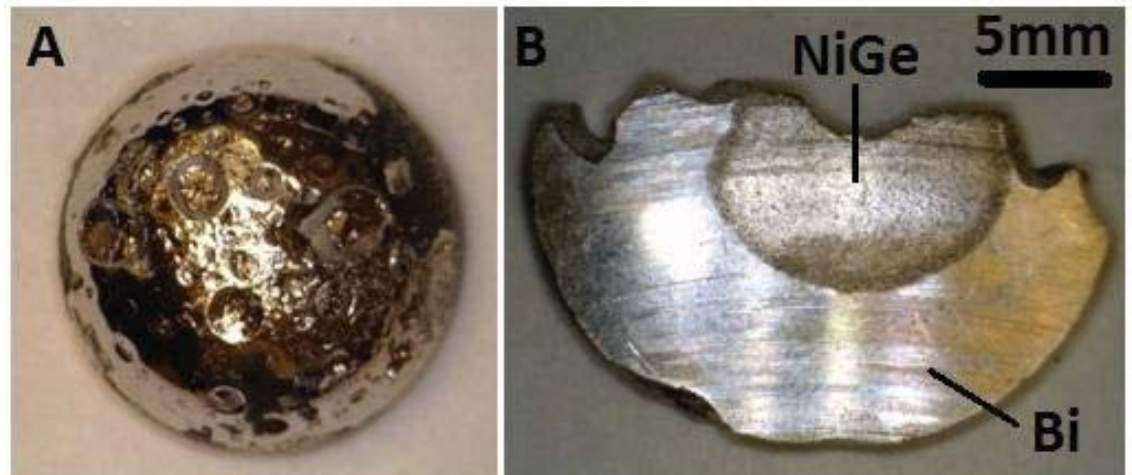
A={La,Ce,Nb,Yb,Ca,...}

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

X={P,As,Sb,Bi}

X'={Ge,Sn}

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



## Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p-type skutterudite with improved properties
- Study behavior of the ternary skutterudite  $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$

## Systems Investigated

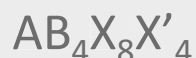
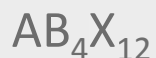
- Ternary systems studied with combination of solidification and powder processing



- Grytsiv et. al has reported a  $\text{Ni}_4\text{Sb}_8\text{Sn}_4$  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).

## Ternary SKD Systems



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

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

X={P,As,Sb,Bi}

X'={Ge,Sn}

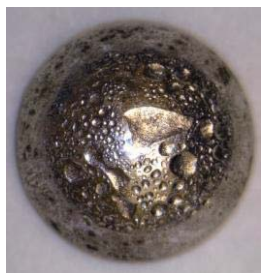
Bauer et. al Acta Phys. Polon. B **34** (2003).

skutterudite phase was not obtained



## ICP analysis of an ingot

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

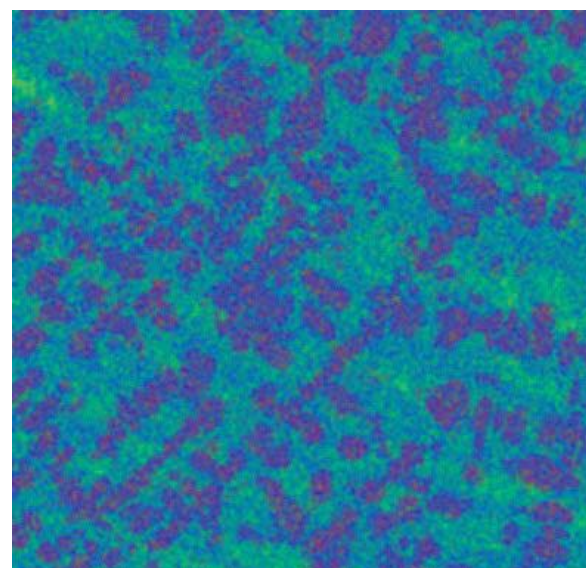
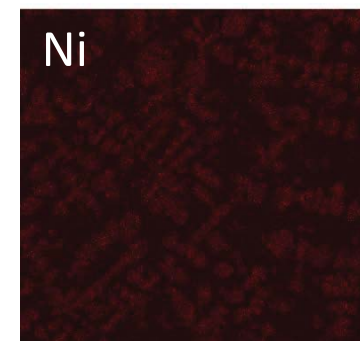
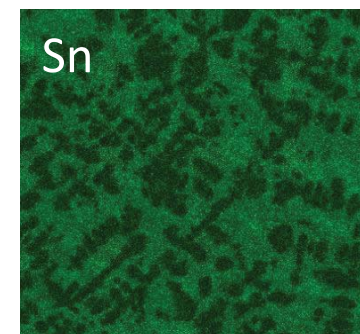
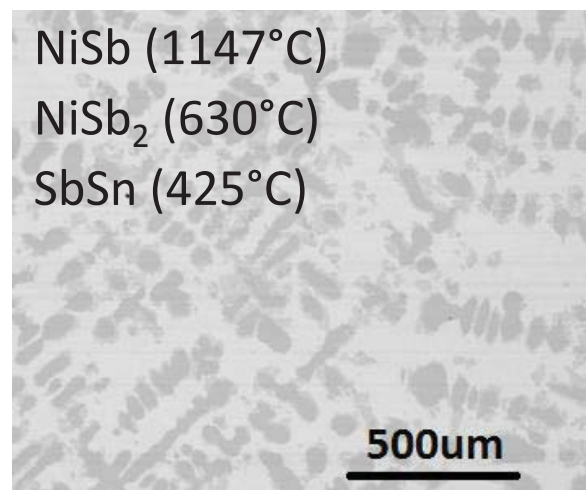


Target



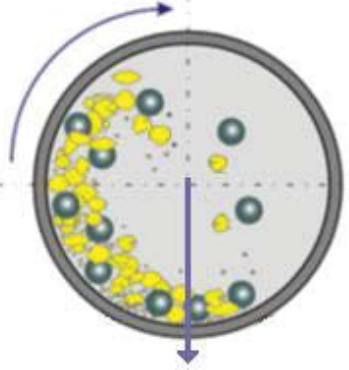
	at%	at%	at%	at%
Co	<b>9.4</b>	9.1	7.3	9.0
Ni	<b>15.6</b>	14.9	13.7	14.6
Sb	<b>43.7</b>	42.4	43.7	44.1
Sn	<b>31.2</b>	33.5	35.3	32.2
Ca	<b>0</b>	2e-4	7e-4	7e-4
Mg	<b>0</b>	1e-4	2e-4	2e-4
Na	<b>0</b>	3e-3	4e-3	4e-3

## EDS map of an ingot

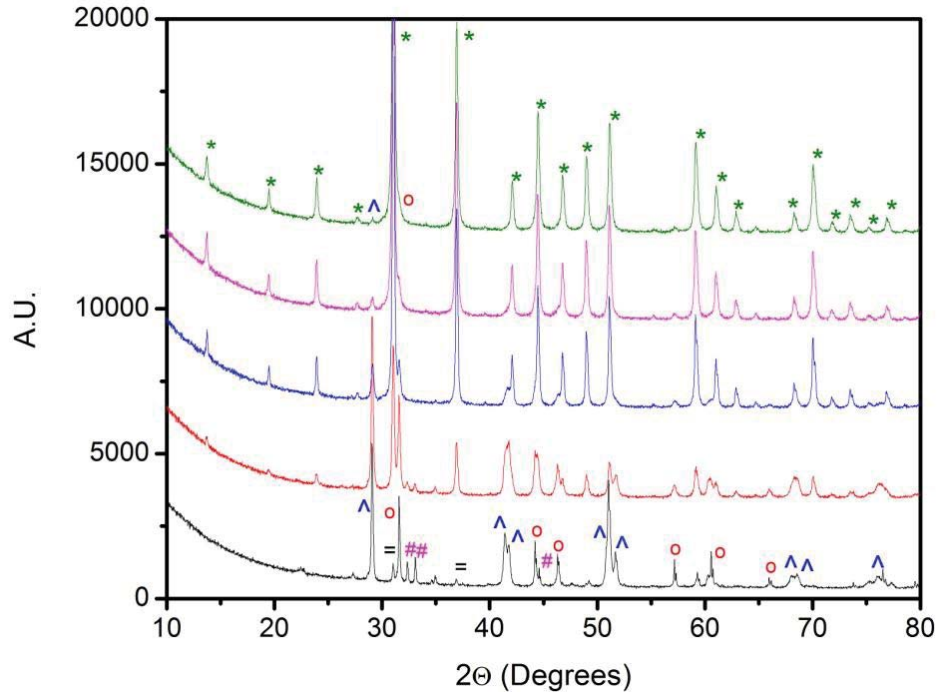
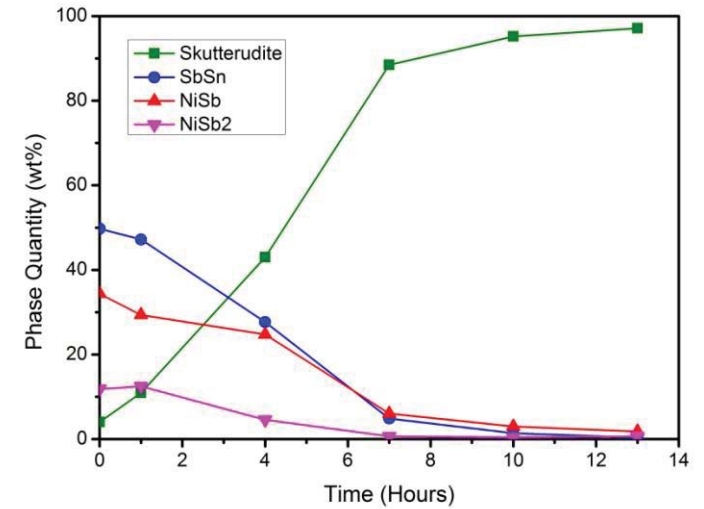


## Milling Details

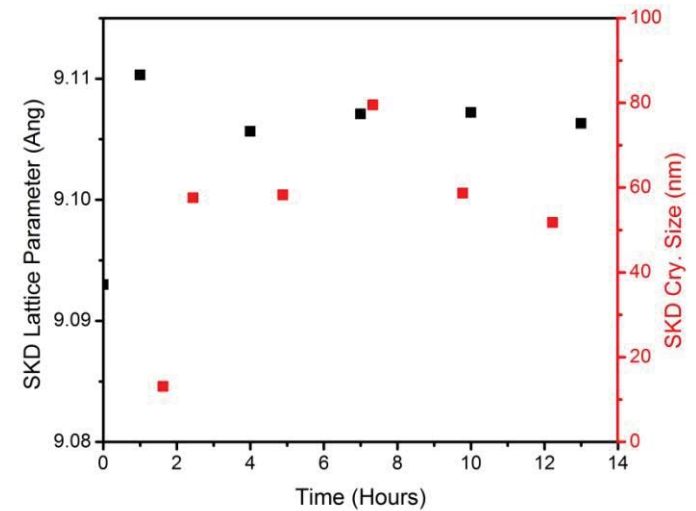
- Ingots crushed by hand
- Planetary mill
  - 550 rpm
  - Ball to powder weight ratio 3.8
  - Ar atmosphere



## Ni<sub>4</sub>Sb<sub>8</sub>Sn<sub>4</sub> Milling



\* SKD  
 ^ SbSn  
 o NiSb  
 # NiSb<sub>2</sub>  
 = Sn<sub>3</sub>Ni<sub>4</sub>



# Introduction

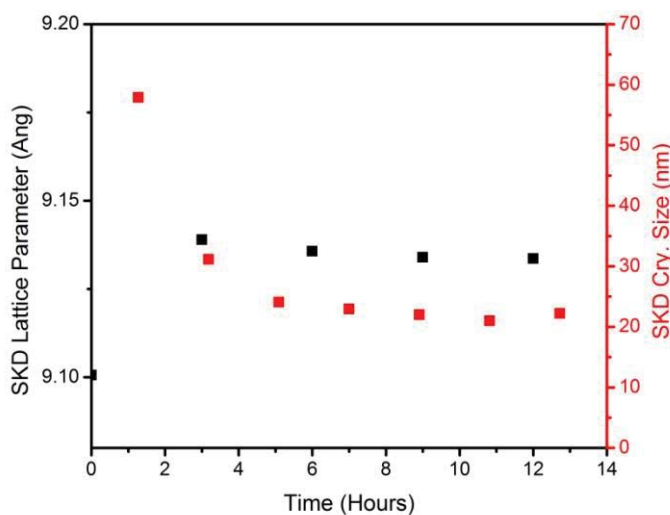
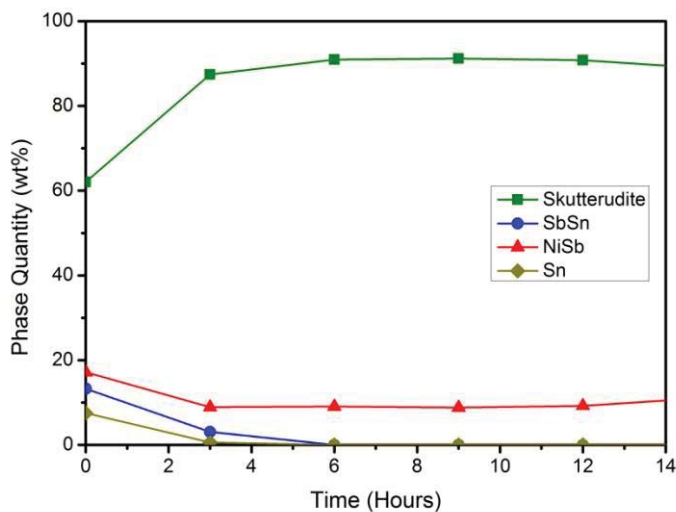
# Processing

# Properties

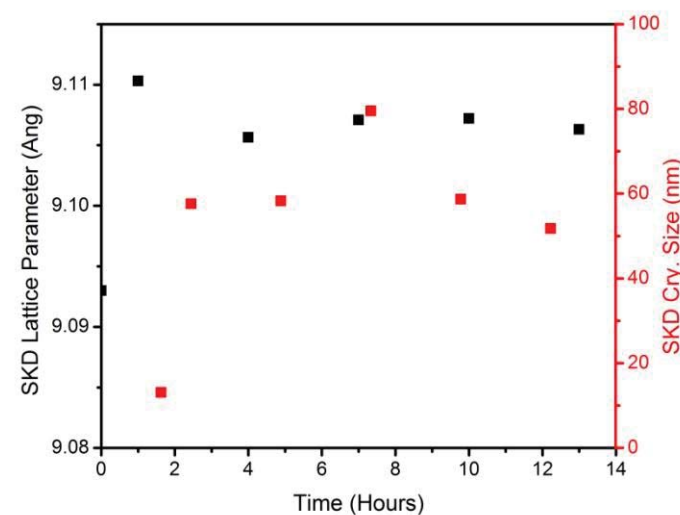
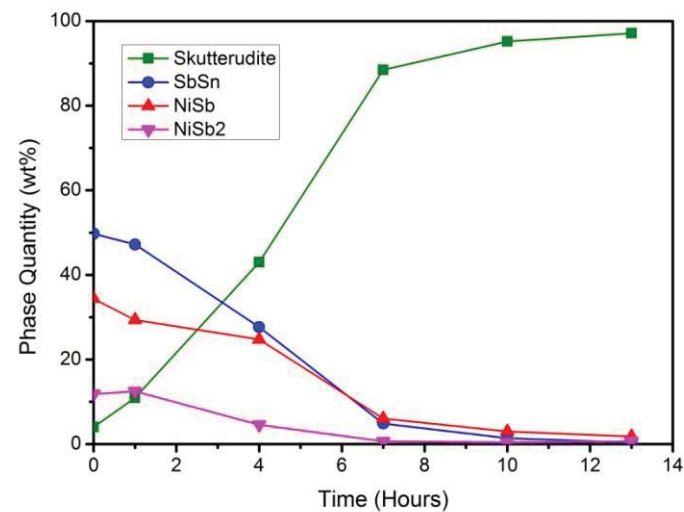
M

- I
- P

## Co<sub>1</sub>Ni<sub>3</sub>Sb<sub>7</sub>Sn<sub>5</sub> Milling

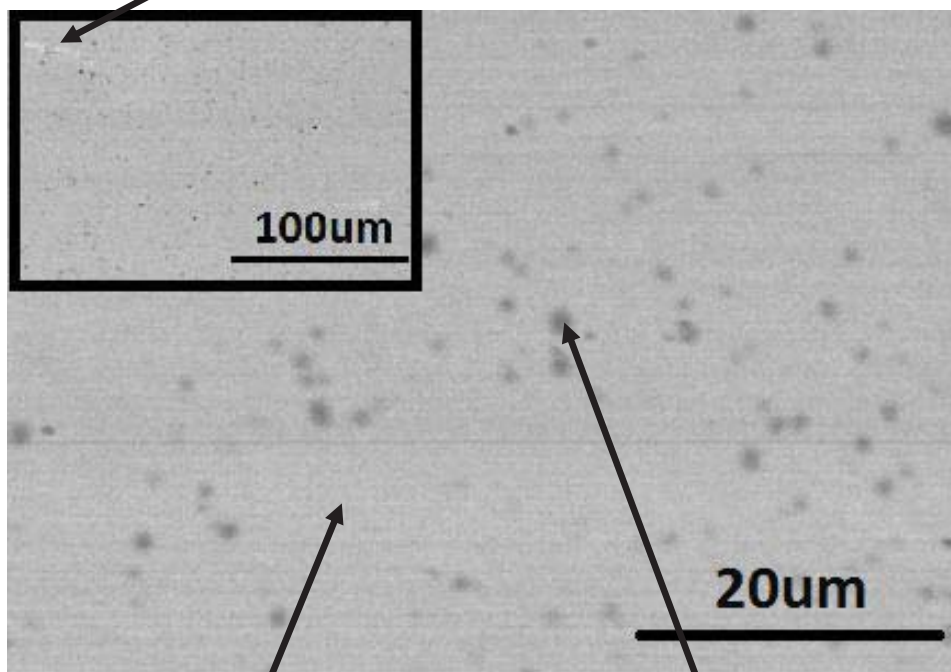


## Ni<sub>4</sub>Sb<sub>8</sub>Sn<sub>4</sub> Milling

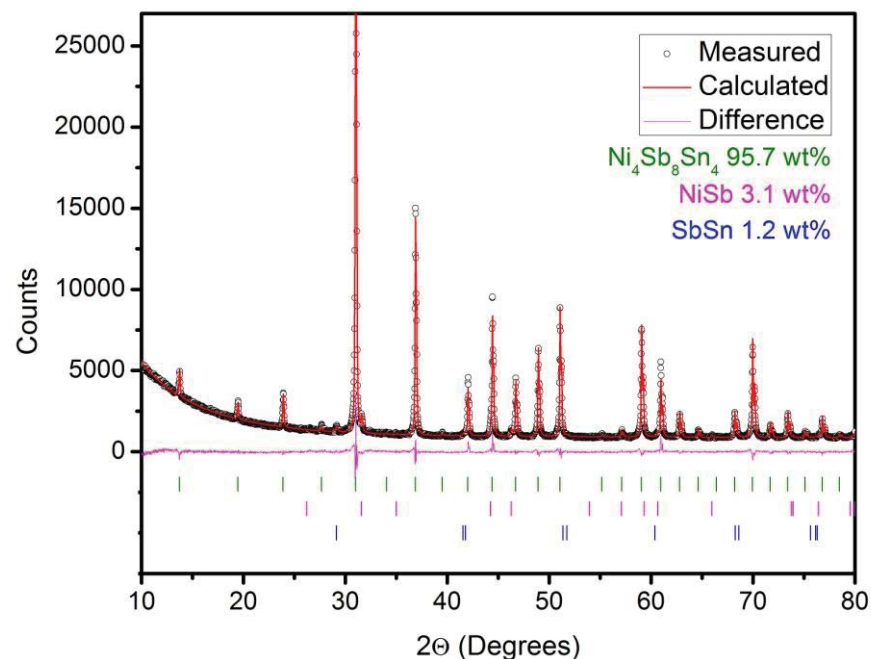


SEM/EPMA on Hot PressedNominal Composition  $\text{Ni}_4\text{Sb}_8\text{Sn}_4$ 

SbSn (242°C)

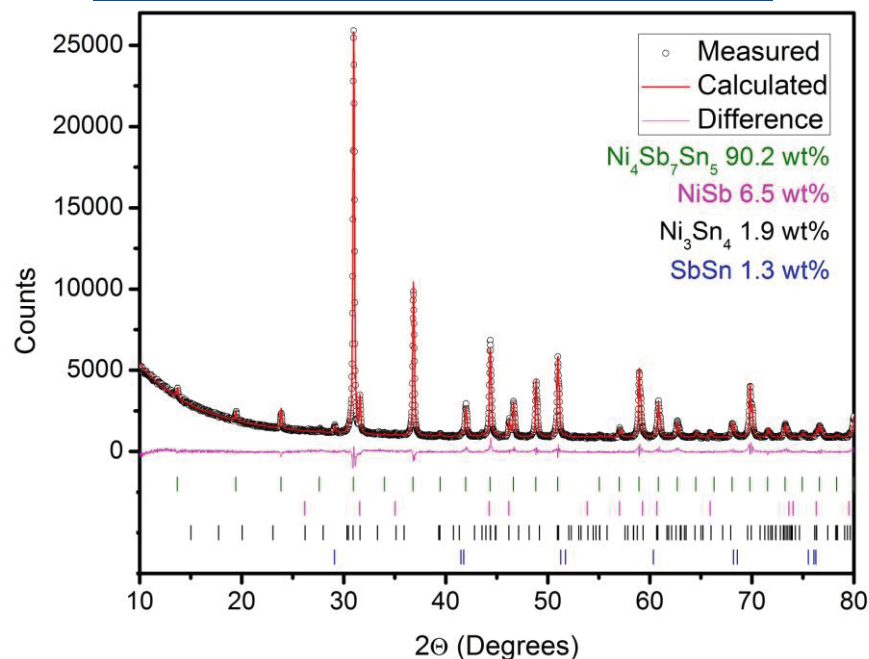
 $\text{Sn}_{0.3}\text{Ni}_{4.0}\text{Sb}_{8.4}\text{Sn}_{4.2}$  $\text{Sb}/(\text{Sb}+\text{Sn})=0.65$ 

NiSb (1147°C)

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

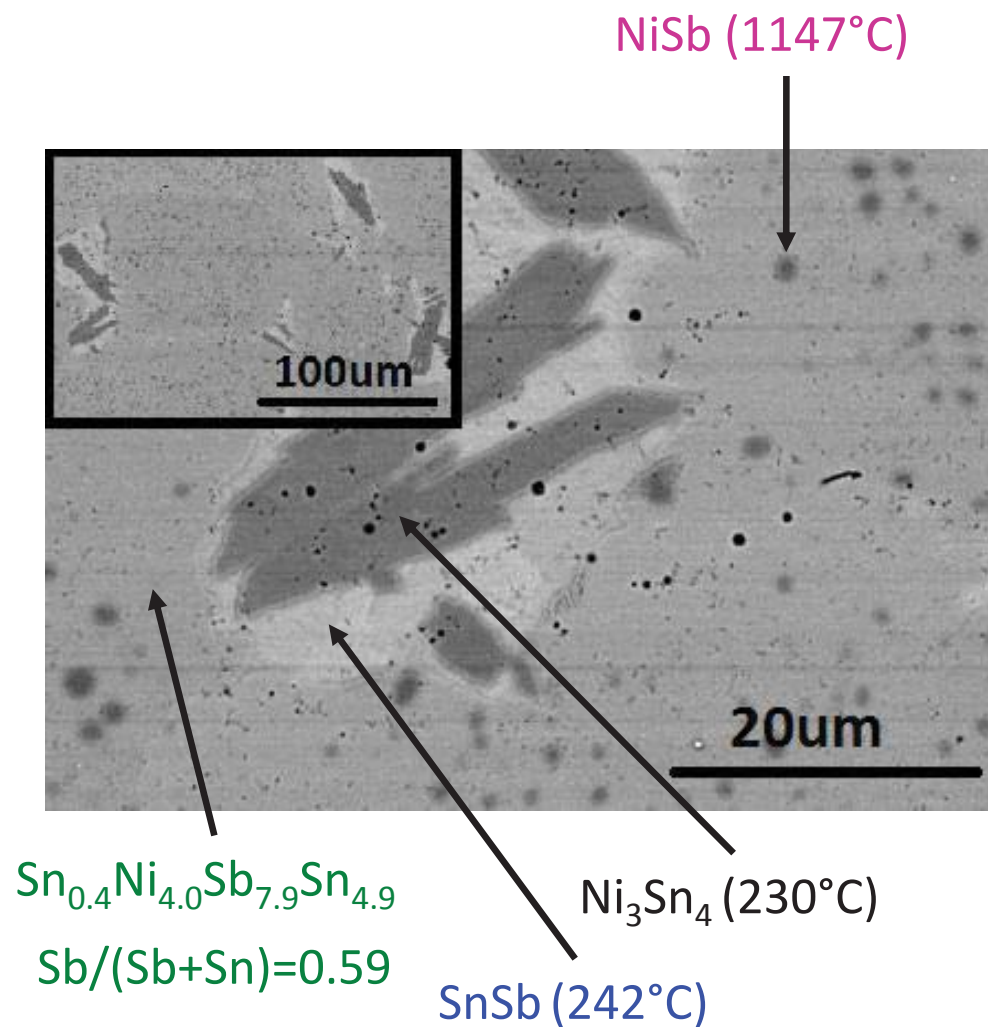
## Rietveld on Hot Pressed



Parameter	$\text{Ni}_4\text{Sb}_7\text{Sn}_5$	$\text{Ni}_4\text{Sb}_8\text{Sn}_4$
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

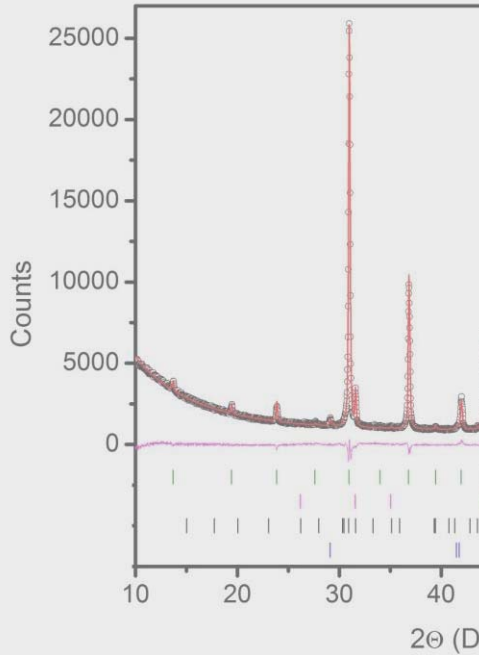
## SEM/EPMA on Hot Pressed

Nominal Composition  $\text{Ni}_4\text{Sb}_7\text{Sn}_5$





## Rietveld on Hot Pressed

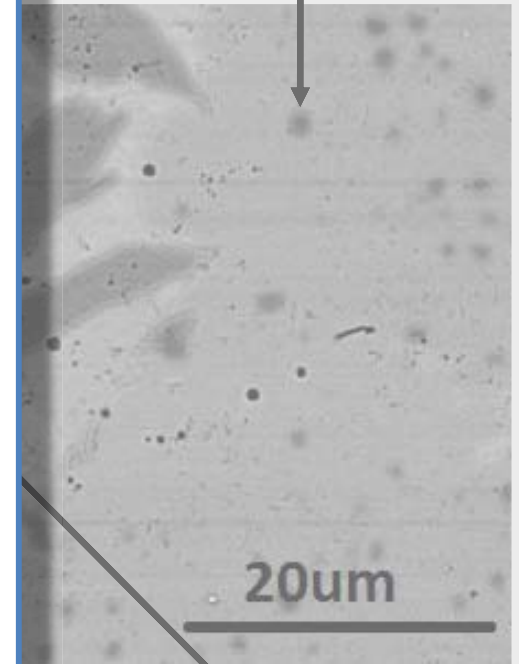


Parameter	Ni <sub>4</sub> S <sub>7</sub> Sn <sub>5</sub>
GOF	1.0
Lattice (Å)	9.1
Y	0.1
Z	0.3
2a Occ. (Sn)	0.9
24g Occ. (Sb+Sn)	0.95

## SEM/EDMA on Hot Pressed

position Ni<sub>4</sub>Sb<sub>7</sub>Sn<sub>5</sub>

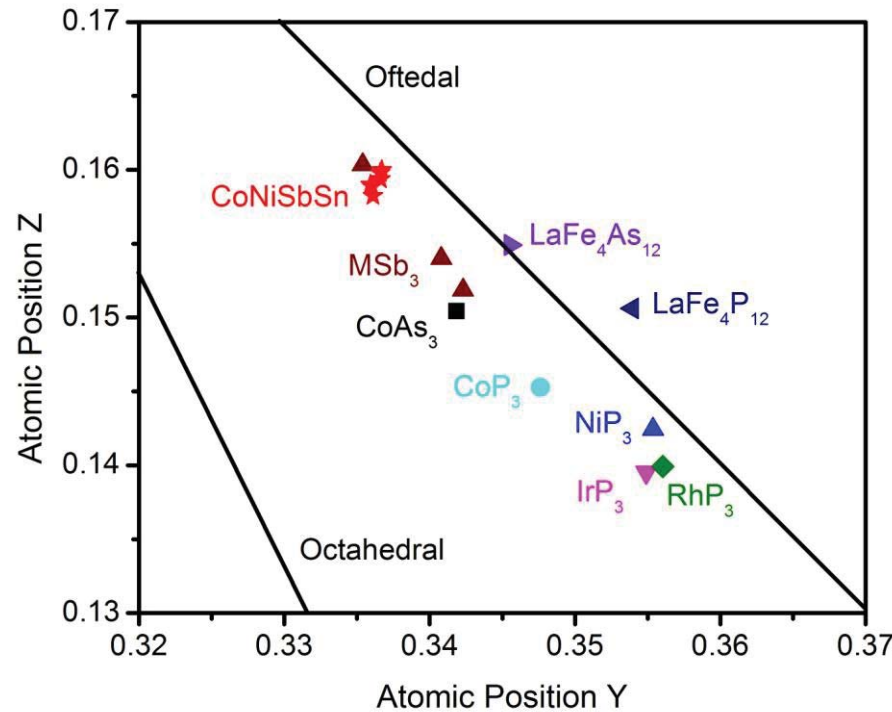
NiSb (1147°C)



Ni<sub>3</sub>Sn<sub>4</sub> (230°C)

SnSb (242°C)

## Pnictogen Atomic Position



★ This Work

N. Mandel et al. Acta Cryst. (1971)

A. Kjekshus et al. Acta Chem. Scand. (1974)

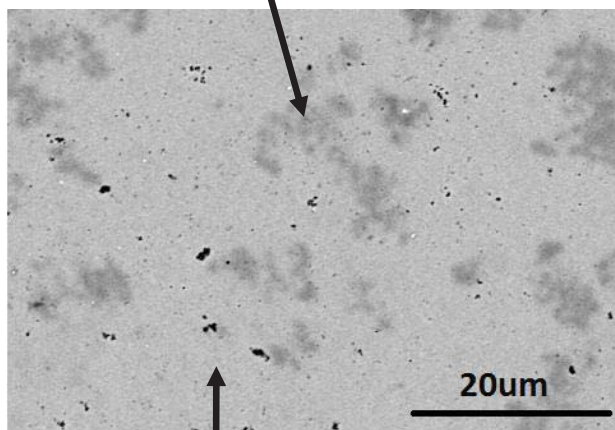
# Introduction

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

Density  $7.64 \text{ g/cm}^3$

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	82.6
$\text{Ni}_3\text{Sn}_4$	8.7
Sn	6.2

$\text{Ni}_3\text{Sn}_4$  (230°C)



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

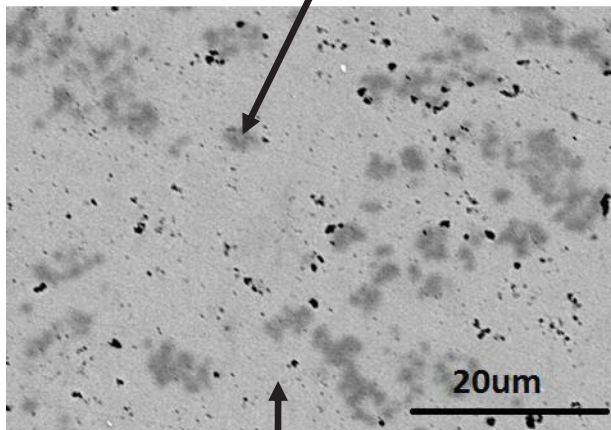
# Processing

## 200°C Anneal 72 Hrs

Density  $7.25 \text{ g/cm}^3$

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	80.0
$\text{Ni}_3\text{Sn}_4$	11.9
Sn	7.6

$\text{Ni}_3\text{Sn}_4$  (230°C)



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

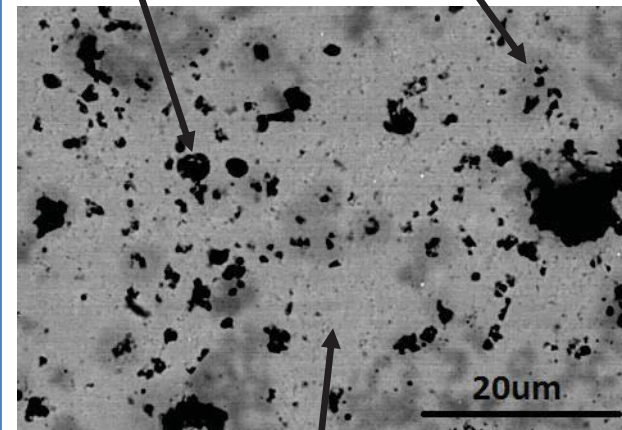
# Properties

## 400°C Anneal 72 Hrs

Density  $6.75 \text{ g/cm}^3$

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	73.6
$\text{Ni}_3\text{Sn}_4$	14.7
Sn	10.0

Porosity  $\text{Ni}_3\text{Sn}_4$  (230°C)

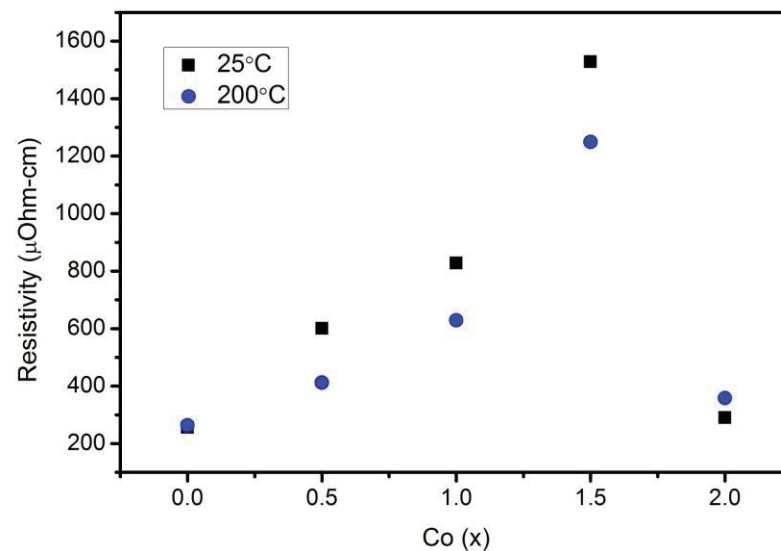
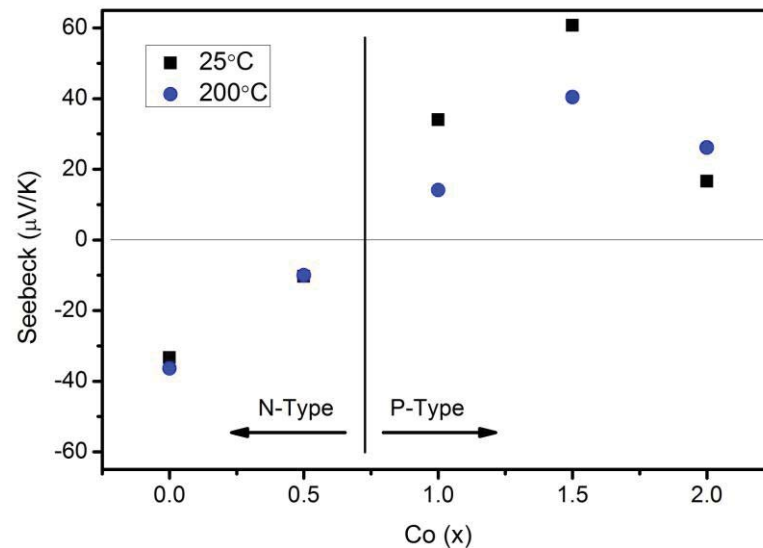
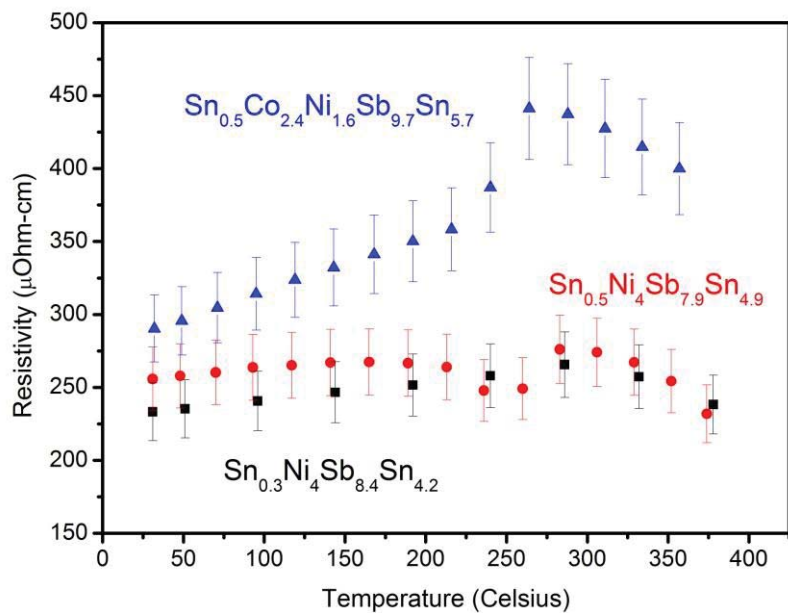
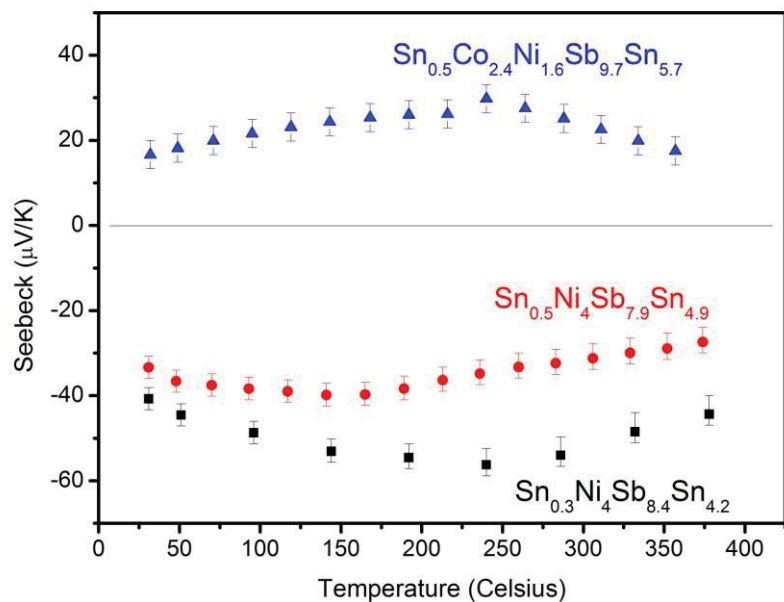


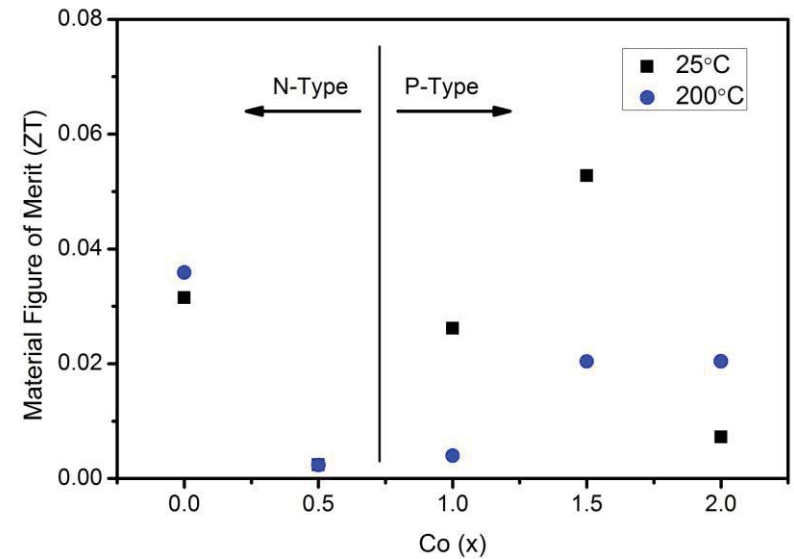
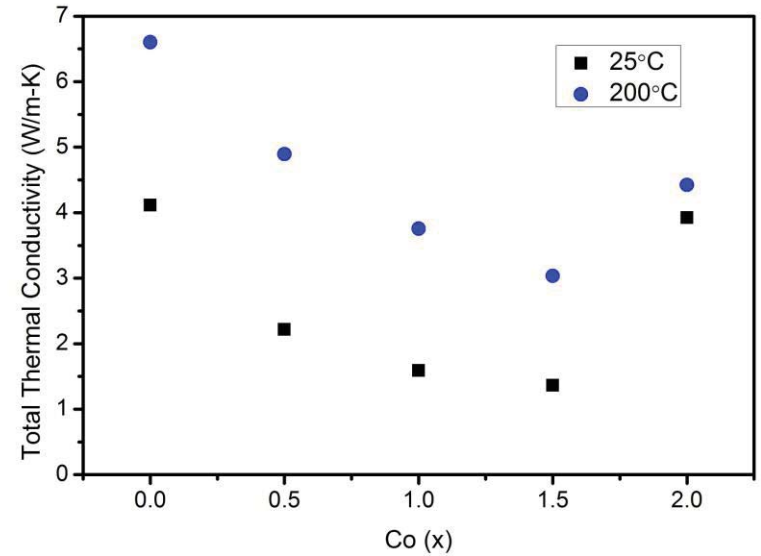
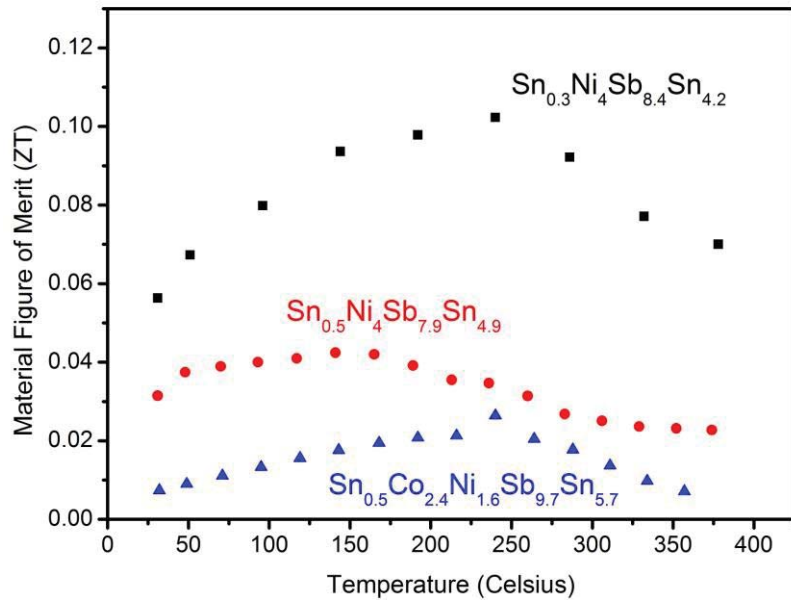
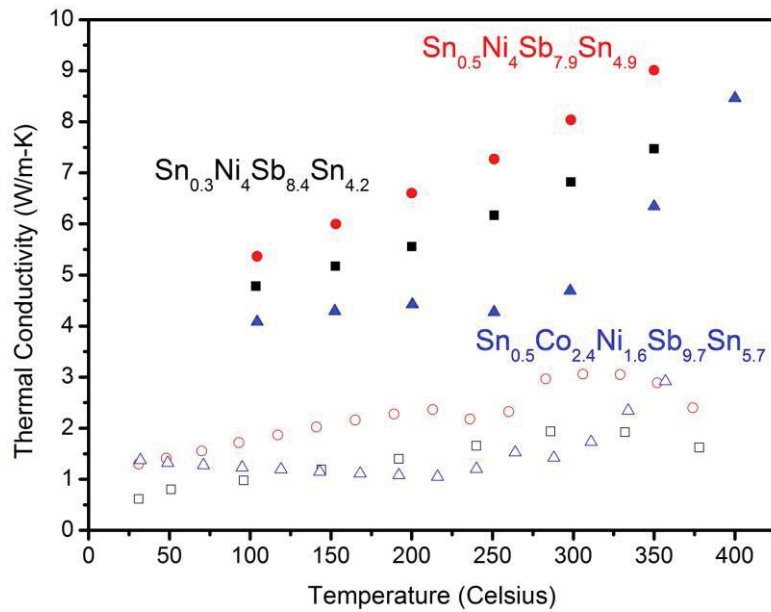
$\text{Sn}_{0.5}\text{Co}_{2.4}\text{Ni}_{1.6}\text{Sb}_{9.7}\text{Sn}_{5.7}$

# Introduction

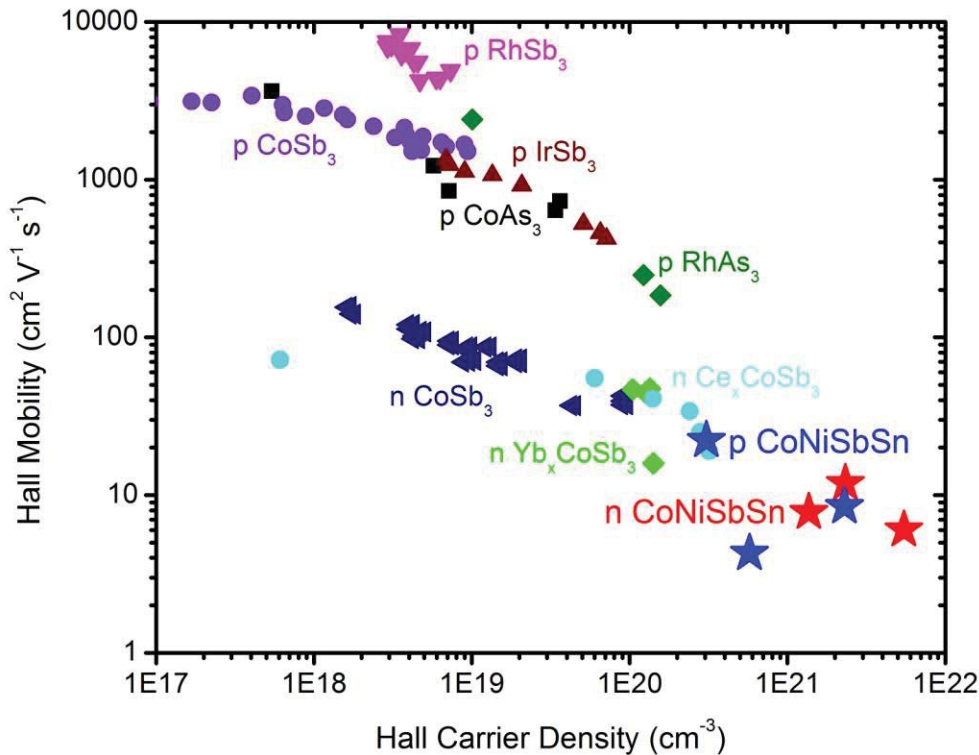
# Processing

# Properties





## Mobility and Carrier Comparison



★ ★ This Work

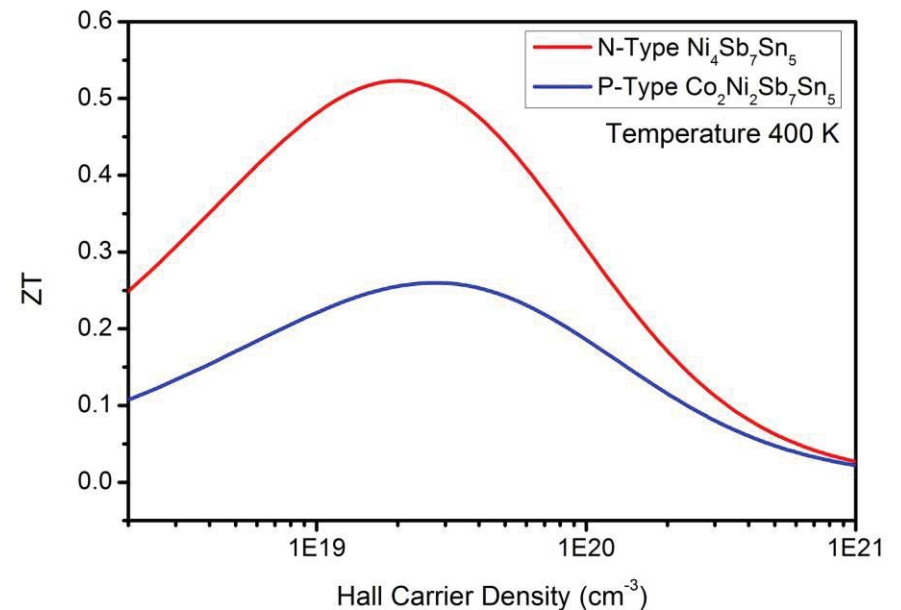
$\text{Yb}_x \text{CoSb}_3$ : L. Fu et al. Intermetallics (2013)

$\text{Ce}_x \text{CoSb}_3$ : 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 ( $m/m_e$ )
  - 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

## Acknowledgements

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

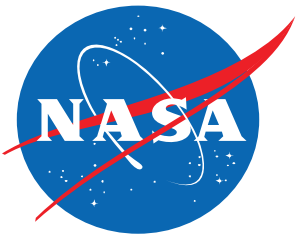
NASA Glenn Research Center

Dr. Sabah Bux, Dr. Jean-Pierre Fleurial

JPL

NASA Cooperative Agreement:  
NNX08AB43A

NASA/USRA Contract:  
04555-004



The  
University  
of Akron

