Poster presentation for MRS Spring 2011, April 27, San Francisco, CA

National Nuclear Security Administration

Final Poster layout

Thermoelectric properties of nanostructured $(Bi, Sb)_2Te_3$ alloys using spark-plasma sintering (SPS)

Nancy Yang, R. Nishimoto, and J. Chames Sandia National Laboratories, CA.
Z. Zhang, Y. Zhou and E. Lavernia, University of California, CA

Abstract

SPS consolidated nanostructured $(Bi, Sb)_2Te_3$ alloy is a promising thermoelectric (TE) material. The effect(s) of a nanocrystalline structure and Te dopant on the TE properties of $(Bi_{0.25}Sb_{0.75})_2Te_3$ were investigated. The bulk nanostructured $(Bi_{0.25}Sb_{0.75})_2Te_3$ alloy was prepared via mechanical milling followed by spark plasma sintering (SPS) with excess Te addition (0- 8 wt.%). The microstructure, electrical resistivity, Seebeck coefficient, thermal conductivity, and texture relative to the SPS loading directions were examined. We found the SPS consolidated nanostructured $(Bi_{0.25}Sb_{0.75})_2Te_3$ exhibits weak texture and contains nanopores and Te phase, 20-30 nm, mostly along grain boundaries. These SPS induced chemical and physical characteristics raise the resultant electrical resistivity, therefore lower the figure of merit (ZT).

Thermoelectric Generator Fundamentals

•***Electricity*** can be produced from ΔT temperature gradient generated by applying a heat source on one end and taking heat out on the other end of thermopile leading to ΔV, voltage gradient.

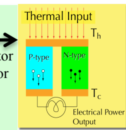
•***TE performance*** is expressed by figure of merit (*ZT*)

$$ZT = \frac{S^2}{\rho\kappa}T$$

Where
- *S* = Seebeck coefficient
- *ρ* = electrical resistivity
- *κ* = thermal conductivity
- *T* = temperature

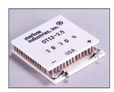
(S, ρ, κ) Experimentally measured

P type-acceptor
N-type-donor



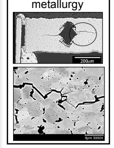
Background and Motivation

Typical TE module design

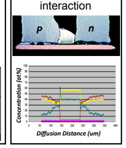


Performance, aging and reliability of materials must be understood

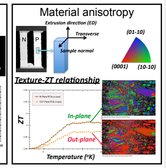
Physical / chemical metallurgy



Material-device interaction



Material anisotropy



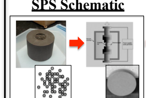
Experiments

SPS consolidation

SPS Model: SPS-825S Dr. Sinter® at UCD

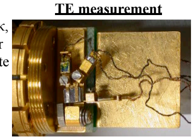
- $(Bi_{0.25}Sb_{0.75})_2Te_3$ was mechanically alloyed using pure Bi_2Te_3 and Sb_2Te_3 powders.
- The $(Bi_{0.25}Sb_{0.75})_2Te_3$ alloy powders with 0, 2, 5, 6, 8 wt.% Te addition were milled in a planetary ball mill (Fritsch p-7 premium line) for 3 hrs in a nitrogen glove box to achieve 100-200nm nanocrystaline structure.
- The nanostructured powders were sintered in a 14mm cylindrical graphite die at 80MPa and 400°C for 3 minutes using Syntex system.

SPS Schematic



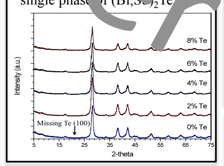
TE measurement

TE Transport properties, κ, S, and ρ were measured for 2°K- 390°K range at the rate of 0.2°K/m step (2 -20°K); 0.5 K/min step (20-390°K) using PPMS, Quantum Design system

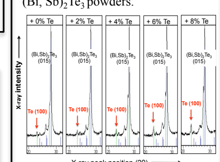


Experimental results

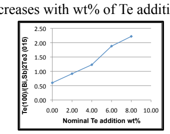
All mechanically milled starting powders are supersaturated single phase of $(Bi,Sb)_2Te_3$



XRD detects a second phase of Te in all SPS consolidated nanostructured $(Bi, Sb)_2Te_3$ powders.



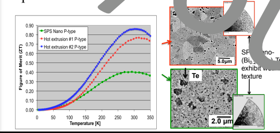
Volume fraction of the Te phase increases with wt% of Te addition

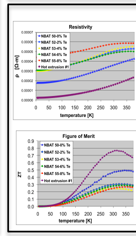


Texture, measured by orientation factor, increases with wt% of Te doping

Sample ID	Consolidation	Orientation Factor	Nominal Te added (wt%)	Texture
NBAT50	SPS	0.023	0	Weak
NBAT52	SPS	0.021	2	Weak
NBAT53	SPS	0.028	4	Weak
NBAT54	SPS	0.023	6	Weak
NBAT55	SPS	0.027	8	Weak
Pure Bi…	Hot extrusion	0.168	0	Strong

The SPS nanostructured $(Bi,Sb)_2Te_3$ contains Te 2[nd] phase and dense nanopore that may be responsible for the reduced ZT seen.





- The electrical resistivity increases with Te addition, therefore lowers ZT.
- The adverse effects on the resistivity and ZT most likely are attributed to the increases in Te phase separation and nanoporosity, induced during the SPS consolidation.

Conclusions

- SPS consolidated nanostructured $(Bi,Sb)_2Te_3$ is not only susceptible to nanopores formation and Te phase separation but also exhibit exhibits weak texture.
- The Te phase separation, dense nanopore and weak texture have adverse effect on TE transport properties, especially electrical resistivity.
- SPS process optimization to mitigate Te-phase separation and nanopore formation are underway.
- The mechanism of the Te phase transformation and how does it influence the electrical resistivity is being studied.

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Sandia National Laboratories

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Abstract

Nanostructured (Bi, Sb)$_2$Te$_3$ alloy is a promising thermoelectric (TE) material. The effect(s) of a nanocrystalline structure and Te dopant on the TE properties of p-type (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ were investigated. The nanostructured (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ alloy was prepared via mechanical milling followed by spark plasma sintering (SPS) with excess Te addition (0- 8 wt. %). The microstructure, electrical resistivity, Seebeck coefficient, thermal conductivity, were relative to the SPS loading directions were examined. We found the SPS consolidated nanostructured (Bi$_{0.25}$Sb$_{0.75}$)$_2$Te$_3$ possesses weak texture and contains nano-pores and Te phase, 20-30 nm along grain boundaries. These SPS induced chemical and physical characteristics impact the resultant electrical resistivity, and Seebeck coefficient, therefore figure of merit (ZT).

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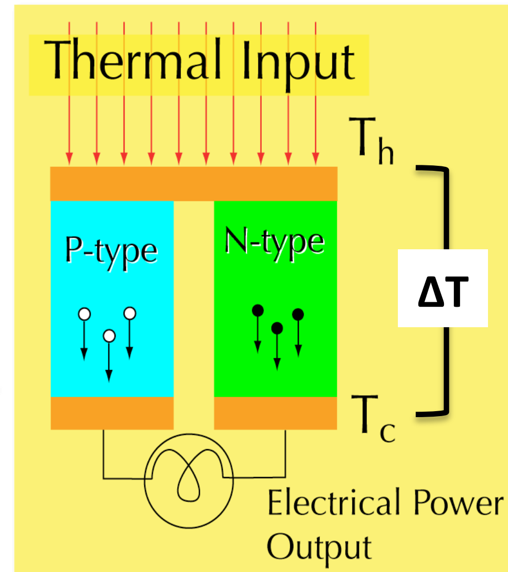
Thermoelectric Generator Fundamentals

• ***Electricity*** can be produced from ΔT, temperature gradient, generated by applying a heat source on one end and taking heat out on the other end of thermopile leading to ΔV, voltage gradient .

•***<u>TE performance</u>*** is expressed by figure-of-merit (*ZT)*

$$ZT = \frac{S^2}{\rho\kappa}T$$

P type-acceptor
N-type-donor



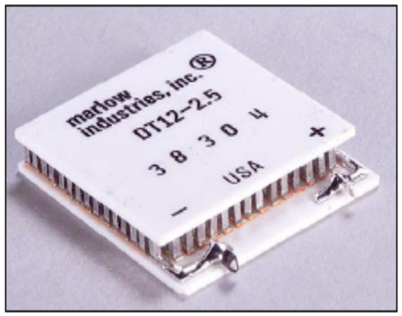
Courtesy of J. Sugar

S =Seebeck coefficient
ρ =electrical resistivity
κ= thermal conductivity
T=Temperature

Experimentally measured

Background and Motivation

Typical TE module design



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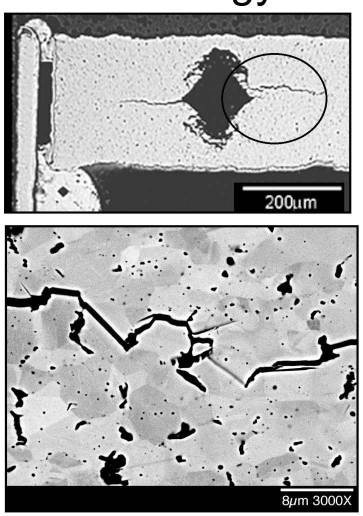

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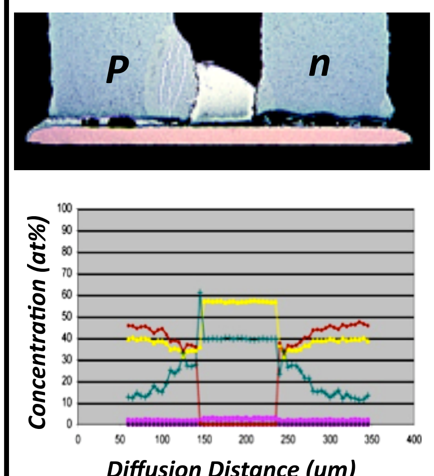

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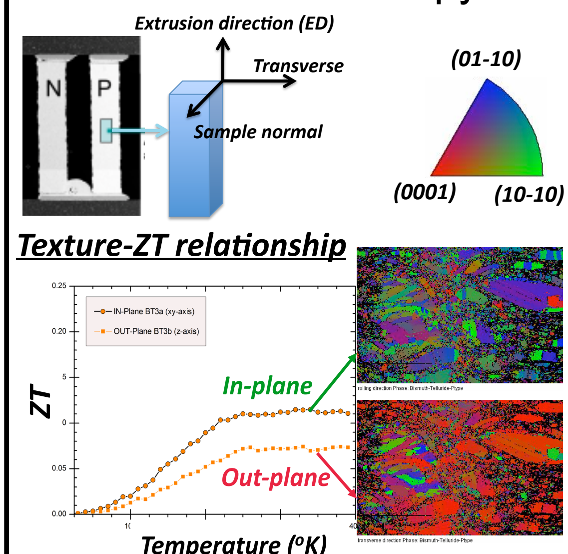

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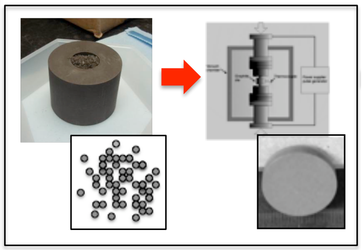

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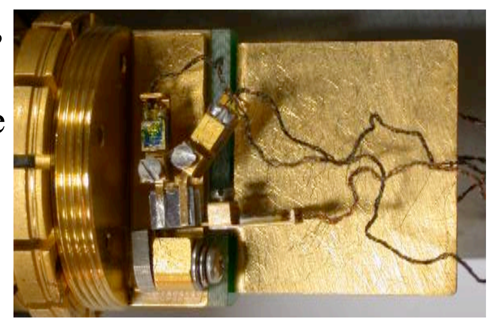

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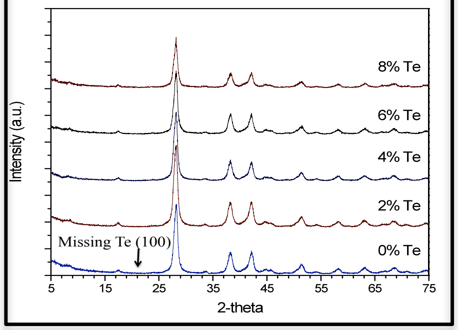
Experimental Results

All mechanically milled starting powders are Te-supersaturated $(Bi,Sb)_2Te3$ single phase.



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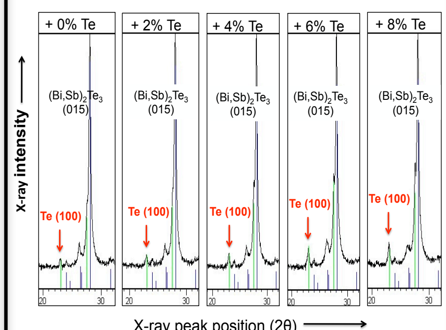

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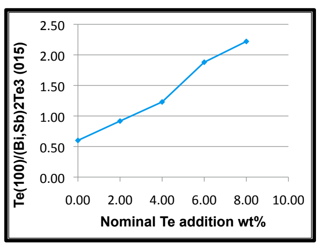

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pure Bi_2Te	Hot extrusion	0.168	0	Strong

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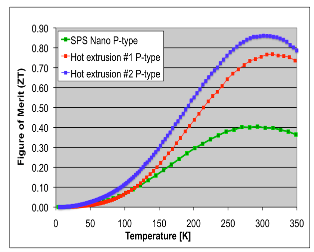

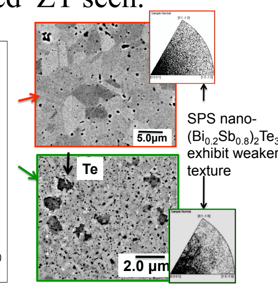

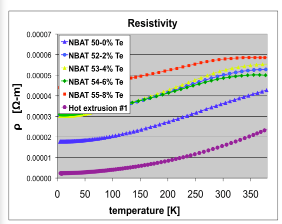

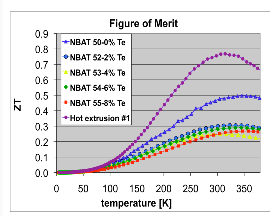

- The electrical resistivity increases with Te addition, therefore lowers ZT.
- The adverse effects on the resistivity and ZT most likely are attributed to the increases in Te phase separation and nanoporosity, induced during the SPS consolidation.

Conclusions

•SPS consolidated nanostructured $(Bi,Sb)_2Te_3$, without process optimization, exhibits exhibits weak texture and is susceptible to nanopore formation and Te phase separation.

•The Te phase separation, dense nanopore and weak texture have adverse effect on TE transport properties, especially electrical resistivity.

•SPS process optimization to mitigate Te-phase separation and nanopore formation is underway.

•The mechanism of the Te phase transformation and its influence the electrical resistivity is being studied.