Improving the thermoelectric properties of Half Heusler compounds

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March 31th, 2011

Outlines

- Introduction of thermoelectrics and applications
- TE properties improvement via:
  - Seebeck coefficient
  - Thermal conductivity
- Bulk Half Heusler with nano-inclusions
- Nanostructured HH and Predictions

Seebeck Effect

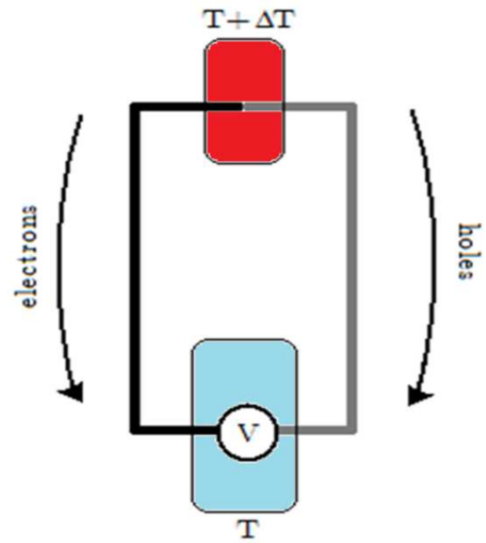
- Temperature gradient deducing Voltage gradient or vice visa

$$S=-\Delta V/\Delta T$$

- Thermal conductivity: κ
- Dimensionless figure of Merit:

$$ZT= S^2T/\rho\kappa$$

- Efficiency- the higher ZT is, the closer the efficiency of TE circuit getting to Carnot Engine.



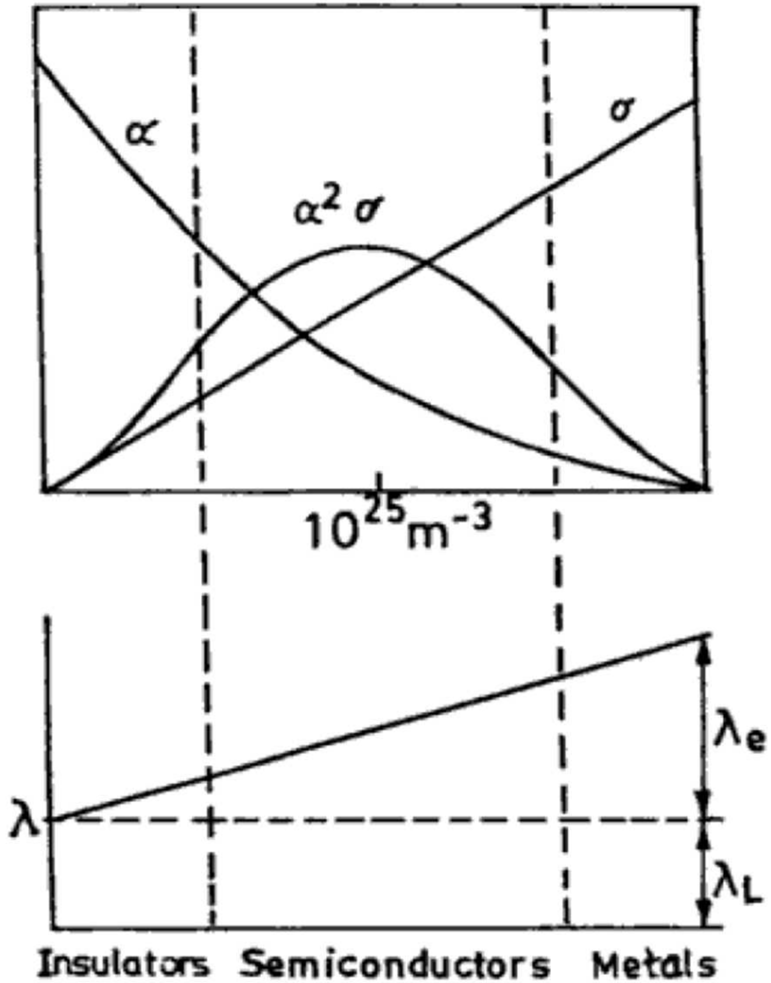
$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}$$

Semiconductor is the best TE material

- α = Seebeck coefficient
- σ = Electrical Conductivity
- λ = Thermal Conductivity

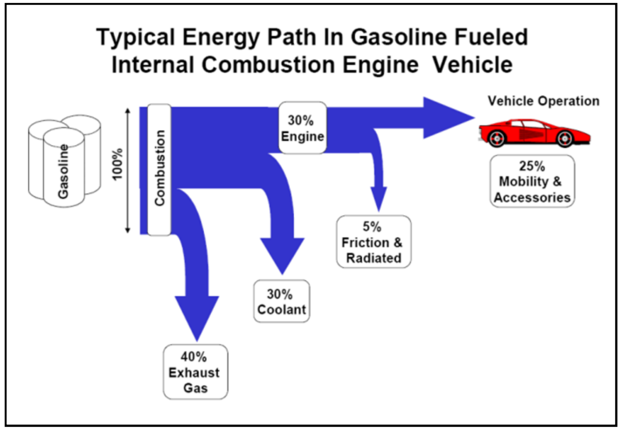
- Power factor combined with thermal conductivity shows semiconductor is the best choice for TE materials

  $ZT = \alpha^2 \sigma T / \lambda$

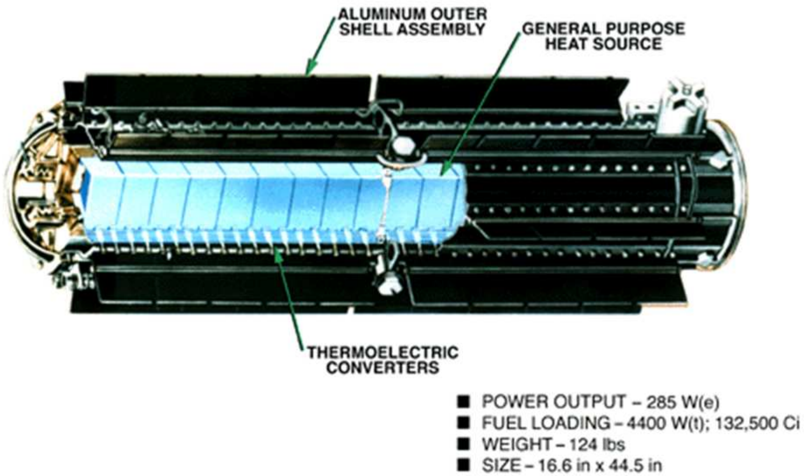


Thermoelectrics Applications

Waste Heat Recovery

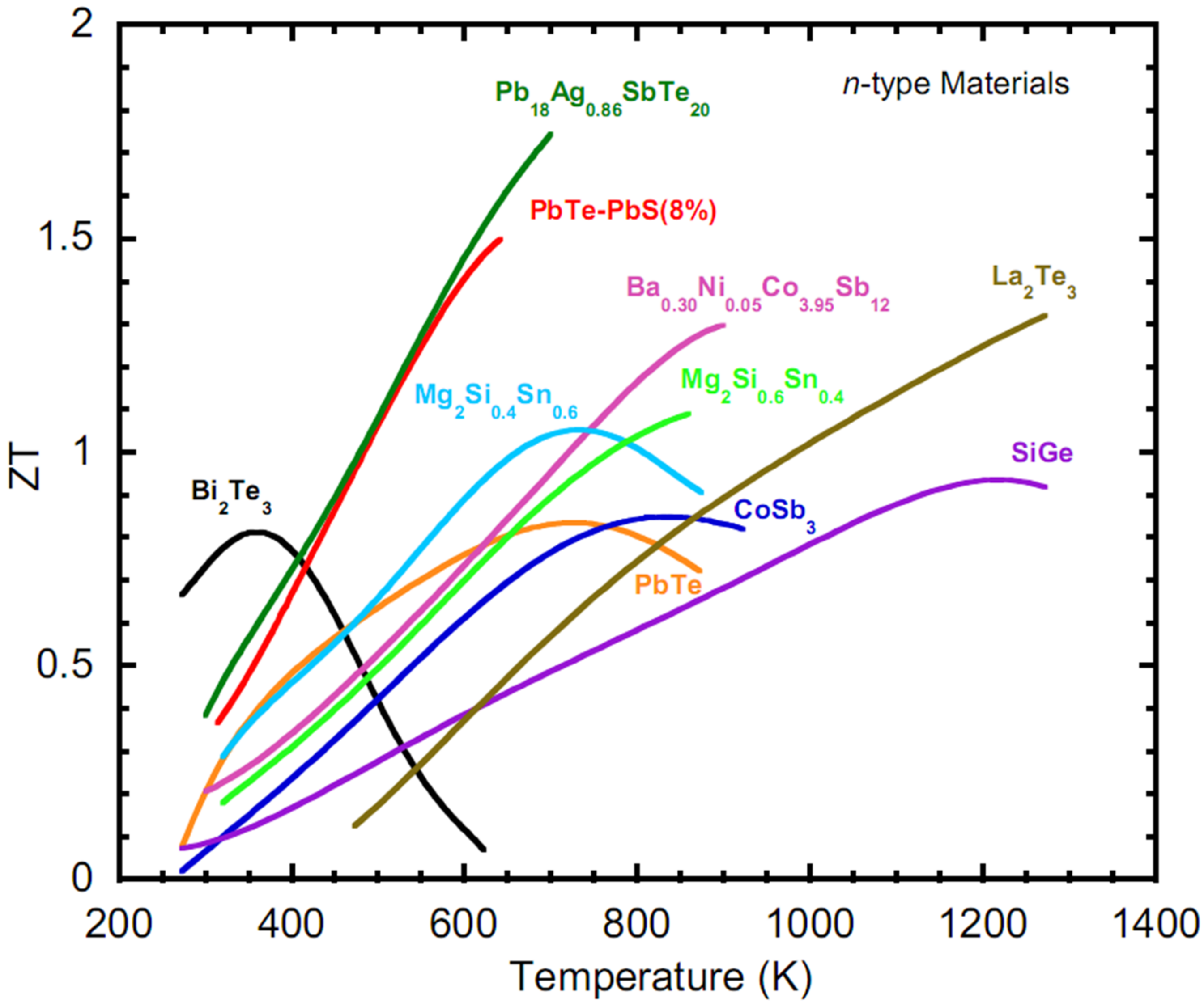


Thermoelectric Generator

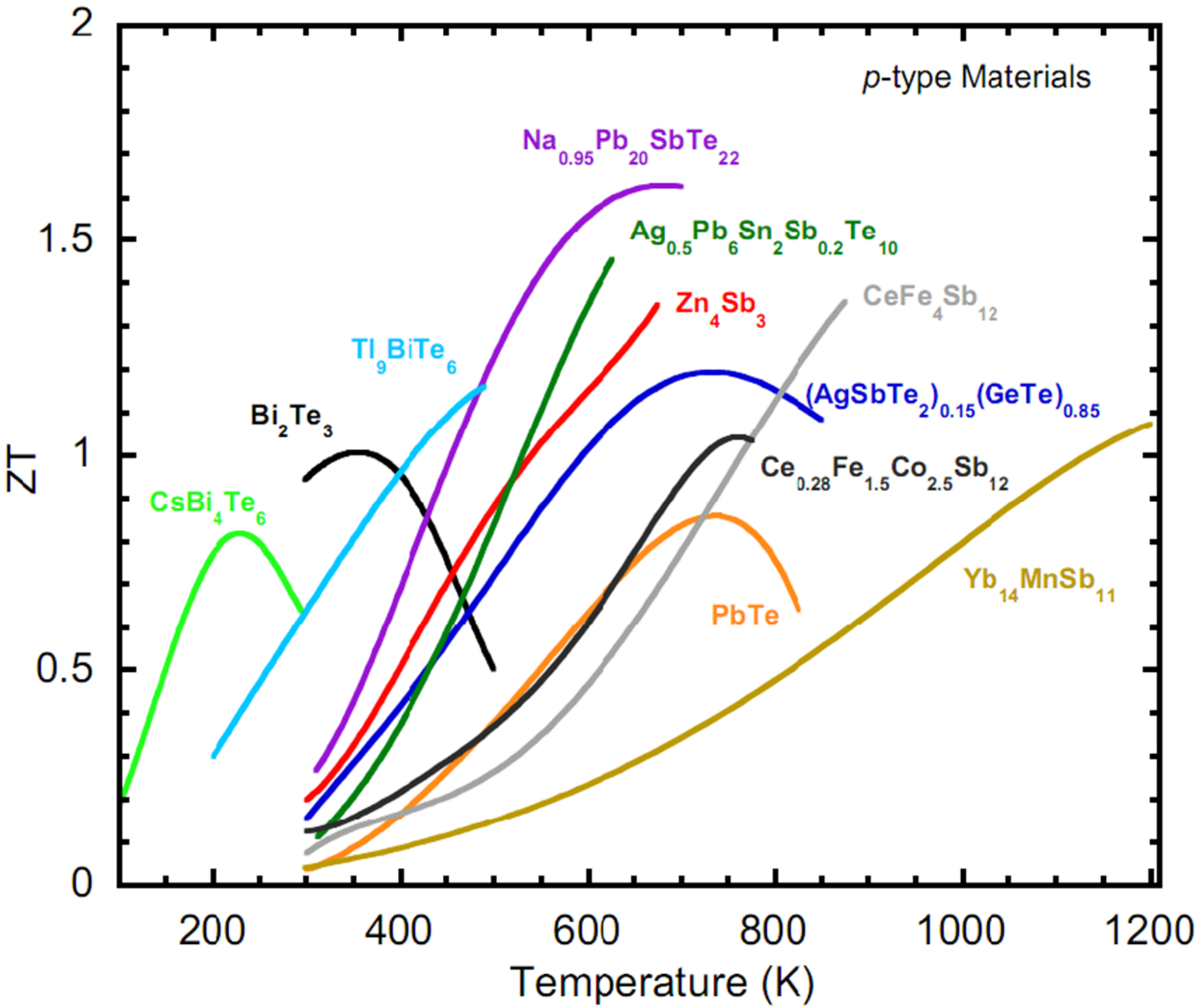


Thermoelectric Cooler

State of the Art TE materials (n-type)

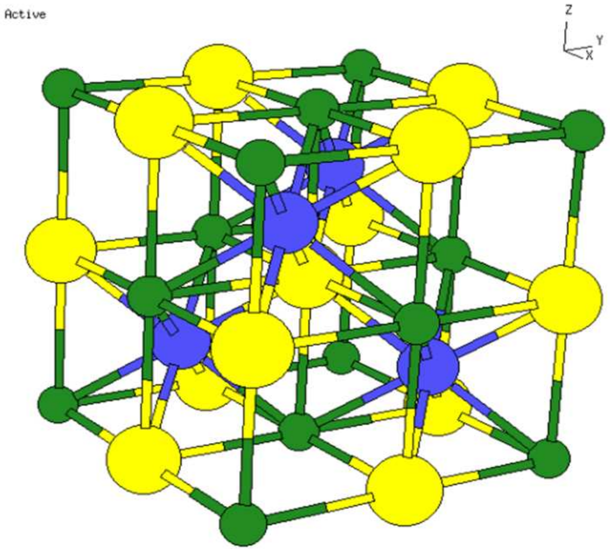


State of the Art TE materials (p-type)



Half Heusler alloys

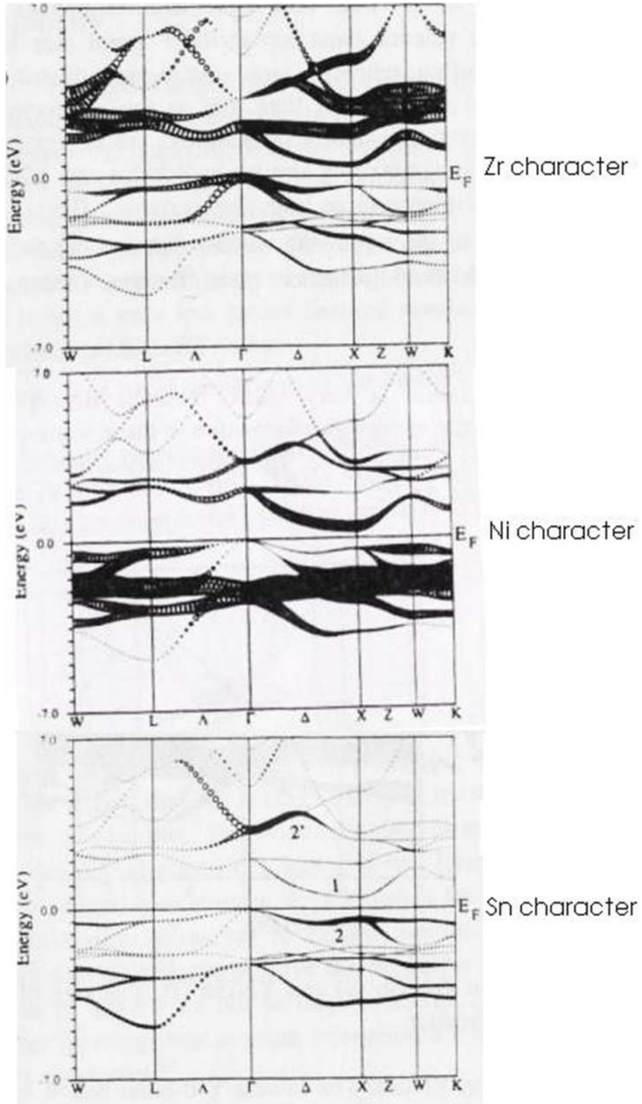
Ti-Ni-Sn



Ti and Sn atoms forms a rock salt structure and Ni atoms fill half of the hollows at the center of Ti-Sn cubic.

Pros: Easy preparation, mulitiple doping options, non-toxic, high electrical conductivity
Cons: comparably high thermal conductivity

Band Structure of MNiSn



S.D. Mahanti, P. Larson, D.Y. Chung, S. Sportouch, and M.G. Kanatzidis. Mater. Res. Soc. Symp. Proc. ***545*** *(1999) 23.*

? How can we improve the properties of Thermoelectric materials

$$ZT = \frac{S^2 T}{\rho \varkappa} = \frac{S^2}{L_e + \frac{\varkappa_L \rho}{T}}$$

$L_e - electrical\ Lorentz\ number$

$\varkappa_L - Lattice\ thermal\ conductivity$

$\boldsymbol{\rho} - electrical\ \ resistivity$

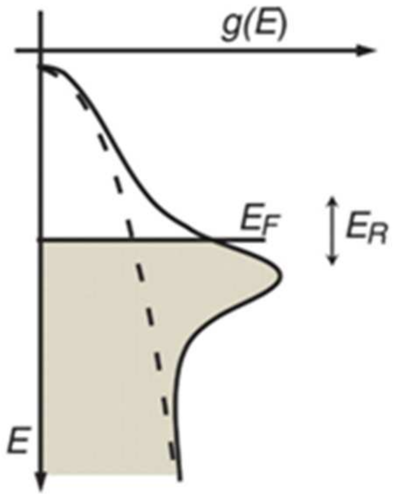
$K_e = L * \sigma * T$

$\varkappa_L$?

S ?

resonant states

Mahan-Sofo Theory



Mott Expression

$$S = \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{d[\ln(\sigma(E))]}{dE}\right\}_{E=E_F}$$

$$= \frac{\pi^2}{3}\frac{k_B}{q}k_B T\left\{\frac{1}{n}\frac{dn(E)}{dE} + \frac{1}{\mu}\frac{d\mu(E)}{dE}\right\}_{E=E_F}$$

n(E)=g(E)*f(E)

Band Structure Engineering

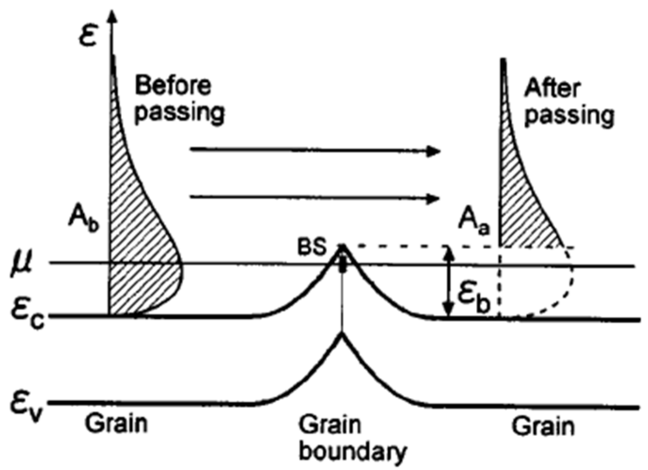
Doping isovalent atoms with higher/lower electronegativity to resonate with corresponding conduction(n-type)/valence band edge of the majority component.

J.P. Heremans; V. Jovovic, E.S. Toberer, A. Saramat, K.Kurosaki, A.Charoenphakdee, S. Yamanaka, G.J. Snyder, Science, v321, July 2008

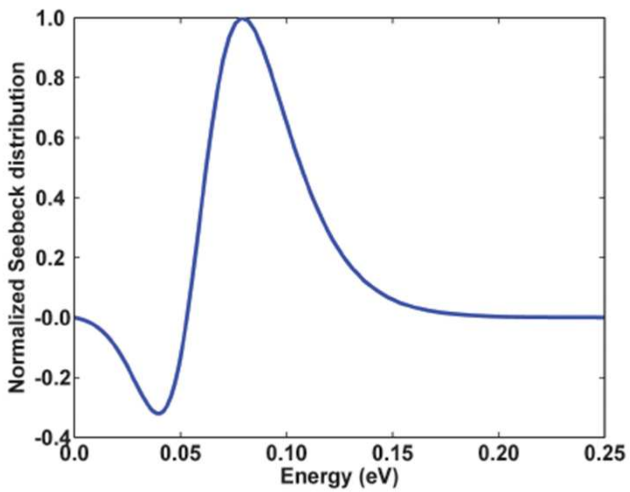
Energy Filtering

Carriers →

(1)



Carriers which have lower energy than ε_b are greatly scattered



(2)

Calculated normalized seebeck distribution *vs* electron energy for heavily doped bulk n-type $Si_{80}Ge_{20}$ at RT. Low energy electrons contribute negatively to the Seebeck coefficient. This is also one of the motivation of our nano-inclusions bulk materials.

1) K.kishimoto, M.Tsukamoto, T. Koyanagi Journal of Allplied Physics, v92, n9, 2002
2)Minnich,A.J.;Dresselhaus, M.S.; Ren, Z.F.; Chen, G. Energy and Environmental Science, v 2, n 5, p 466-479, 2009

Thermal conductivity

thermal conductivity $\kappa_T = \kappa_C + \kappa_e + \kappa_p$

κ_p
photon contribution κ_p negligible

electronic contribution κ_e

Wiedemann–Franz law

K_e= L * σ * T , where L is Lorentz number L=2.44*10^{-8} W*Ω*K^{-2}

Lattice contribution κ_C ***is exactly what we are working on………***

LatticeTC model

Callaway's Lattice TC

$$\kappa_C = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta/T} \tau_C(x,T)\frac{x^4 e^x}{(e^x-1)^2}dx$$

relaxation time

$$\tau_C^{-1} = \tau_I^{-1} + \tau_U^{-1} + \tau_B^{-1}$$

where :

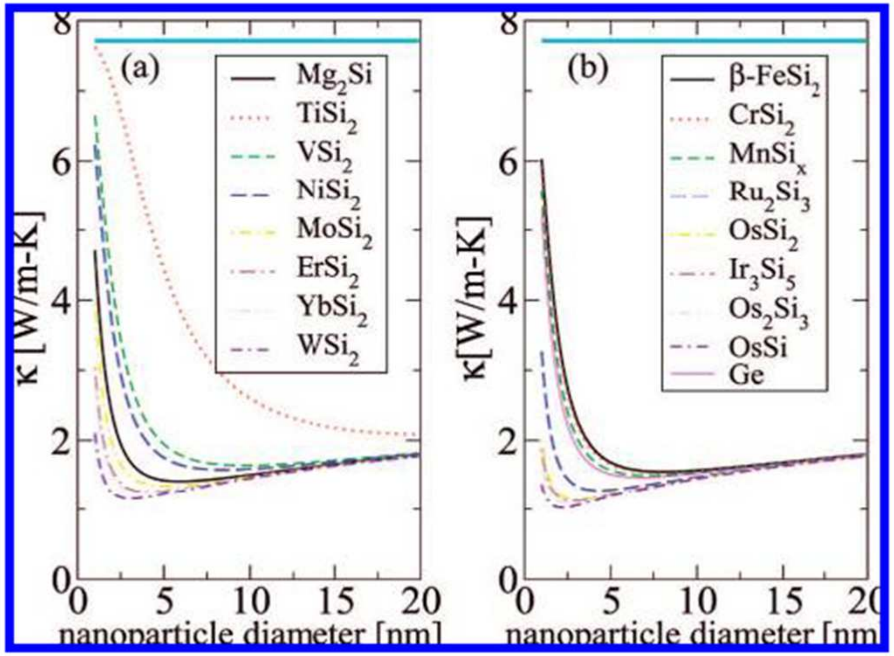
$$x = \hbar\omega / k_B T$$

Impurity scattering $\tau_I^{-1} = A\omega^4$

Umklapp scattering $\tau_U^{-1} = B_U T^3 \omega^2$

Boundary scattering $\tau_B^{-1} = v/L$

J. Callaway, Physics Review, v113, n4, 1959



Mingo developed the grain boundary term to deal with bulk materials involving nano-particles

$$\tau_{np}^{-1} = \upsilon(\sigma_s^{-1} + \sigma_l^{-1})^{-1}\rho$$

Short wavelength $$\sigma_s = 2\pi R^2$$

Long wavelength $$\sigma_l = \pi R^2 \frac{4}{9}(\Delta D/D)^2(\omega R/\upsilon)^4$$

ρ is the volume density of the nano-inclusions

This is TC of various silicide nanoparticles (0.8% volume fraction) into $Si_{50}Ge_{50}$ main matrix at T=300K:

1) TC decrease greatly even with small fraction of nanoinclusions.

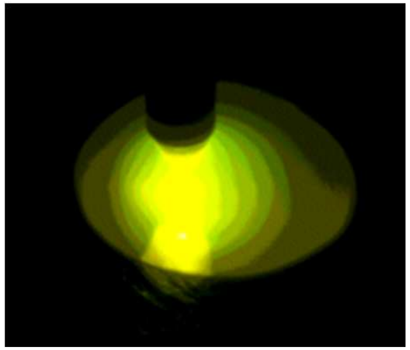
2) It is not necessary to make accurate nanoparticle size control

N. Mingo, D. Hauser, N. P. Kobayashi, M. Plissonnier, and A. Shakouri, Nano Lett., 2009, 9(2), 711-715

Preparing bulk HH with nano-inclusions

2% ZrO_2 nanoparticles dispersed $Hf_{0.3}Zr_{0.7}CoSn_{0.3}Sb_{0.7}$

Arc Melting



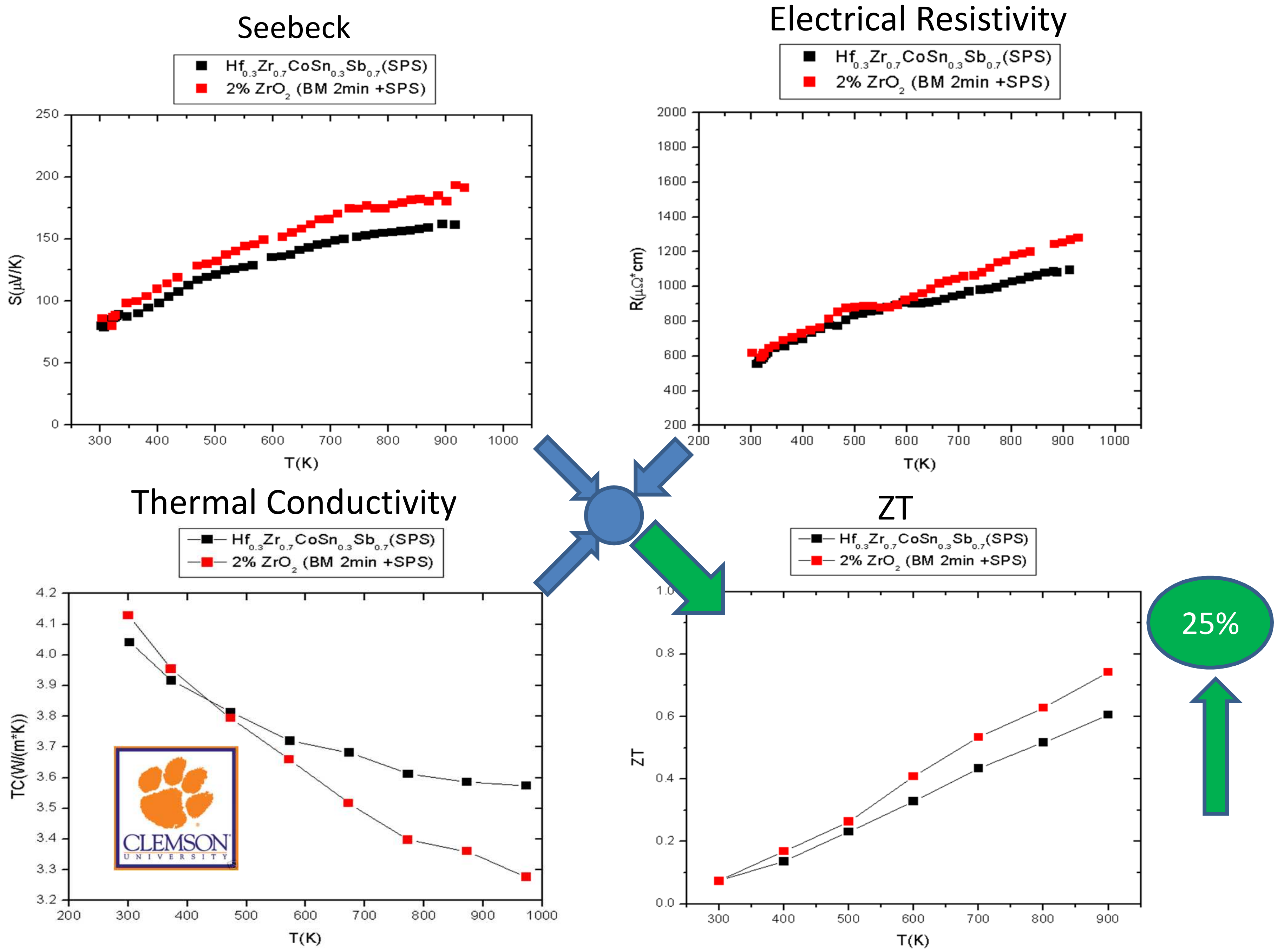
Main Matrix preparation

Ball milling/mixing

ZrO_2 nanoparticles involving

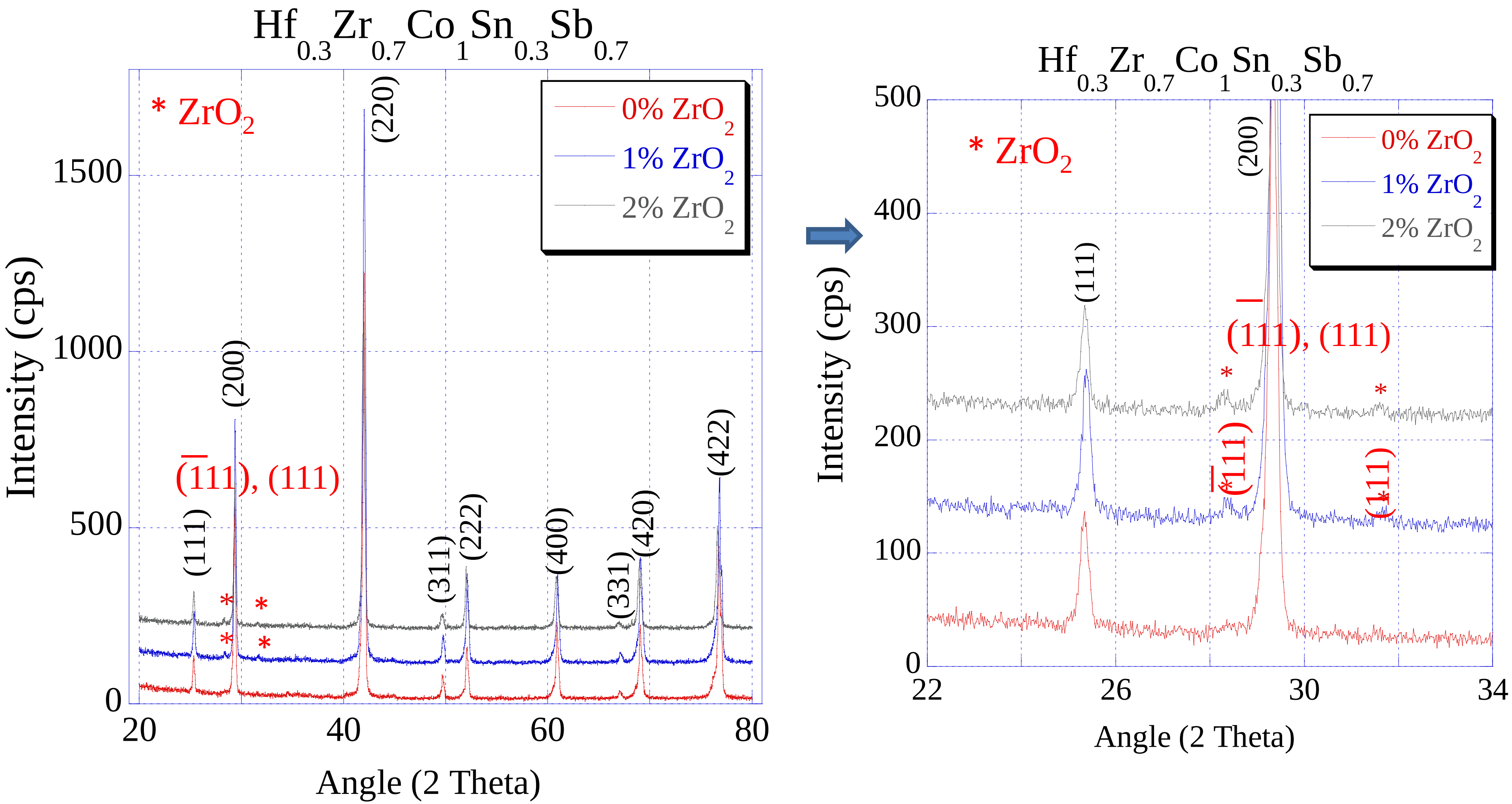
SPS (Spark Plasma Sintering)

Clemson University, SC



Seebeck
Hf0.3Zr0.7CoSn0.3Sb0.7(SPS)
2% ZrO2 (BM 2min +SPS)
S(μV/K)
T(K)
Electrical Resistivity
Hf0.3Zr0.7CoSn0.3Sb0.7(SPS)
2% ZrO2 (BM 2min +SPS)
R(μΩ*cm)
T(K)
Thermal Conductivity
Hf0.3Zr0.7CoSn0.3Sb0.7(SPS)
2% ZrO2 (BM 2min +SPS)
TC(W/(m*K))
T(K)
CLEMSON
UNIVERSITY
ZT
Hf0.3Zr0.7CoSn0.3Sb0.7(SPS)
2% ZrO2 (BM 2min +SPS)
ZT
T(K)
25%

X-Ray Pattern as proof of existence of ZrO2



SEM and TEM in process….

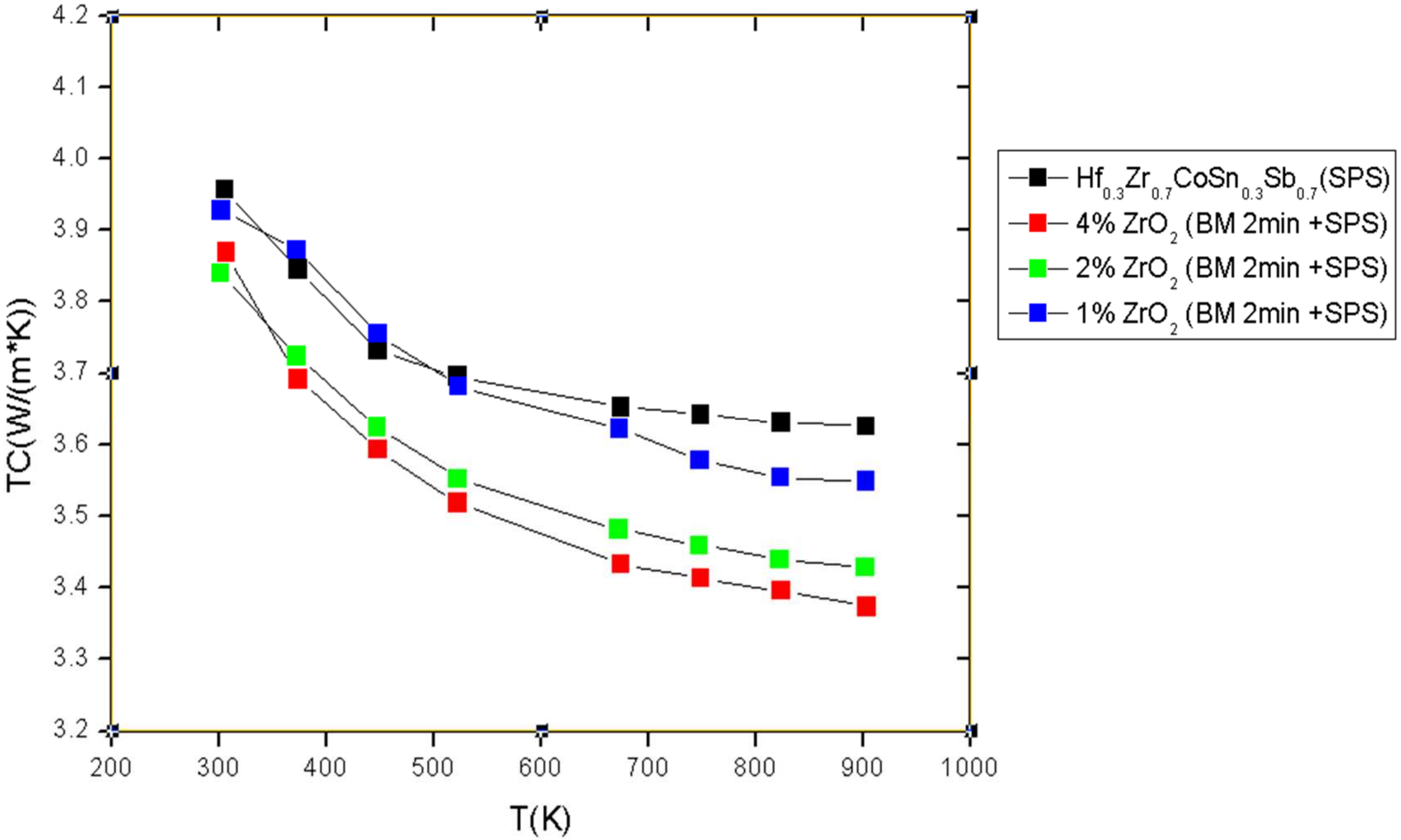
SEM and EDS

SEM is used to determine the gain size of the main matrix as well as existence of ZrO_2 nano-inclusions.
EDS is used to determine HH compound's uniform distribution as well as rough chemical composition.

SEM

Providing accurate proof for nano-inclusions existence as well as information of their grain size and position in main matrix

Higher naonparticles dispersion level will further decrease TC



Nano-structure instead of nano-inclusions?

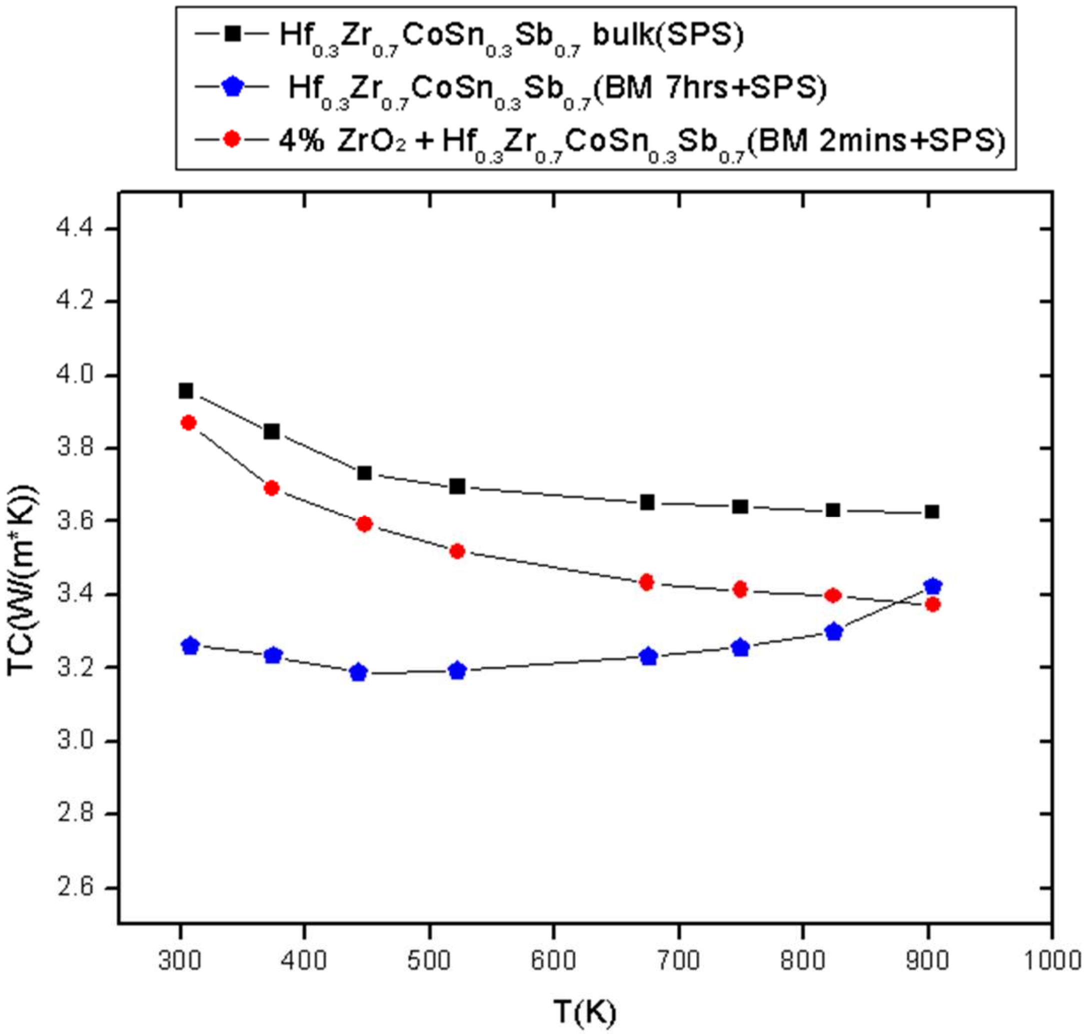
How about ball milling the main matrix over hours?

grinding the main matrix to nano-scale?

	Main matrix grains	Inclusion grains	Ball milling time
Nano-inclusions	Micron scale	Nano scale	<5 mins
Nano-structure	Nano scale	Nano scale	hours

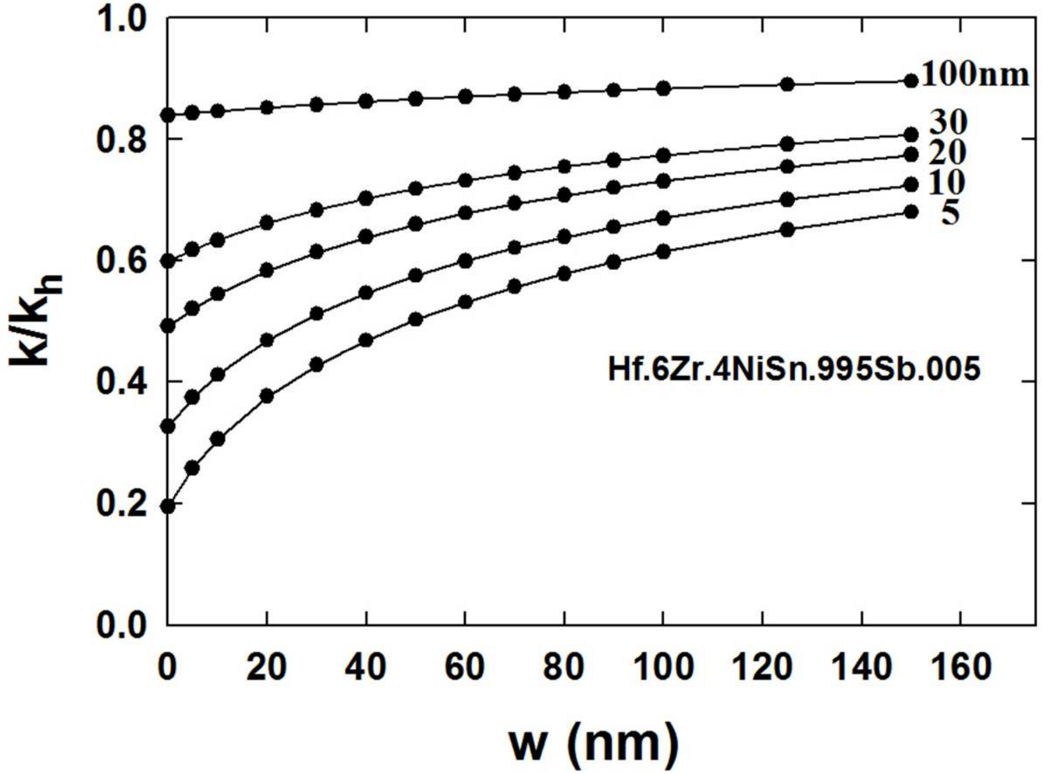
Investigation in process.....

1) ***Prevent oxidization while ball milling***
2) ***Prevent contamination from the vial itself***



Further decreasing in thermal conductivity shows nano-structure bulk more promising than nano-inclusions bulk.

Further predictions……….



k/k_h - Lattice TC of nano-structured Half Heusler alloy normalized to the reference regular bulk alloy

w - the size range of the particles

What ZT can we expect from this theoretical model?

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

For N-type HH $Hf_{0.6}Zr_{0.4}NiSn_{0.995}Sb_{0.005}$ at 900K

Grain size	Lattice TC	ZT
20 to 100μm (bulk)	1.10	0.91
100 to 200 nm	0.99	0.93
20 to 60 nm	0.704	0.99
5 to 25 nm	0.418	1.07

Acknowledgement

- *Many thanks to Dr. Poon for his work on lattice TC prediction for nanostructured Half Heusler*

- *Appreciate the help of Thermal conductivity measurement and SPS from Clemson University*

Thanks for your attendance!