

Thermoelectric Performance Enhancement of Bi_2Te_3 and Ag_2Te Using Surrounding Metallic Nano-bridges

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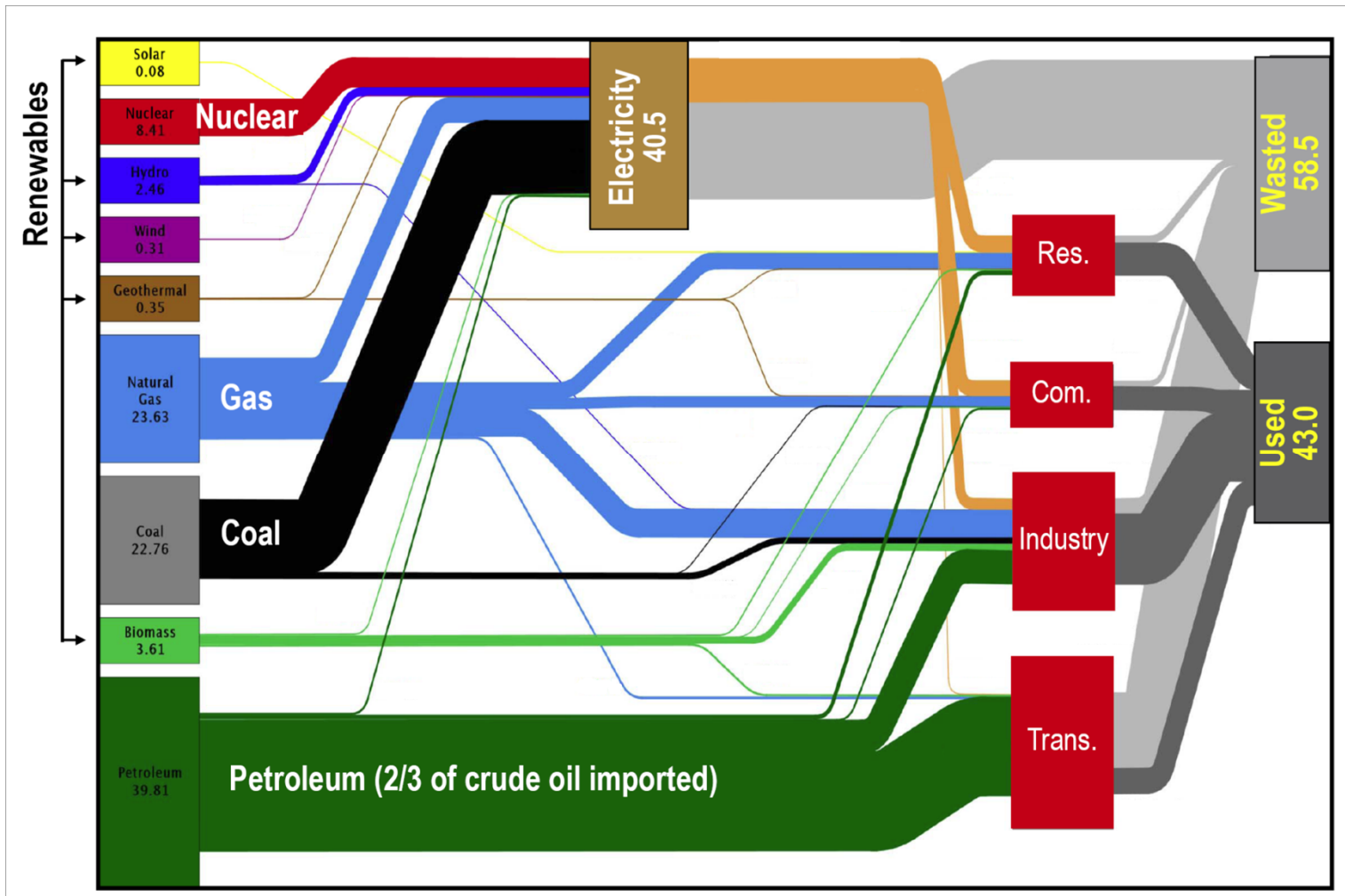
- Potential of Thermoelectrics
- Overview of Thermoelectricity
- New Design to Yield Enhanced Performance in Bulk Systems
- Bi_2Te_3 / Ag_2Te Decorated with Metallic Nanoparticles
 - Model validated by experiment
- Newly emerging research directions
 - ✓ Novel methods for synthesis and assembly of TE materials
 - ✓ Self assembled composite nanostructures
 - ✓ Novel 3D crystalline materials with metallic nanoparticles
 - ✓ Novel tools for thermoelectric characterization
- Summary

Potential of Thermoelectrics



U.S. Energy Consumption ~ 102 Quads (2007)

“Waste Heat” Can Be Utilized Using Thermoelectrics



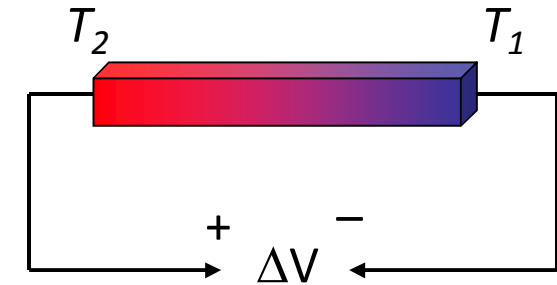
Introduction to Thermoelectricity



- Seebeck coefficient

$$S = -\frac{\Delta V}{T_2 - T_1}$$

Measure of how much energy can be converted to electrical energy, $S > 0$ for p-type, $S < 0$ for n-type



- Efficiency determined by
Dimensionless figure of merit

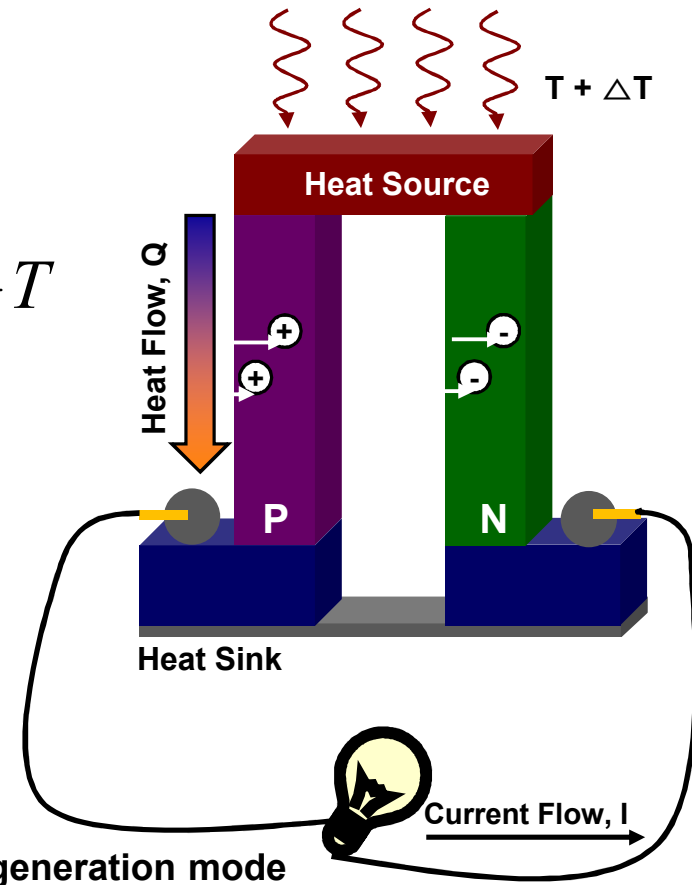
$$ZT = \frac{\sigma S^2}{\kappa} T$$

σ = electrical conductivity

κ = thermal conductivity

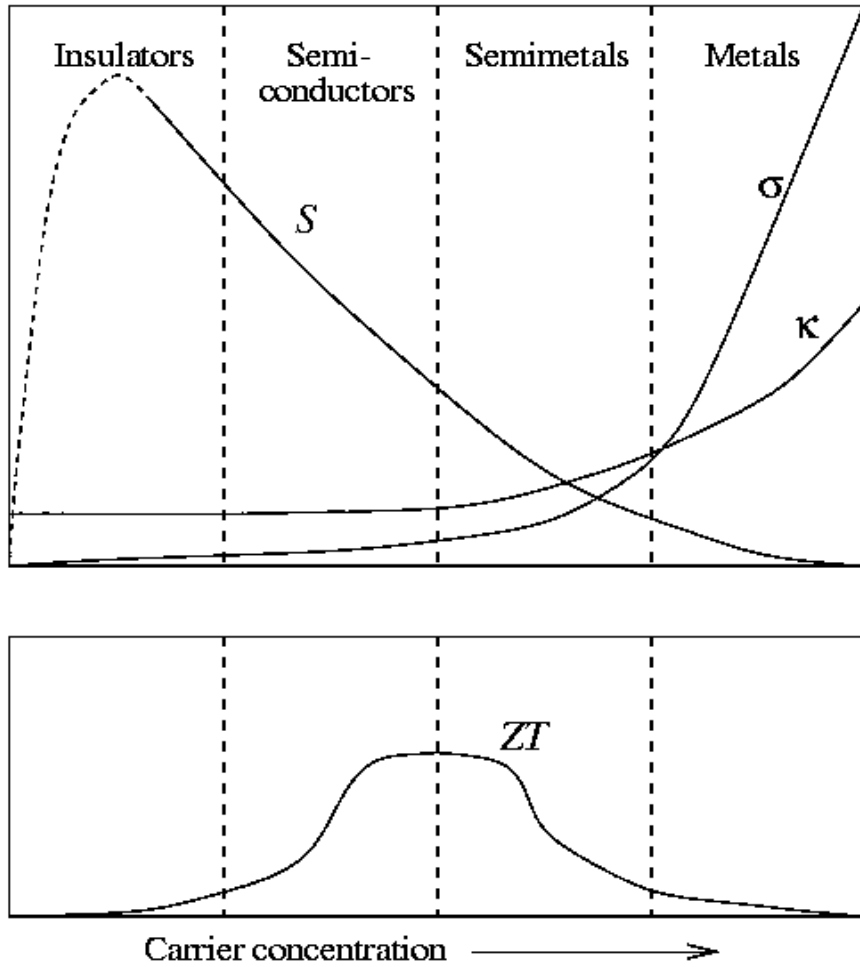
ε = efficiency of a TE device for electricity generation

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



Power generation mode

Thermoelectric Properties of Conventional Materials



For most bulk materials...

$$ZT = \frac{S^2 \sigma}{\kappa} T = \frac{S^2 \sigma}{\kappa_e + \kappa_{ph}} T = \frac{S^2}{L + (\kappa_{ph} / \sigma T)}$$

To increase ZT , we want

$$S \uparrow, \sigma \uparrow, \kappa \downarrow$$

but

$$S \uparrow \Leftrightarrow \sigma \downarrow$$

$$\sigma \uparrow \Leftrightarrow \kappa \uparrow, S \downarrow$$

- Increasing σ increases κ_e (Weideman-Franz-Lorenz Law)
- Decreasing κ_{ph} by adding defects decreases mobility (and σ)
- Reducing m^* increases mobility (and σ), but decreases S
- Increasing carrier concentration decreases S

L: Lorentz constant, κ_e and κ_{ph} correspond to carrier and phonon contribution to thermal conductivity, respectively.

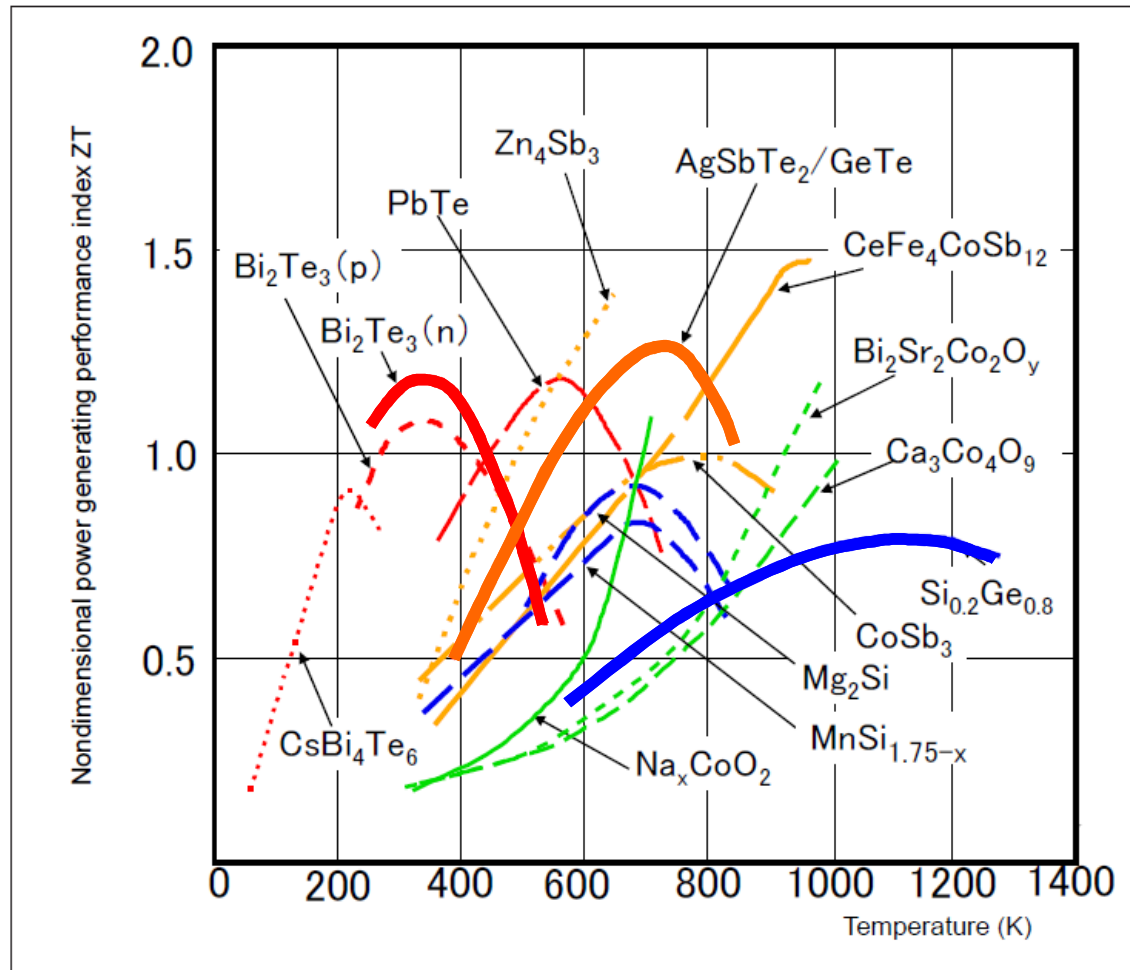
m^* : carrier effective mass

Improving Thermoelectric Efficiency



Try different material compositions ...

still $ZT < 1$ for 40 years!



"Thermoelectric Conversion Materials," ed. By The Ceramic Society of Japan/
Thermoelectrics Society of Japan, Nikkan Kogyo Shimbun, Ltd. (2005)

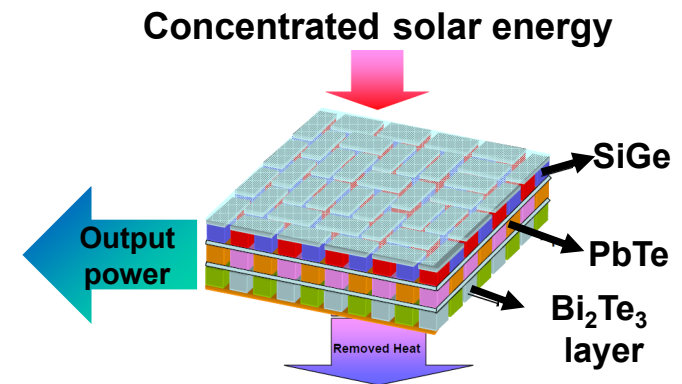
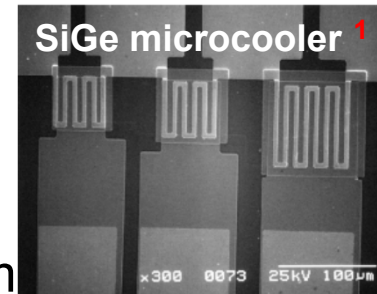
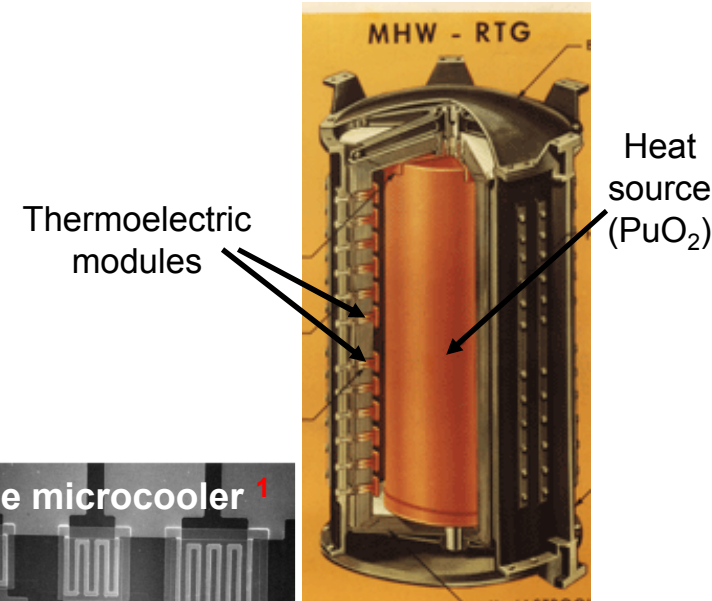
Low-dimensional materials give additional control:

- Enhanced density of states due to quantum confinement effect
⇒ Increase S without reducing σ
- **Boundary scattering** at interfaces reduces κ more than σ
- Decrease in κ
⇒ **phonon group velocity reduction** caused by the spectrum change, the interface thermal resistance and interface scattering, phonon interference and tunneling, and dislocation.
- **Phonon scattering**
⇒ Phonon scattering from free surfaces and grain boundaries decreases the lattice contribution to the thermal conductivity, thereby increasing ZT
- **Solid-solution alloying** to reduce K_{ph}
- **Possibility of materials engineering** to further improve ZT

Real-World Thermoelectric Devices (Applications)



- Power generation, waste heat recovery, cooling
- Radioisotope TE generators powering deep space probes
- Thermoelectric **thin films** being researched
 - On-chip sensor/cooling
 - Local (renewable) power generation
- Advanced Thermoelectric System in tandem mode²
 - Formation of regenerative cycles of solar thermal energy for cascade efficiency
 - PV + TE

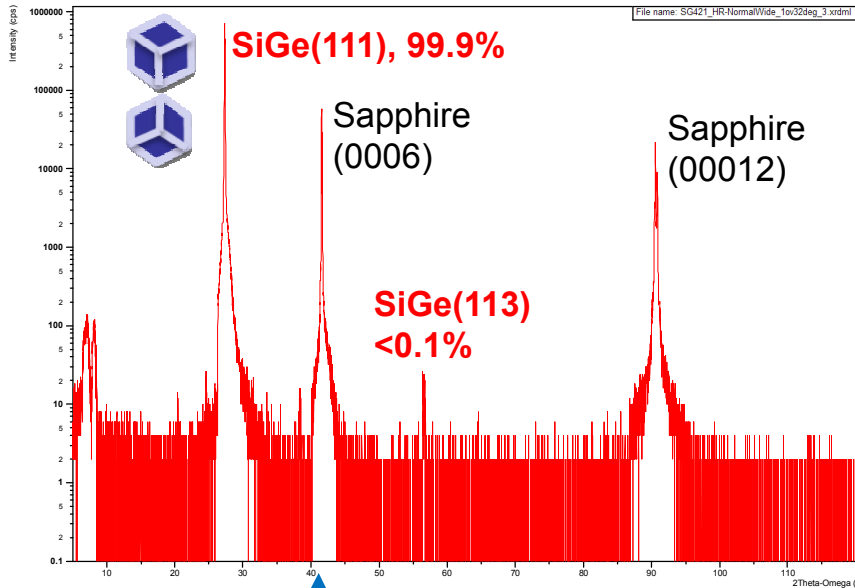


1. Shakouri and Zhang, IEEE trans. 28, 65 (2003)
2. Sang H. Choi, SPIE Newsroom. DOI: 10.1117/2.1200604.0234 (2006)

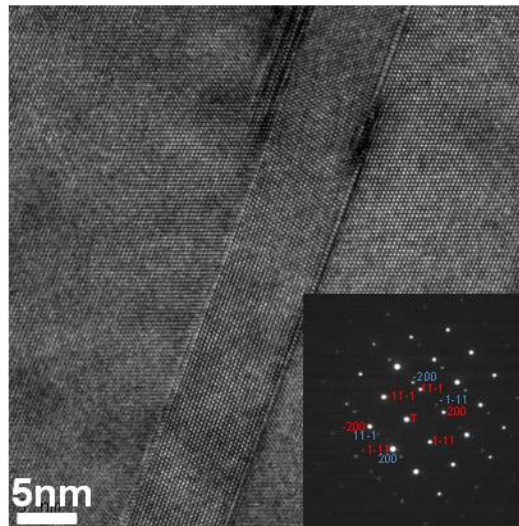
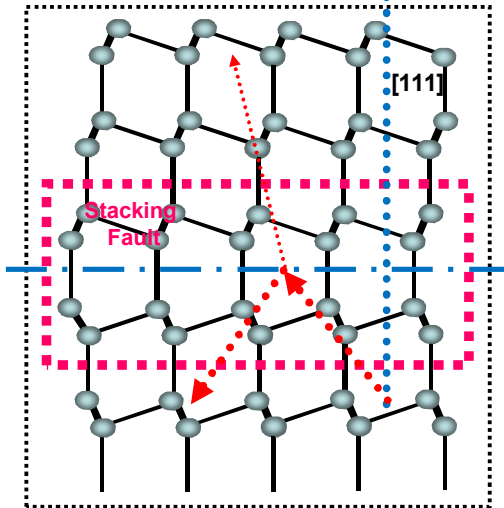
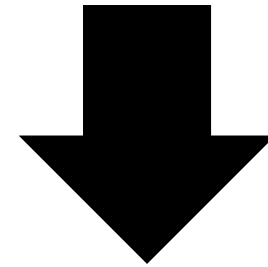
SiGe Twin Crystal for High Temperature Application



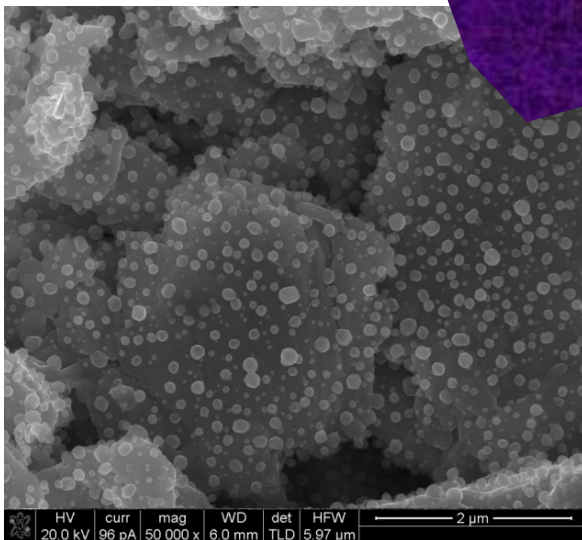
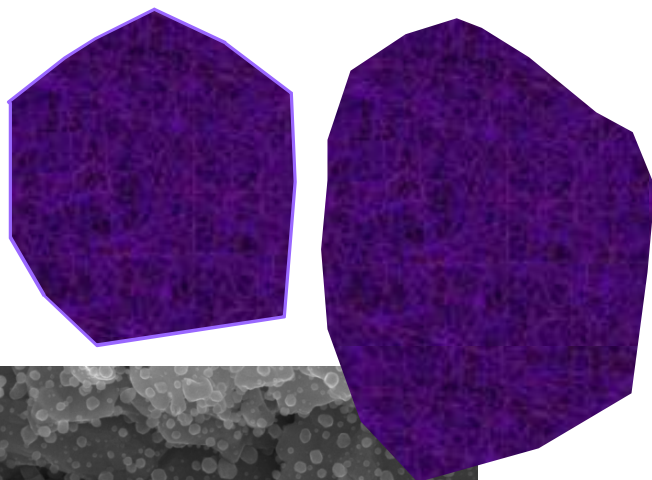
2Theta-Omega Normal Scan



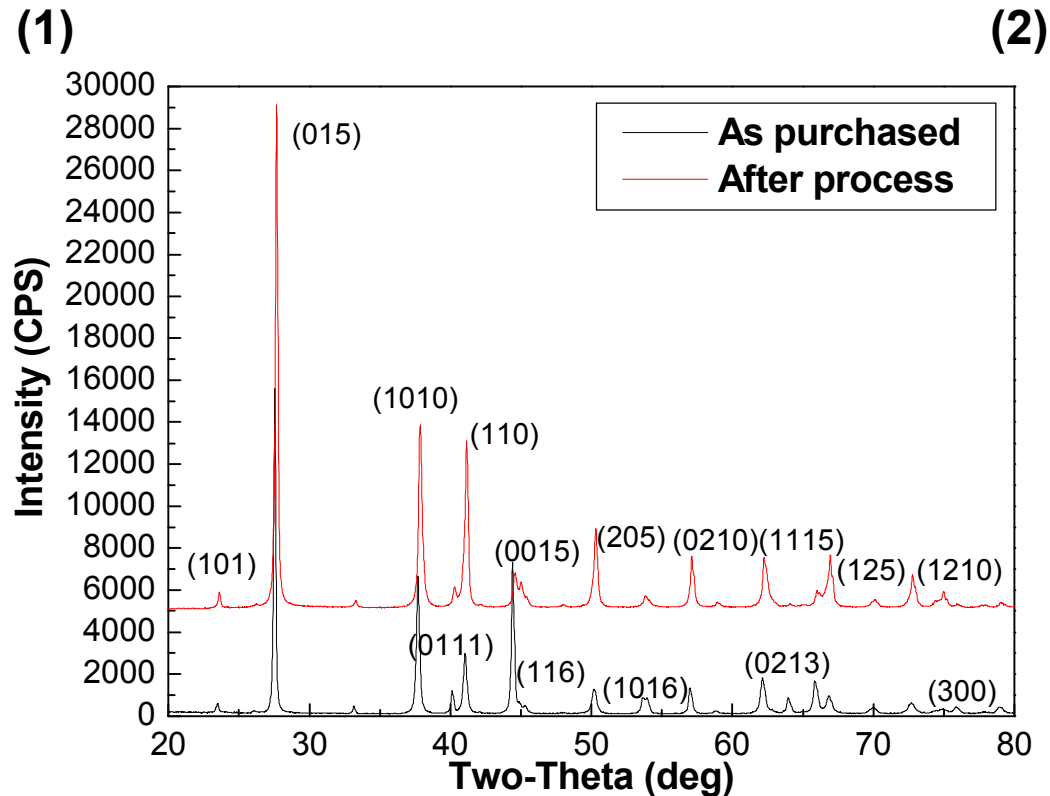
To develop a crystalline structure for phonon scattering using NASA Langley invented “**twinned lattice structure (TLS)**”. TLS is superior to superlattice structure.



- Thin-film deposition techniques is not suitable for large scale and economical applications due to its high manufacturing cost and difficulty to scale up for large scale applications



Synthesis of Nanostructured Bismuth Telluride Powder



(2)



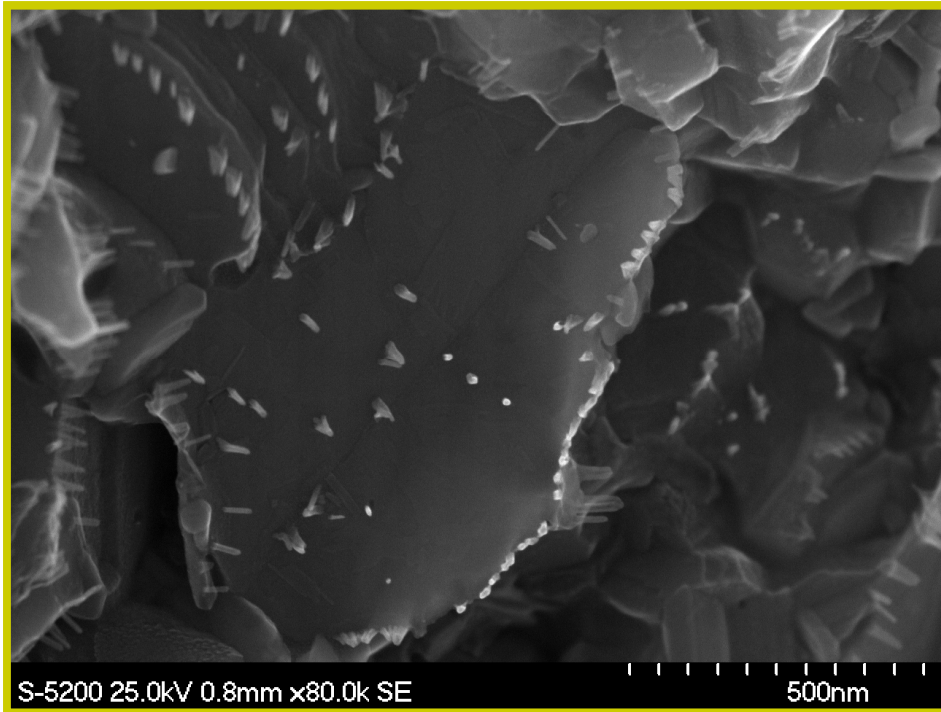
Figure 1 shows XRD patterns of the as purchased (black) and hydrothermally synthesized (red) Bi_2Te_3 powders. All the peaks in Figure can be indexed to Bi_2Te_3 (JCPDF, no. 15-0863).

Figure 2 shows TEM images of Bi_2Te_3 nanoparticles and Diffraction Pattern with measured d -values

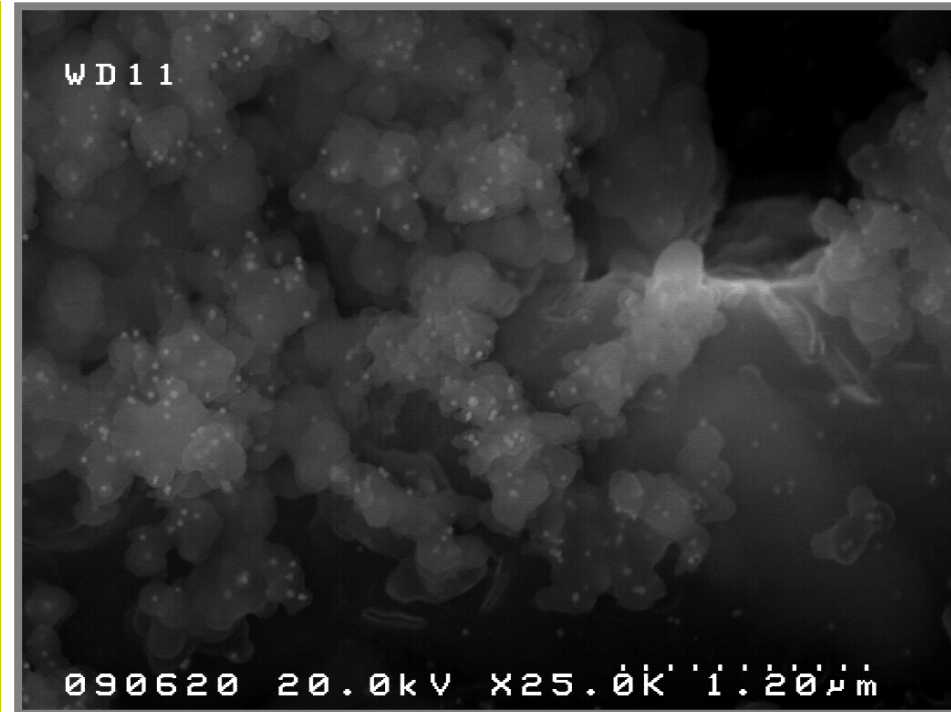
Au and Ag Particle Distribution in Hot-pressed Bi_2Te_3



0.5 wt% Au / Bi_2Te_3

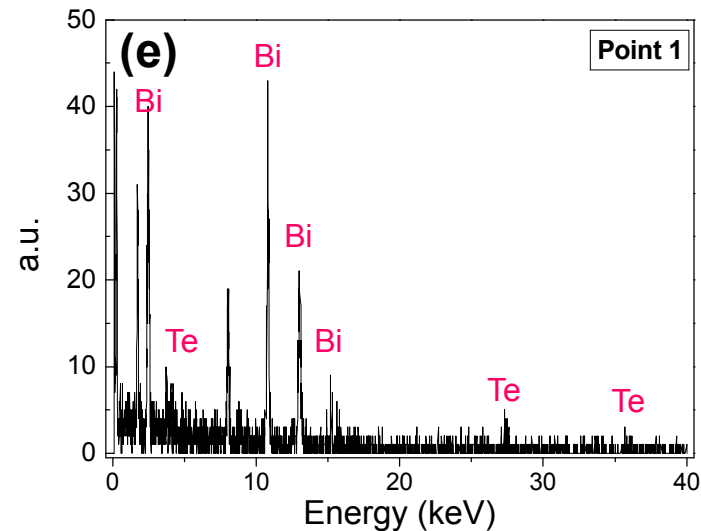
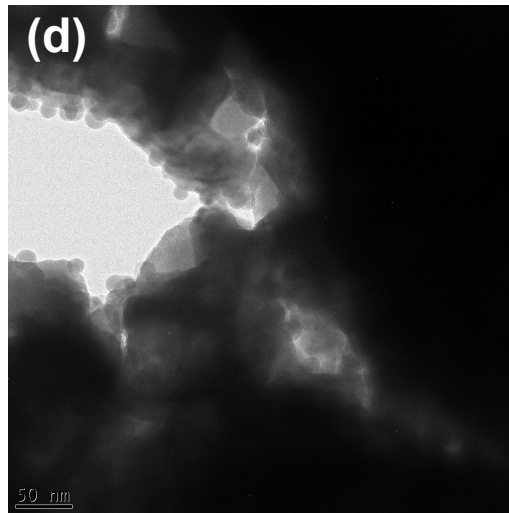
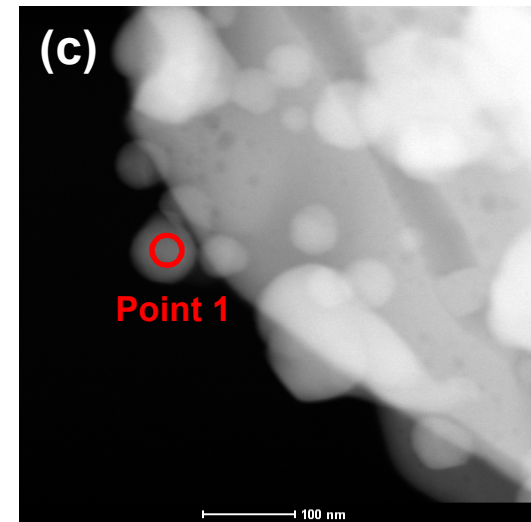
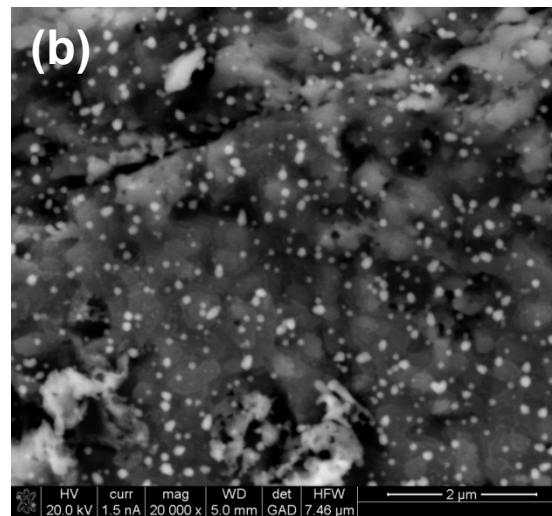
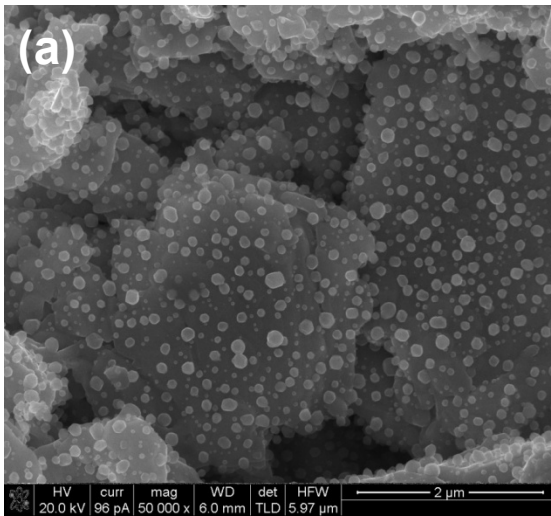


0.5 wt% Ag / Bi_2Te_3



➡ *It is crucial to distribute the metallic nanoparticles uniformly.*

Ag₂Te Particles Decorated with Metallic Nanoparticles



A cleavage surface SEM images ((a) and (b)) and TEM images ((c) and (d)) of the Ag₂Te-based Bi nanoparticles decorated sample. (e) EDS spectra of nanoparticle (red circle in (c))

TE Characterization System

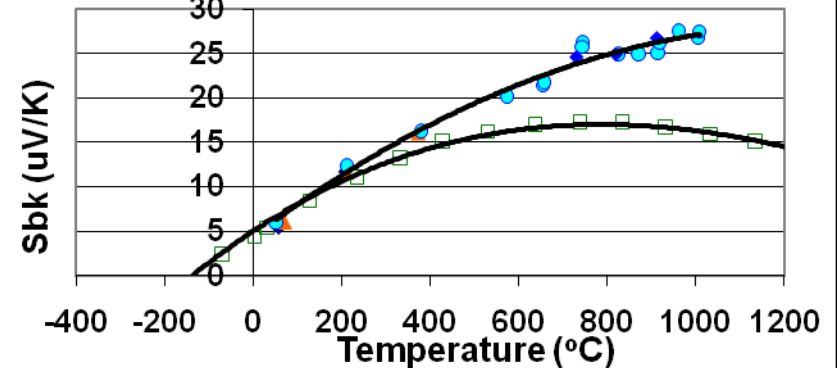


(b)

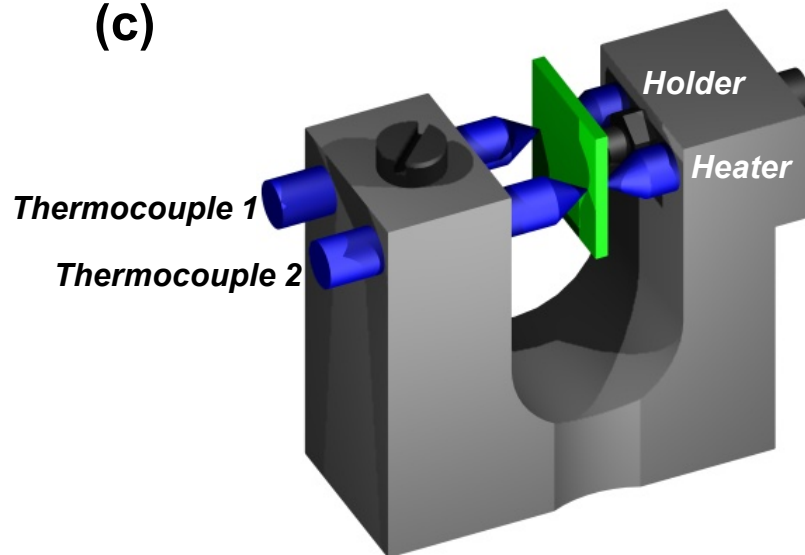
Sbk vs. temp In Argon gas S-type

Moly sample

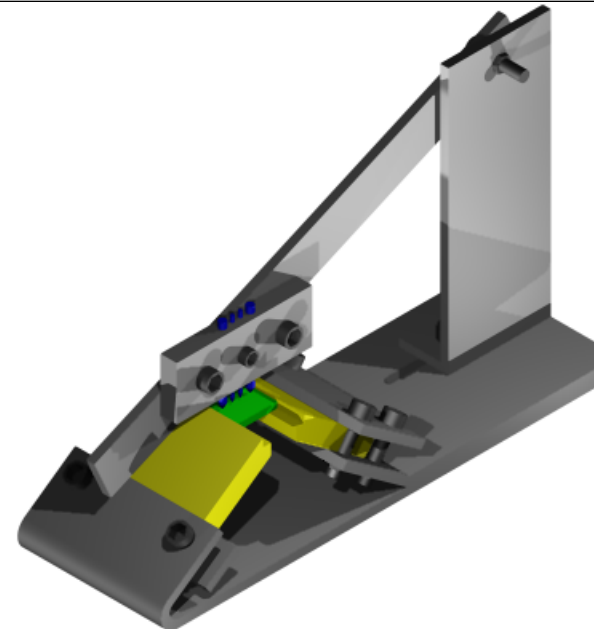
Raw data



(c)

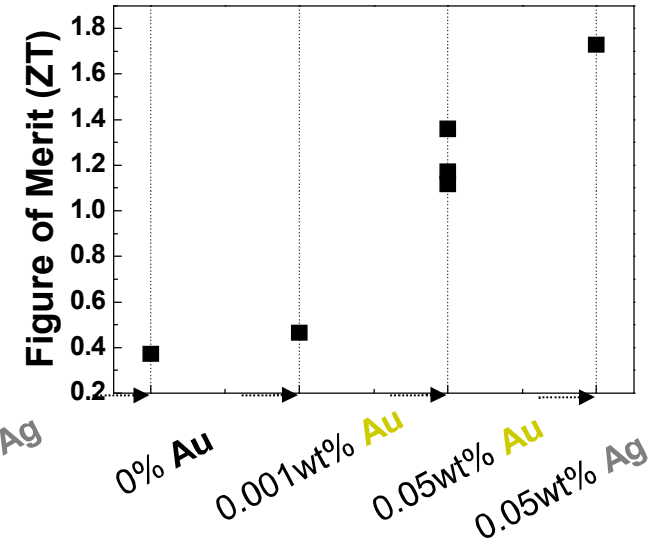
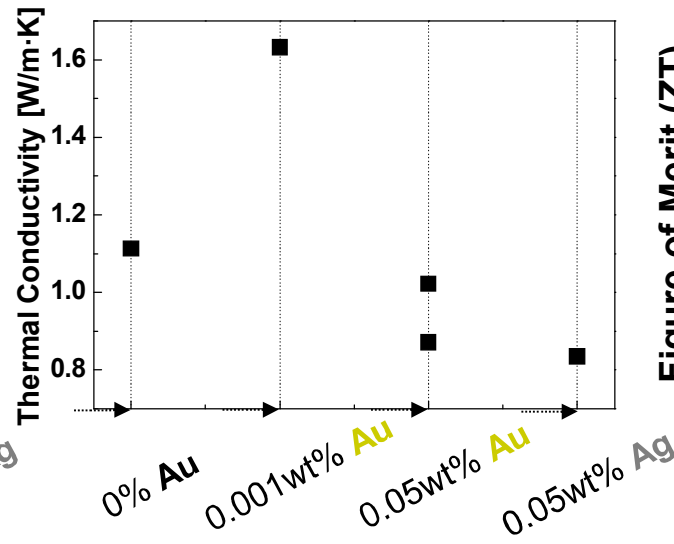
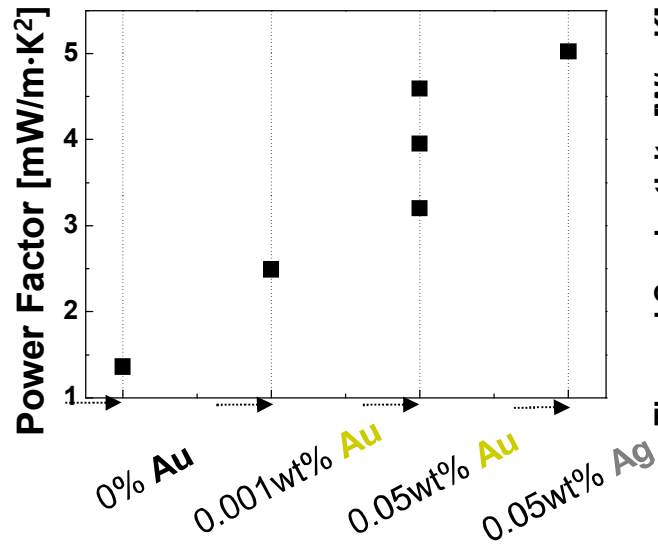


(d)



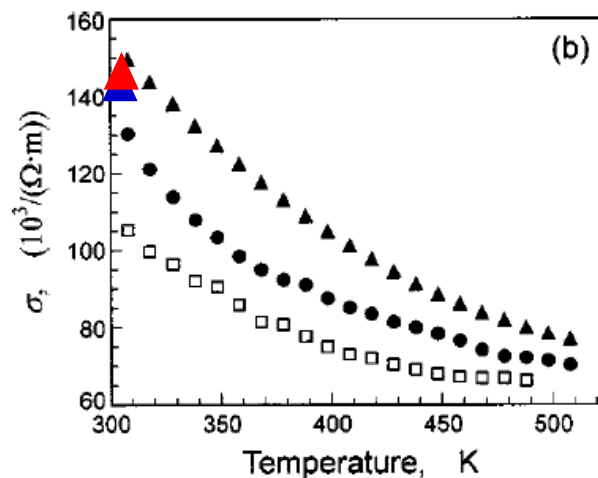
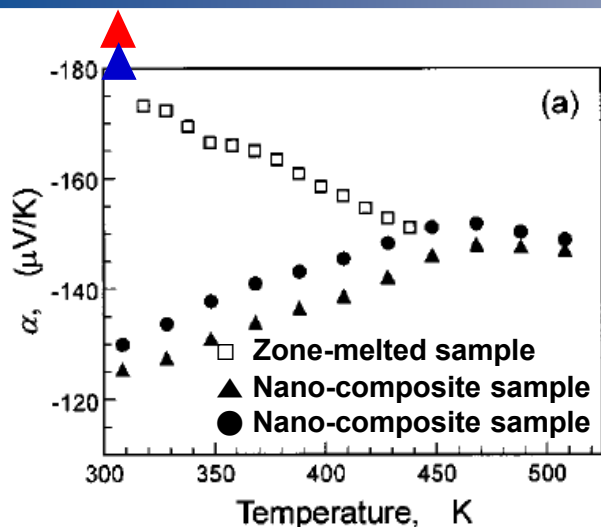
(a) TE characterization chamber system (b) Seebeck coefficient measurement of a molybdenum sheet. (c), (d) CAD drawing of hand-built sample holders with 2 and 4 probes, respectively.

Bi₂Te₃ (n-type) Performance



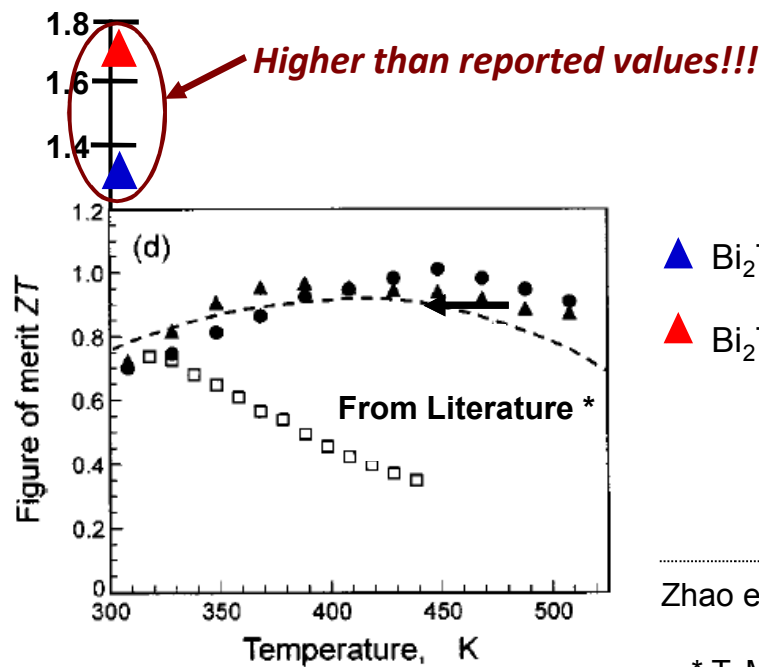
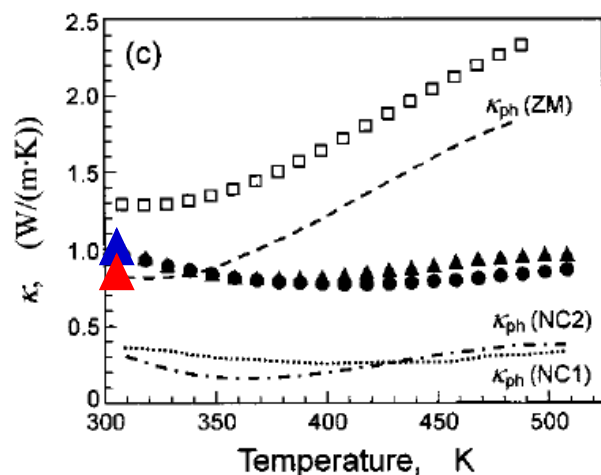
Sample	Au	ρ	C_p	α	S	σ	κ	Z	ZT
Au	wt%	kg/m ³	J/kg·K	cm ² /s	μ V/K	1/ Ω ·cm	W/m·K	K ⁻¹	(303K)
1	0	5780	154.15	0.0125	-159	537	1.112	0.0012	0.371
2	0.001	5780	154.4	0.0183	-176	805	1.632	0.0015	0.463
3	0.05	5780	133.25	0.0113	-163	1205.1	0.870	0.0037	1.117
4	0.05	5780	133.25	0.0133	-181	1205.1	1.022	0.0039	1.171
5	0.05	5780	133.25	0.0133	-181	1400	1.022	0.0044	1.359
Sample	Ag	ρ	C_p	α	S	σ	κ	Z	ZT
Ag	wt%	kg/m ³	J/kg·K	cm ² /s	μ V/K	1/ Ω ·cm	W/m·K	K ⁻¹	(303K)
6	0.05	5780	186	0.00776	-188	1420	0.8342	0.0057	1.727

Test Results and Comparison of Bi_2Te_3



- Bi_2Te_3 nano-structured powder was hydrothermally synthesized with an additive for *n*-type Bi_2Te_3 TE materials

- The mixed powder was hot pressed in vacuum at 350 °C for 30 min using a pressure of 50 MPa in a graphite die with a diameter of 16 mm.



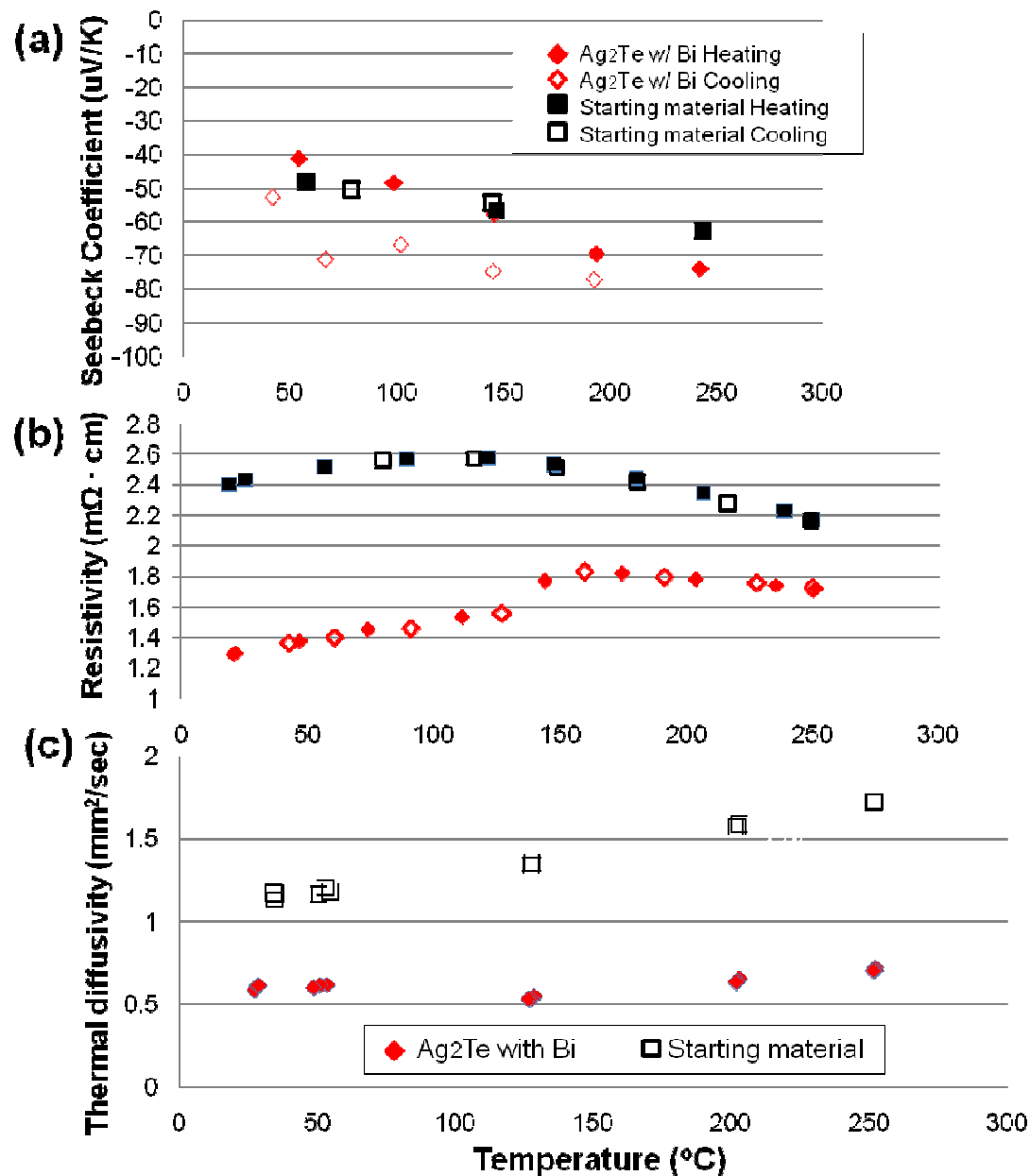
▲ Bi_2Te_3 , 0.05 wt% Au particles

▲ Bi_2Te_3 , 0.05 wt% Ag particles

Zhao et al., Appl. Phys. Lett. **86**, 06211 (2005)

* T. M. Tritt, Science 283, 804 (1999)

Ag₂Te (n-type) Performance



Summary



Achieved:

- Fabrication and shape modification of Bi-Te samples
- Development of metallic nanoparticle-decorated Bi_2Te_3 ($ZT=1.36_{\text{Au}}$, 1.72_{Ag}) materials whose FoMs are higher than the known values so far ($ZT=0.82$)
- Ag_2Te : Thermal conductivity required (in process of measurement) to derive the FoM. Improved Seebeck coefficient and electrical conductivity observed after decoration.
- Demonstration of a bulk and thin film measurement system that measures Seebeck coefficient, electrical conductivity, and thermal diffusivity simultaneously at temperature up to 1000[K]
- Hand-built sample holder to measure various nano/micro structures in high temperature range for thermoelectric material applications (to be tested)
- ***Ways to enhance the FoMs of our TE material designs with metallic nanoparticles by***
 - Metallic nanoparticles, which act as conduction bridges between $\text{Bi}_2\text{Te}_3/\text{Ag}_2\text{Te}$ grains
 - Phonon scattering source
 - Electron energy filtering effect
- ***- Next step: control bulk doping concentration***