Nano Structured Composite Materials for Thermoelectric Applications

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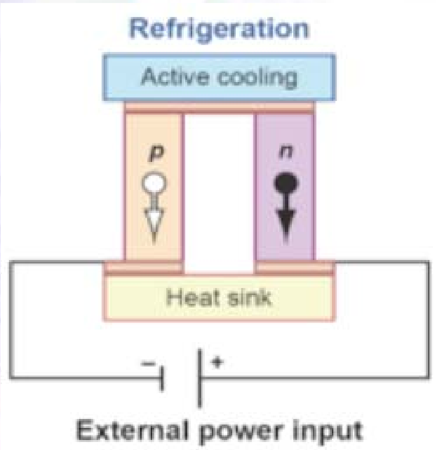
Thermoelectricity

연구분야

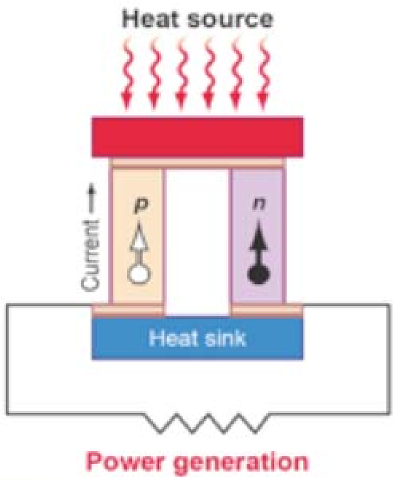
온도차에 의해 기전력이 발생하는 현상(Seebeck 효과) 또는 전류에 의해 열이 흡수,발생이 생기는 현상 (Peltier효과)

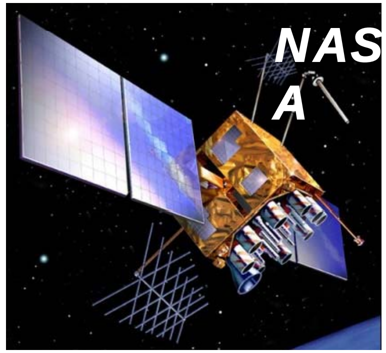
응용분야

열전냉각 (Thermoelectric cooling)



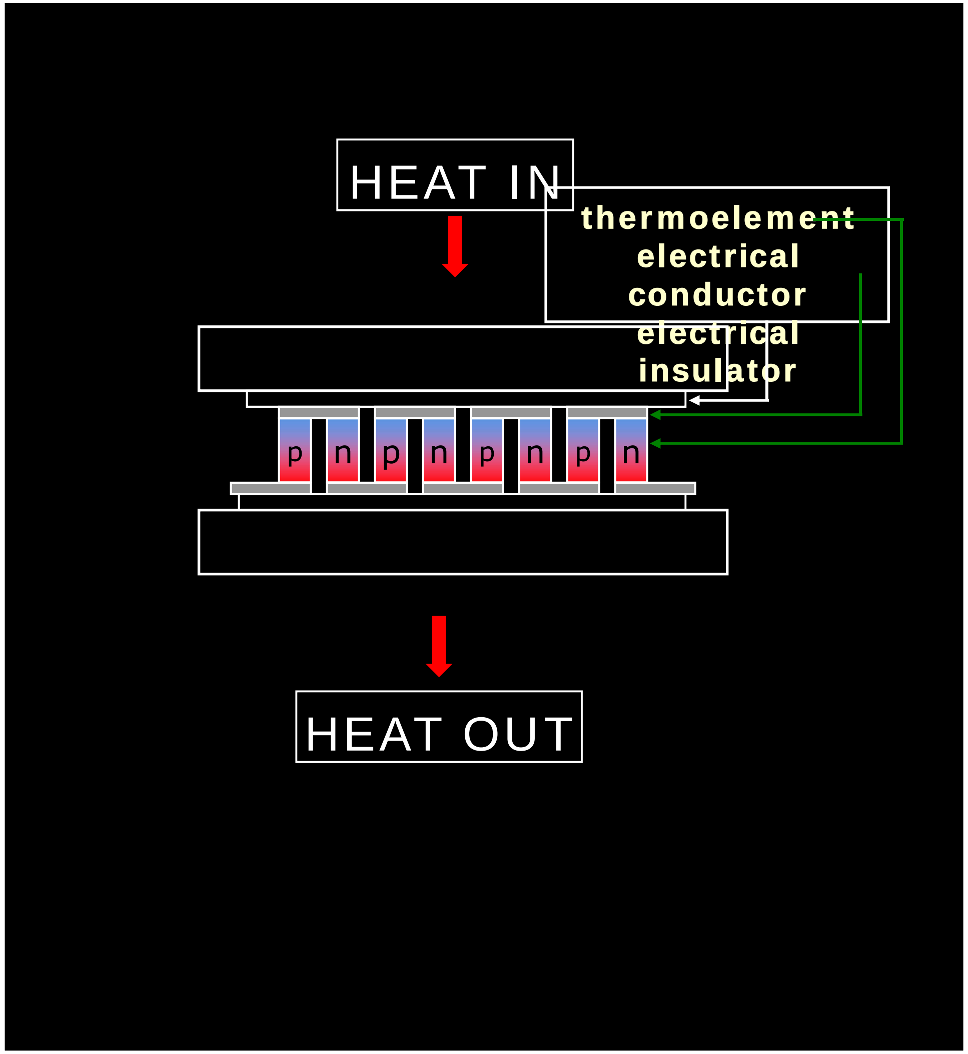
열전발전 (Power generation)

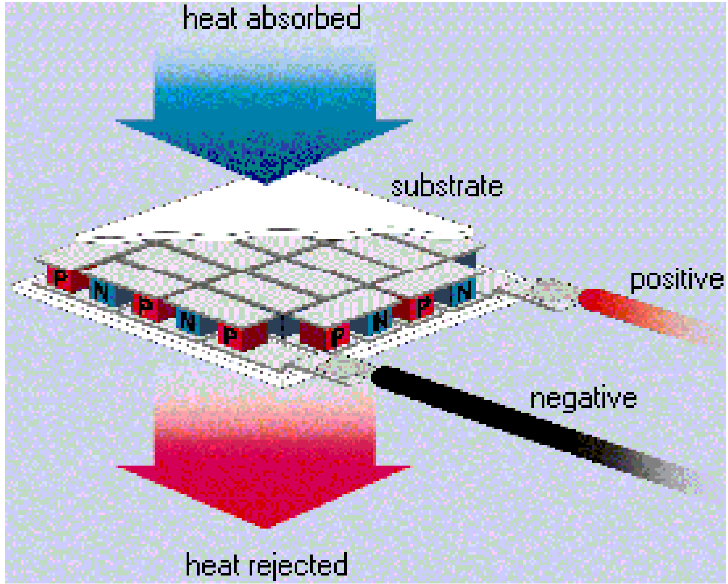


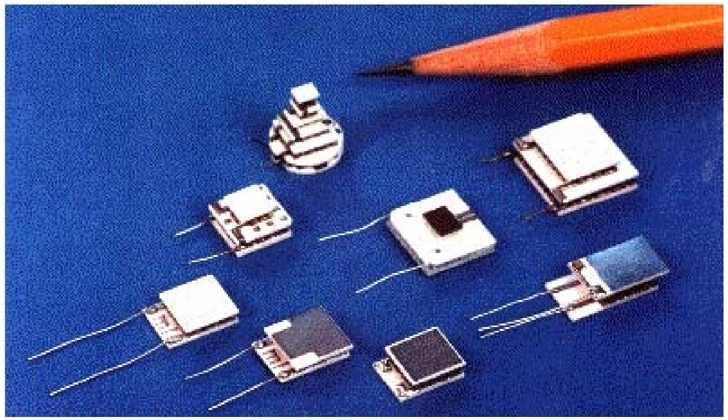


www.spaceref.com/news/viewpr.html?pid=18796

Configuration of Thermoelectric Module







Thermoelectric Figure of Merit

$$Z=\alpha^2\sigma/\kappa$$

- Seebeck coeff. (α) : morphology, doping state
- Electrical conductivity(σ) : carrier concentration
- Thermal conductivity (κ) : phonon scattering

Optimum Transport Coefficients

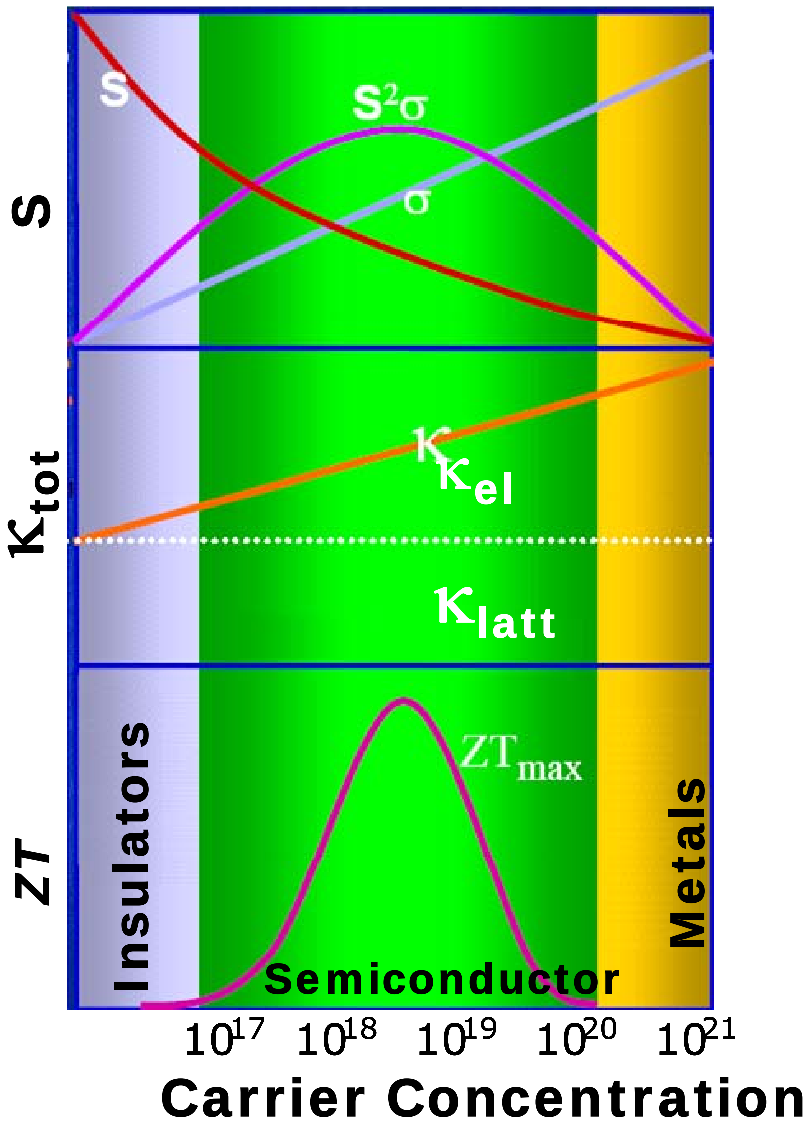


Figure of Merit : ZT

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

$$\kappa = \kappa_e + \kappa_{ph}$$

- High Seebeck coefficient
- High electrical conductivity
- Low thermal conductivity

Difficulties in increasing ZT in bulk materials :

S ↑ ↔ σ ↓

σ ↑ ↔ **S** ↓ **and k** ↑

Selection Criteria for Candidate Materials

$$Z_{\max} \propto \gamma \frac{T^{3/2}\tau\sqrt{\frac{m_x m_y}{m_z}}}{k_{latt}} e^{(r+1/2)}$$

m = effective mass
τ = scattering time
r = scattering parameter
k_{latt} = lattice thermal conductivity
T = temperature
γ = band degeneracy

Guiding Principles:

- Narrow band-gap semiconductors : Single carrier systems
- Heavy elements : High μ, low κ
- Large unit cell, complex structure : low κ
- Highly anisotropic or highly symmetric
- Complex compositions : low κ, complex electronic structure
- Mass Fluctuation : low κ
- High density of states near the Fermi level : high Seebeck coefficient

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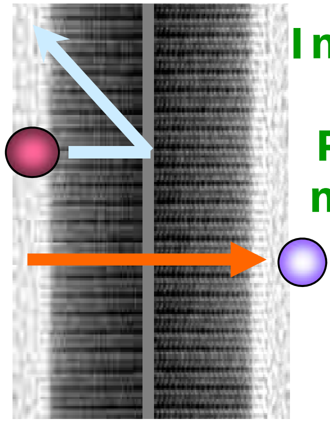
New direction : Nano-based Thermoelectrics

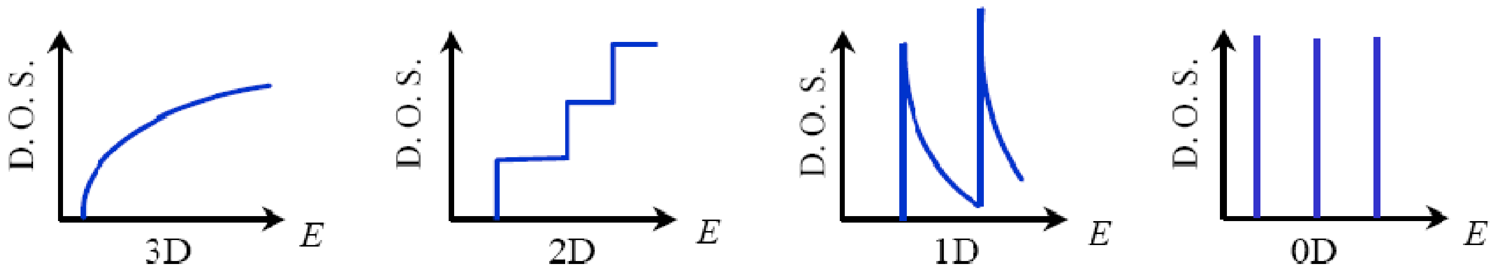
- **Minimizing the thermal conductivity :** Thermal conductivity can be significantly reduced by the **scattering of unwanted heat flow** at the interfaces

	Phonons	Electrons
Mean Free Path	Λ = 10-100 nm	Λ = 1-10 nm
Wavelength	λ = 10-50 nm	λ = 1 nm

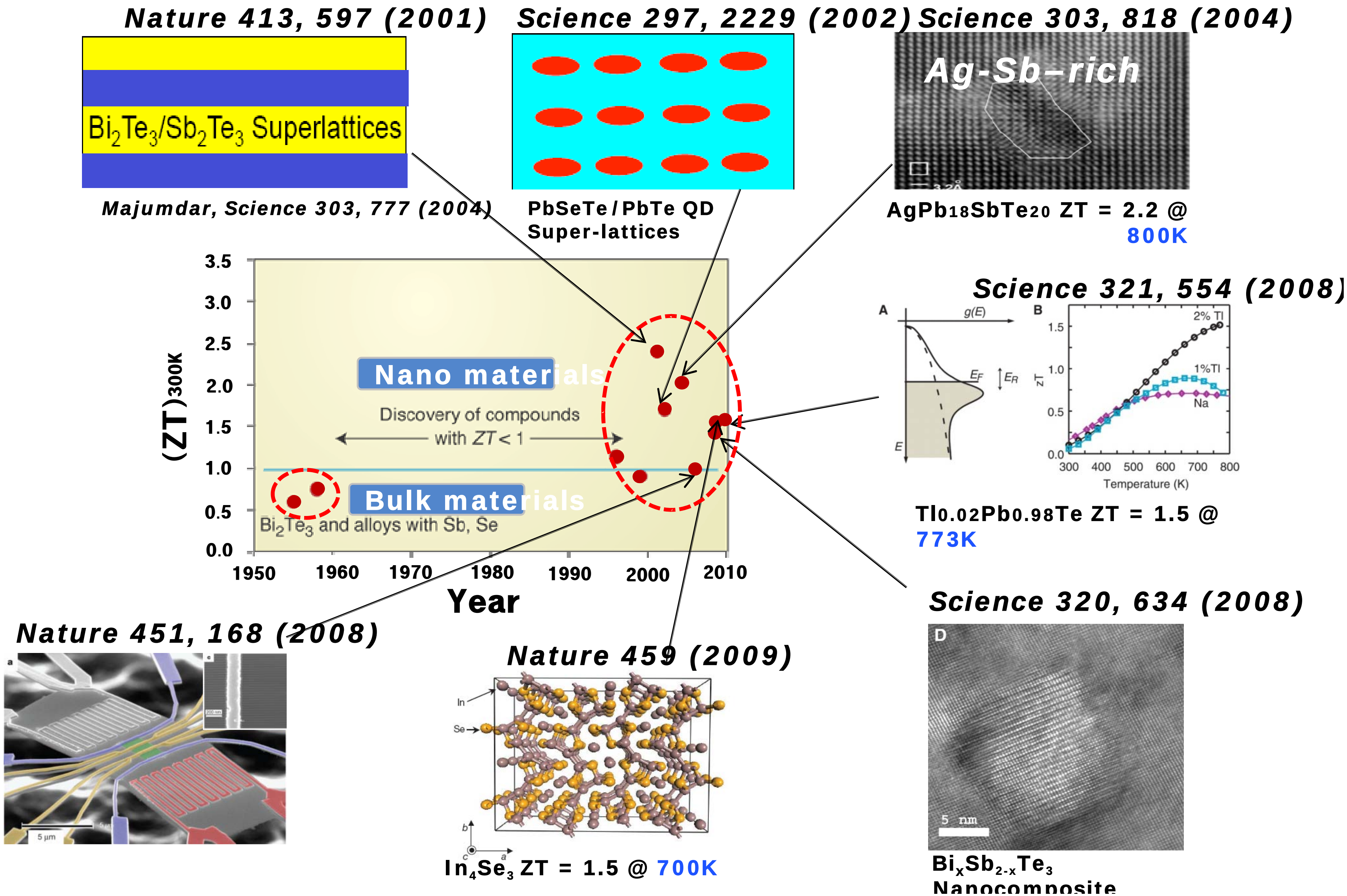


Interfaces that Scatter Phonons but not Electrons

- **Maximizing Seebeck coefficient:** Electronic properties may be dramatically modified due to **the electron confinement** in nanostructures which exhibit low-dimensional behaviors.

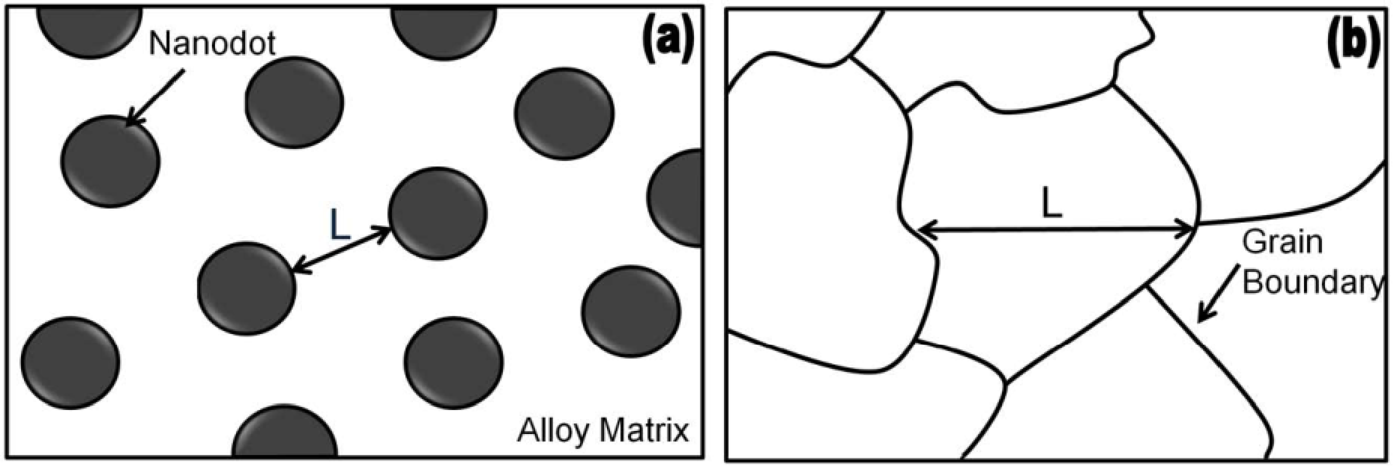


New Classes of Promising Thermoelectric Materials



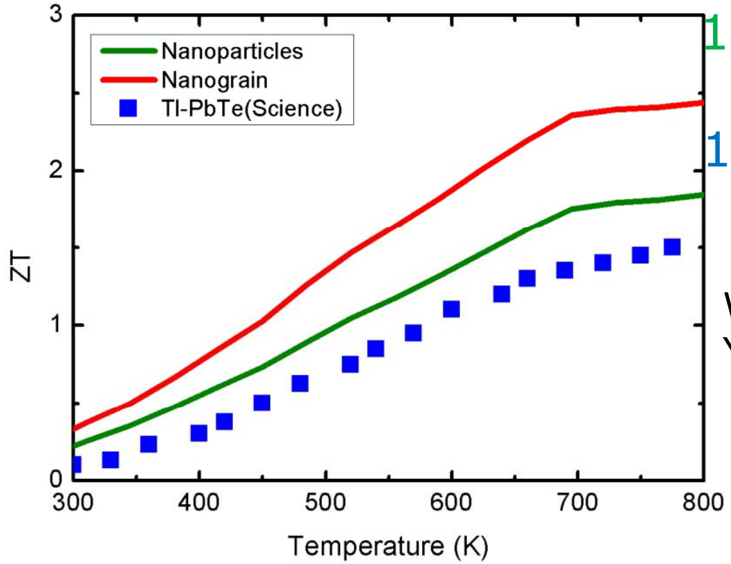
Theoretical studies

Nanodot Nanocomposites **Nanograined Nanocomposites**



Λ = 1-10 nm < L

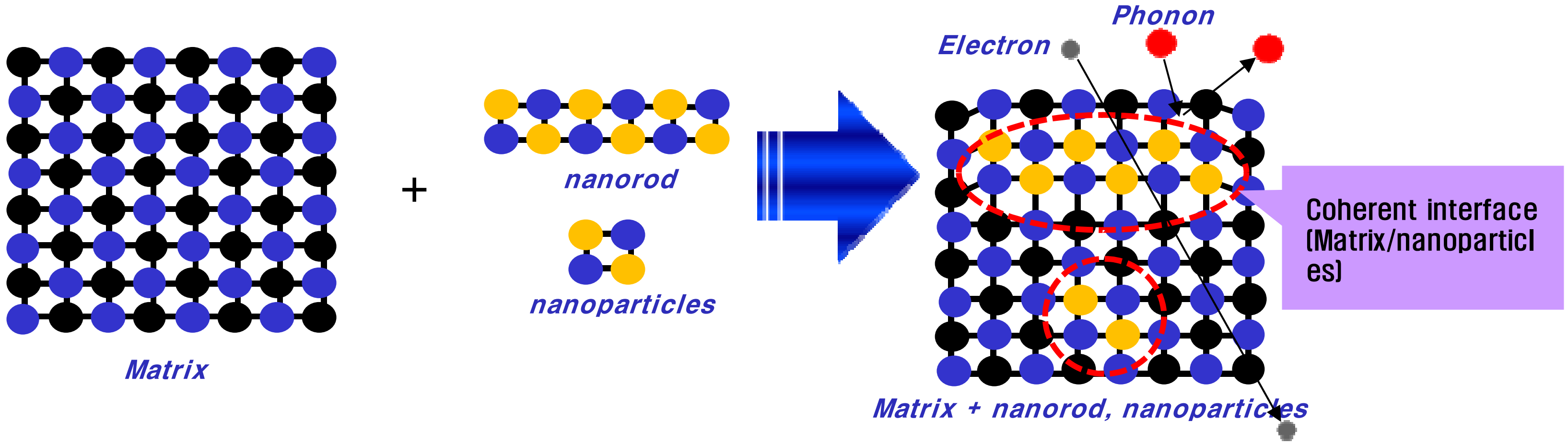
Electron mean free path



Woochul Kim,
Yunsei Univ.

New Approach

Nanoparticles Embedded in Bulk Thermoelectric Materials



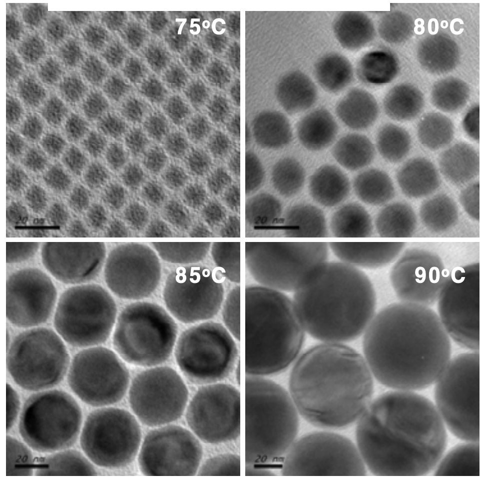
Type of Bull Matrixes	Nanoparticles	Nanorods
PbTe Bi_2Te_3 In_2Te_3	Bi_2Te_3 Bi_2Se_3 Sb_2Te_3 $Bi_xSb_{2-x}Te_3$ Bi	Bi_2Te_3 CdSe Te

Synthesis of Various Nanoparticles

$Bi(C_2H_3O_2)_3$
(or $Sb(C_2H_3O_2)_3$)
+
Te-TOP
(or Se-TOP)

1-Dodecanthiol
Oleylamine, 1-Octadecene
Various reaction temperature

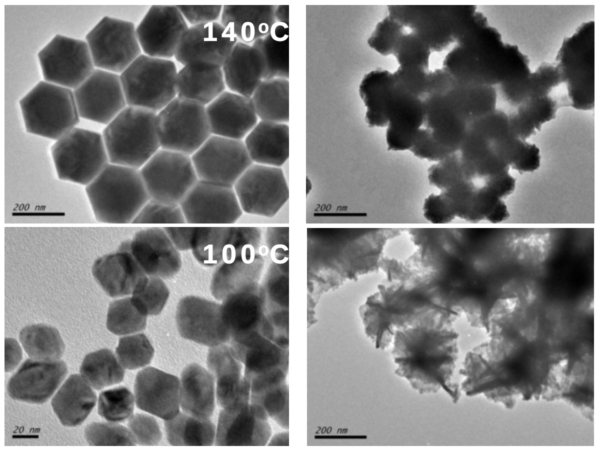
◆ Size Control



Bi_2Se_3

Various Source

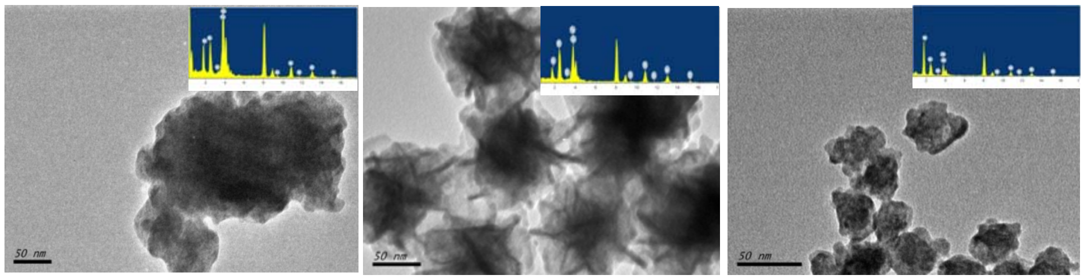
◆ Morphology Control



Bi Bi_2Te_3

Oleic acid, 1-Octadecene
1-Dodecanthiol
Various surfactant

◆ Composition Control



$Bi_{0.9(3)}Sb_{0.9(2)}Te_3$ $Bi_{1.5(3)}Sb_{0.5(1)}Te_3$ $Bi_{1.9(3)}Sb_{0.1(1)}Te_3$

Sample preparation and measurements

◆ Sample Preparation

Rocking furnace

Nanocomposite ingot

sawing

Polishing (400 – 2000 – micro)

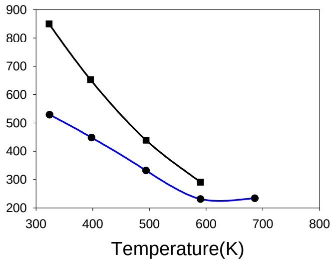
◆ Measurements

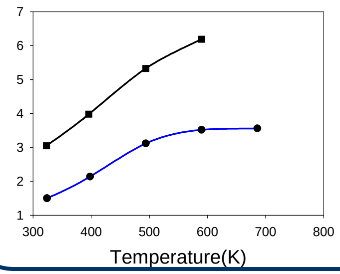
Seebeck Coefficient & Electrical conductivity measurement

Thermal conductivity measurement

Nanocomposite sample

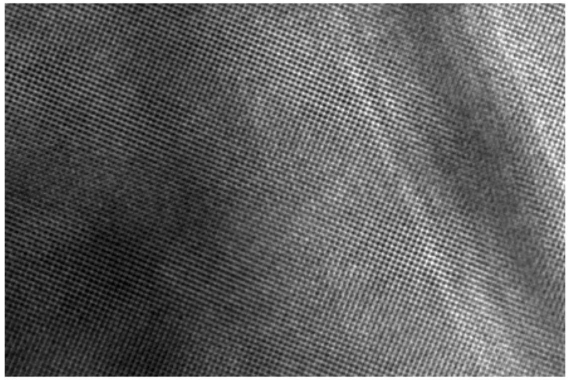
◆ Data Analysis



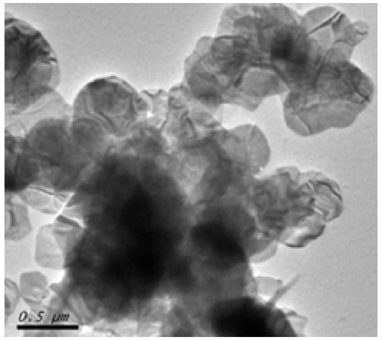


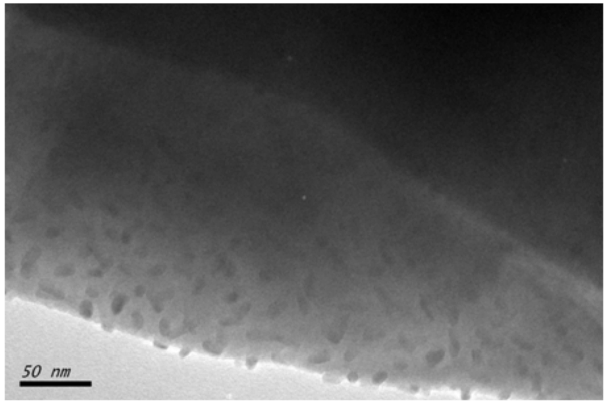
Nano-structured Bulk Thermoelectirc Material

PbTe ingot with Bi_2Te_3 nanoparticle



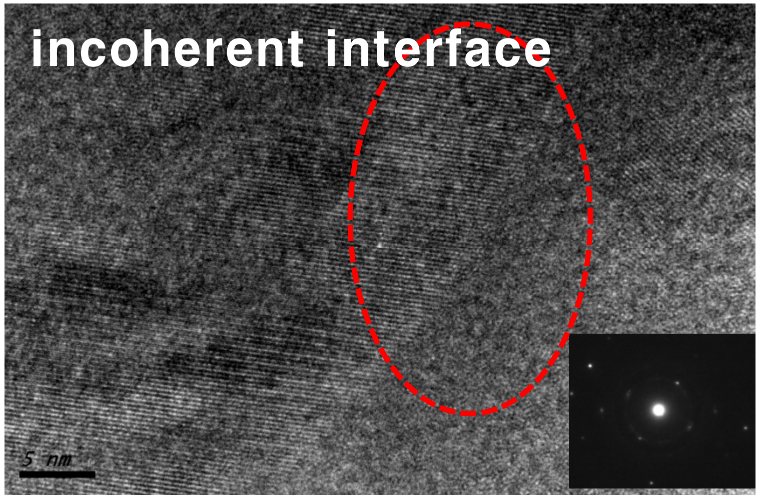
PbTe





Bi_2Te_3 nanoparticles(~150nm)

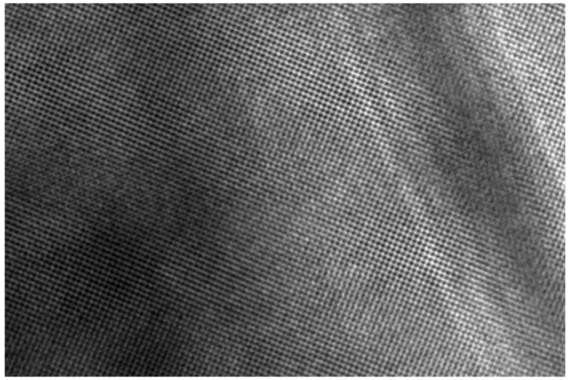
Materials	Lattice parameter	Structure	Lattice mismatch
PbTe	6.3462A	Rock salt	30% (a/a)
Bi_2Te_3	a=4.385A, c=30.48A	Rhombohedral	



PbTe with Bi_2Te_3 ingot

Nano-Bulk Composite Thermoelectric Material

PbTe ingot with Bi_2Se_3 nanoparticle



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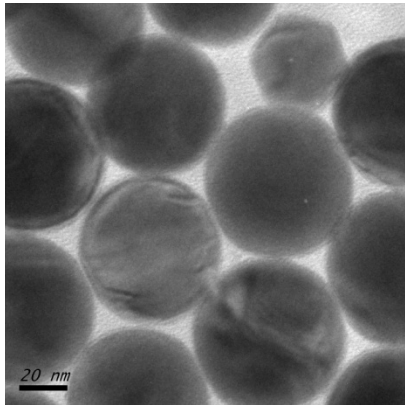
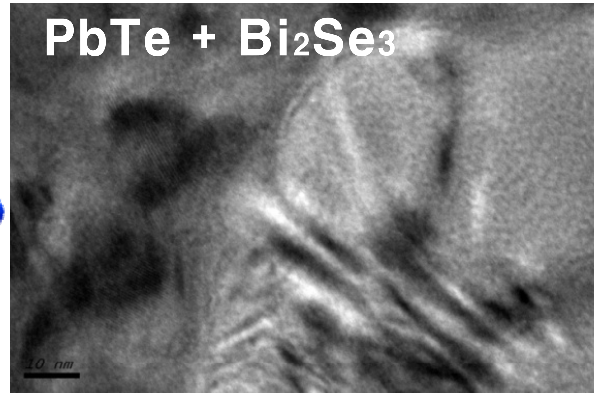
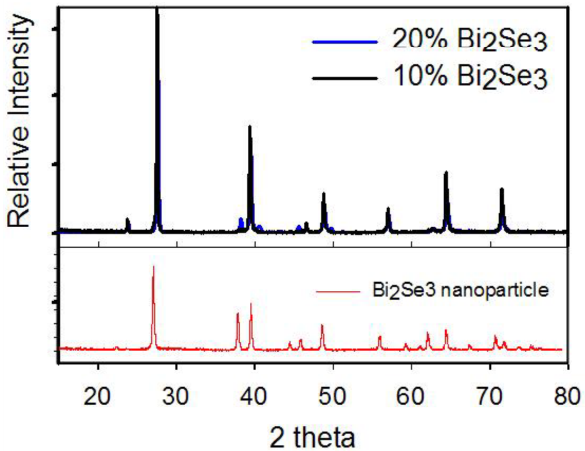
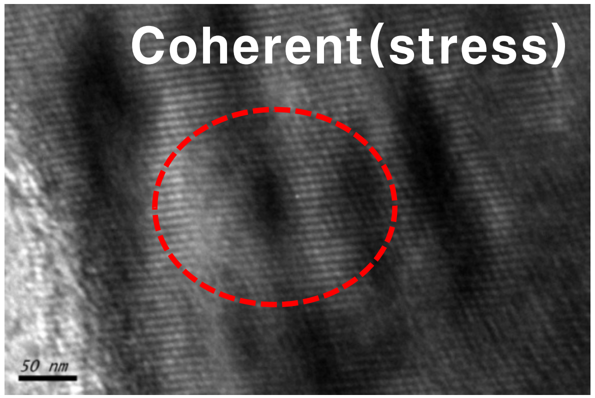


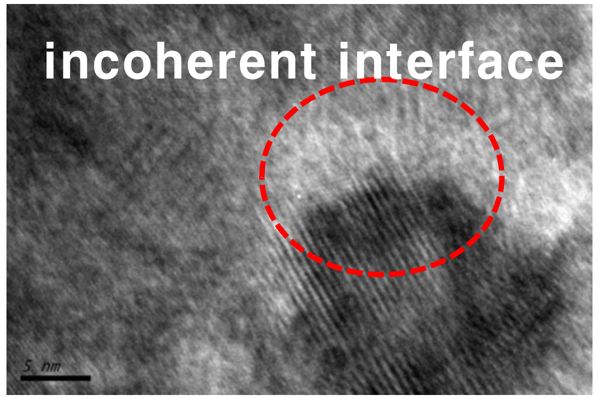


PbTe

Bi_2Se_3 nanoparticles(~80nm)

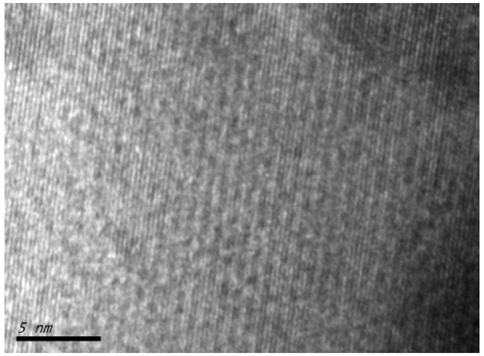






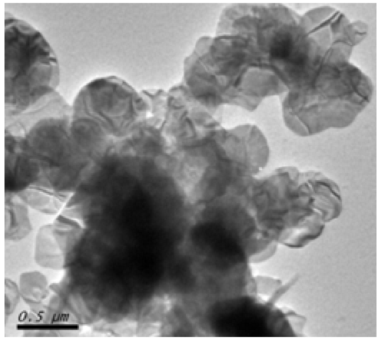
Nano-Bulk Composite Thermoelectric Material

In_2Te_3 ingot with Bi_2Te_3 nanoparticle

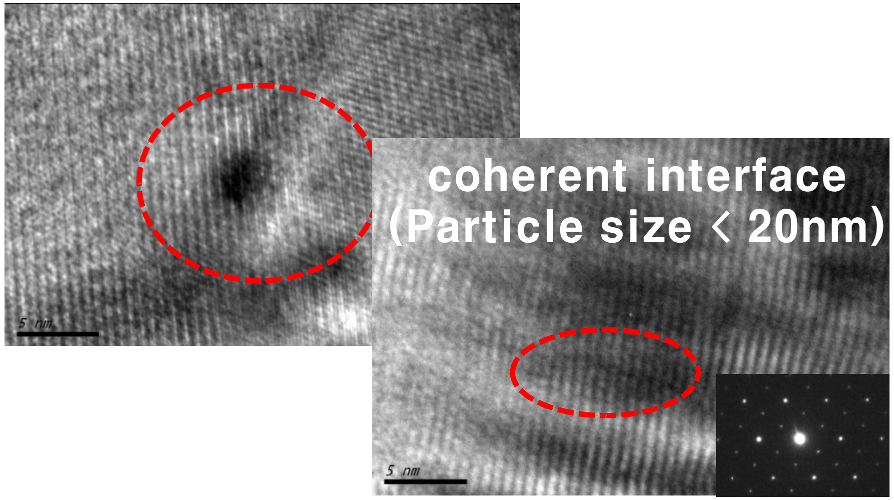


In_2Te_3 Matrix

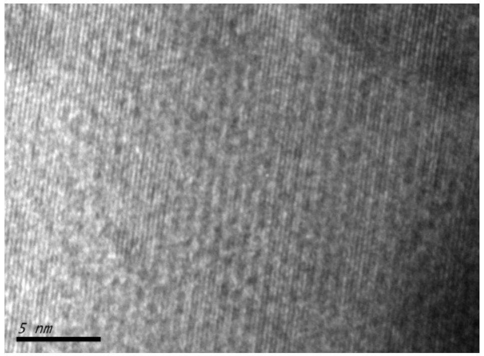
+



Bi_2Te_3 nanoparticles
(~150nm)

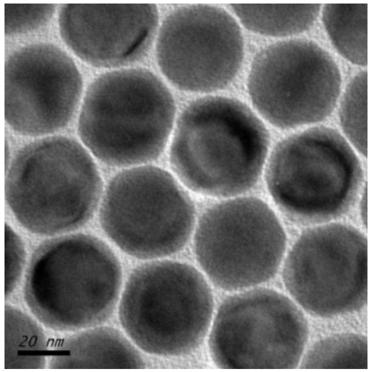


In_2Te_3 ingot with Bi_2Se_3 nanoparticle

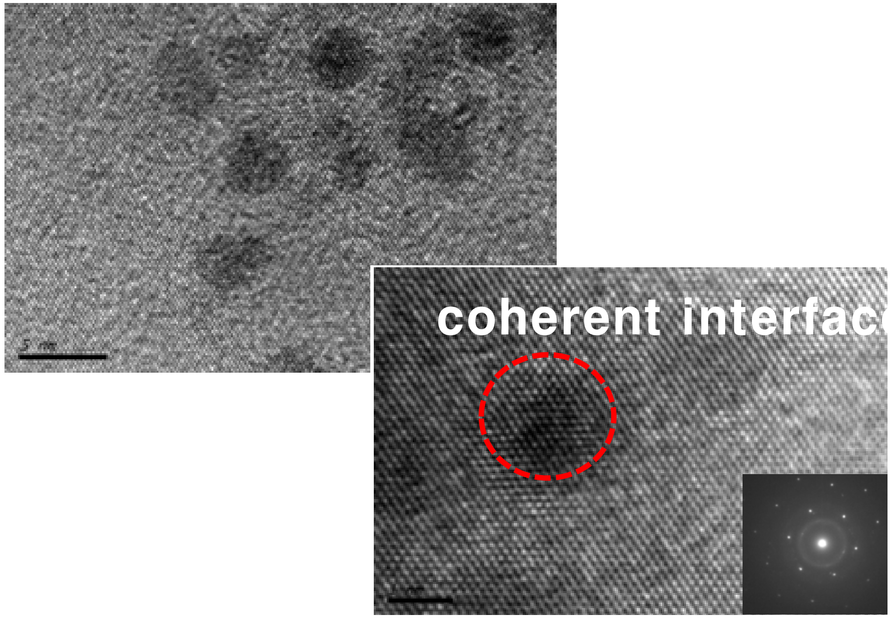


In_2Te_3 Matrix

+

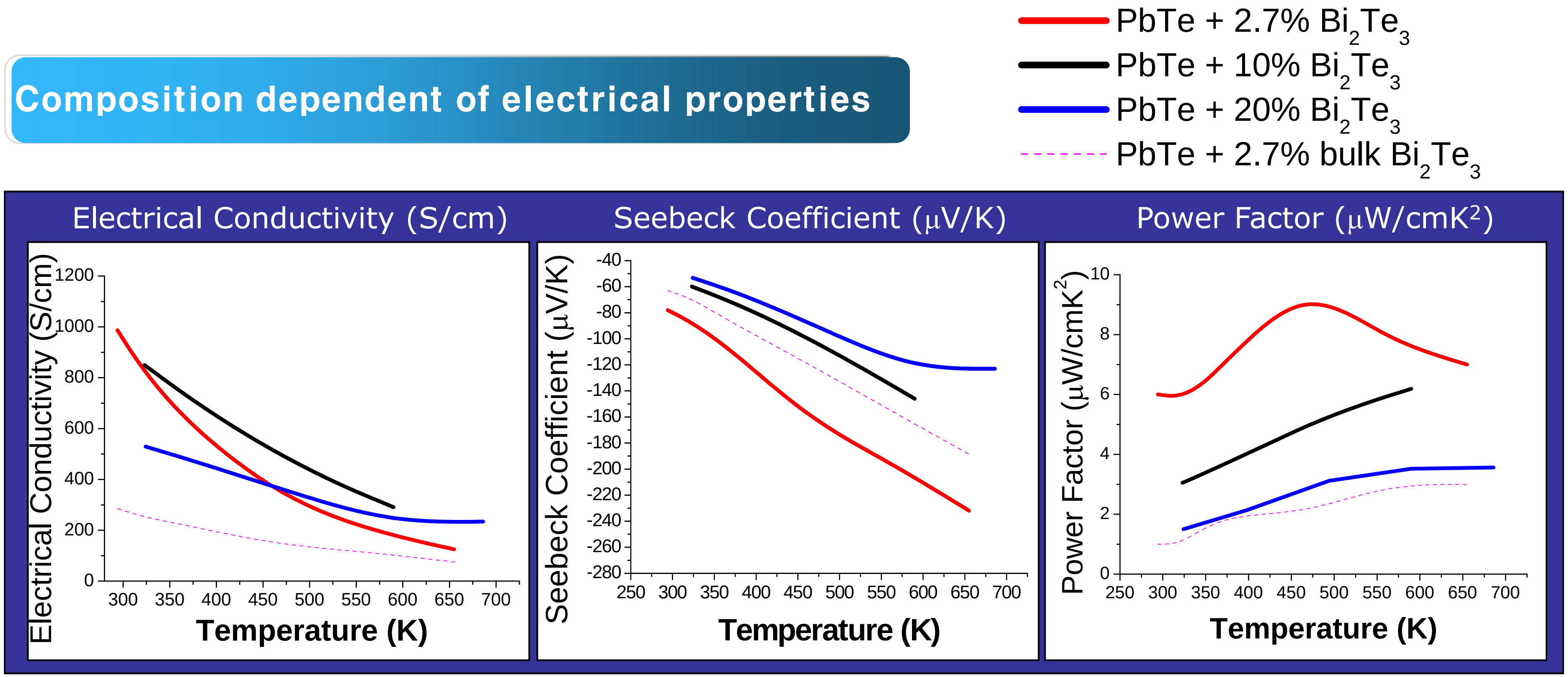


Bi_2Se_3 nanoparticles
(~80nm)



Nano-Bulk Composite Thermoelectric Material

Composition dependent of electrical properties



- The values :

  ~1000 S/cm at R.T.

- Negative value
- Majority of charge carriers :

  Electrons

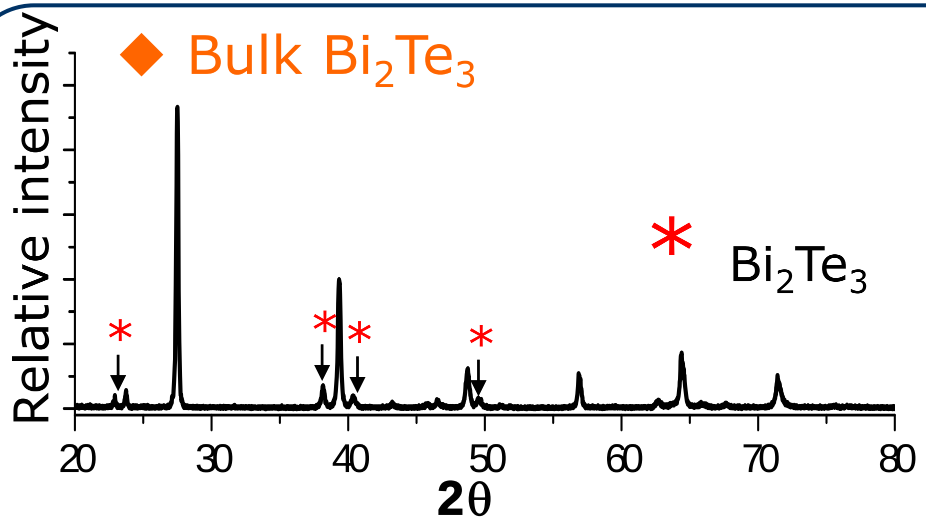
- The values : ~ -60~-220μV/K

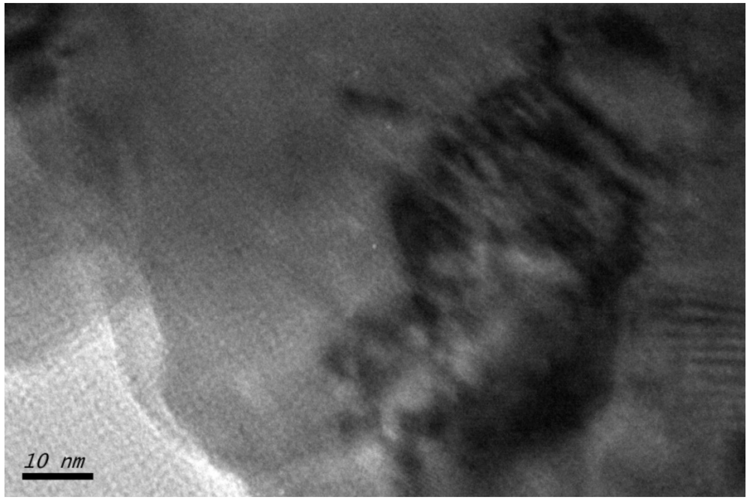
- The values :

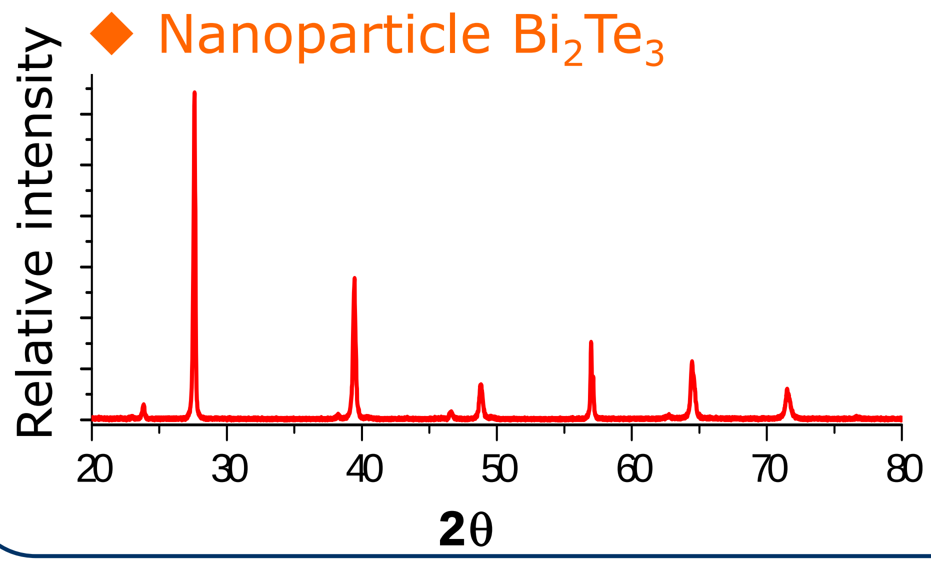
  1.5 ~9 W/cmK²

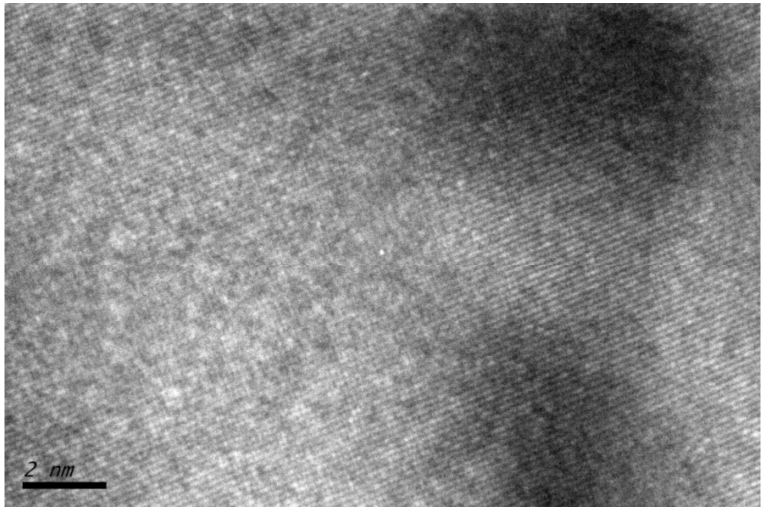
Power Factor increase with decreasing nanoparticle content

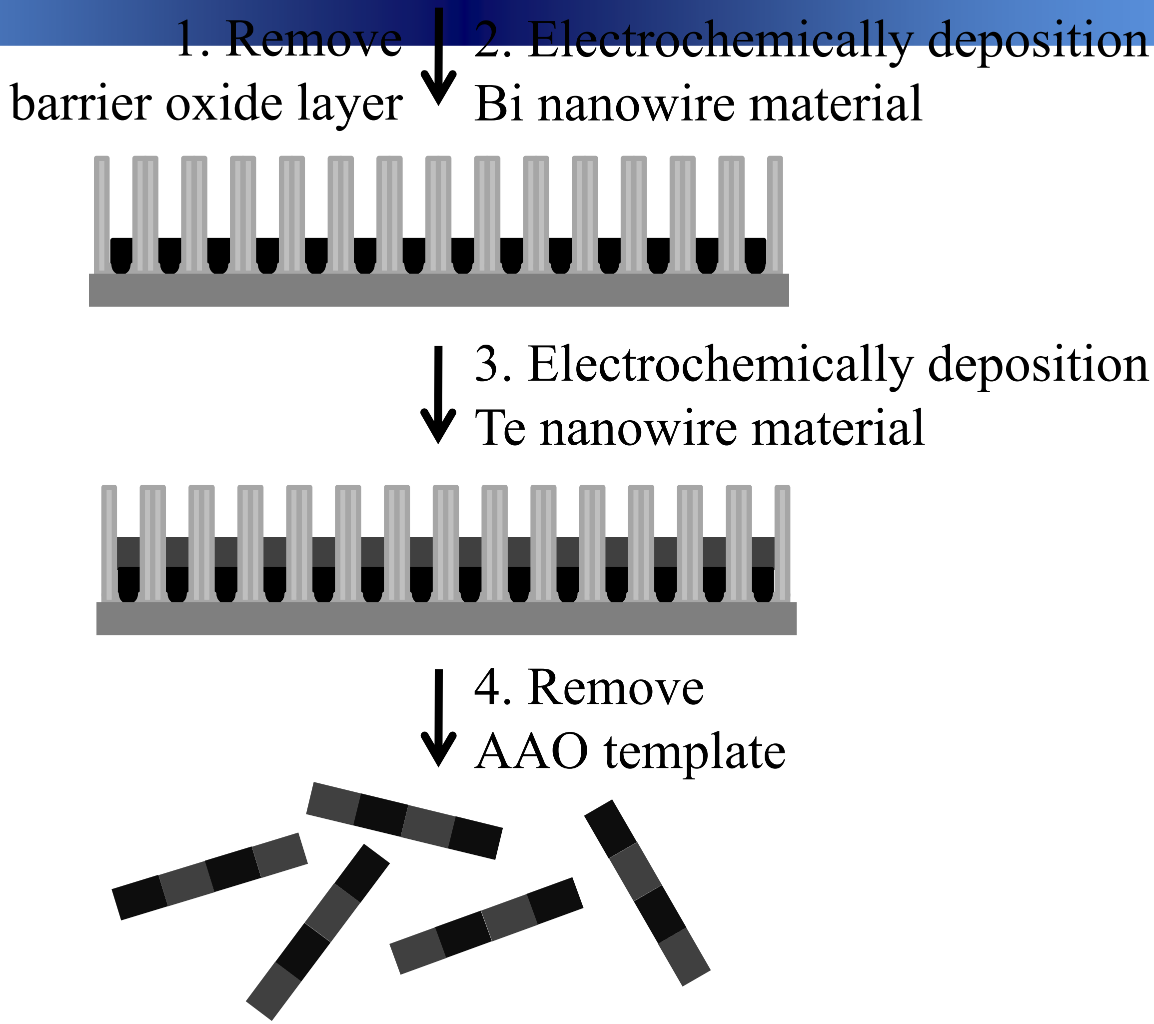
Nano-Bulk Composite Thermoelectric Material

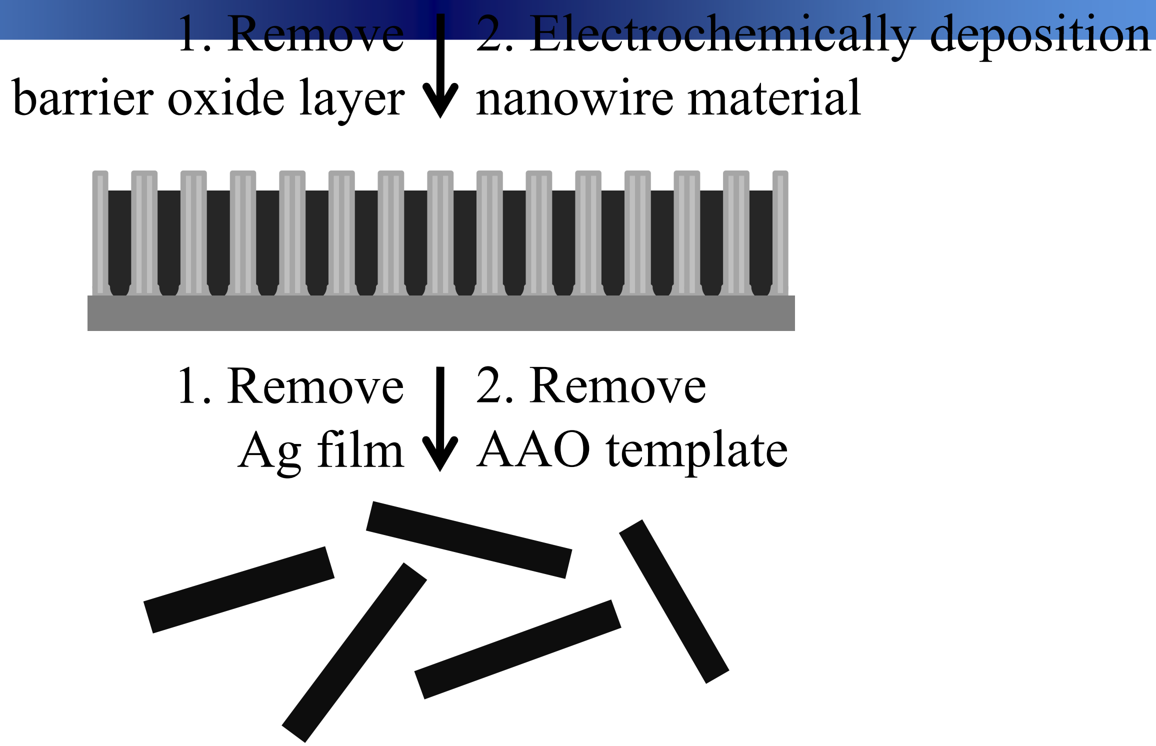






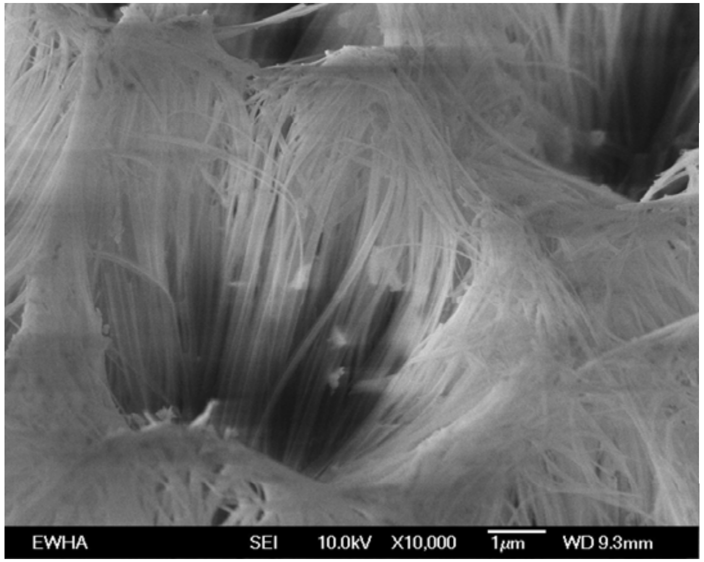


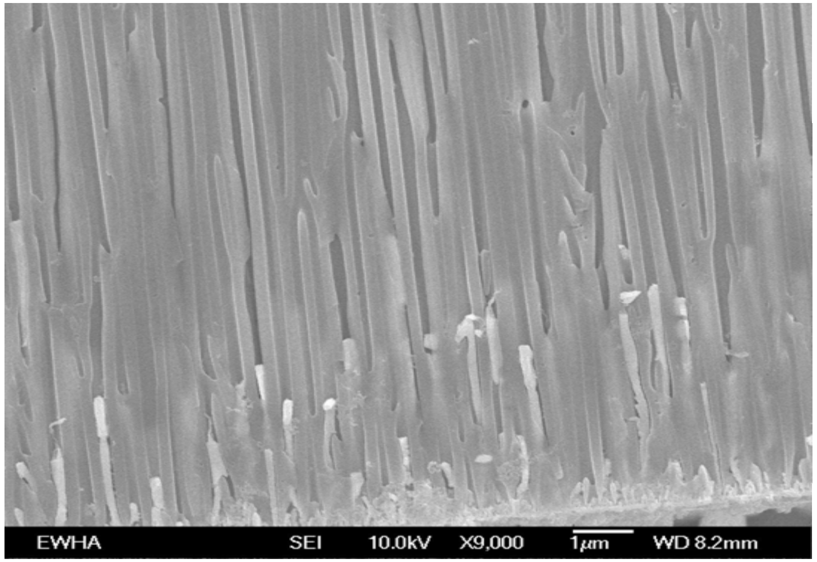

1. Remove
barrier oxide layer
2. Electrochemically deposition
Bi nanowire material
3. Electrochemically deposition
Te nanowire material
4. Remove
AAO template

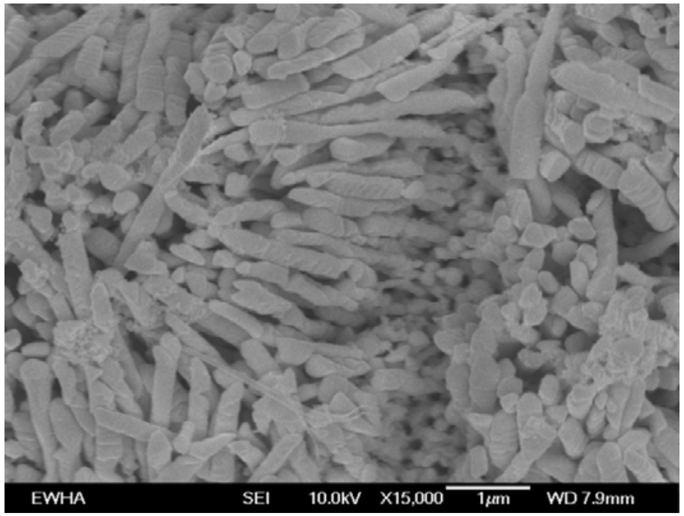


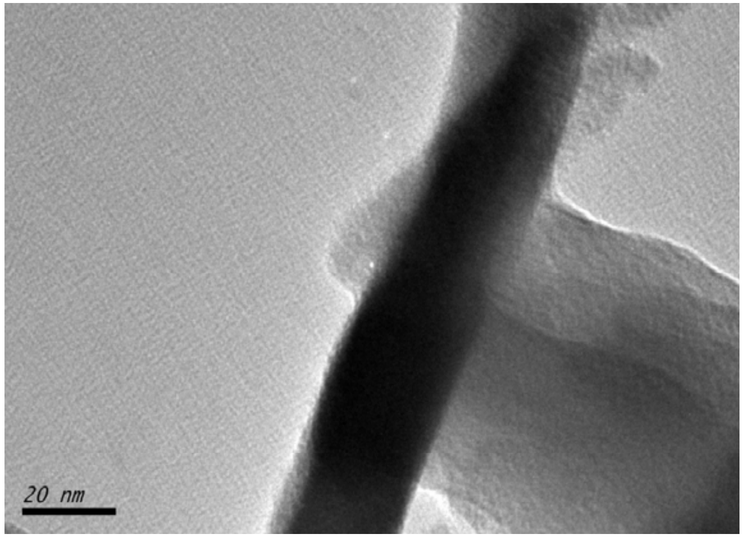
•Scheme 1. Schamatic of the process employed to produce (a) superlattice structure (b) one element or binary nanowire arrays by pulsed-potential deposition into porous anodic alumina template

SEM image Bi and Te NWs

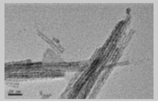
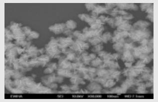
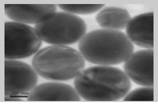
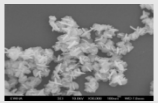
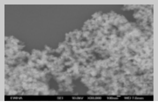
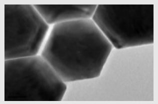
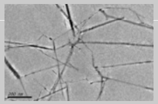
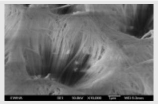


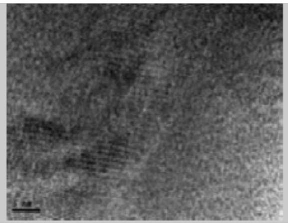
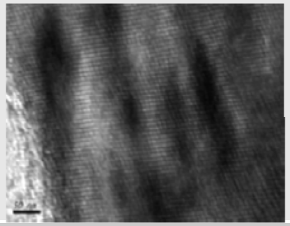
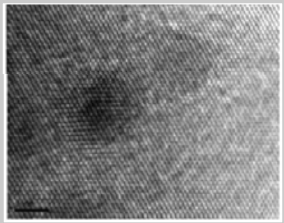
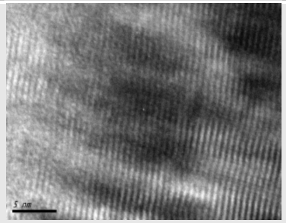






Summary

열전재료용 나노입자, 나노선 제조	
Hydrothermal법을 이용한 Bi_2Te_3의 morphologies	
Colloidal법을 이용한 Bi_2Te_3 나노입자	
Bi_2Se_3나노입자	
Sb_2Te_3 나노입자	
$Bi_xSb_{2-x}Te_3$ 나노입자	
Bi 나노입자	
CdSe 나노선	
전기화학법을 이용한 Bi, Te 나노선	

Bulk에 나노입자, 나노선 삽입	
PbTe ingot with Bi_2Te_3	
PbTe ingot with Bi_2Se_3	
InTe ingot with Bi_2Se_3	
InTe ingot with Bi_2Te_3	

Conclusions

- **Nanostructured bulk CompositeTE materials**

  - New approaches are promising in raising ZT
  - Strong thermal conductivity reduction can be achieved through nanostructuring
  - Doping studies and processing conditions are important in ZT optimization

- **Nanoparticles**

  - Nano particles of various TE materials are obtained

- **Nanocomposites**

  - New approaches was provide to control the size and concentration of the nanocomponent in bulk TE materials

Acknowledgment

Ha Yeong Kim Jieun Park, Hee Jin Kim
Dr. Mi-Kyung Han
Prof. WooChul Kim   Yonsei University
Prof. Wooyoung Lee Yonsei University

Grant:

21st Century Frontier
R&D Programs

NRF,