Innovative Nano-structuring Routes for Novel Thermoelectric Materials; Phonon Blocking & DOS Engineering

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1st approach;

Atomic scale engineering

"Electron – Phonon Coupling"

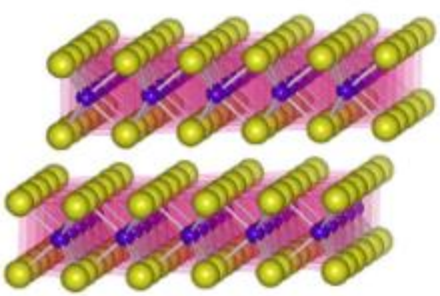
2nd approach;

Nano-scale engineering

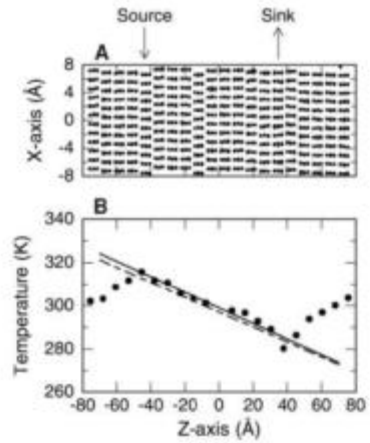
Lattice distortion (2-D) system for low κ

Extreme low thermal conductivity in disordered & layered structure

❑ WSe_2



Crystal structure of WSe_2



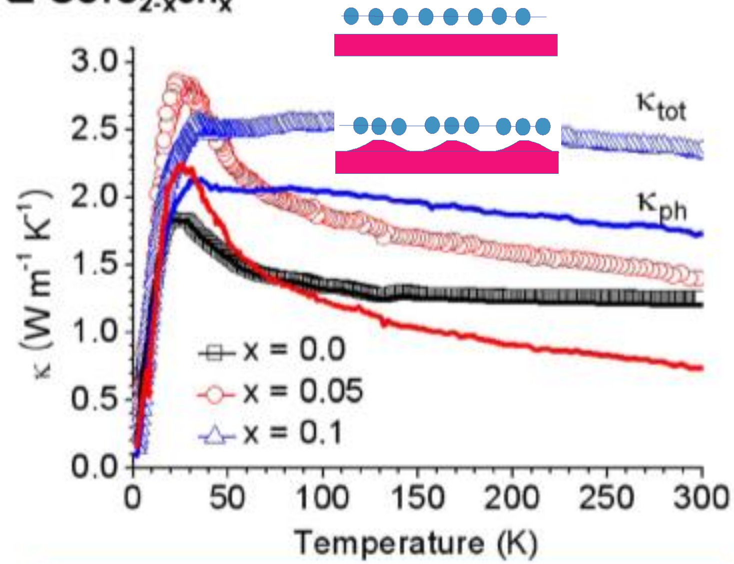
MD simulation of disordered & layered structure

◈ **Extreme low thermal conductivity of WSe_2**

- Thin film: 0.04 W/m·K @300K
- Random stacking of 2-D crystalline sheet

➔ Low thermal conductivity in CDW?
(CDW: Charge Density Wave)

❑ $CeTe_{2-x}Sn_x$



◈ **Very low thermal conductivity**

- Low lattice conductivity κ_{ph}
- κ is comparable to that of Bi_2Te_3

◈ **Low κph : originated from the CDW**

- in-plane disordered crystalline of $CeTe_2$

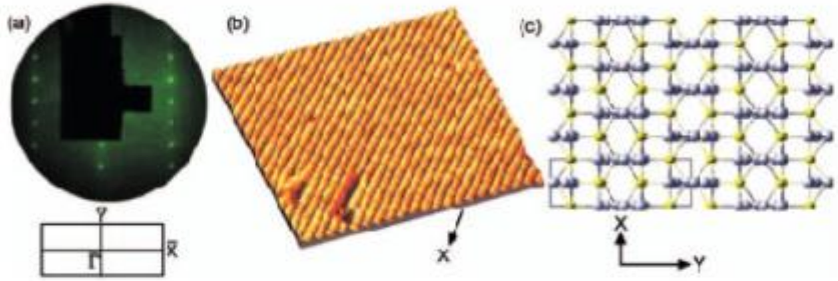
C. Chiritescu et al. *Science* **315**, 351 (2007)

J. Appl. Phys. 107, 053705 (**2010**)
J. Appl. Phys. 105, 053712 (**2009**)

Quasi 1-D structure for low κ & large S

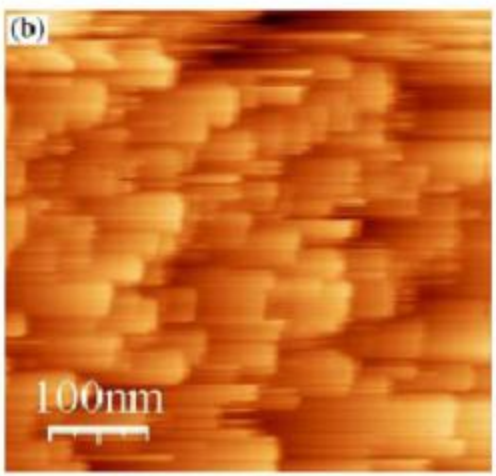
Quasi 1D structure of In_4Se_3

- Anisotropic electrical transport of In_4Se_3



Quasi one dimensional In chain in In_4Se_3 (100) plane

Y. B. Losovyj et al. *Appl. Phys. Lett. (92) 122107 (2008)*

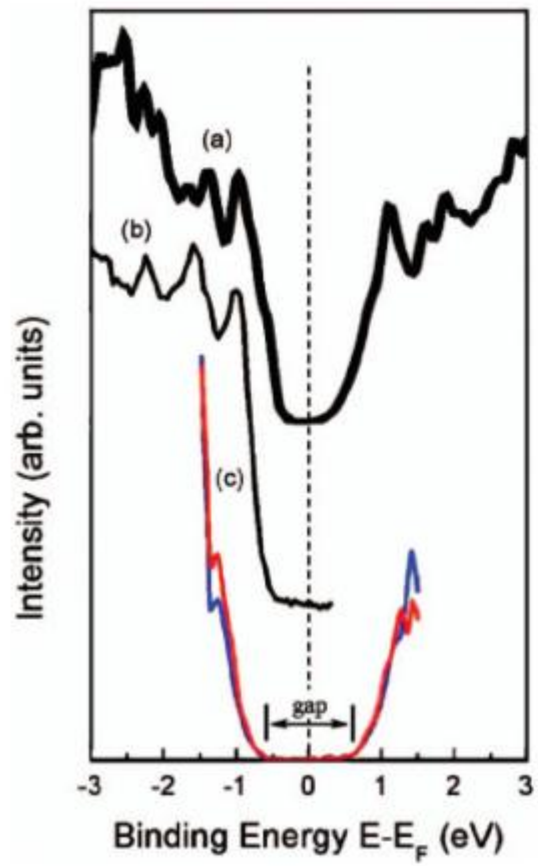


STM picture of the In_4Se_3 single crystal

Nano wire-like structure along the cleaved (100) surface

O. A. Balitskii et al. *Physica E* **22**, 921 (2004)

In_4Se_3 → doping → gap ↓

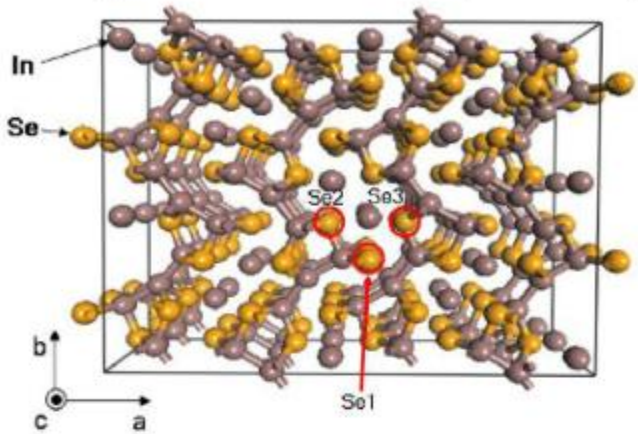


(a) Theory, (b) Photoemission, and (c) dI/dV measurements of In_4Se_3

Quasi 1-D structure for low κ & large *S*

Quasi 1D structure & electronic transport of In_4Se_{3-x}

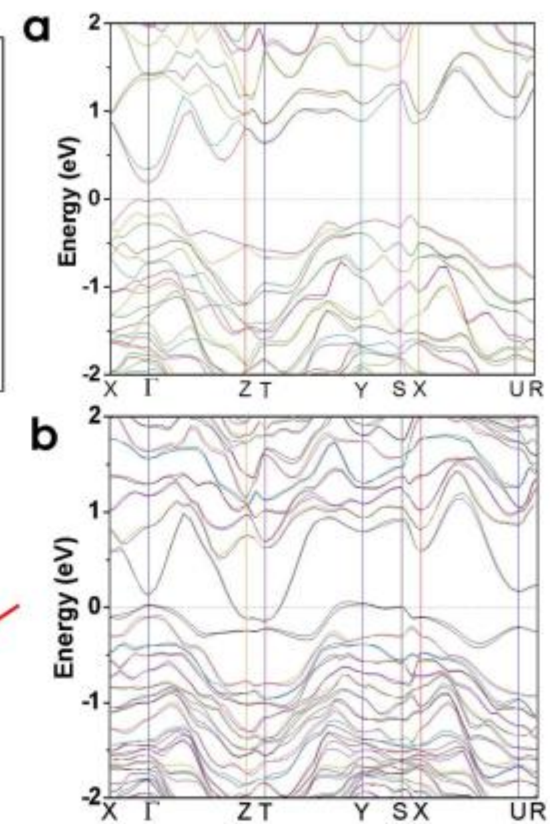
❑ Anisotropic electrical transport of In_4Se_3



a-axis:
Z-T, S-X, U-R

b-axis:
X-Γ, Y-S

c-axis:
Γ-Z, T-Y, X-U



Electronic band structure of (a) In_4Se_3 and (b) In_4Se_{3-x} (x=0.25)

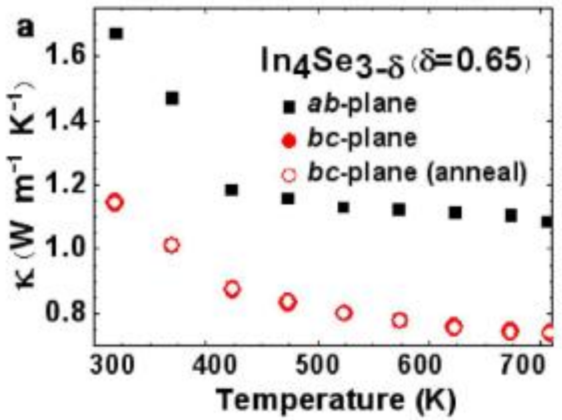
- ◈ **Semiconducting band gap of 0.2 eV in In_4Se_3**
- ◈ **Semi-metallic character of In_4Se_{3-x} (x=0.25)**
  - van der Waals gap along the *a*-axis
  - localized hole band along the *b*-axis
  - highly dispersed electron band along the c-axis
- ◈ **Quasi 1-D electronic transport**
  - Possible emergence of **Peierls distortion** in In_4Se_{3-x}

Appl. Phys. Lett. 97, 152104 (**2010**)
Appl. Phys. Lett. 95, 212106 (**2009**)

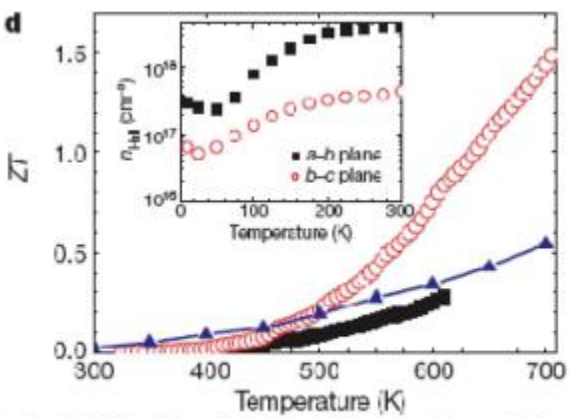
Extreme low κ by Peierls distortion: In_4Se_{3-x}

Thermoelectricity & Peierls distortion in $In_4Se_{3-\delta}$

❑ Thermoelectric properties of $In_4Se_{3-\delta}$

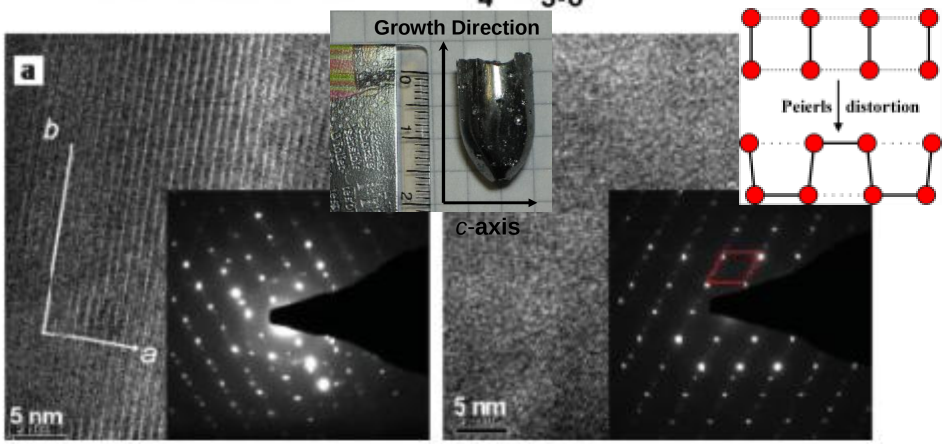


Thermal conductivity of $In_4Se_{3-\delta}$

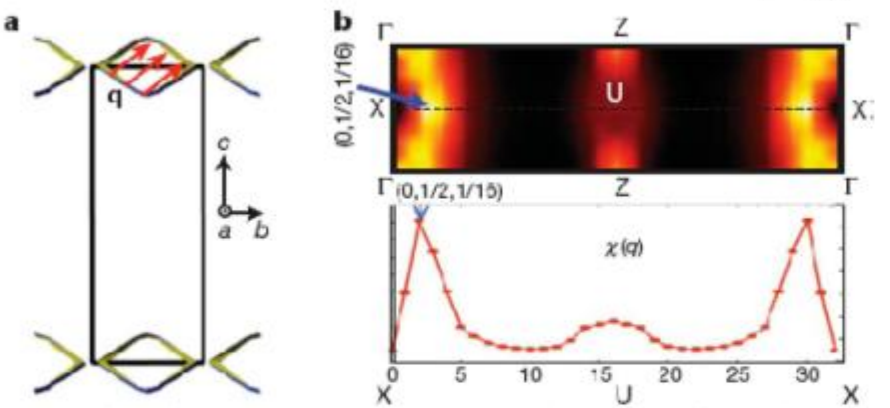


High ZT (1.48 at 705 K) in $In_4Se_{3-\delta}$(δ= 0.65)

❑ Peierls distortion in $In_4Se_{3-\delta}$



Quasi-one-dimensional lattice distortion in $In_4Se_{3-\delta}$

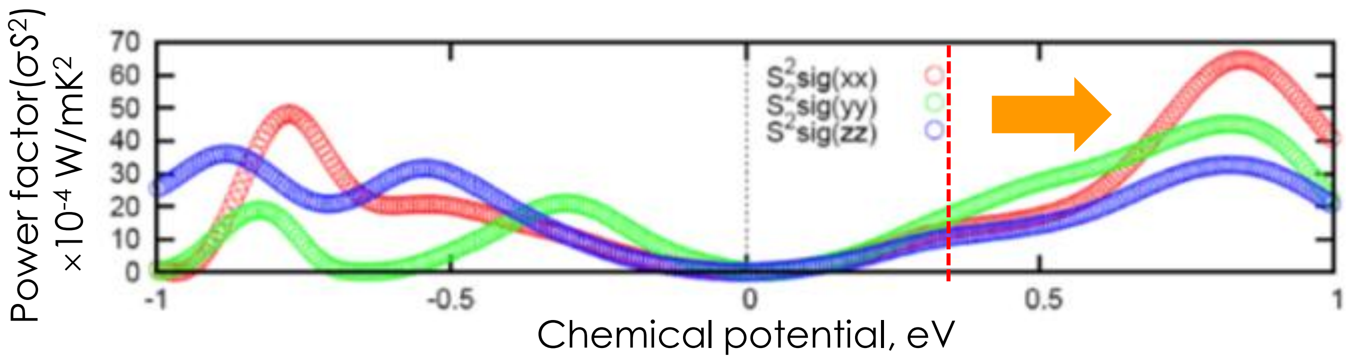


Fermi surface and Charge modulation in $In_4Se_{3-\delta}$

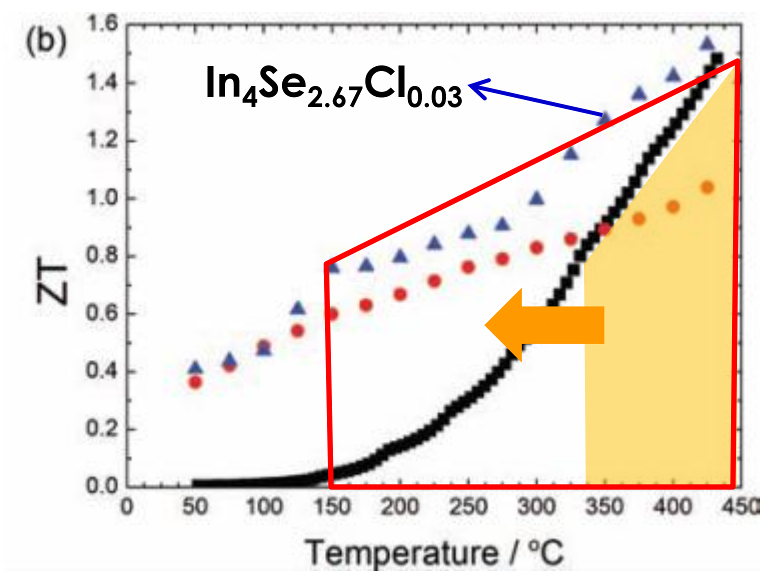
Nature 459, 965 (**2009**)

Enhancement of *ZT* / Evidence for Peierls distortion

- **Boltzman transport calculation at 600 K**

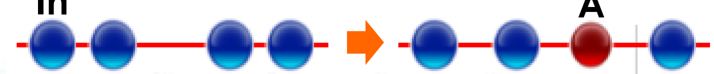


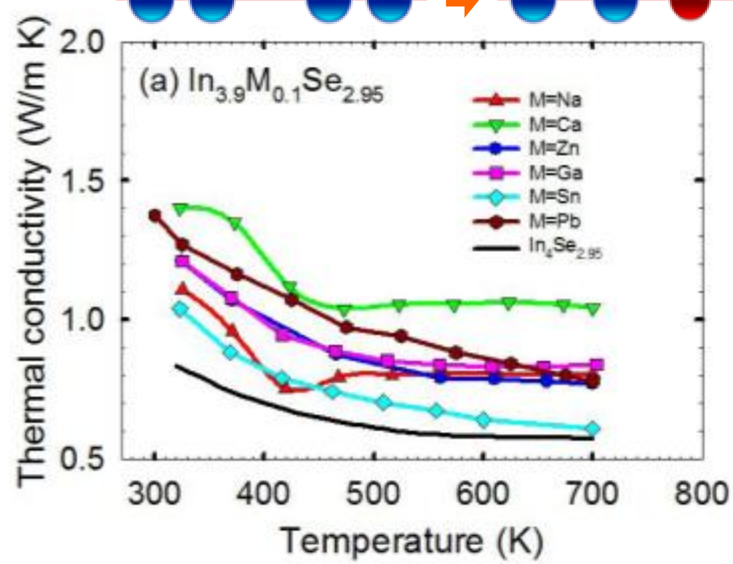
- **Anion(Se)-site doping: $In_4Se_{3-x-y}H_y$ (H = H, Cl, I, Br)**



Adv. Mater. 23, 2191 (**2011**)
J. Mater. Chem. 22, 5730 (**2012**)

- **Cation(In)-site doping: $In_{4-x}A_xSe_{3-y}$**





Appl. Phys. Lett. 99, 102110 (**2011**)

Summary

- **Charge density wave is an effective way to realize the disordered and layered structure with extremely low lattice thermal conductivity.**

- **Peierls distortion is a new way of thermoelectric materials development.**

  1) High thermoelectric performance

  - **In_4Se_{3-x} :** high thermoelectric figure-of-merit **(*ZT* = 1.48 @ 705K)**

  2) Enhanced *ZT* over a wide temperature range (300K – 705K) has been obtained by **chemical potential positioning**.

  3) Thermal conductivity reduction by Peierls distortion was experimentally verified.

- **Seebeck coefficient enhancement was achieved by orbital hybridization.**

  1) High density of states near the Fermi level

  - Localized *f*-band can be tuned by *dp*-hybridization strength control in transition metal doped rare-earth dichalcogenide systems.

1st approach;

Atomic scale engineering

2nd approach;

Nano-scale engineering

"Interface Engineering for Bi(Sb)-Te(Se)"

BST : p-type $(Bi,Sb)_2Te_3$

BTS : n-type $Bi_2(Te,Se)_3$

κ reduction : Strategy Overview

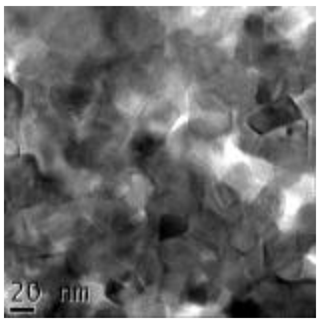
- Lattice thermal conductivity (κ_{latt}) reduction by interface phonon scattering

κ_{latt}	0.6	0.4	0.32	0.25

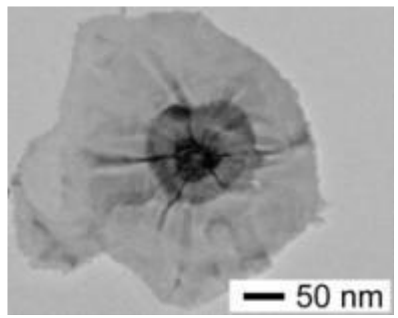
Incoherent interface

Grain-boundary

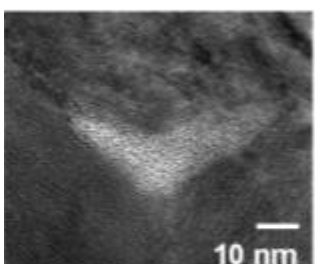
Nanoparticle



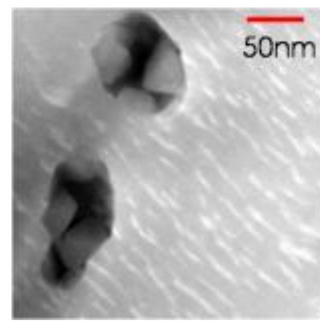
Nanoplate



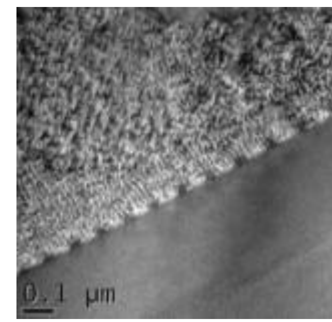
Surface (nanophase)



Coherent interface (strain)



Semi-coherent Interface (dislocation)

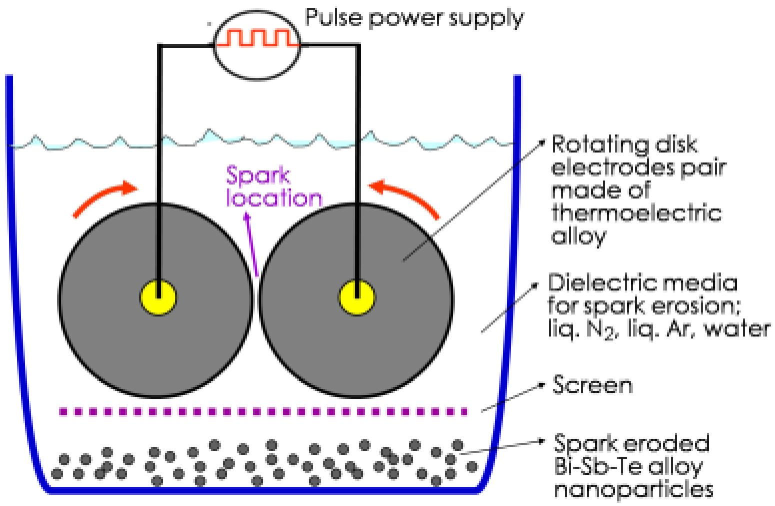


ZT	1.0	1.4	1.6	1.75

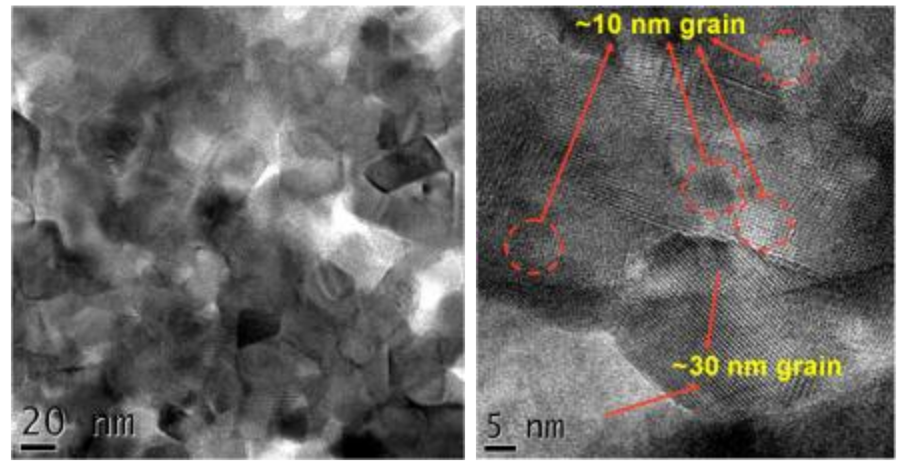
κ reduction: experimental limit by nano-grain approach

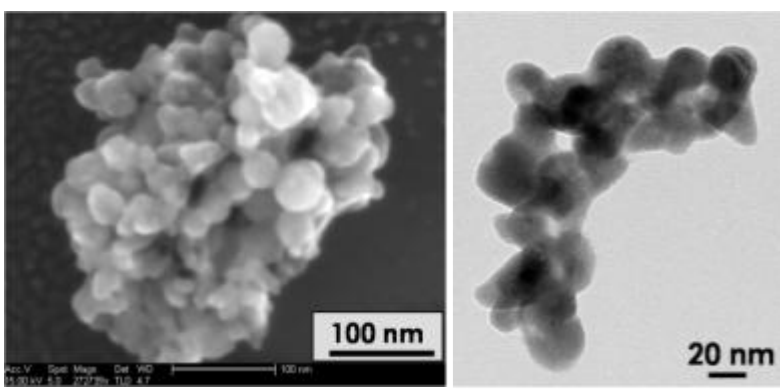
- Phonon scattering by grain boundary → **κ**(lattice) **~0.4 W/mK** → ***ZT*** **~1.4**

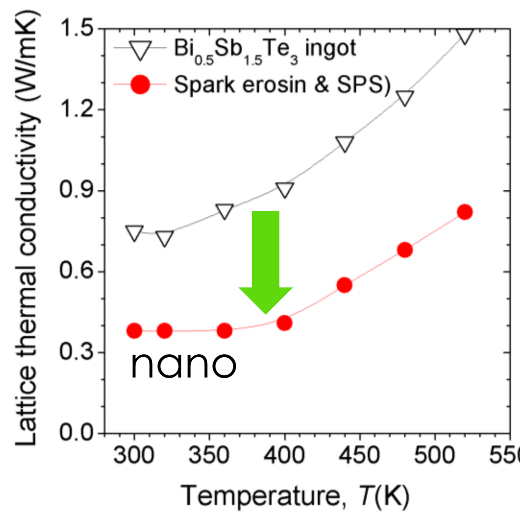
BST nano-powder by spark erosion

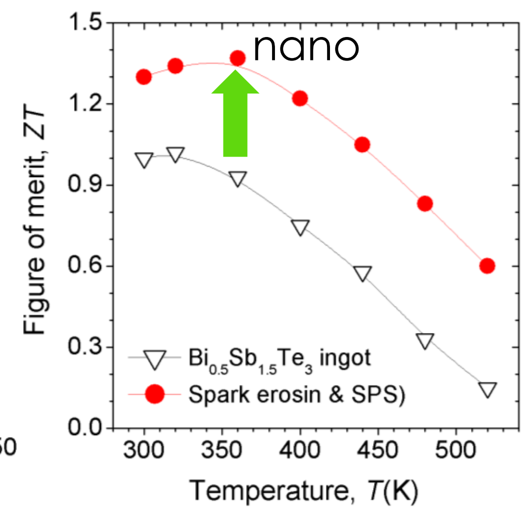


Bulk with nano-grain(spark plasma sintering)





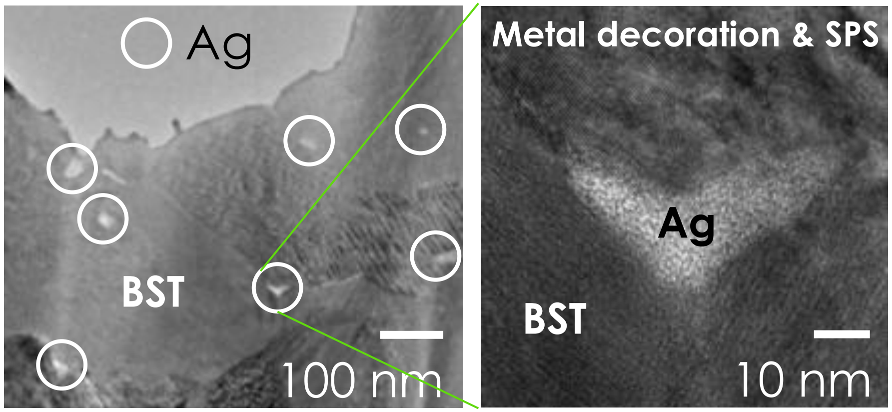


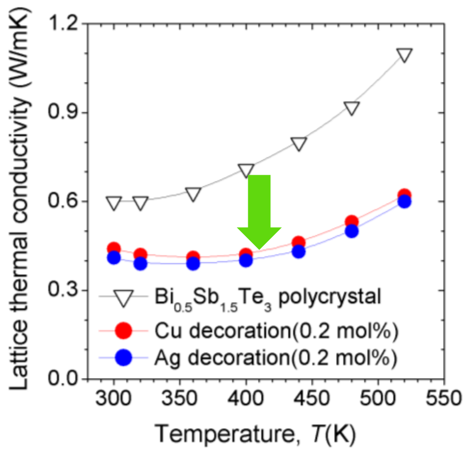


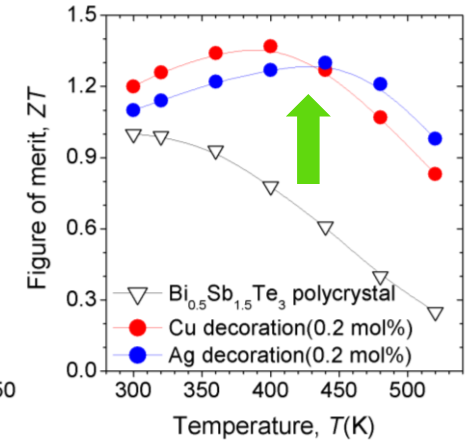
submitted

κ reduction: interface vs. phonon scattering

- **Incoherent** interface → κ(lattice) **~0.4 W/mK → *ZT* ~1.35**

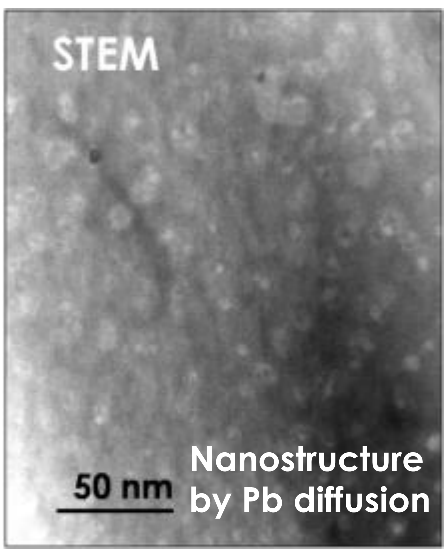


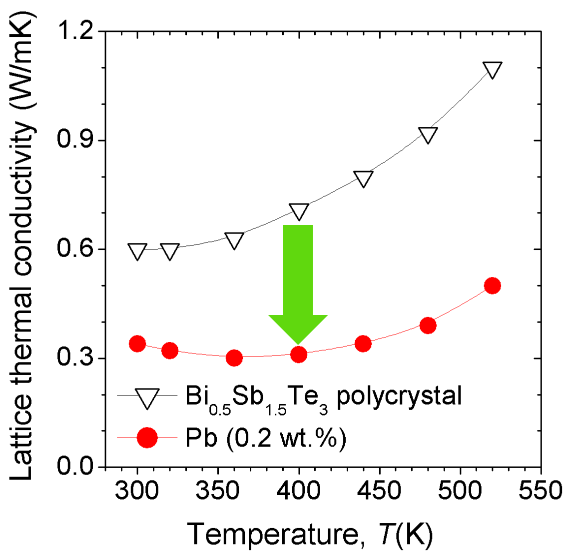


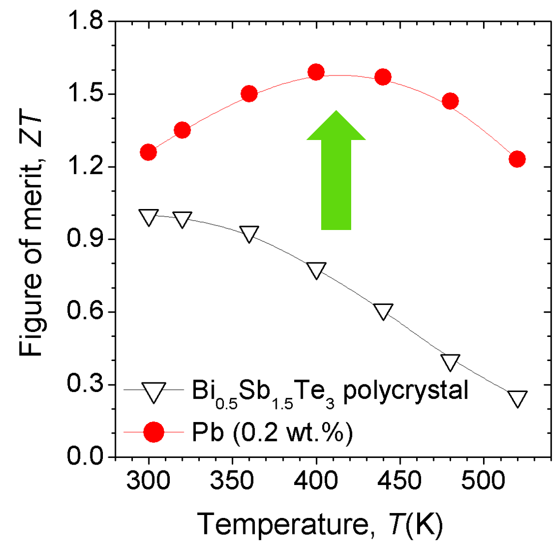


in press (J. Elec. Mater.)

- **Coherent** interface (strain) → κ(lattice) **~0.3 W/mK → *ZT* ~1.5**



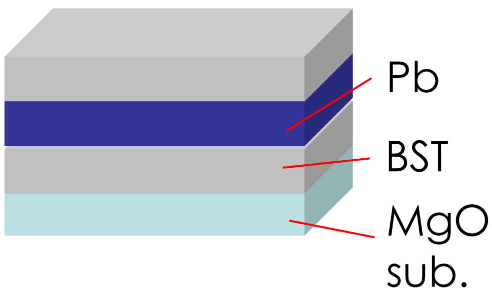


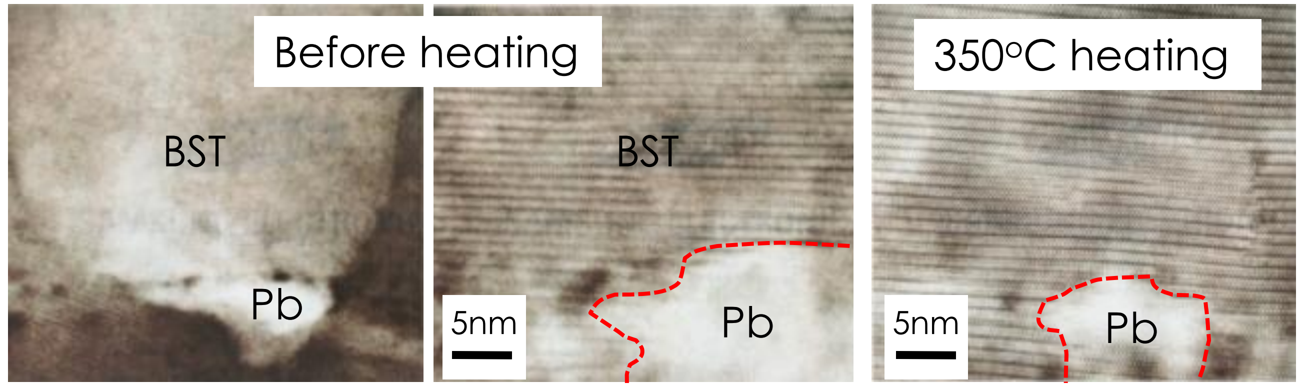


Ongoing Research

In-situ TEM analysis for nanostructuring

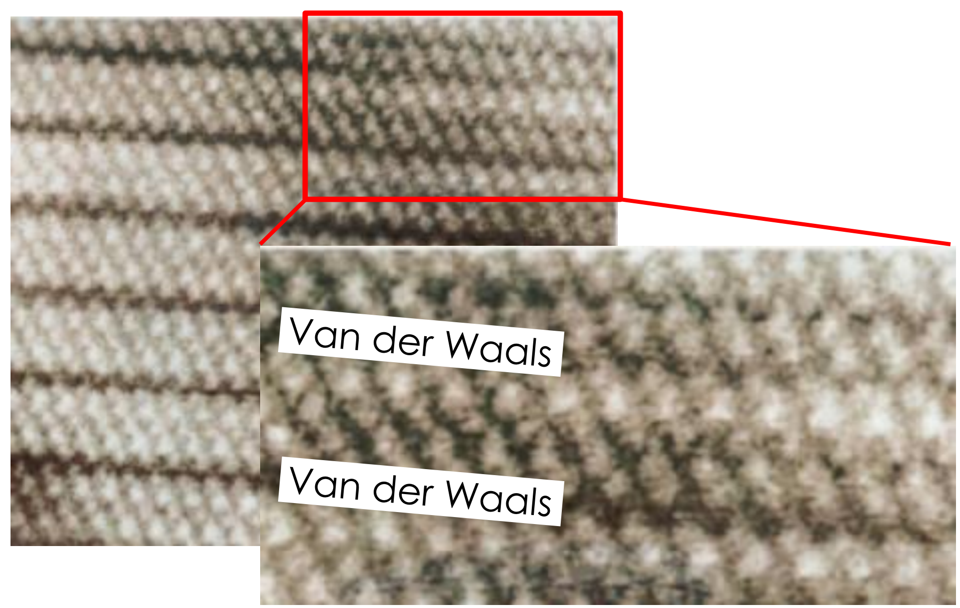
- **Mechanism study by Pb/BST thin film: nanostructuring by Pb diffusion**





Before heating (BST)

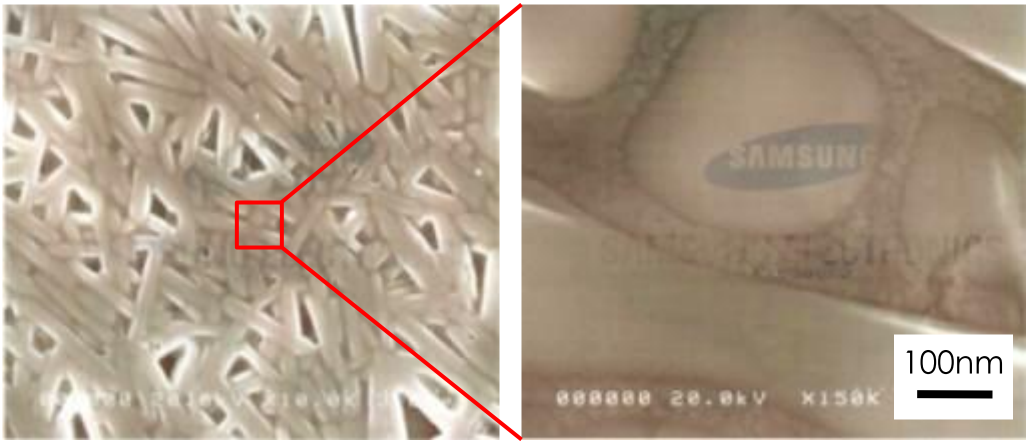
350°C heating (Pb-BST)



Ongoing Research

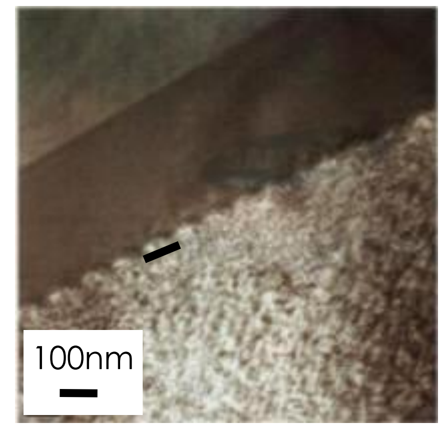
κ reduction: semi-coherent interface formation

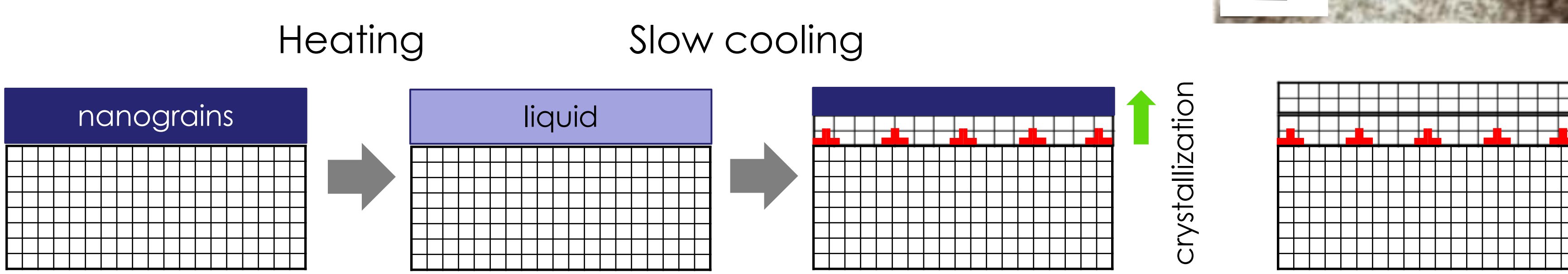
- **Nanostructured ribbon by melt spinning**



- **Bulk with strained interface**

LPER: Liquid Phase Epitaxy Regrowth





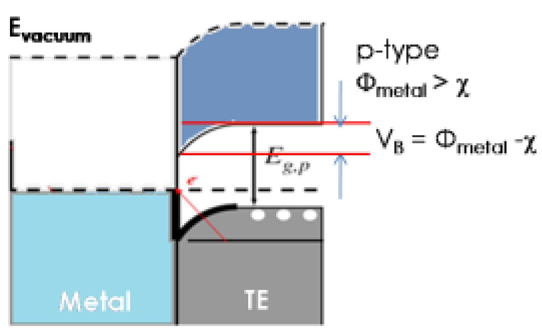
Ongoing Research

Mechanisms for *S* enhancement in bulk

Mechanism	Theory	Simulation	Material
Carrier filtering	**[1999]** Thermionic emission current in heterostructures	**[2008]** Band bending at PbTe/metal interfaces	**[2009]** Bulk(PbTe) **[2010]** Bulk(skutterudite) **[2011]** Bulk(TAGS) **[2011]** Pt-Sb_2Te_3
Resonant State	**[1956]** Virtual bound (resonant) state by doping **[1996]** DOS engineering	**[2006]** Doped PbTe	**[2008]** Tl-doped PbTe **[2009]** Sn-doped Bi_2Te_3

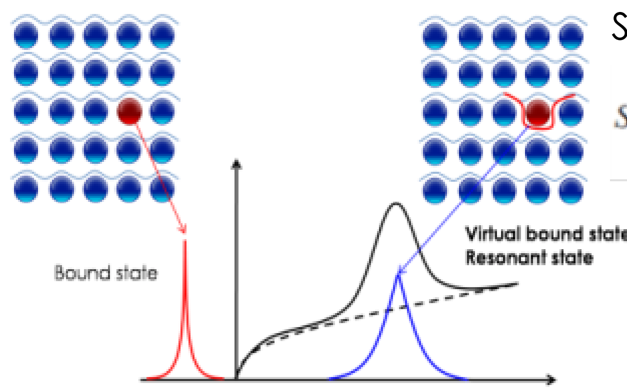
Carrier filtering effect

$$\frac{\pi^2 k_b^2 T}{3q}\left(\frac{d\ln N(E)}{dE} + \boxed{\frac{d\ln \tau(E) v(E)^2}{dE}}\right)_{E=E_F}$$



S.V. Faleev, *Phys. Rev. B* 77, 214304 (2008)

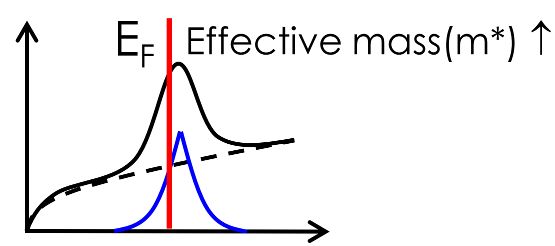
Resonant state



J. Friedel, J. Physics, 1956

If E_F is tuned to near a peak in DOS, $S^2\sigma$ would be sharply increased!

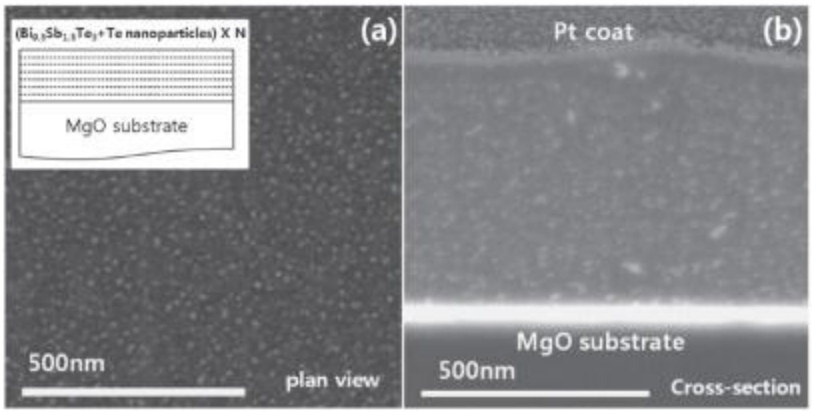
$$S = \frac{\pi^2}{3}\cdot\frac{k_B}{e}\cdot k_B T\left[\frac{g(E)}{n(E)} + \frac{1}{\mu(E)}\cdot\frac{\partial \mu(E)}{\partial E}\right]_{E=E_F}$$

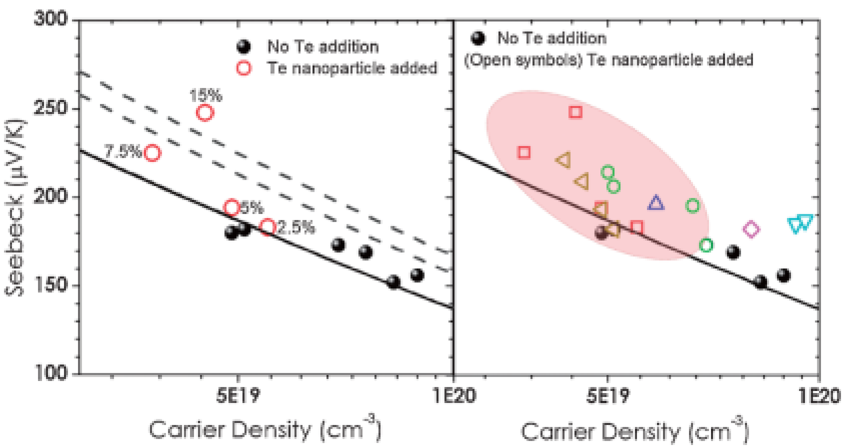


ORNL, PNAS, 1996

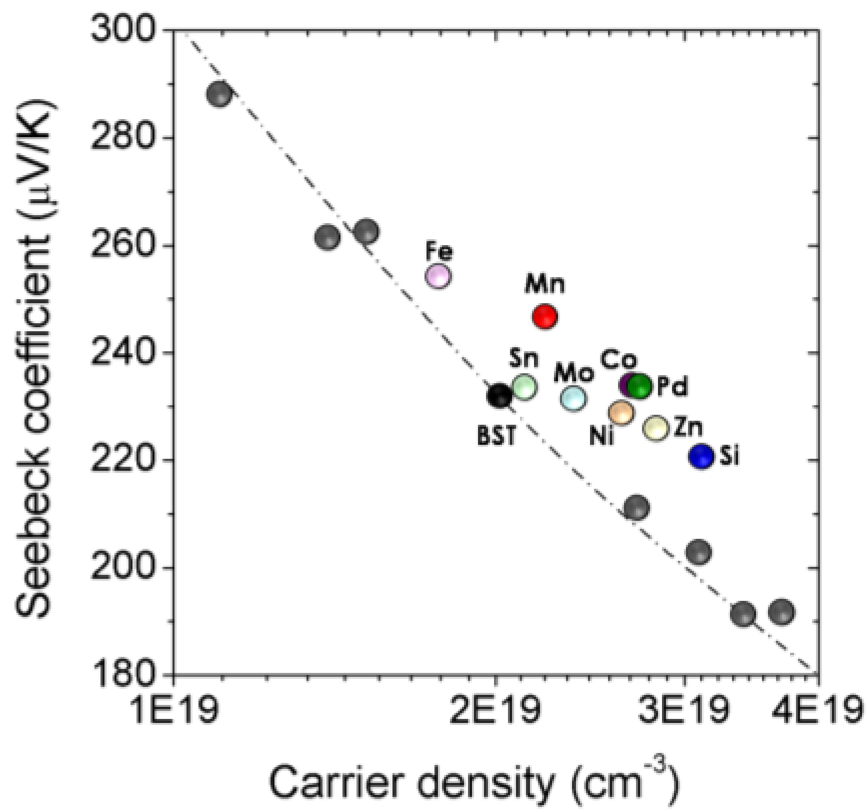
S enhancement : carrier filtering effect

- **Results on the simulation & model experiment (thin film) :** BST + nanoparticles
  1. Required work function value of metal nano-particle: 3.5-4 or 5-5.5 eV
  2. Optimum size & volume fraction : 5nm / 5vol.%





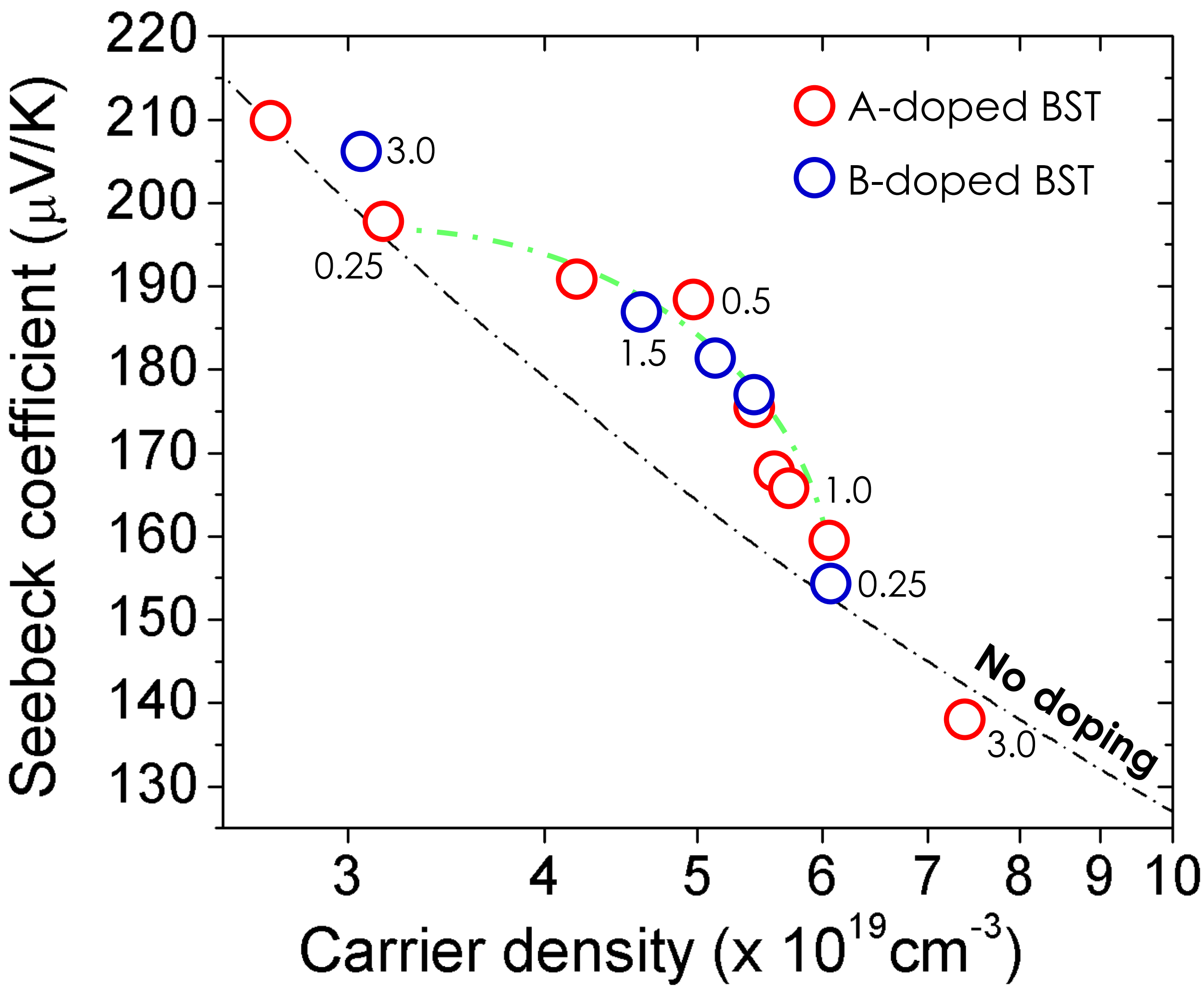
Experimental evidence on *S* enhancement in bulk nanocomposite



Appl. Phys. Express 4(9) 091801 (**2011**)

S enhancement : resonant state formation

- **Results on simulation & experiment in doped BST**



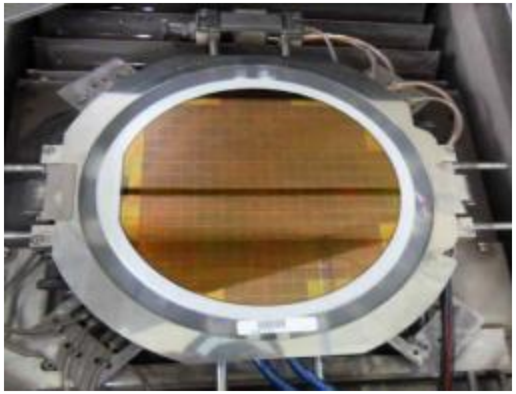
Ongoing Research

Applications

- Memory test chamber

- CPU cooler

- Cold chuck



- Extremely low T chamber

- Water purifier

- HVAC