A new class of high ZT doped bulk nanothermoelectrics through bottom-up synthesis

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- **Students and Post-Doctoral Associates**

  Ramanath group: Dr. Rutvik J. Mehta, Hong Zhu, Peter O'Brien (will be at Intel), Devender, Priyanka Jood (Australia), Dr. C. Karthik (Now at Idaho), Dr. A. Purkayastha (Now at Laird)

  Borca-Tasiuc group: Dr. Yanliang Zhang (now at GMZ), Liang Han, Emmanuel Sachdeva, Ed Castillo, Matt Belley, Wei Jiang.

- **Collaborators**

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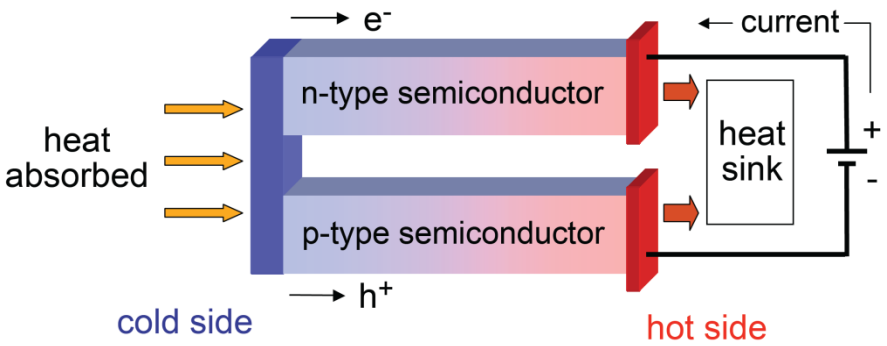
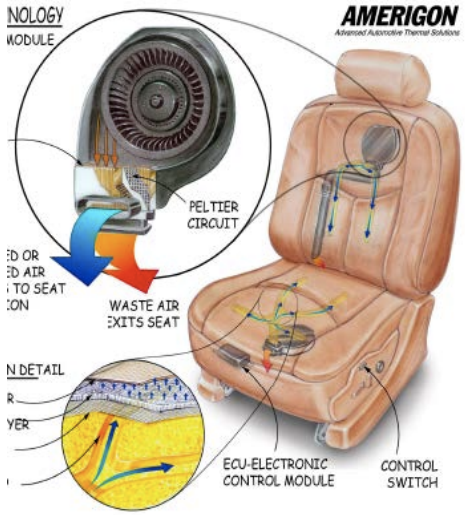
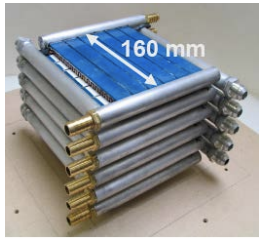
  – National Science Foundation (ECCS, CMMI, DMR, and other grants)
  – NRI-NIST, and NY State

Solid-state electrical ⇔ thermal conversion

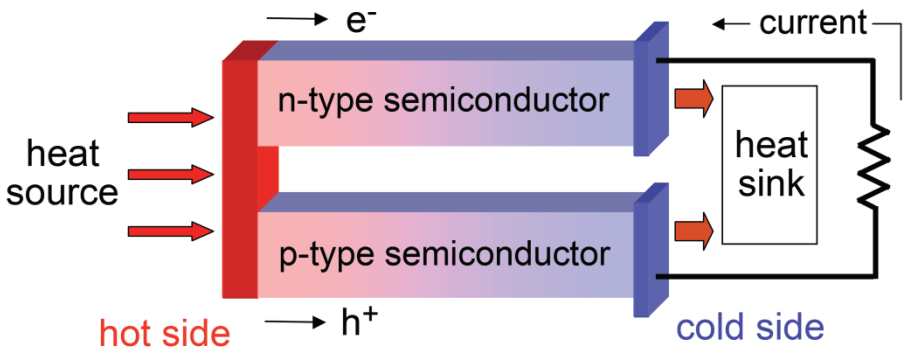
Heat management/refrigeration







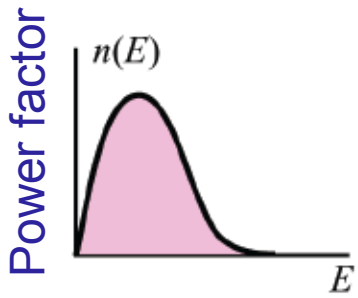
Energy harvesting



Thermoelectrics, a tug-of-war of properties !

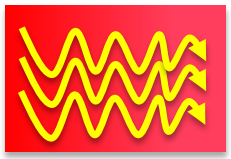
$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

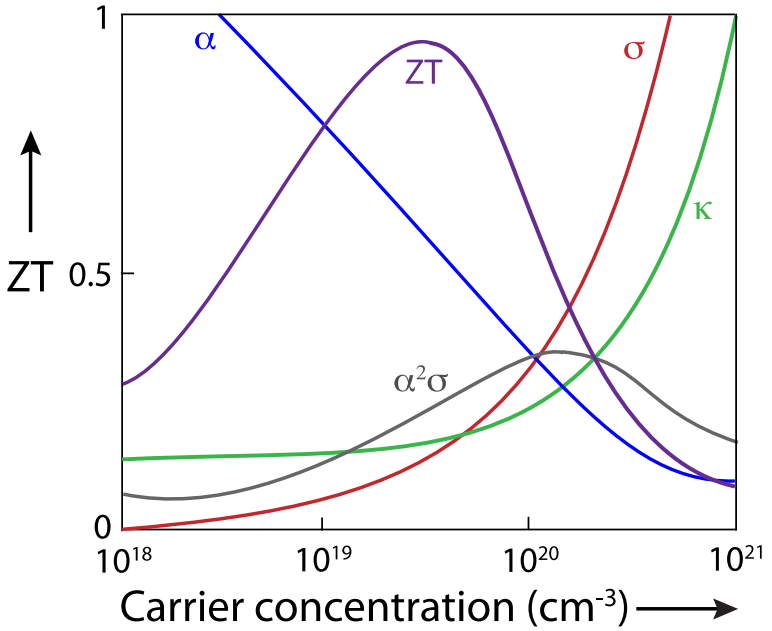
Power factor

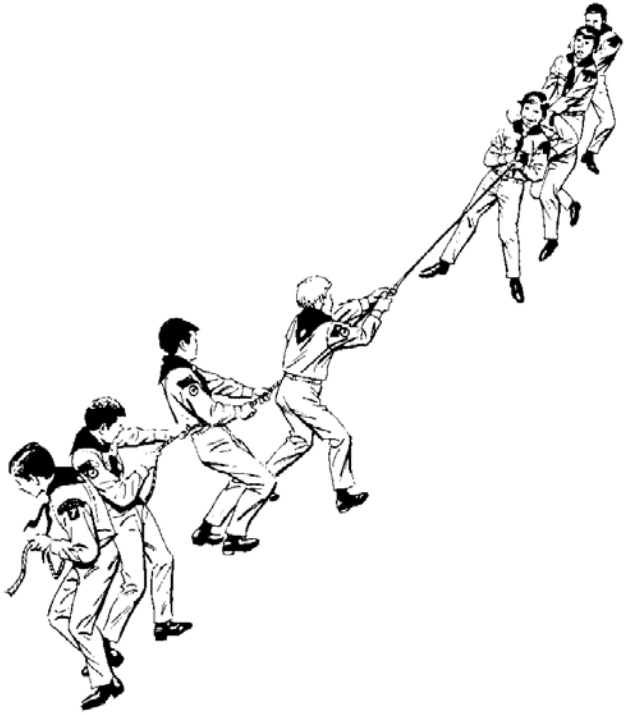


Thermal conductivity

$$= \kappa_L + \kappa_e$$



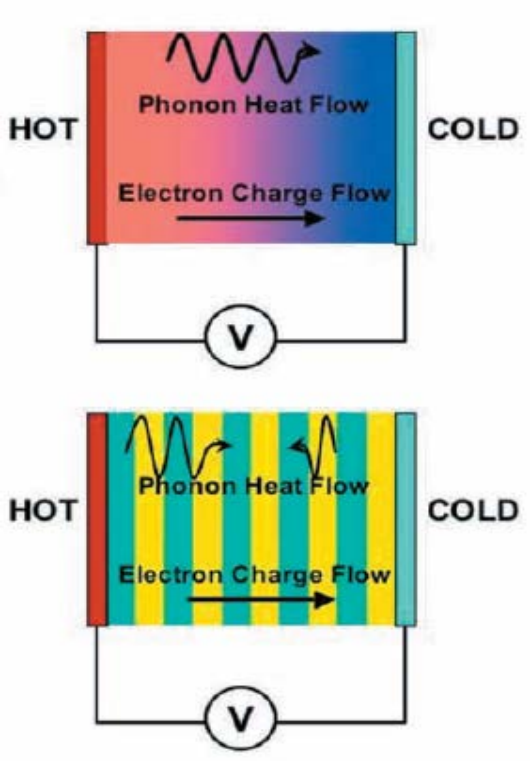


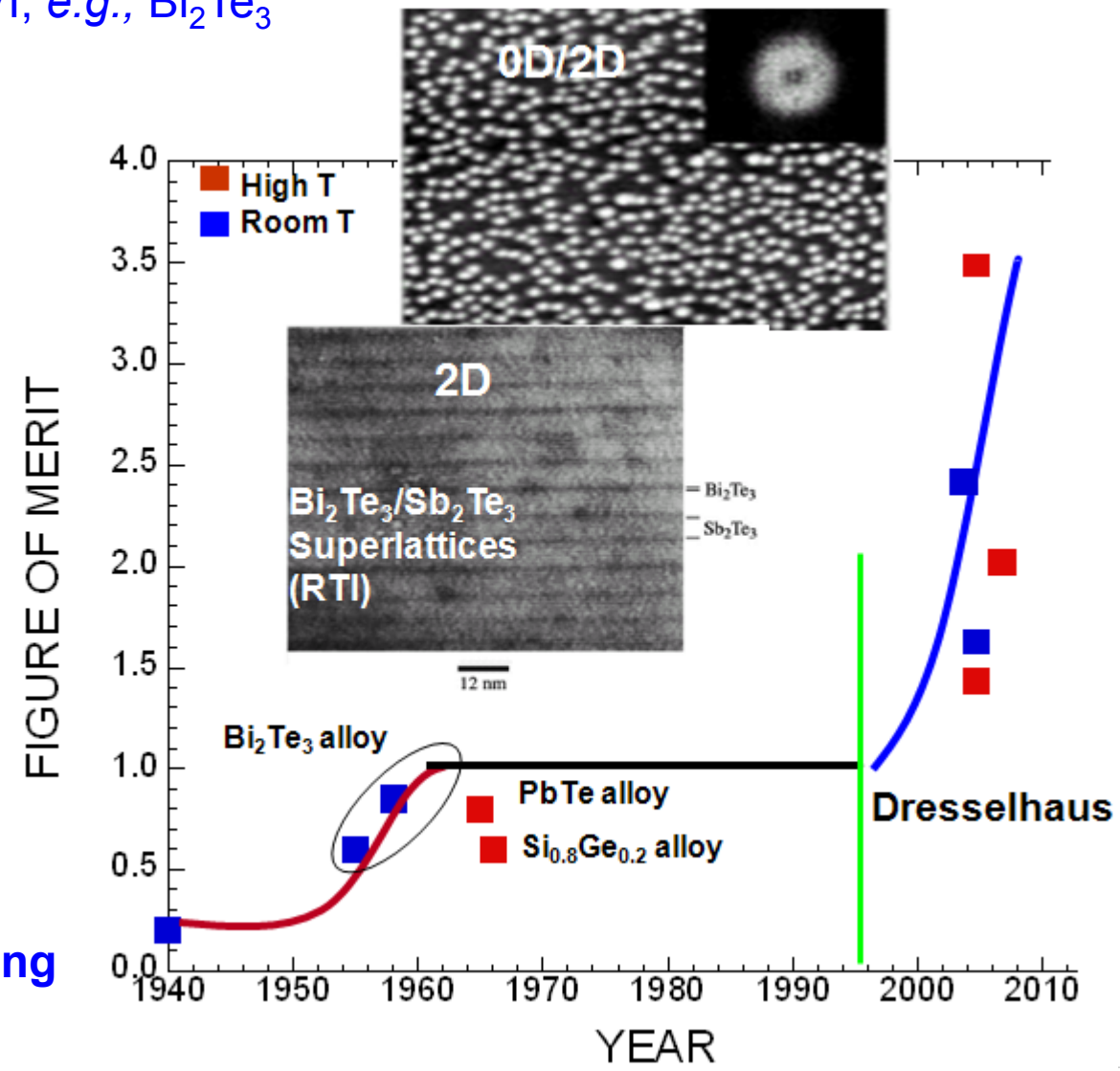


- Nano ➔ κ_L ↓
- But $\alpha^2\sigma$?
- For p- ***and*** n-type ?

High figure of merit nanostructured thermoelectrics

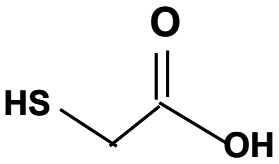
Best materials – Group V + VI, *e.g.*, Bi_2Te_3

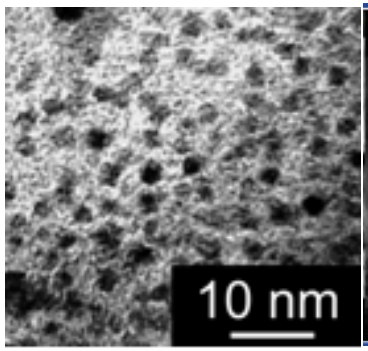


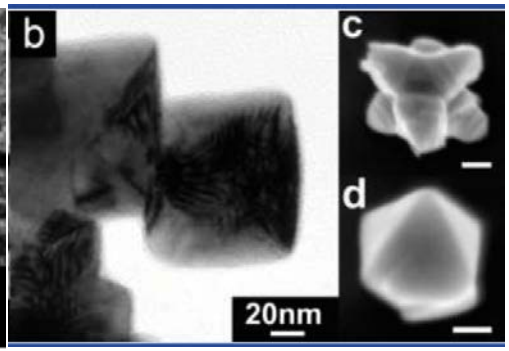


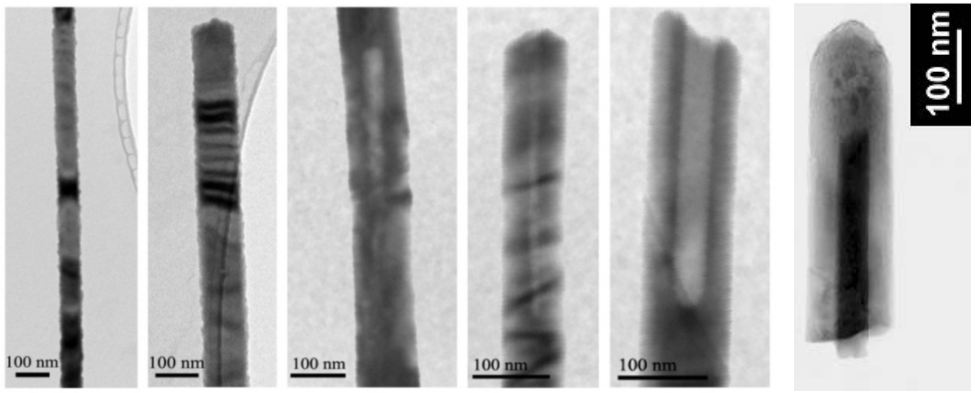
- **Quantum confinement**
  - Increase σ and α
- **Interface phonon scattering**
  - κ decrease

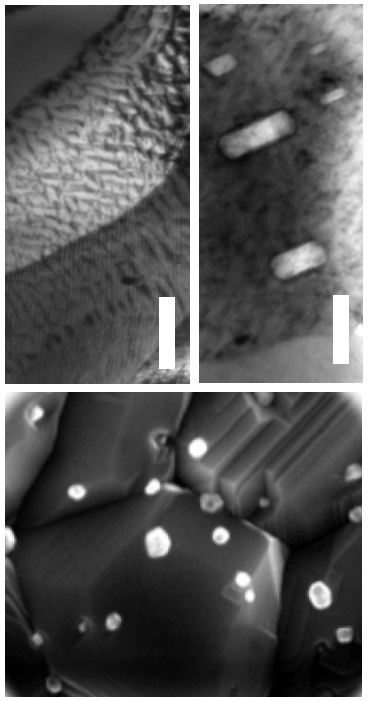
Surfactant-directed nanostructure sculpting and assembly

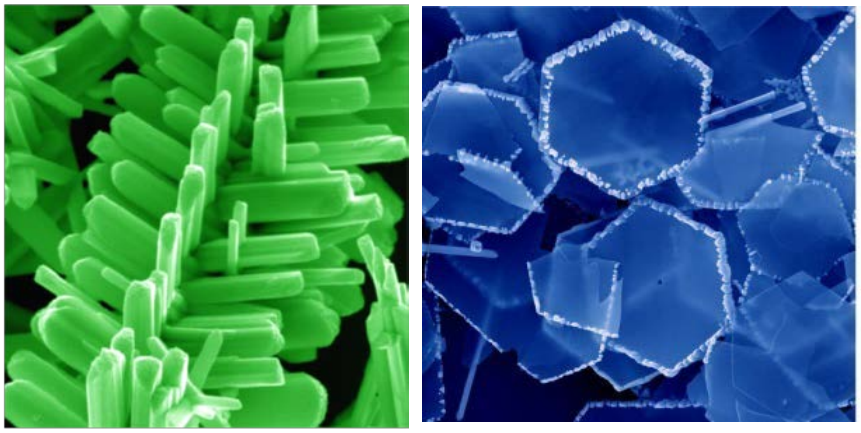






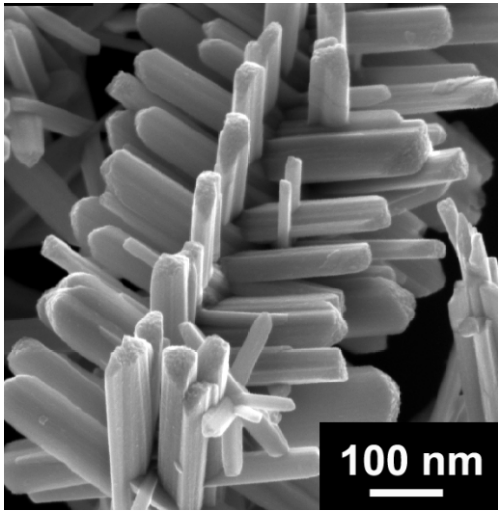


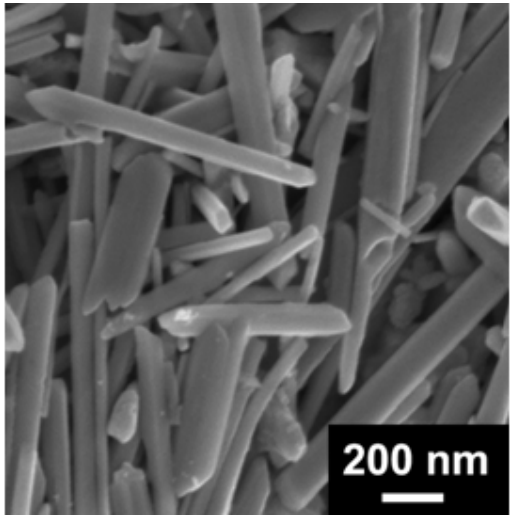


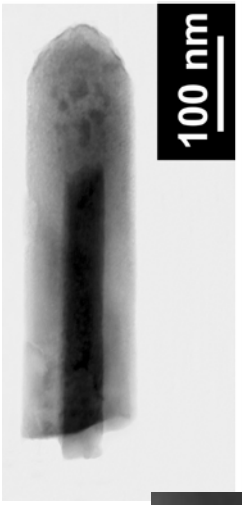


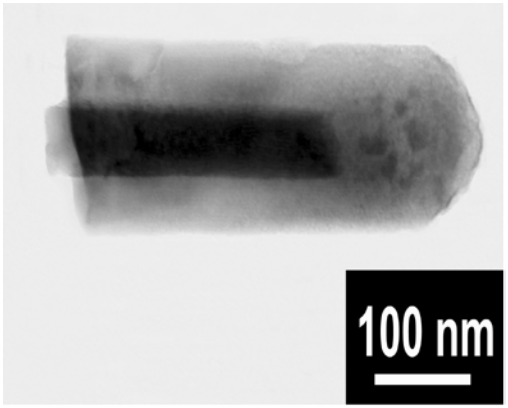
Adv. Mater. (2006-08); Chem Mater. (2008-11), Nano Lett (2010-11), J Phys Chem (2010), ACS Nano (2010), Nature Materials (2012)…

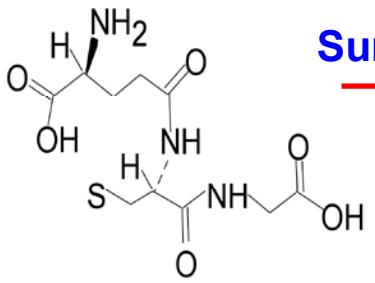
Surfactant-induced branching through twinning



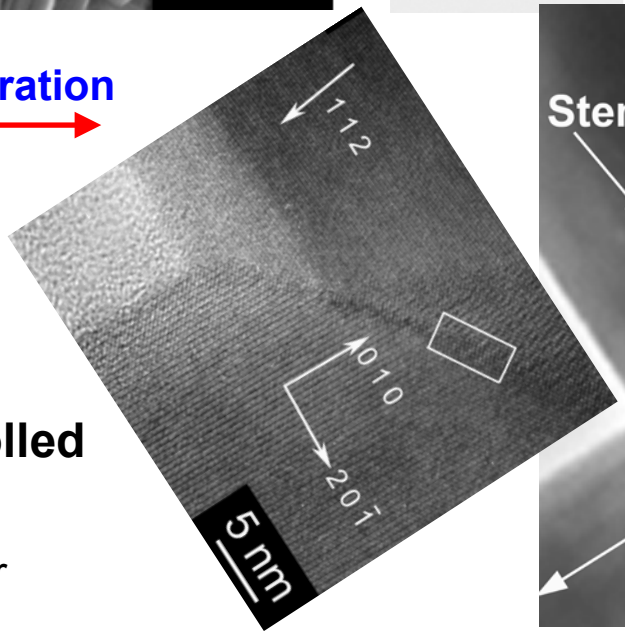


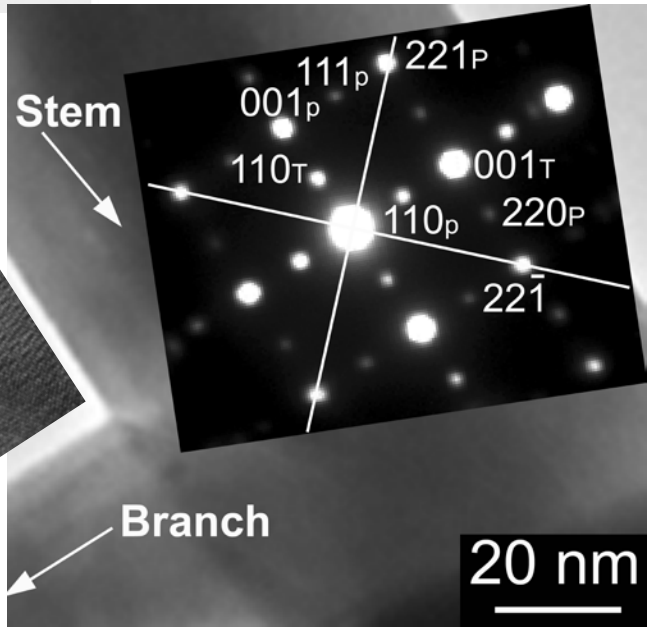






Surfactant concentration →





- **Core-shell structures**
- **Nanoscale features controlled by beaker processing**
  - Twining about (22$\bar{1}$) mirror plane

Purkayastha, Li,…, Borca-Tasciuc, Ramanath, Adv. Mater. 20, 2679 (2008).

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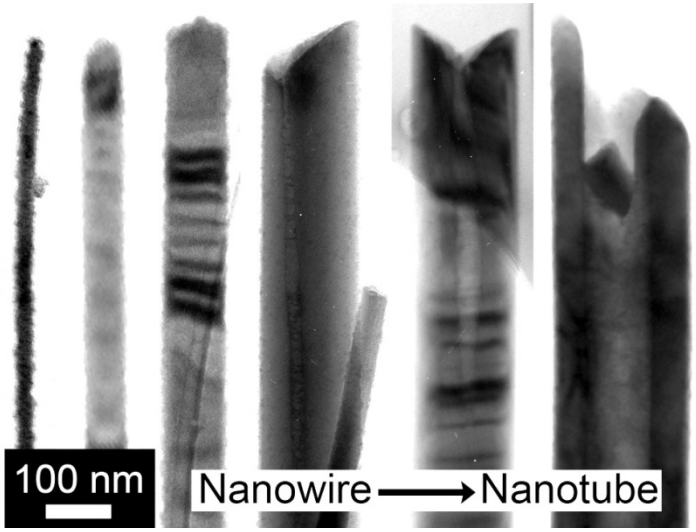
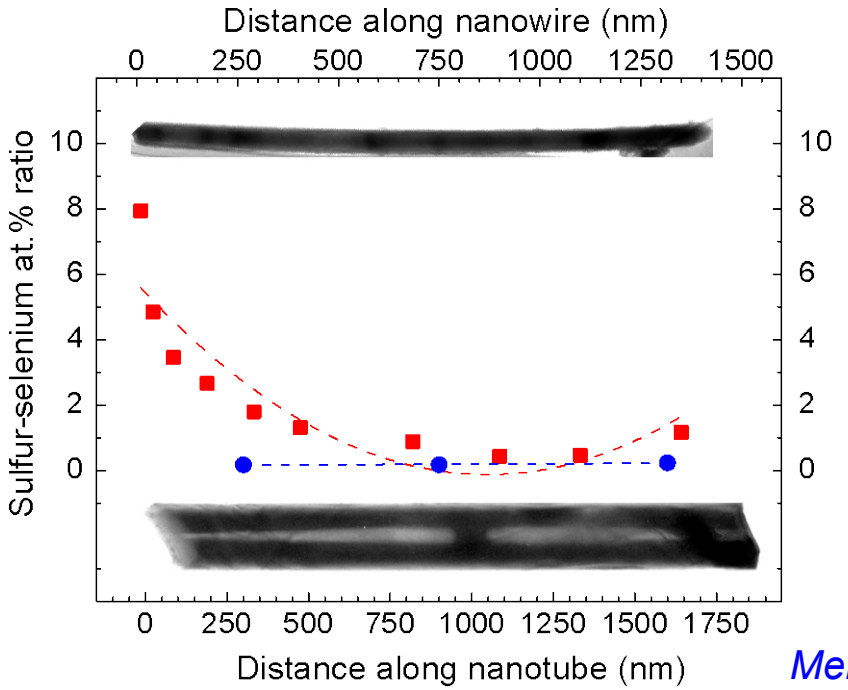
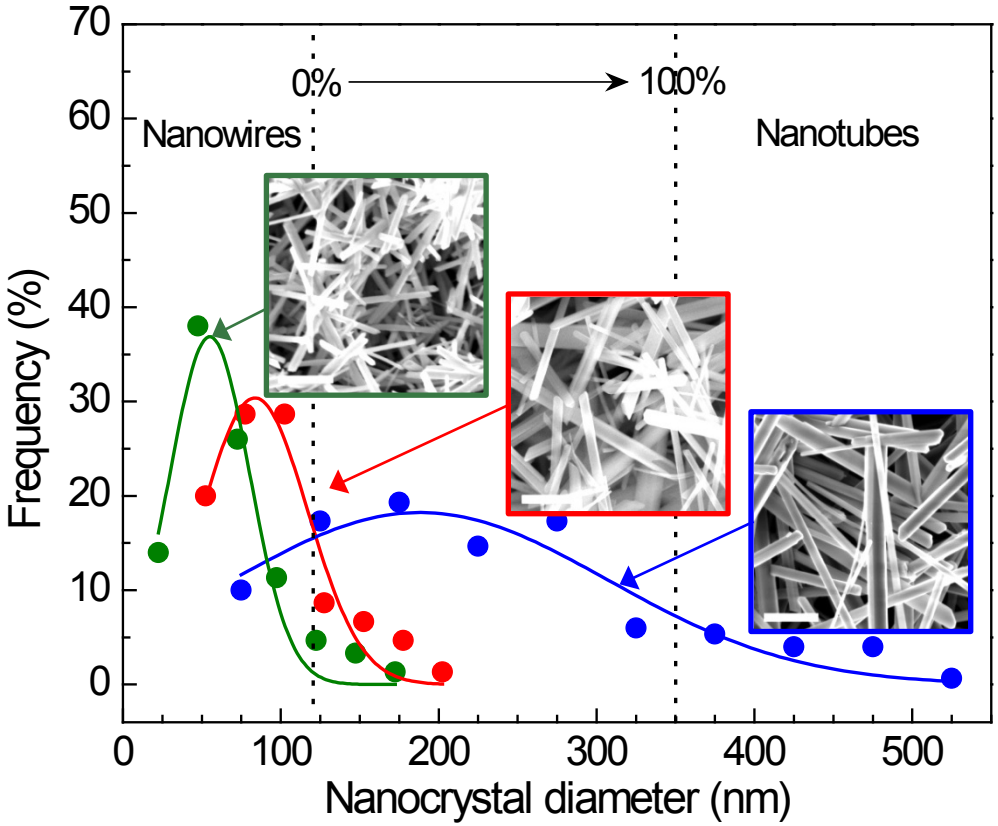
Sulfurized antimony selenide: nanowire → nanotube conversion







- Large $\alpha \sim 1600\ \mu V/K$
- Low $\sigma \sim 10^{-2} - 10^{-5}\ \Omega^{-1}m^{-1}$
- ↑ Microwave dose: nanowire → nanotube
- TGA → sulfurization

Mehta, …, Ramanath, Nano. Lett. 10, 4417 (2010)

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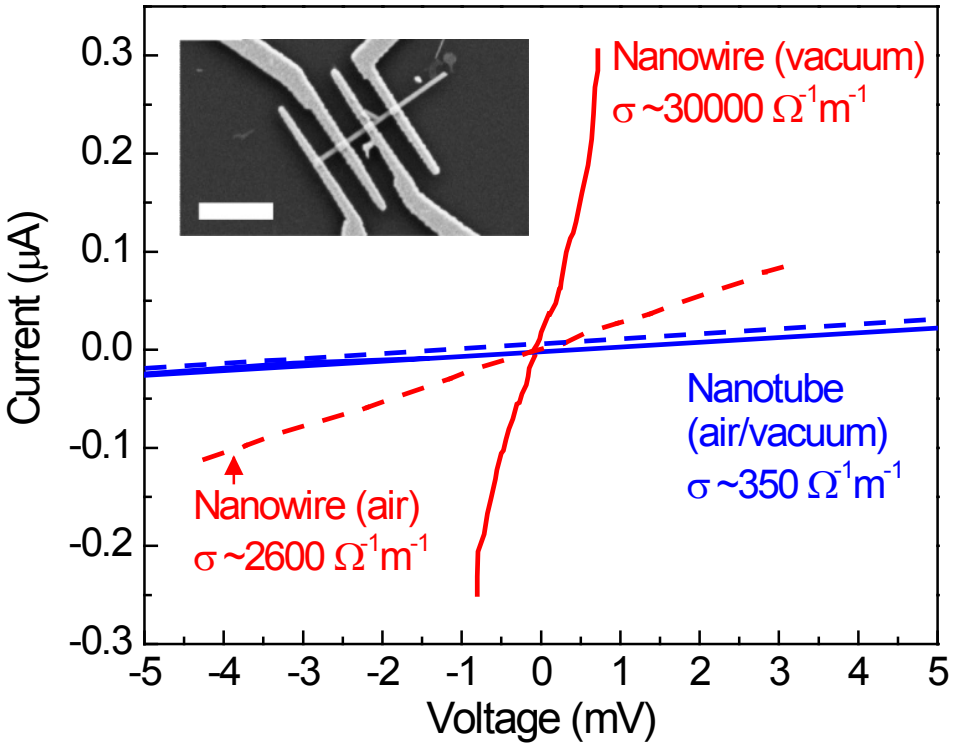
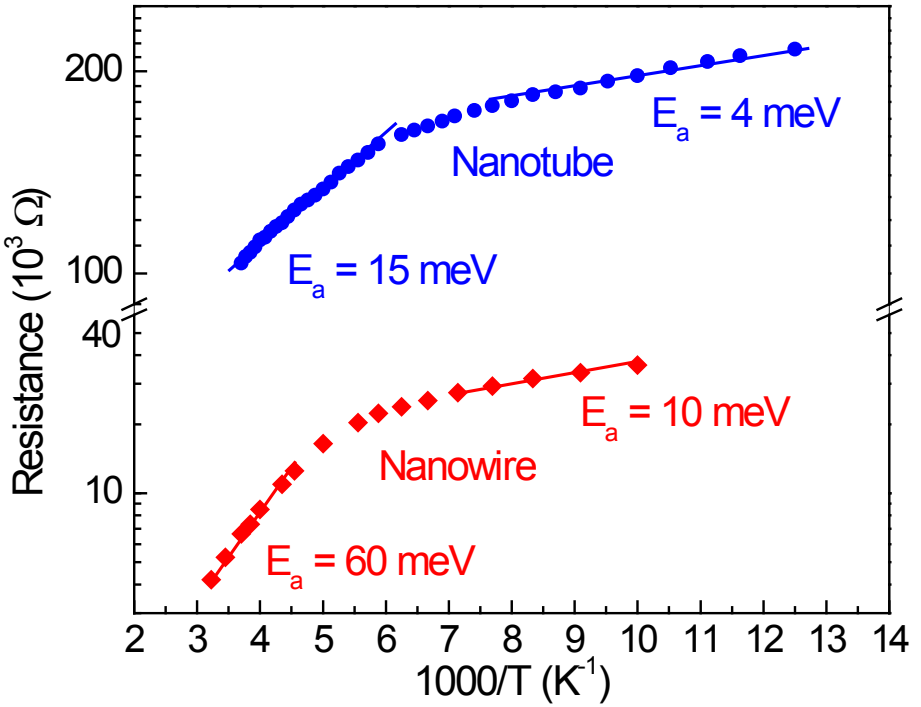
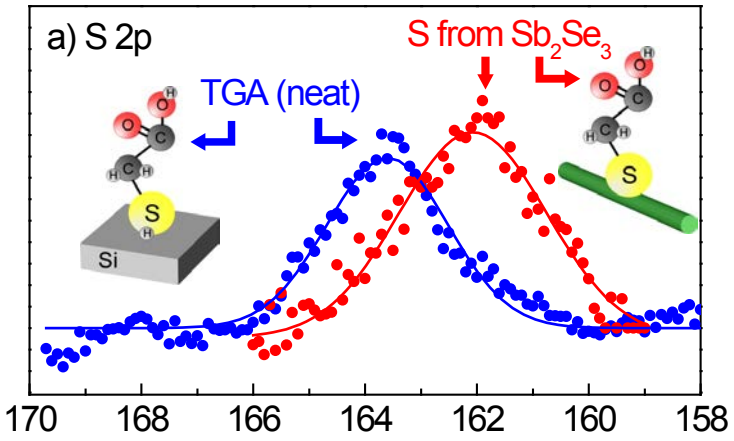
Colossal electrical conductivity enhancement in Sb_2Se_3



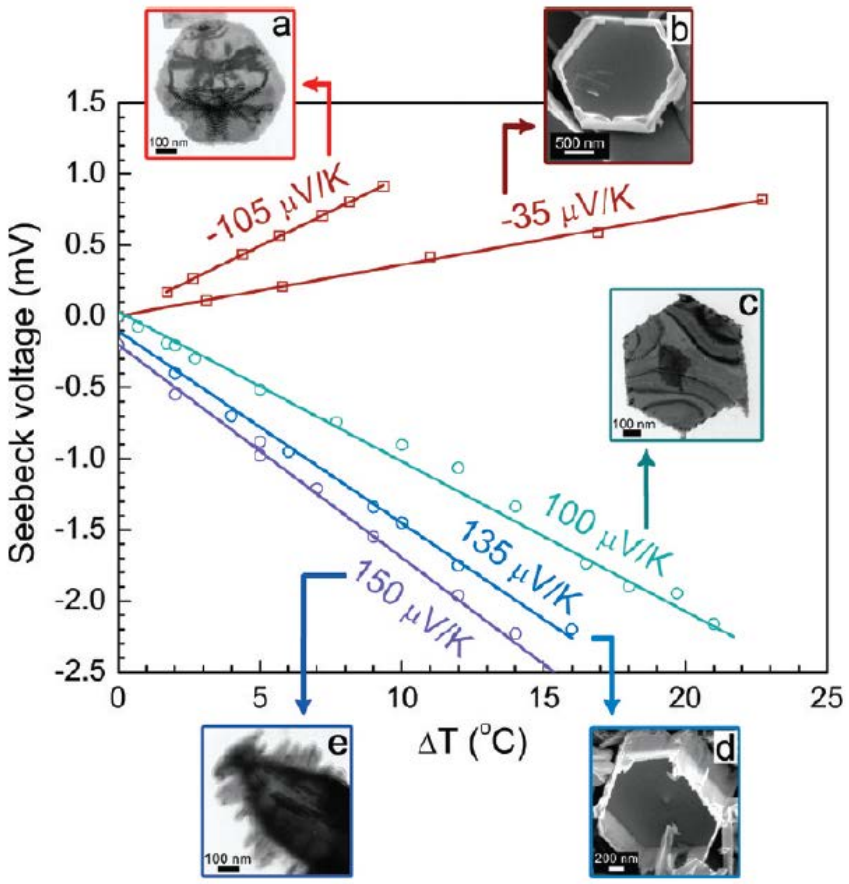


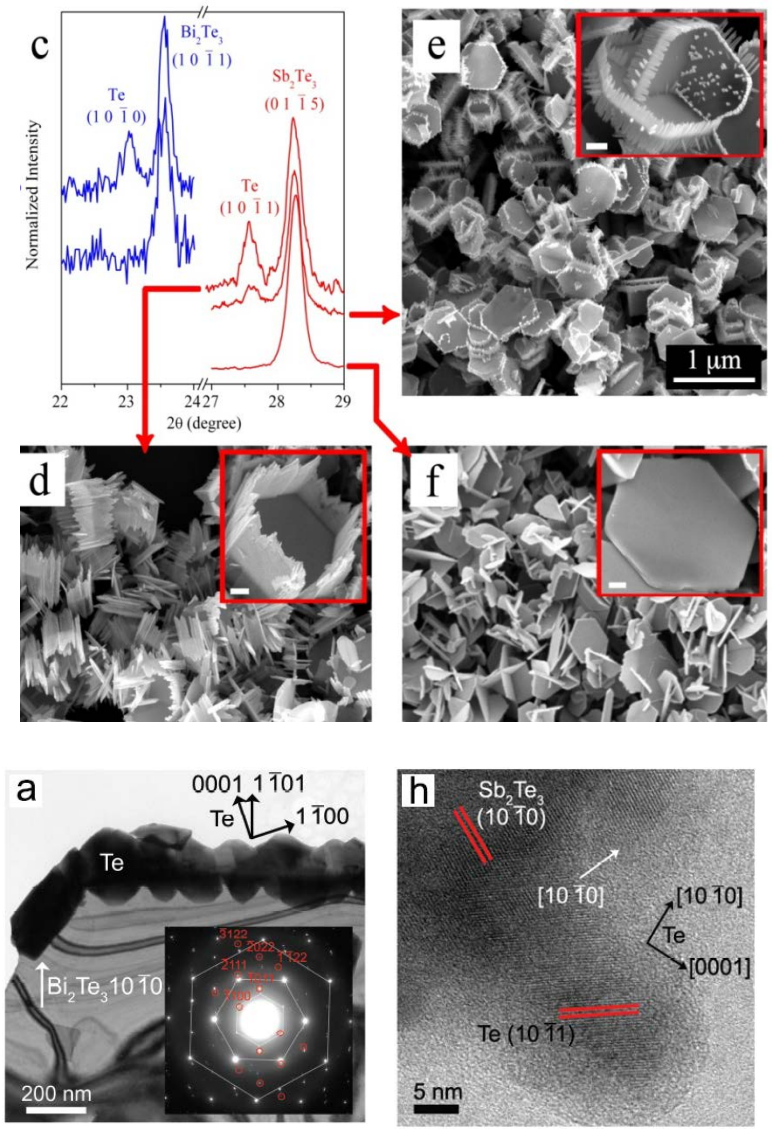


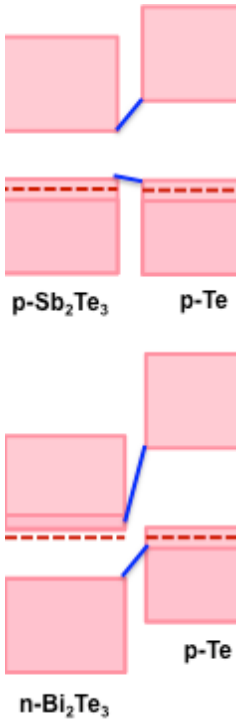
- 10^4-10^{10} higher than bulk; get σ ~ 10 - 10^5 $\Omega^{-1}m^{-1}$
- Only nanowires (S gradients) show
  - high σ and ambient sensitivity
  - Shallow dopant levels from sulfur-surface states

Mehta, …, Borca-Tasiuc, Ramanath, Nano. Lett. 10, 4417 (2010)

Te-heterostructuring-induced α tuning







- **α greater than bulk**
  - Heterointerfaces
  - hot carrier filtering

Mehta, …, Borca-Tasciuc, Ramanath, ACS Nano 4, 5055(2010)

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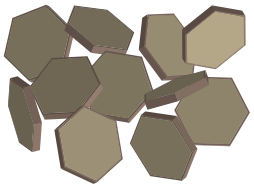
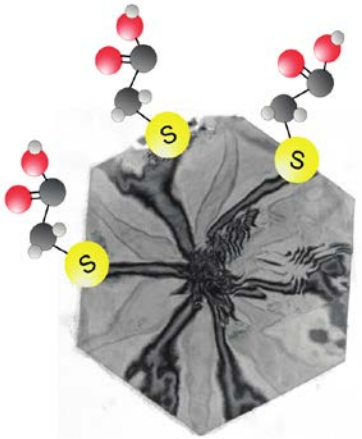
Single-crystal chalcogenide nanoplates and their assemblies





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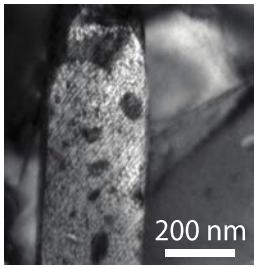

Google:
Ramanath + microwave + thermoelectric

thermaura inc

- **Shaping, sizing, doping and nanostructure/electronic structure control**
  - High ZT; both n- and p-type
  - Very low κ and potential for $\alpha^2\sigma$ enhancement

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

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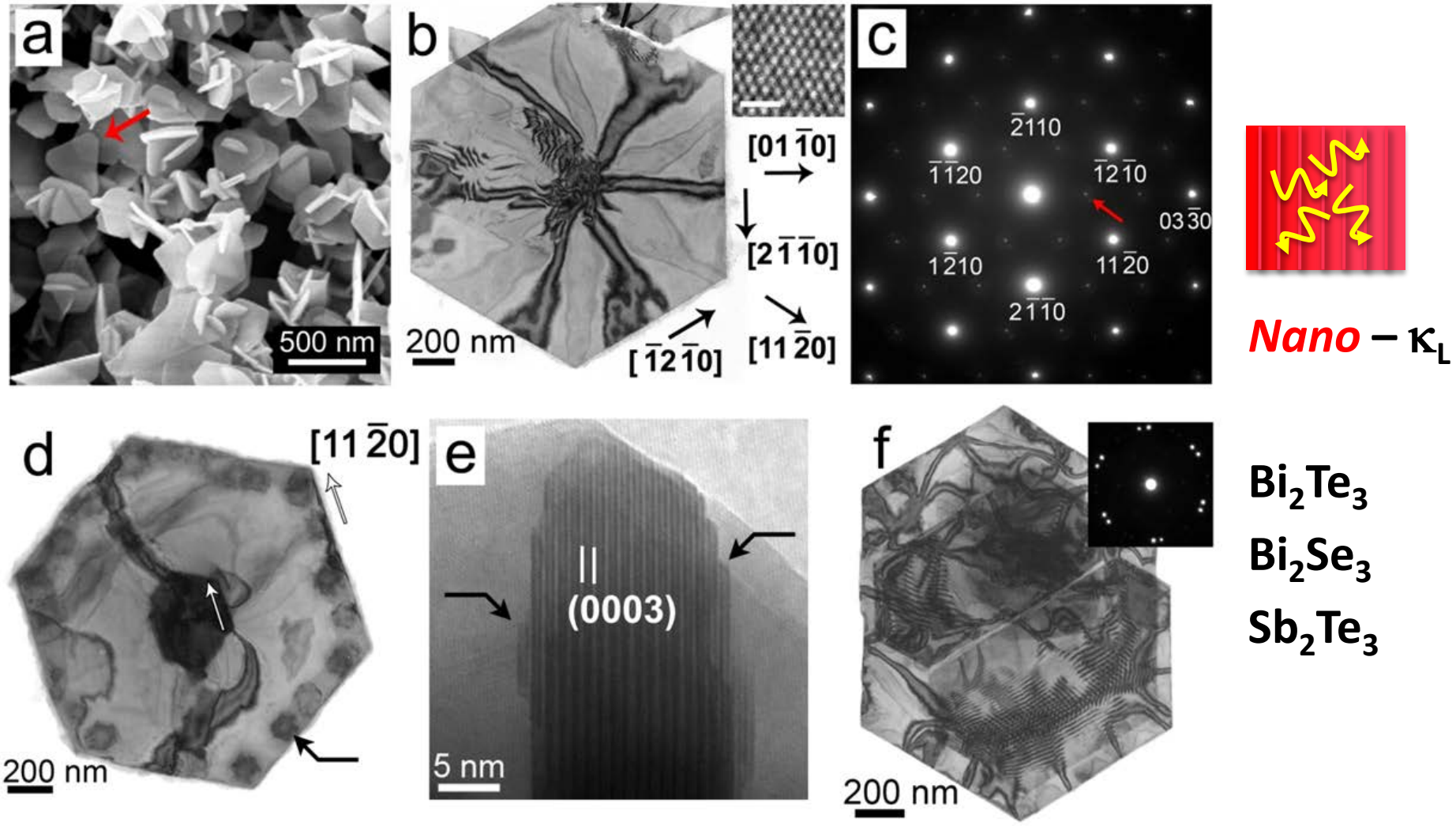
Pnictogen chalcogenide nanoplate building blocks



Nano – κ_L

Bi_2Te_3

Bi_2Se_3

Sb_2Te_3

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

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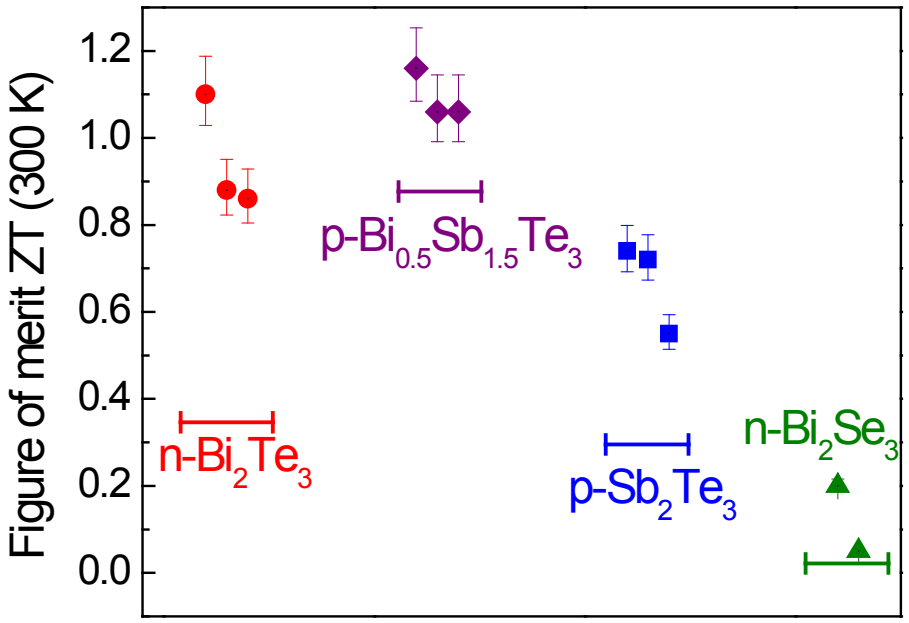
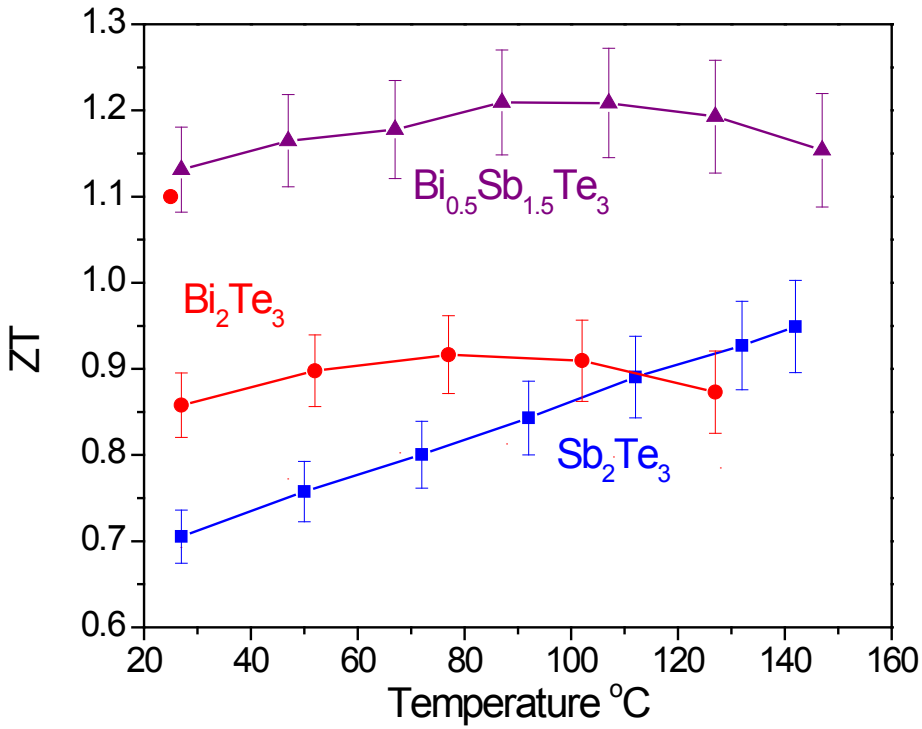
ZT increase for n- *and* p-type nanobulk thermoelectrics





- ZT=1.1 n-Bi_2Te_3, ZT=0.75 p-Sb_2Te_3 with no alloying!!
- ZT increases monotonically up to 0.95 p-Sb_2Te_3 at 400 K
- Blind-samples verification at Marlow and Boston College

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

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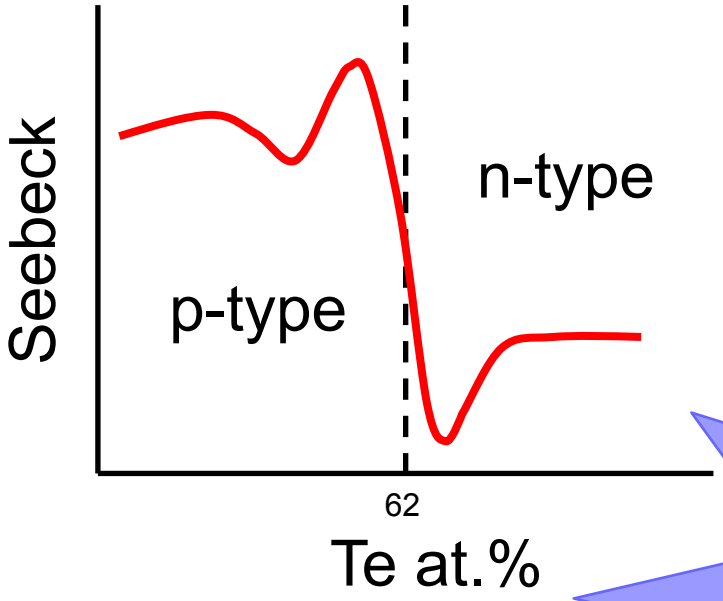
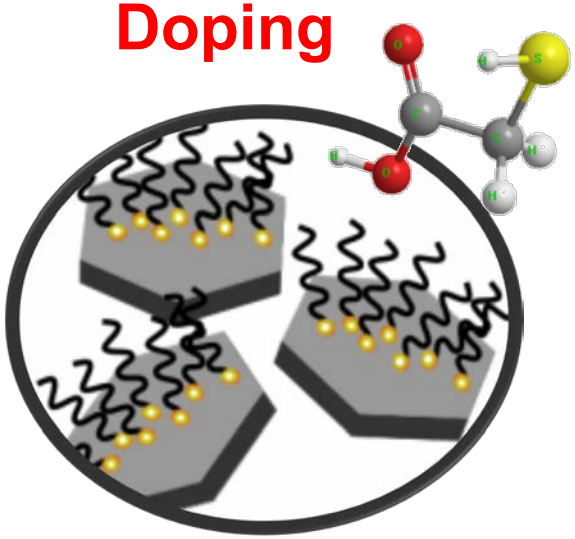
Stoichiometry, composition

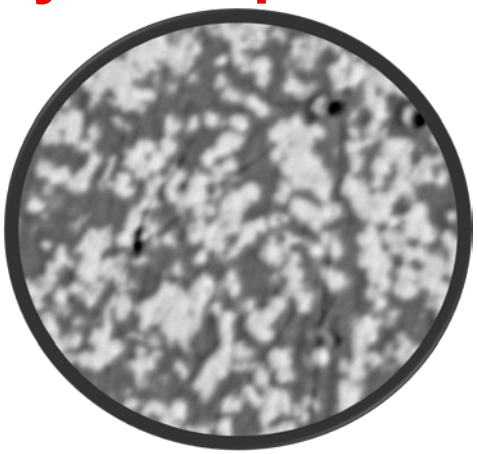


Doping

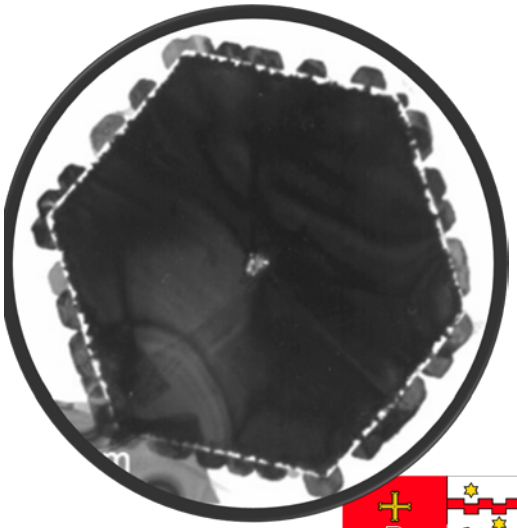


Higher ZT

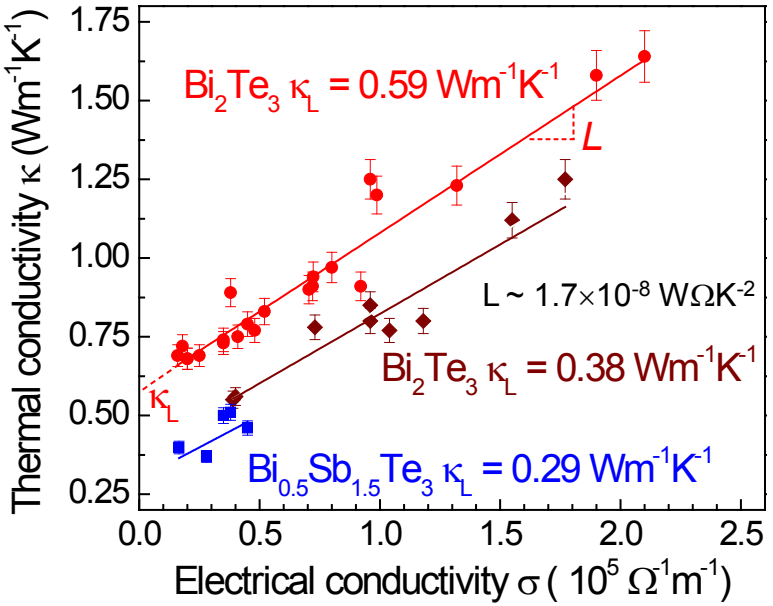
Nanobulk alloys/composites

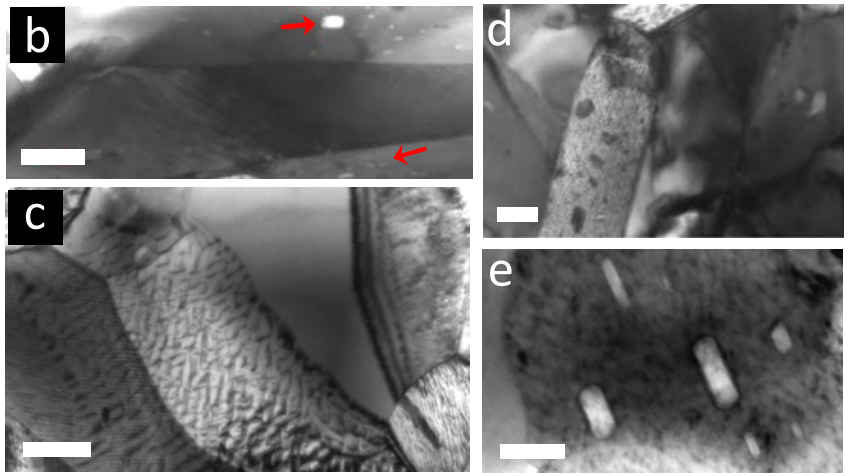


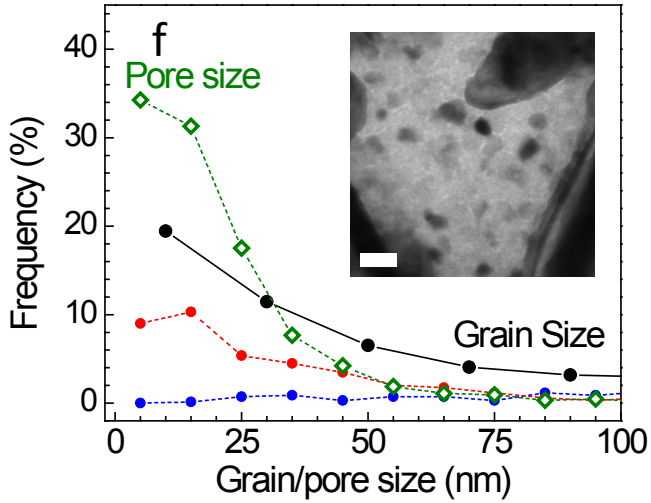
Heterostructuring

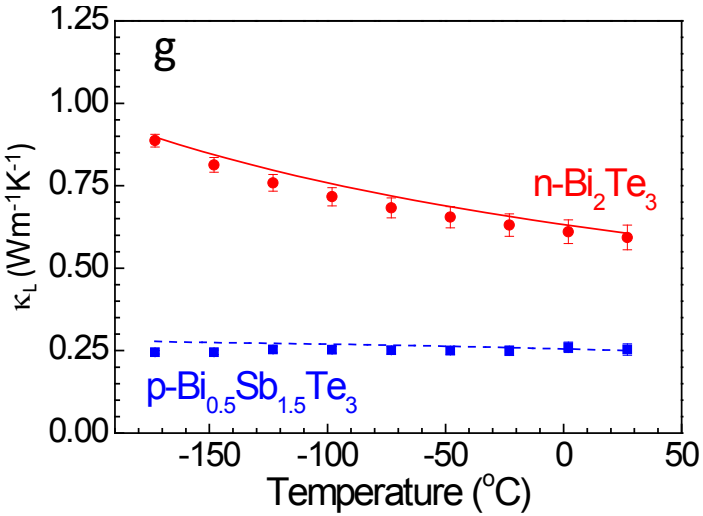


50-75% κ_L diminution due to nanograins and nanopores



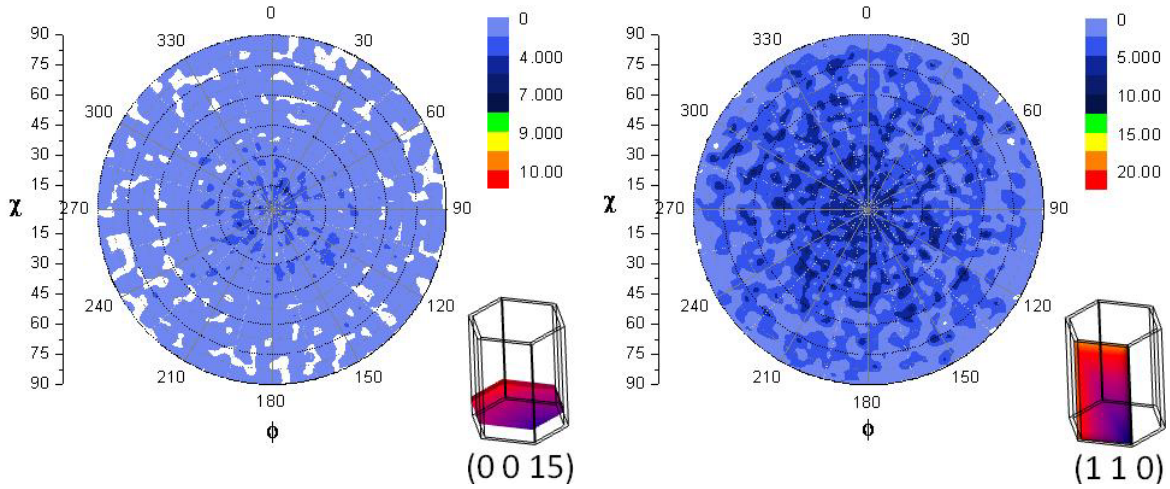


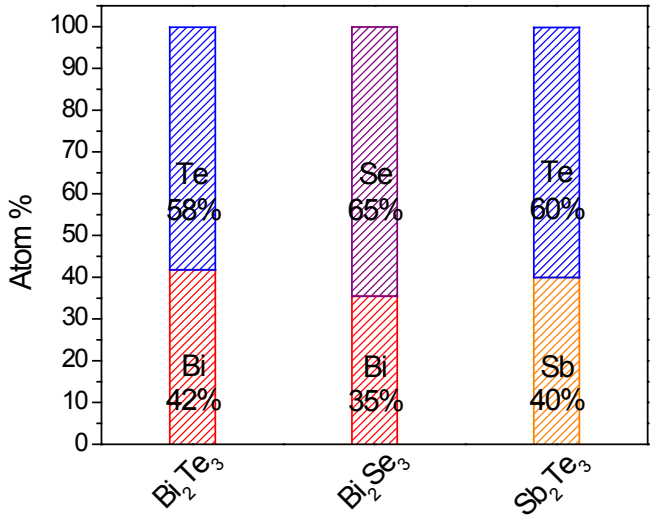


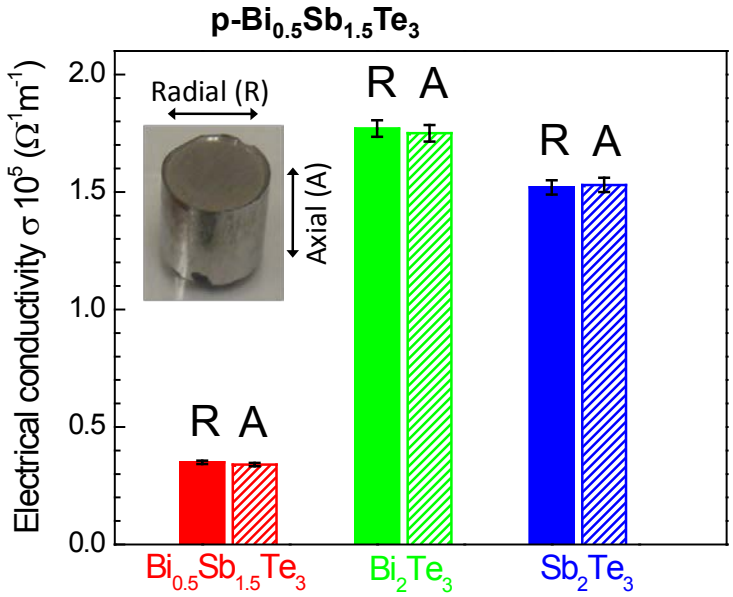


Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

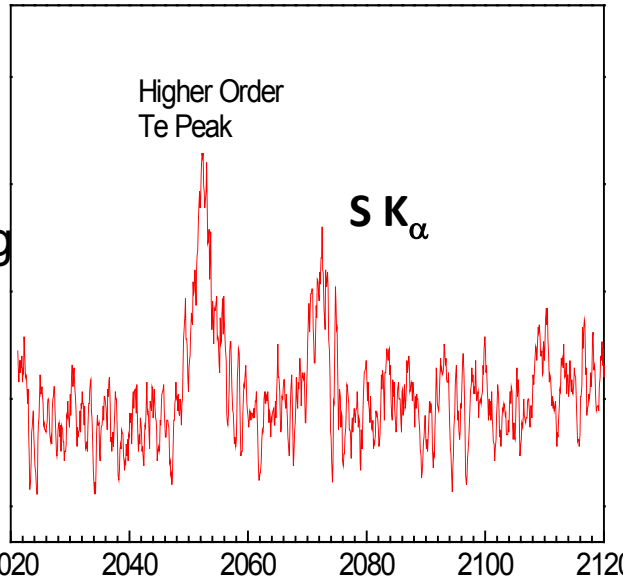
Isotropic properties of bulk-nano thermoelectrics





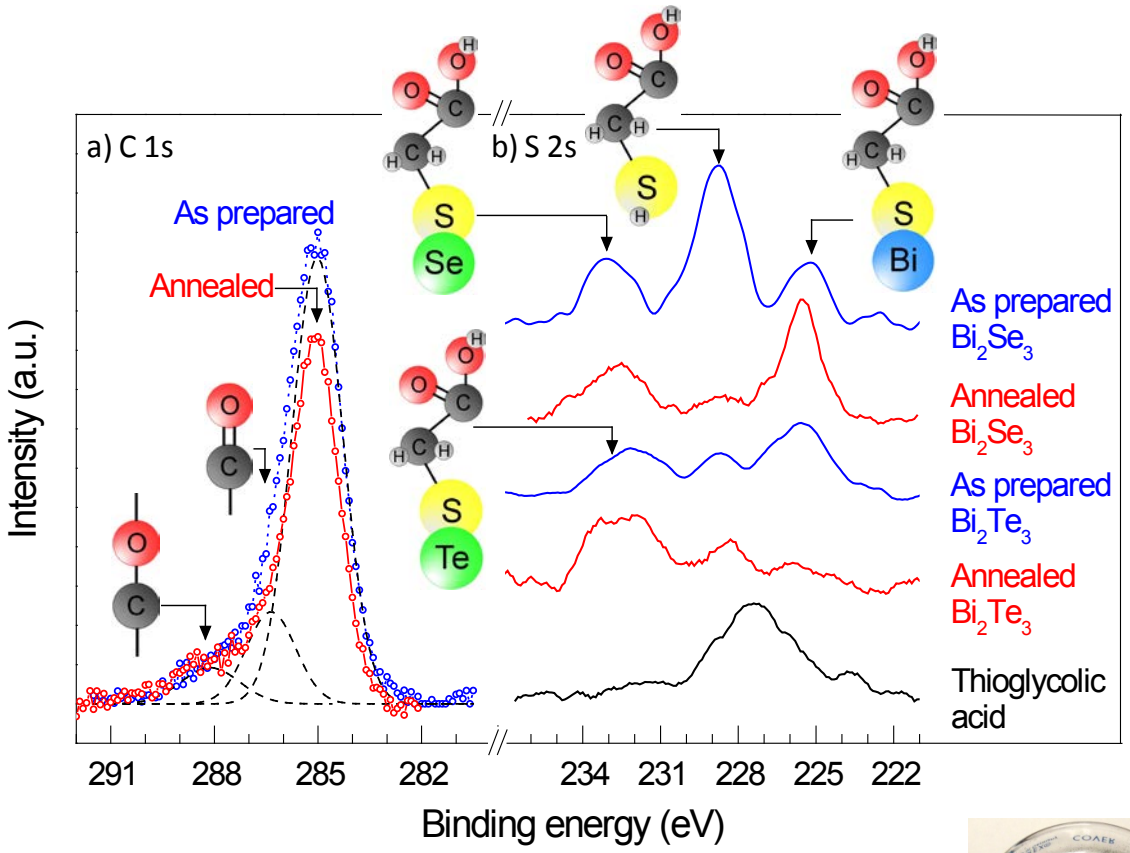


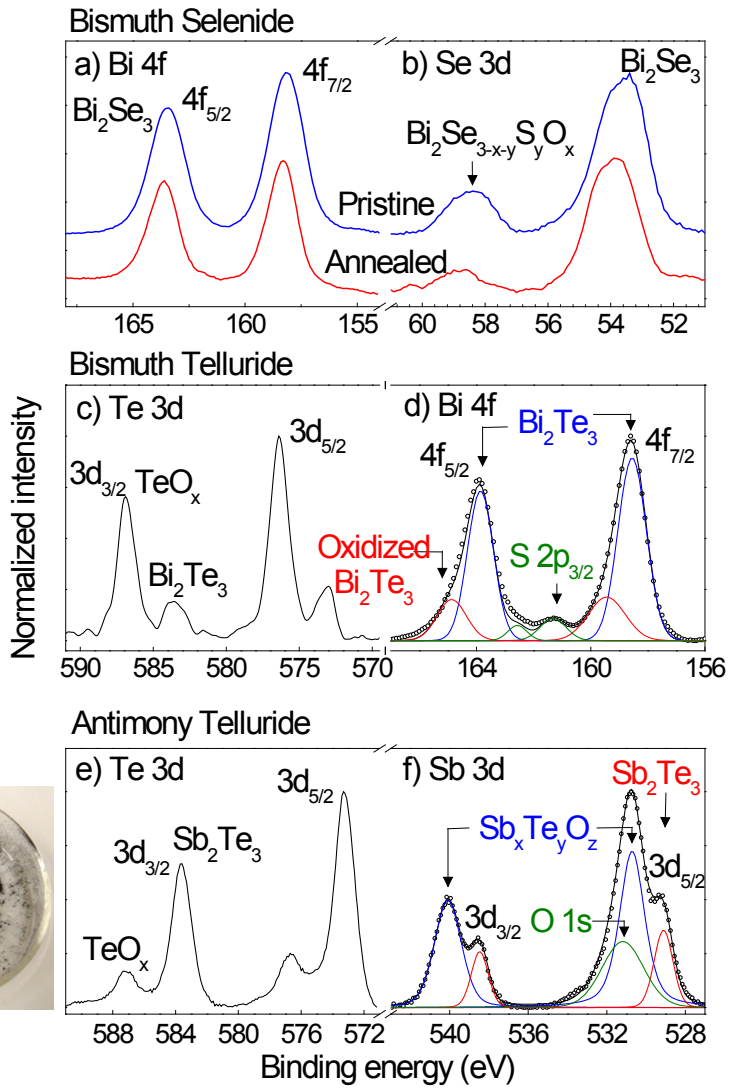
- Random texture
- Isotropic properties
- Near-stoichoimetric
- 0.01-0.25 at.% S doping

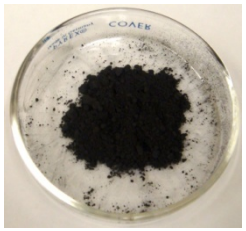


Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

Sulfur doping and oxidation resistance



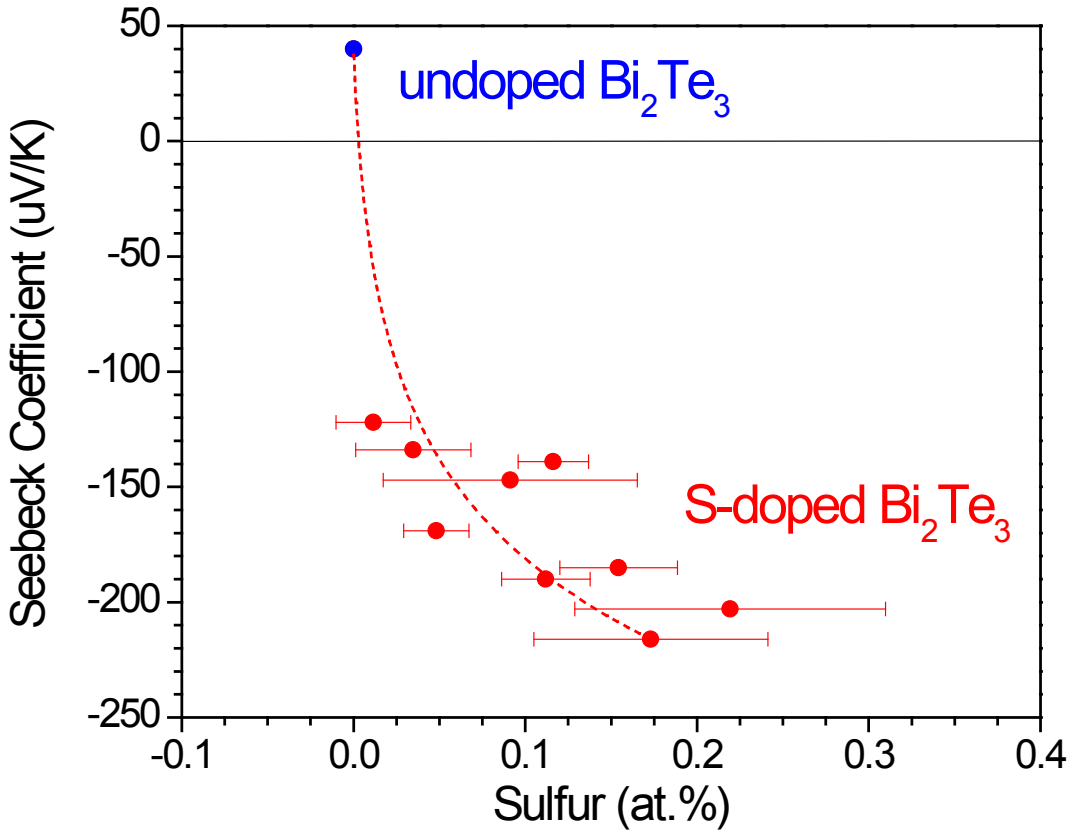




- **Sulfur is in different chemical states**
- **Surfactant capping inhibits oxidation**
  - No oxygen-free handling needed
  - Months/years storage in ambient

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

Effects of sulfur doping on power factor



- **High α, majority carrier reversal, high σ**
  - S doping, Fermi shift, DoS alteration near Fermi level
  - Non-linear dependence on carrier concentration

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

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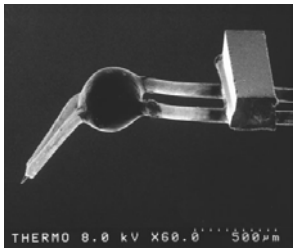
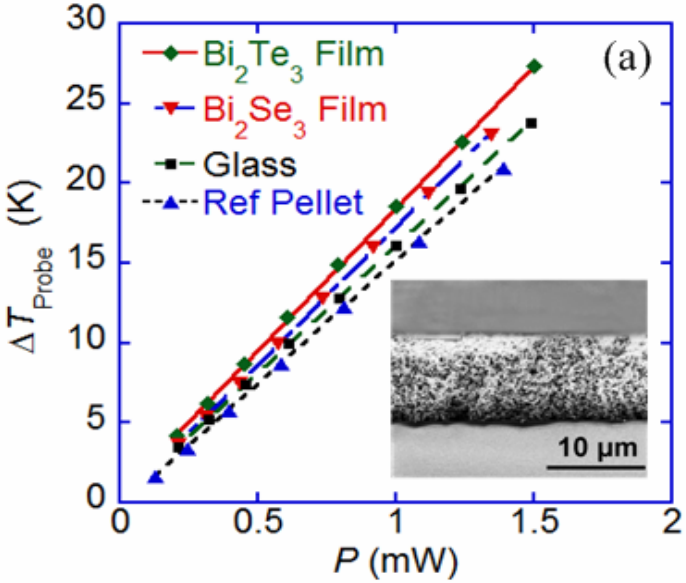
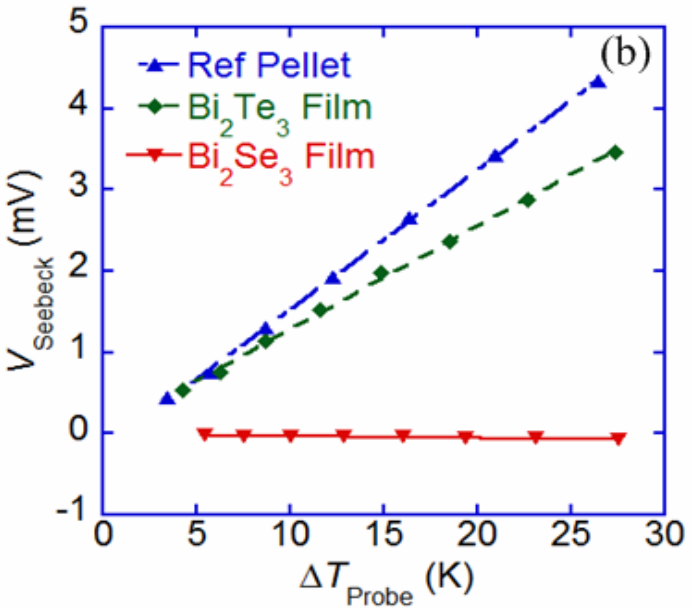
Scanning Thermoelectric μ-Probe







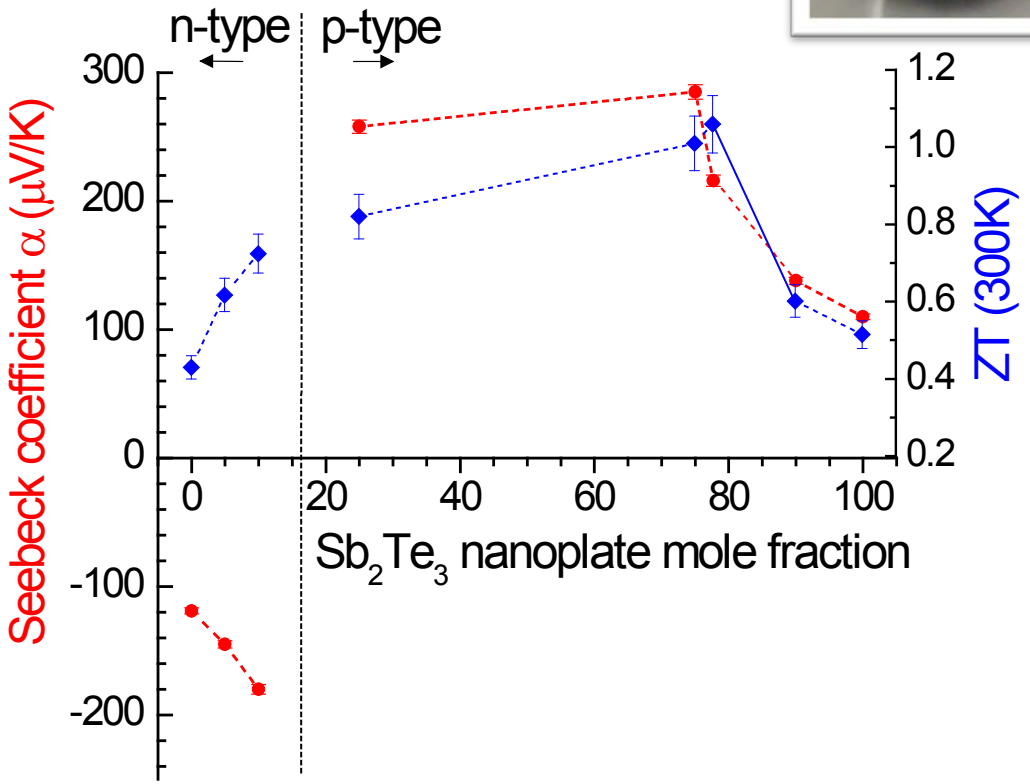
- Simultaneous κ and α on films and nanobulk
- Non-contact κ
- Validated using alternative techniques

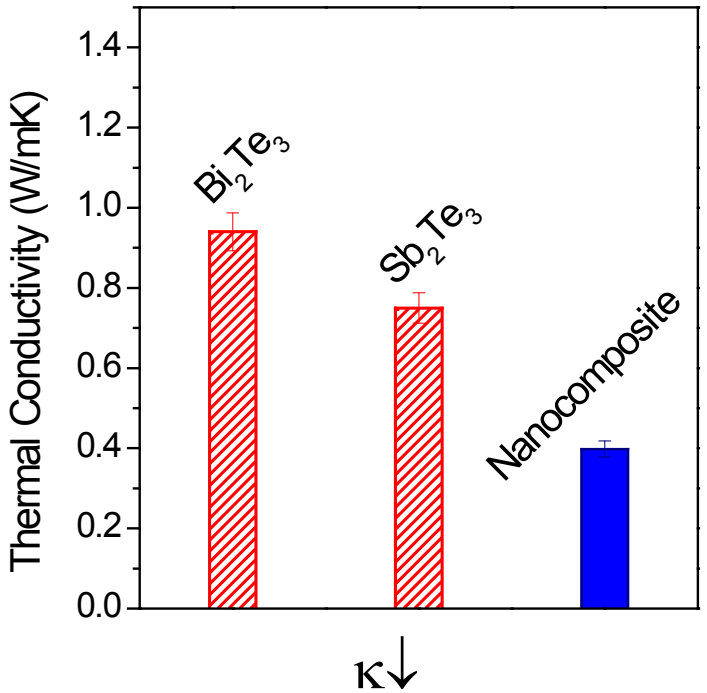
Zhang,.., Ramanath, Borca-Tasciuc, Appl. Phys. Lett. 96, 062107 (2010). Rev Sci Instrum. (2011)

Nanobulk composite alloys: α tuning, κ_L decrease, ZT increase

Bi_2Te_3 – n-type

Sb_2Te_3 – p-type



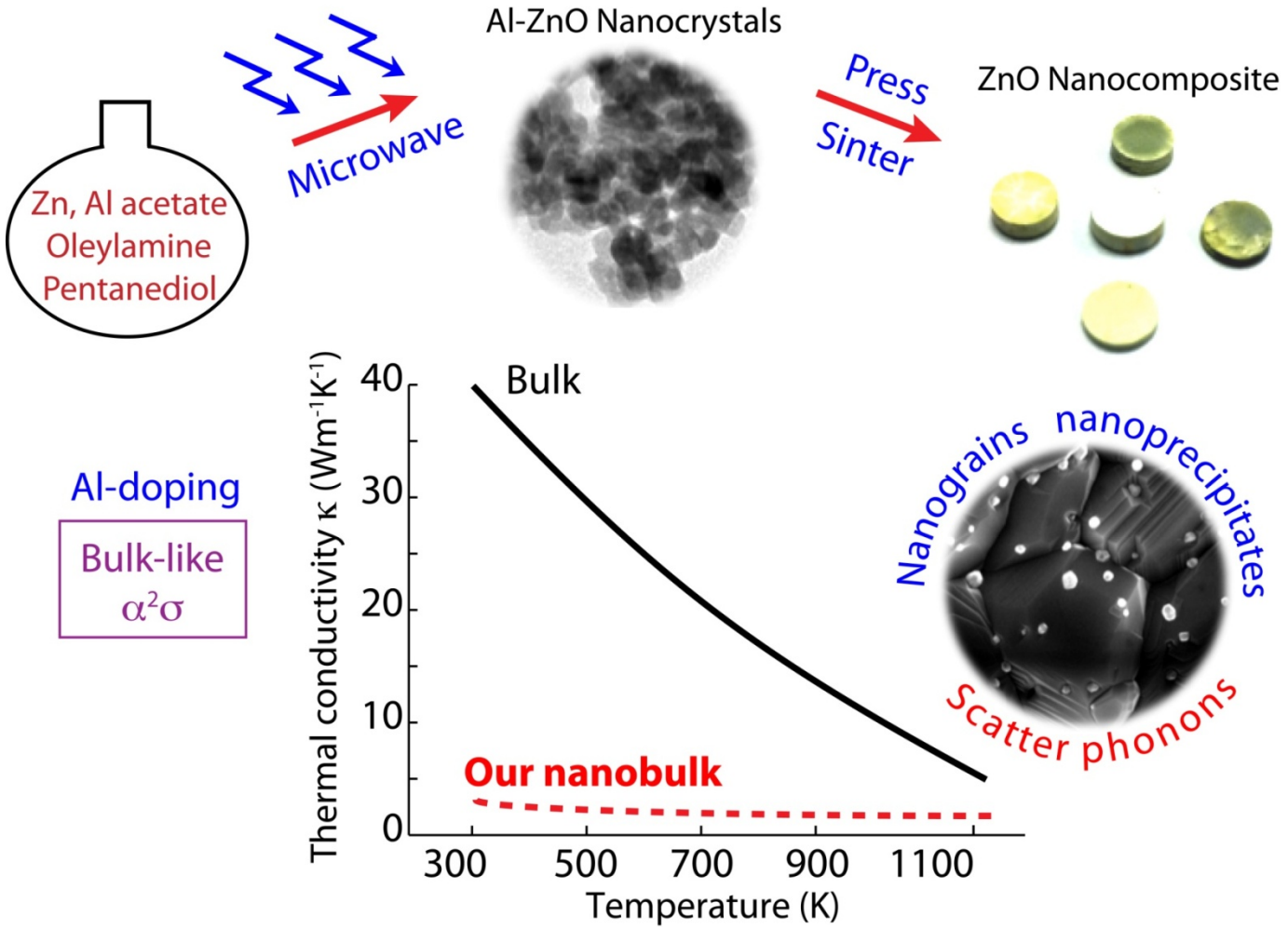


κ↓

2-Fold ↓

Mehta, …, Borca-Tasciuc, Ramanath, Nature Mater. 11, 233-240 (2012).

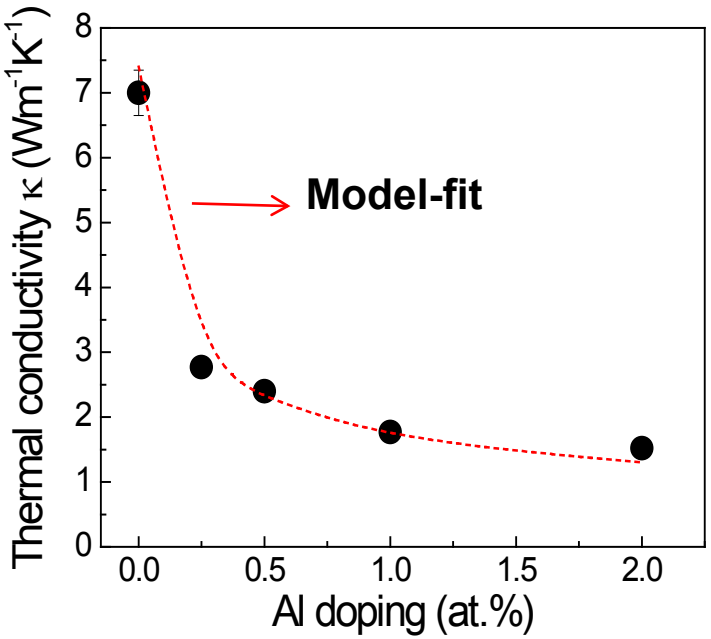
Al-doped ZnO nanocomposites for high ZT @ high T

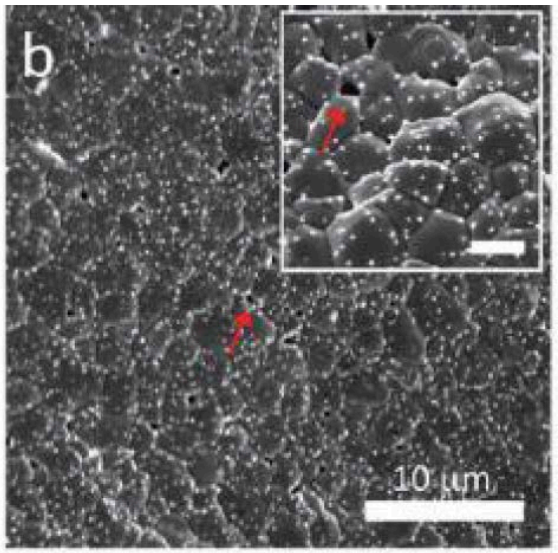


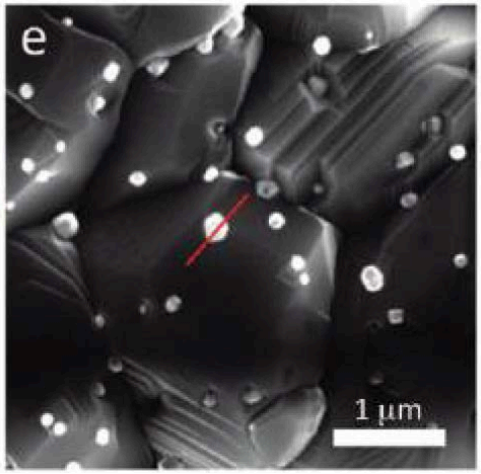
- **Doping + nanostructuring ➔ ZT=0.45 ….50% increase over bulk at 1000 K**

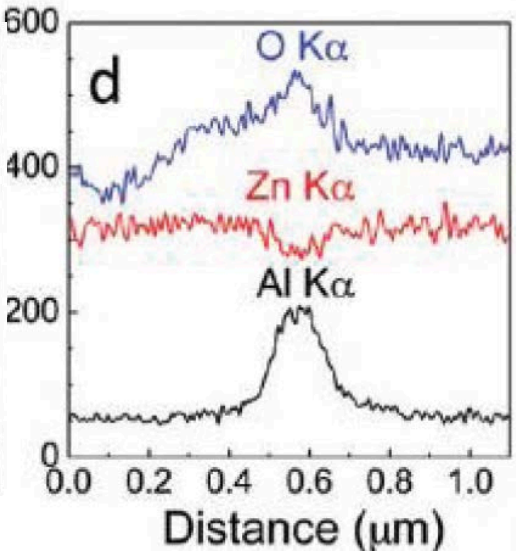
Jood, Mehta…, Dou, Borca-Tasciuc, Ramanath, Nano. Lett.11, 4337 (2011).

Ultralow thermal conductivity due to nanostructuring





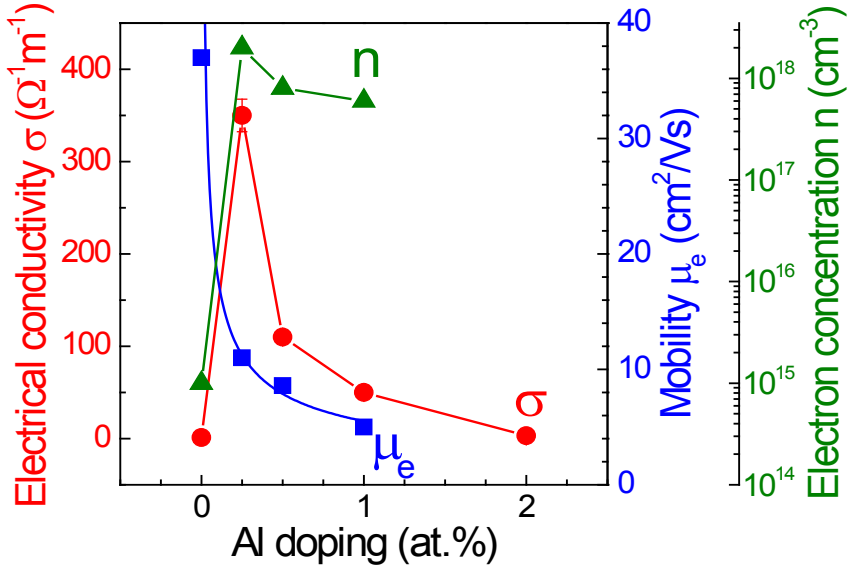


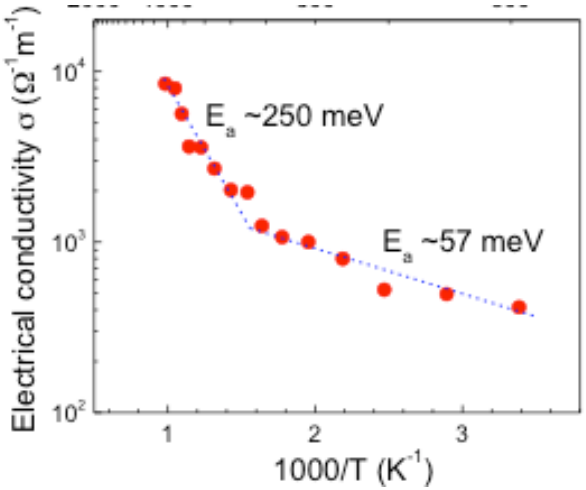


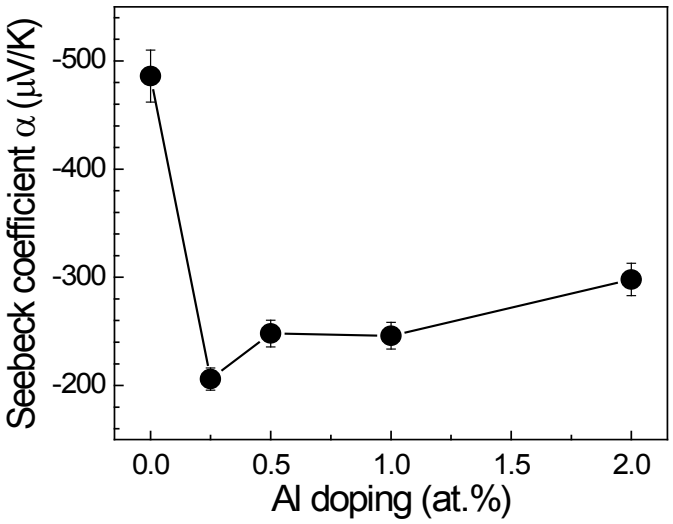
- **Nanograins, nanoprecipitates, nanopores**
  - 20-fold lower κ than bulk

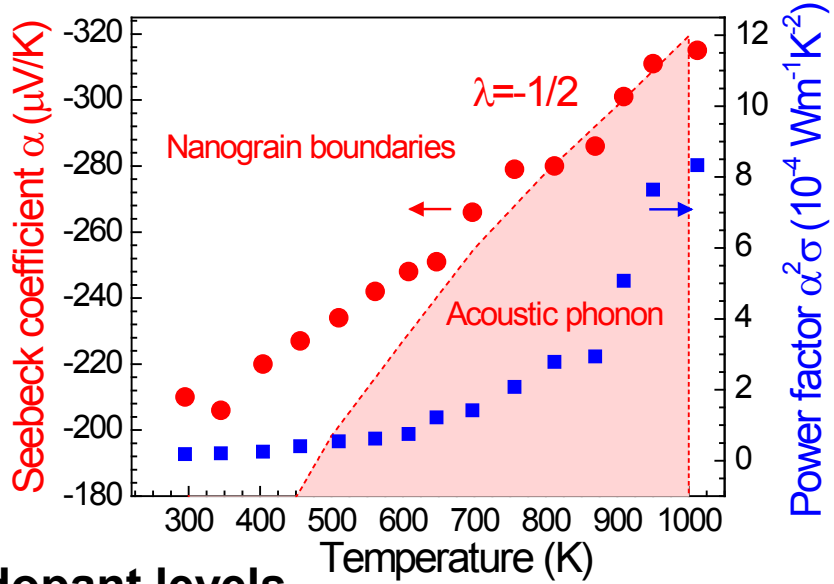
Jood, Mehta…, Dou, Ramanath, Nano. Lett.11, 4337 (2011).

Retention of high α and σ





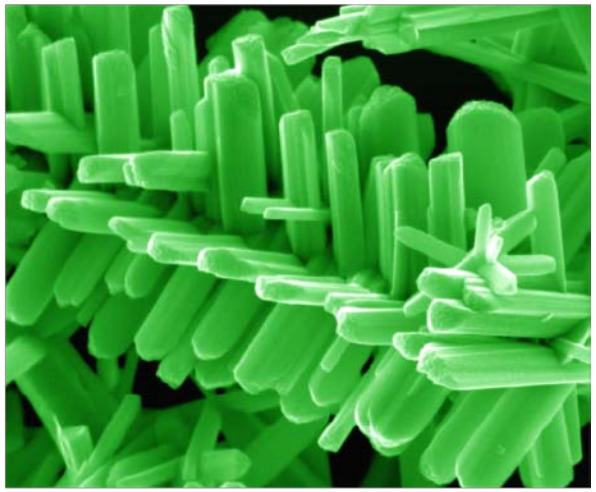


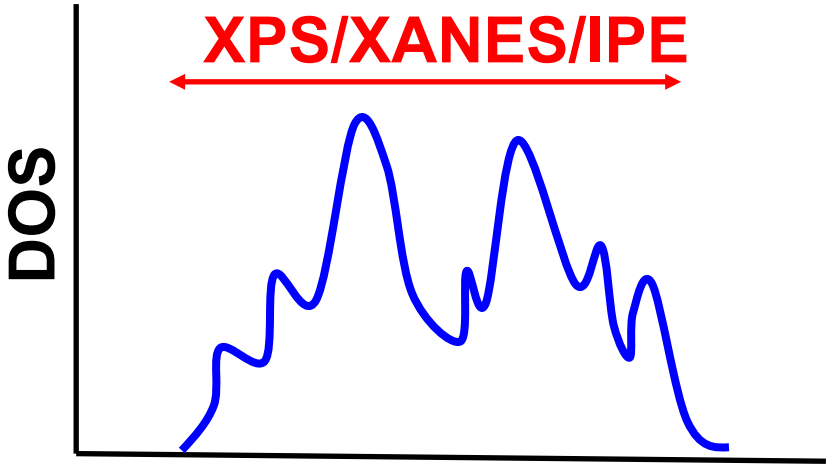


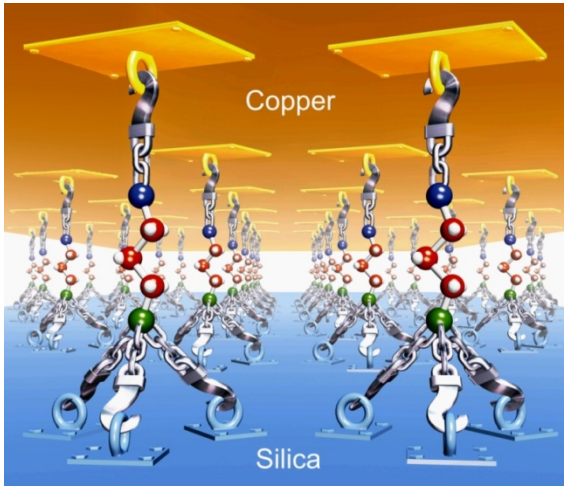
- **Shallow dopant levels**
  - Acoustic phonon scattering at high T—high σ
  - 40-95% higher α than non-nano ➔ high ZT

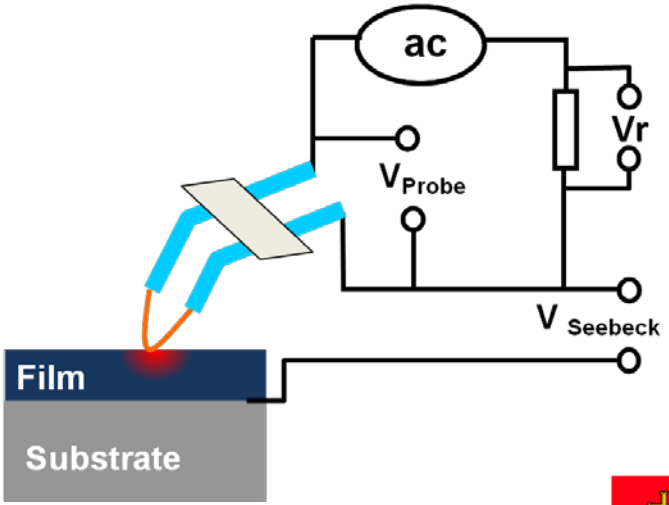
Jood, Mehta…, Dou, Borca-Tasciuc, Ramanath, Nano. Lett. 11, 4337 (2011).

Thank you !!









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