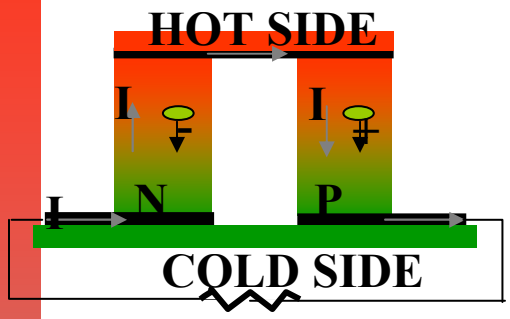
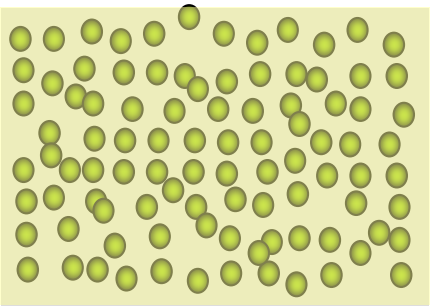
2009 Thermoelectrics Applications Workshop

September 30, 2009





Perspectives on Recent Advances in Thermoelectric Materials Research

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MIT

Perspectives on Recent Advances in Thermoelectric Materials Research

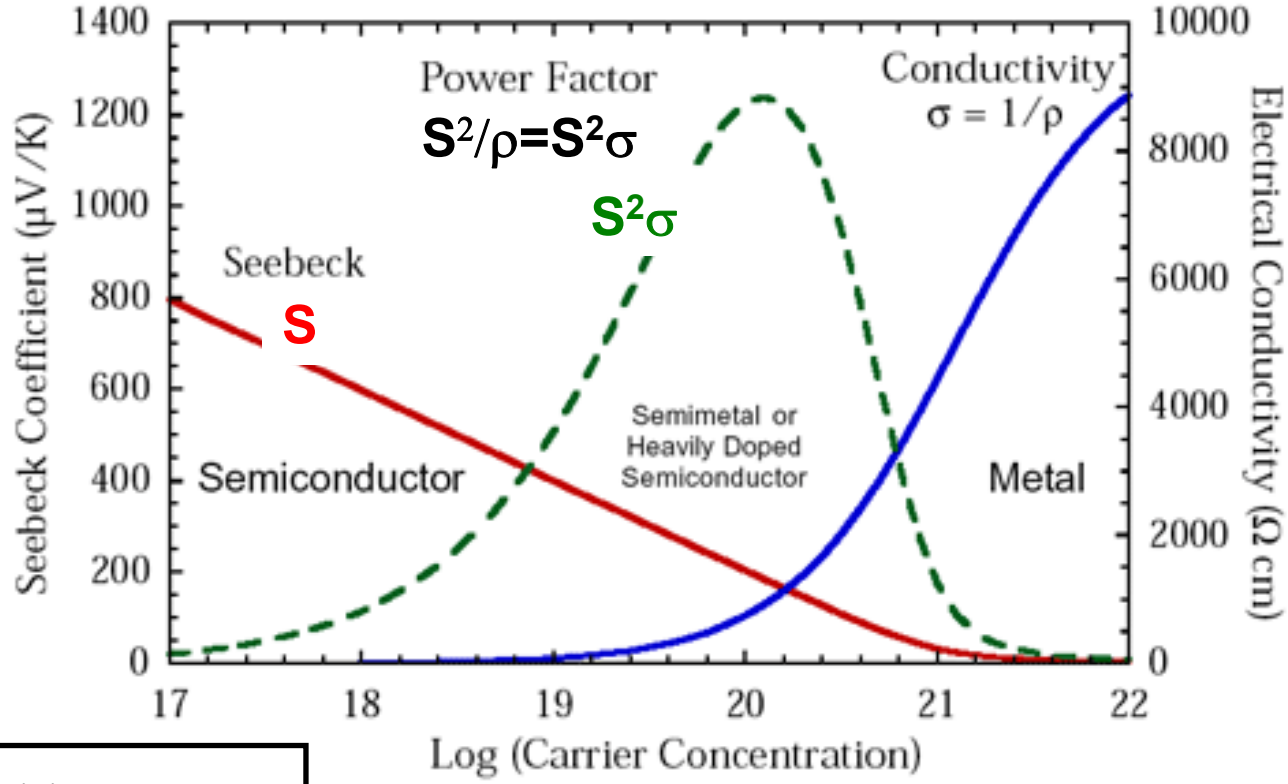
OUTLINE

- Some strategies for enhancing ZT through nanomaterials
- Some recent advances in thermoelectric materials research
- Looking to the future

Why Nanostructural materials are important for Thermoelectric Materials

- New desirable properties are available at the nanoscale but not found in conventional 3D materials, e.g., materials parameters dependent on size in the quantum limit
- Higher surface area to promote catalytic interactions
- Independent control of nanomaterials parameters which depend on each other for 3D materials.

The Thermoelectric Figure of Merit (ZT)



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

Seebeck Coefficient, Conductivity, Temperature, Thermal Conductivity

J. Snyder (2003)
http://www.its.caltech.edu/~jsnyder/thermoelectrics/science_page.htm

For almost all materials, if doping is increased, the electrical conductivity increases but the Seebeck coefficient is reduced.

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Motivation for Nanotech Thermoelectricity

(2D quantum wells, 1D nanowires, 0D quantum dots)

Seebeck Coefficient

Conductivity

Temperature

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

Thermal Conductivity

$ZT \sim 3$ for desired goal

Difficulties in increasing ZT in bulk materials:

$S \uparrow \Longleftrightarrow \sigma \downarrow$

$\sigma \uparrow \Longleftrightarrow S \downarrow$ and $\kappa \uparrow$

$\Rightarrow$ A limit to Z is rapidly obtained in conventional materials

$\Rightarrow$ So far, best bulk material ($Bi_{0.5}Sb_{1.5}Te_3$) has $ZT \sim 1$ at 300 K

Low dimensional physics gives additional control:

- Enhanced density of states due to quantum confinement effects
  - $\Rightarrow$ Increase S without reducing σ
- Boundary scattering at interfaces can reduce κ more than σ
- Possibility of materials engineering to further improve ZT

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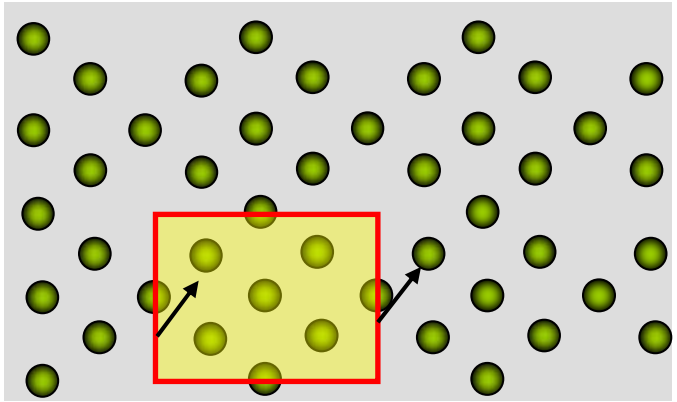
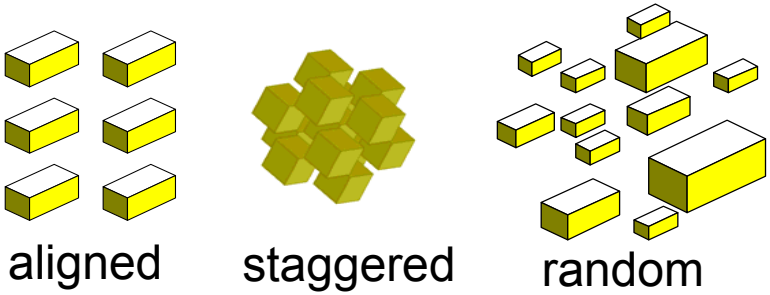
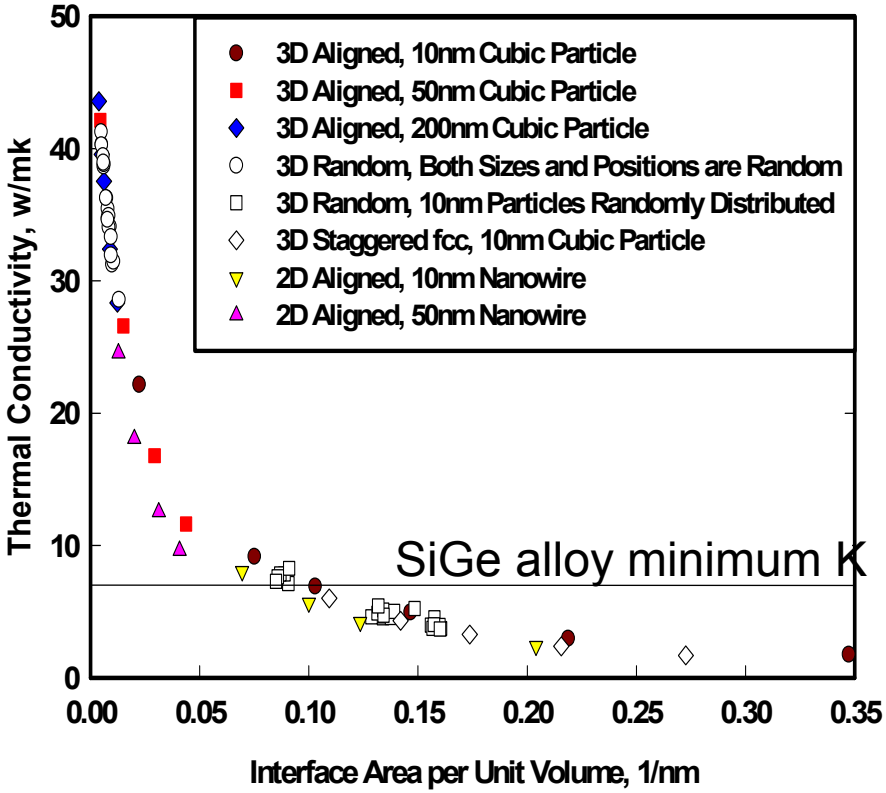
Lowering the Thermal Conductivity by introducing interfaces







(Interface Density)

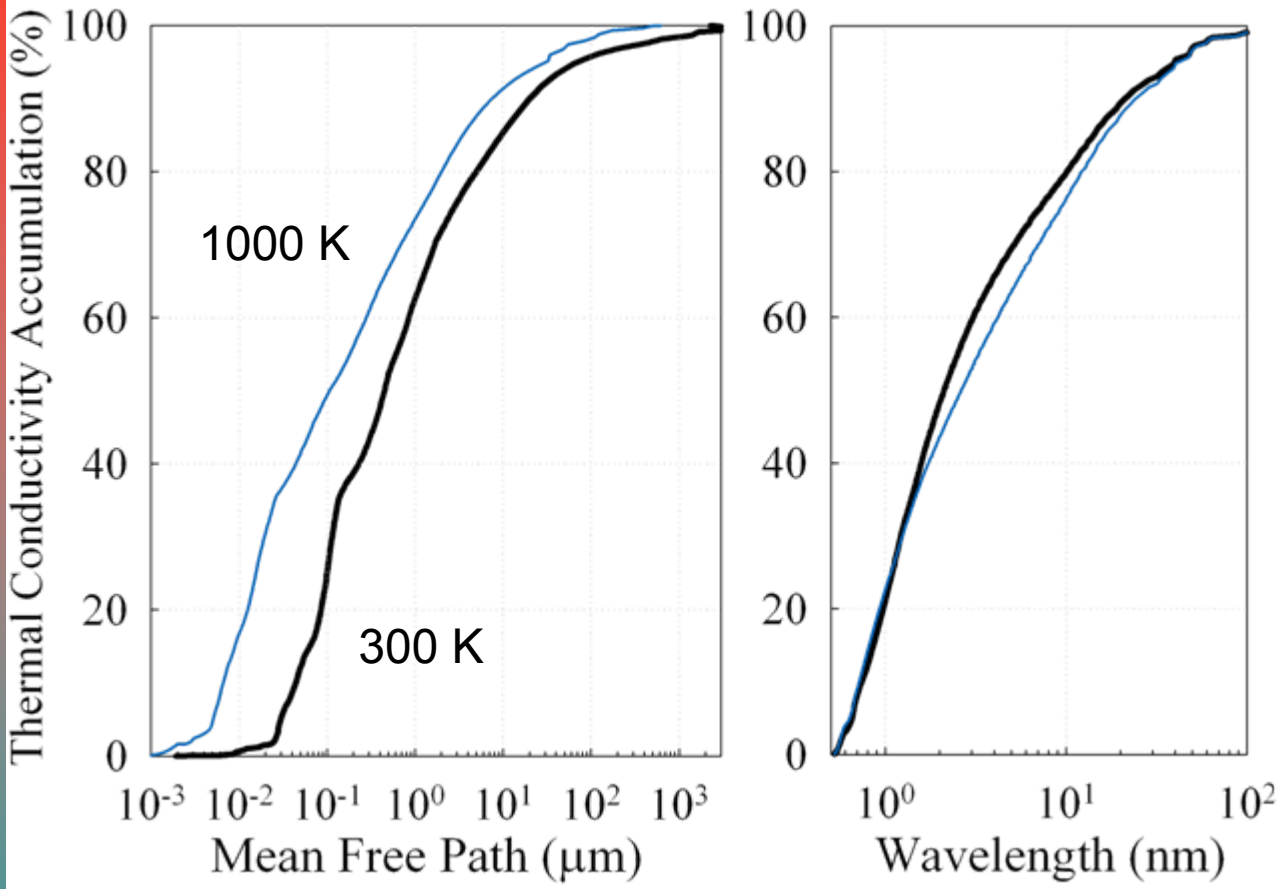
Phonon Mean Free Path (Λ) as Input Parameters to Simulation
Si: Λ=312 nm, Ge: Λ=174 nm at 300 K

Work of Ronggui Yang, MIT Thesis
R. Yang, G. Chen and M. Dresselhaus, PRB **72**, 125418 (2005)

MIT

Modeling

Phonon Mean Free Path in Silicon



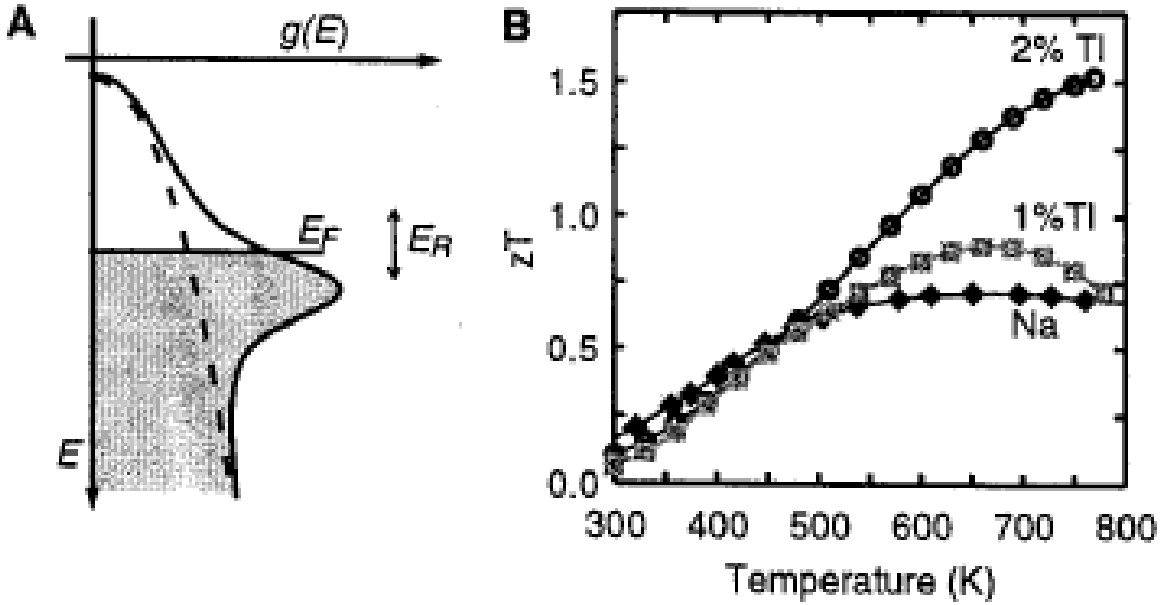
- Phonon mean free path (MFP) spans multiple orders of magnitude
- 80% of the κ at room temperature comes from phonons that travel less than 10 μm
- 40% of the κ at room temperature comes from phonons with MFP<100 nm

This analysis suggests that we need to aim at introducing interfaces to limit the phonon MFP to < 10nm for thermoelectric applications

A. Henry and G. Chen, Journal of Computational and Theoretical Nanosciences, **5**, 141 (2007)

MIT

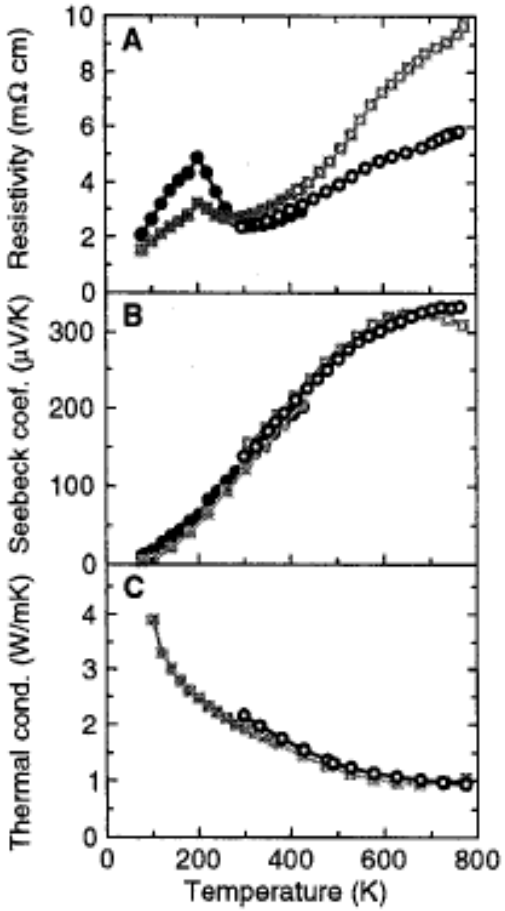
Enhancement of ZT for bulk PbTe by p-type Thallium doping



J.P. Heremans et al., Science 321, 554 (2008)

- Large increase in ZT for bulk PbTe is achieved.
- Thallium doping distorts the electron density of states and increases the hole effective mass

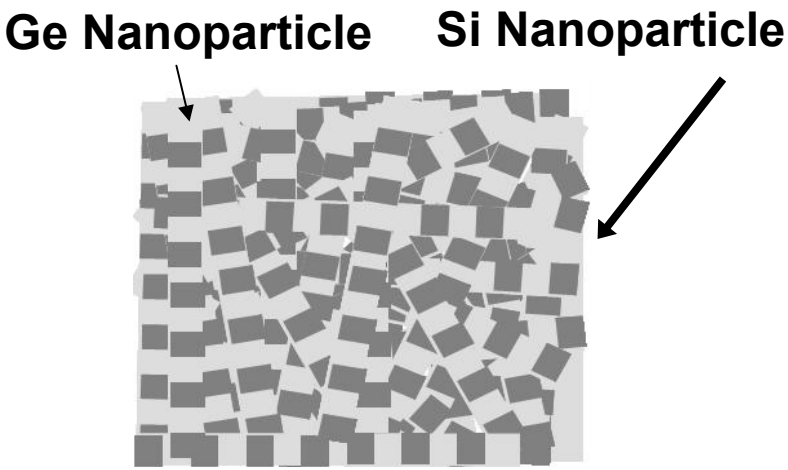
Temperature Dependence of Thermoelectric Parameters

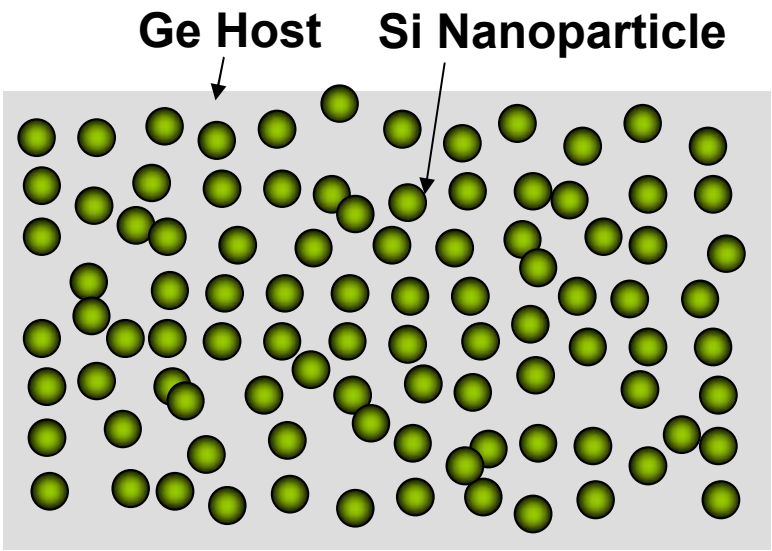


- Increase of Thallium concentration increases carrier conductivity
- The new principle should be applicable to other systems and should be suitable for large scale applications
- Nanostructuring should increase ZT further

J.P. Heremans et al., Science 321, 554 (2008)

Nanoparticle Composite Synthesis to make bulk size samples





- **Nanocomposites**

(1) Cold / Hot Pressing
(2) Induction Heating

- **Nanoparticle composites**

(1) Si nanoparticles in a Ge host
(2) Study core-shell structures

<u>Expectations:</u>

- Reduced thermal conductivity.
- Electrical conductivity comparable to or better than bulk.
- Increased thermoelectric figure of merit.
- Cheap, self-assembly method, and applicable to other materials systems
- Allows easy scale up; M.S. Dresselhaus et al. Adv. Mater. **19**, 1043 (2007)

MIT

Fabricating Nanocomposites

Large scale synthesis of Si, Ge, $Si_{1-x}Ge_x$ nanoparticles

Compaction into dense bulk nanocomposites

Optimization – particle size distribution, processing conditions, and composition

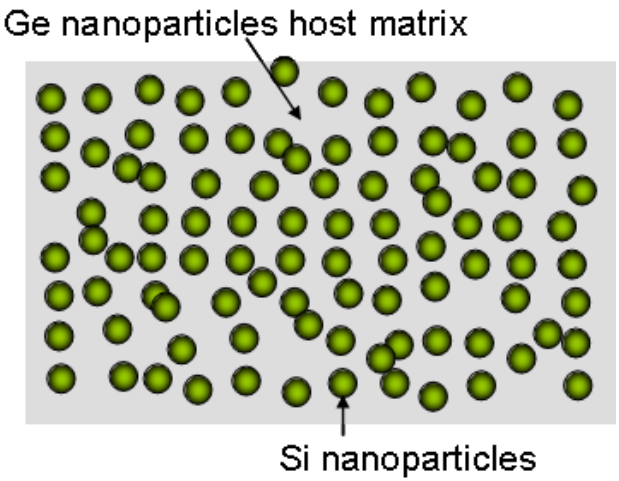
Nanostructure Characterization

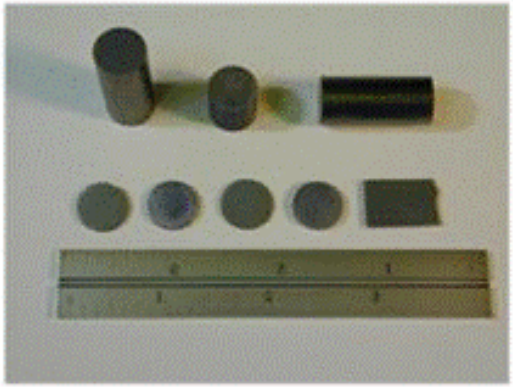
Electron and phonon modeling

TE properties and nanostructure measurement

Experimental validation of ZT values

Stability of TE properties and nanocomposites at high temp





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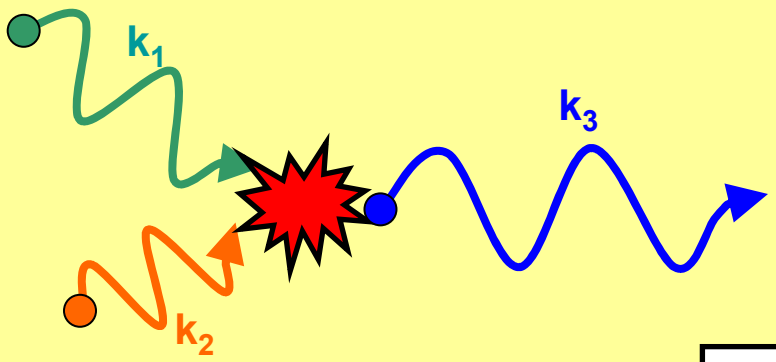
Nano Particle Size Characterization

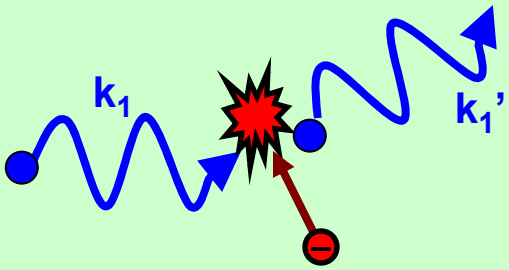
- Dynamic light scattering **(DLS)**
  - Particle/agglomerate size
- Transmission electron microscope **(TEM)**
  - Crystal structure and particle size
  - Limited sampling
- X-ray diffraction **(XRD)**
  - Average particle / crystallite size, phase and purity, lattice strain
- Brunauer – Emmett - Teller **(BET) analysis**
  - Gas absorption technique, to determine surface area and particle/agglomerate size

Phonon Scattering Modeling

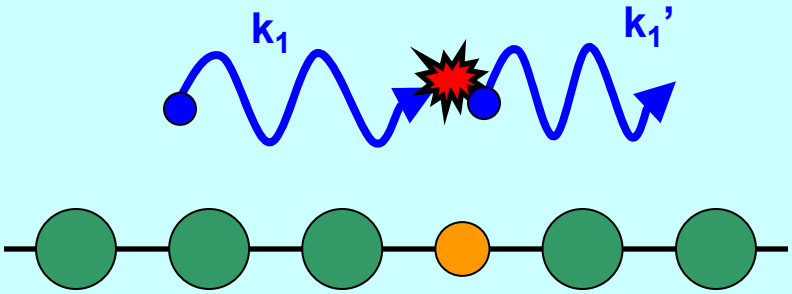
3 Phonon Scattering



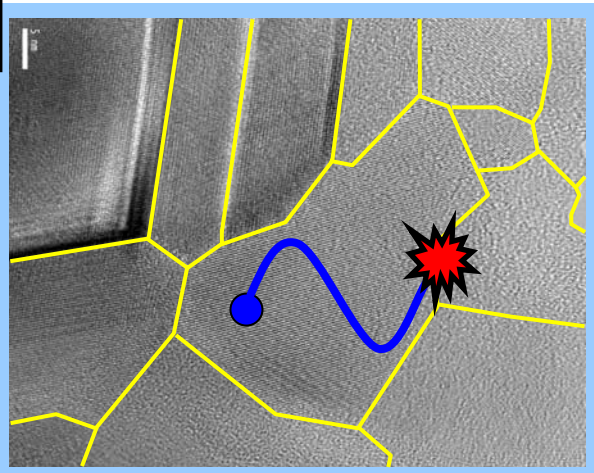
Phonon-electron Scattering



$$\kappa = \frac{1}{3} C v \Lambda$$



Alloy (Point Defect) Scattering



Boundary Scattering

Nanostructuring enhances boundary scattering at grains of different sizes

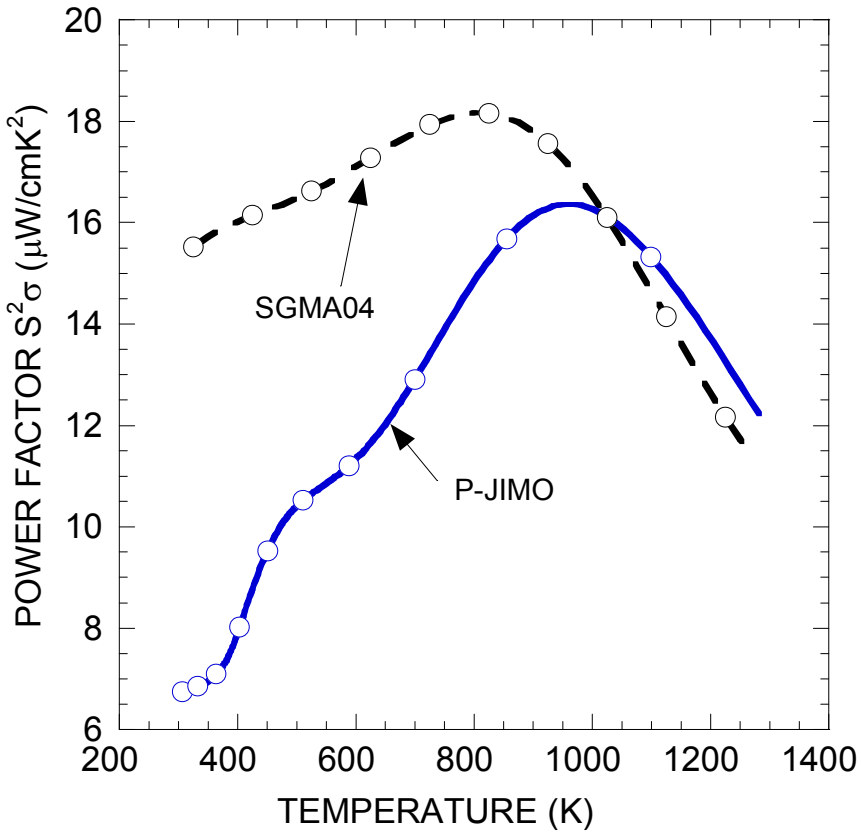
Perspectives on Recent Advances in Thermoelectric Materials Research

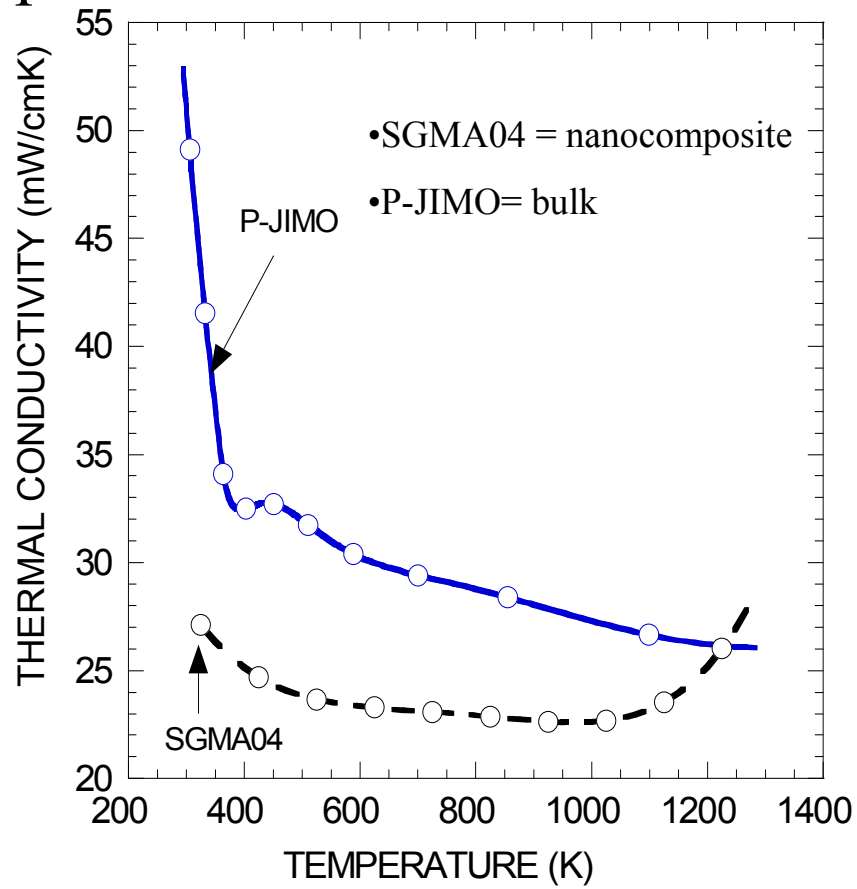
OUTLINE

- Some strategies for enhancing ZT through nanomaterials
- Some recent advances in thermoelectric materials research
- Looking to the future

Experimental Thermoelectric Results

Comparing bulk and nanocomposites of SiGe



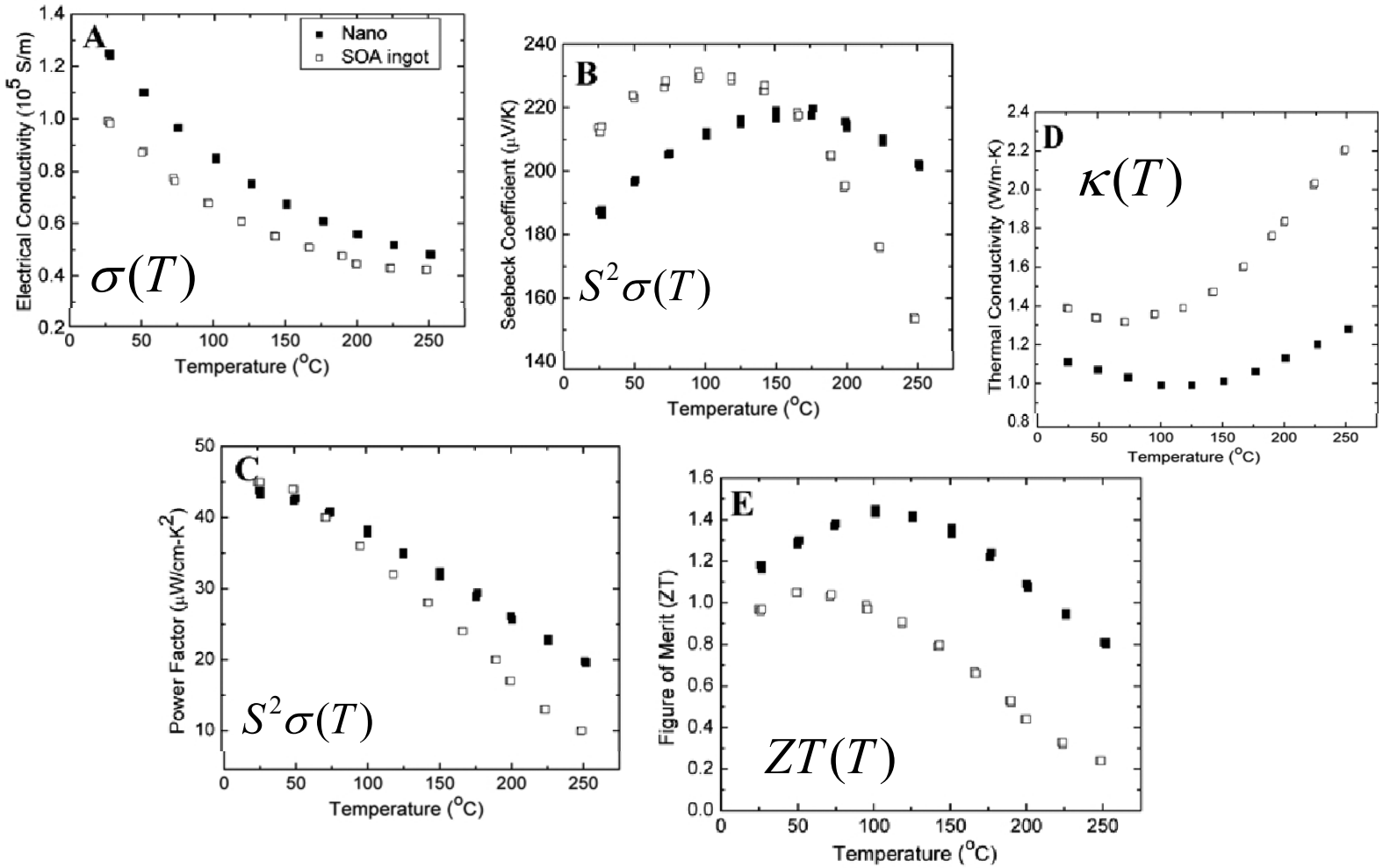


There are large ranges of temperature where the power factor can increase and the thermal conductivity can decrease at the same time. This does not occur in bulk systems.

MIT

Collaboration with Gang Chen , Zhifeng Ren and Jean-Pierre Fleurial

Temperature dependence of Thermoelectric Parameters of a Nanocomposite Bulk $Bi_xSb_{2-x}Te_3$ Alloy Sample Compared to a state-of-the-art bulk ingot

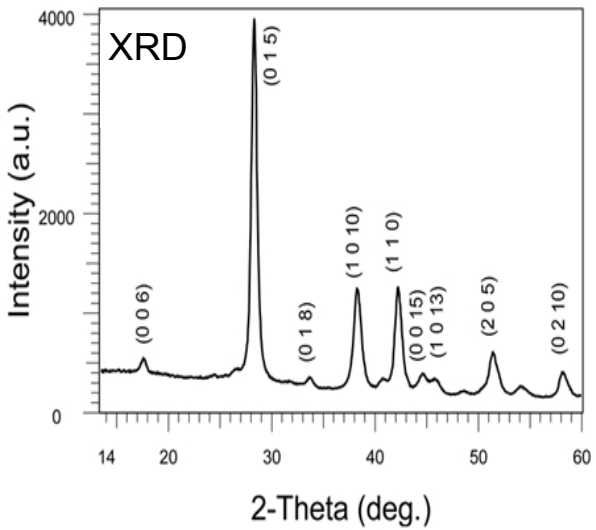


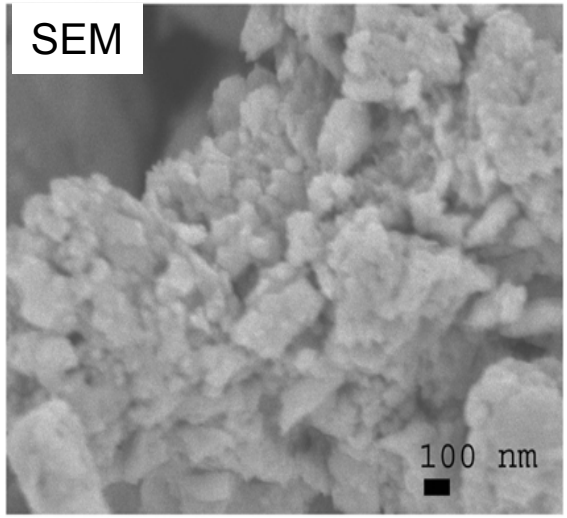
Poudel et al, *Science* **320**, 634 (2008)

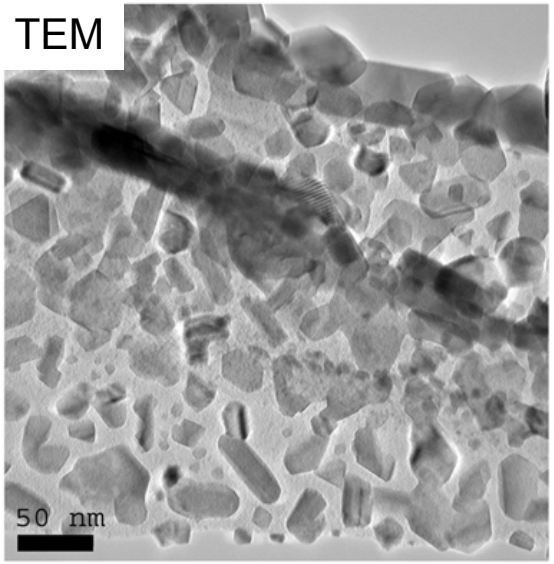
- A 40% increase in ZT relative to the state-of-the-art bulk ingot is achieved

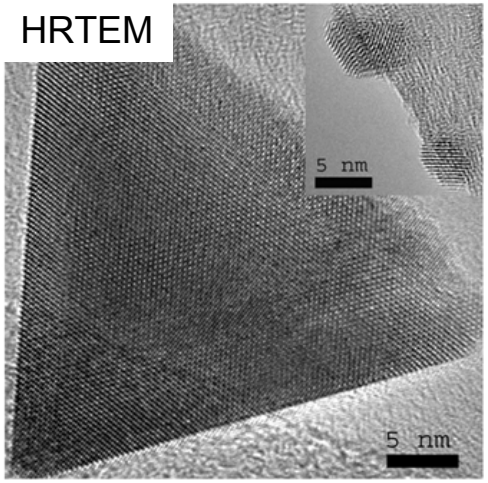
MIT

Characterization of an as-ball-milled $Bi_xSb_{2-x}Te_3$ Alloy Nanopowder









- Nanostructures can scatter phonons preferentially over electrons while also increasing the power factor $S^2\sigma$
- This behavior does not occur in 3D materials
- Nanoparticles of varying sizes and shapes are desirable

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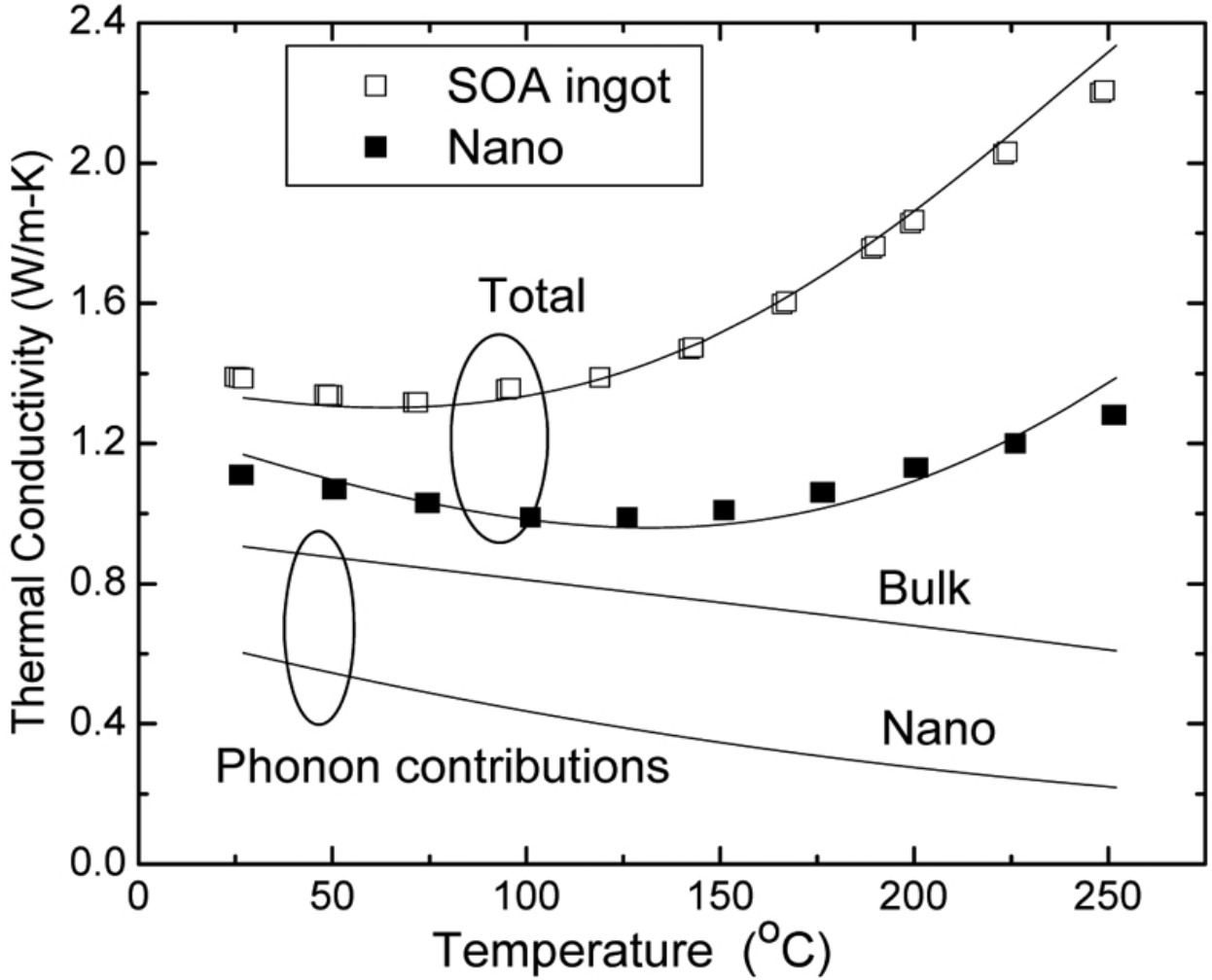
Thermal conductivity of $Bi_xSb_{2-x}Te_3$ Nanocomposite bulk alloy compared to State-of-the-Art Ingot



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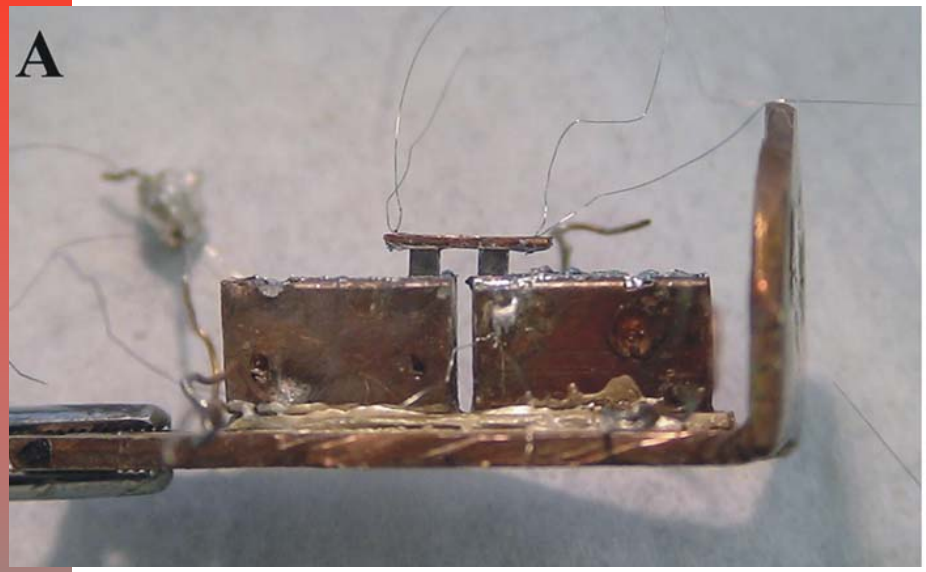
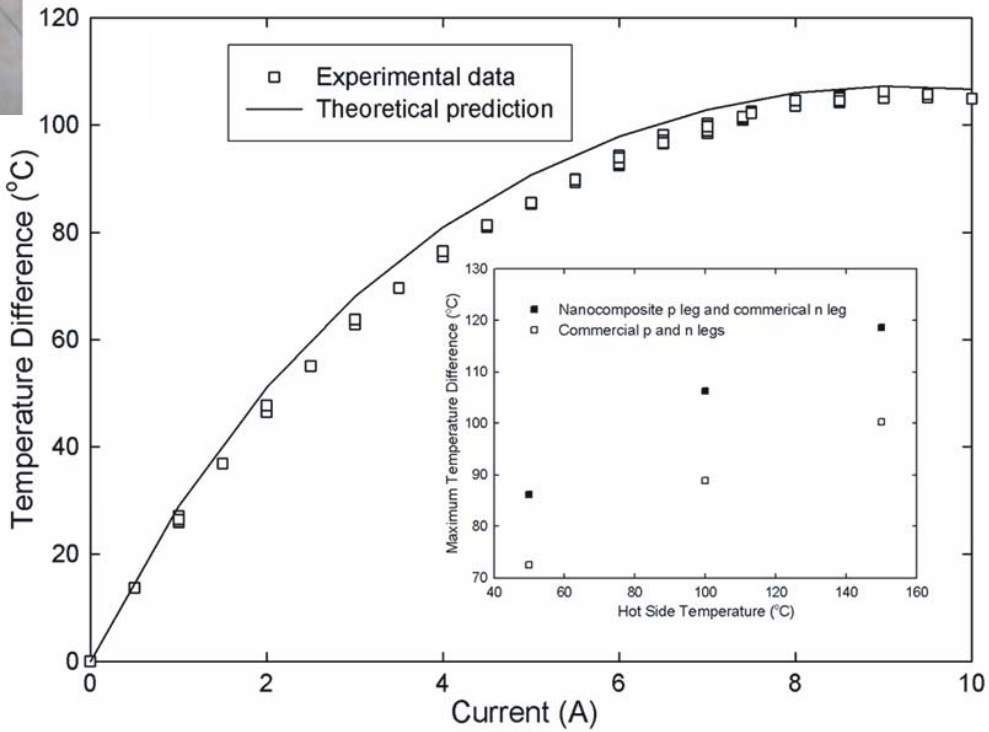
Cooling Test of Thermoelectric Device



- Laboratory tests of the thermoelectric device follow theory predictions
- The next challenge is commercialization of the device/concept



- Cooling Test results (comparison of experiment and theory) are for the hot side fixed at 100°C
- Inset is a comparison to a state-of-the-art bulk ingot

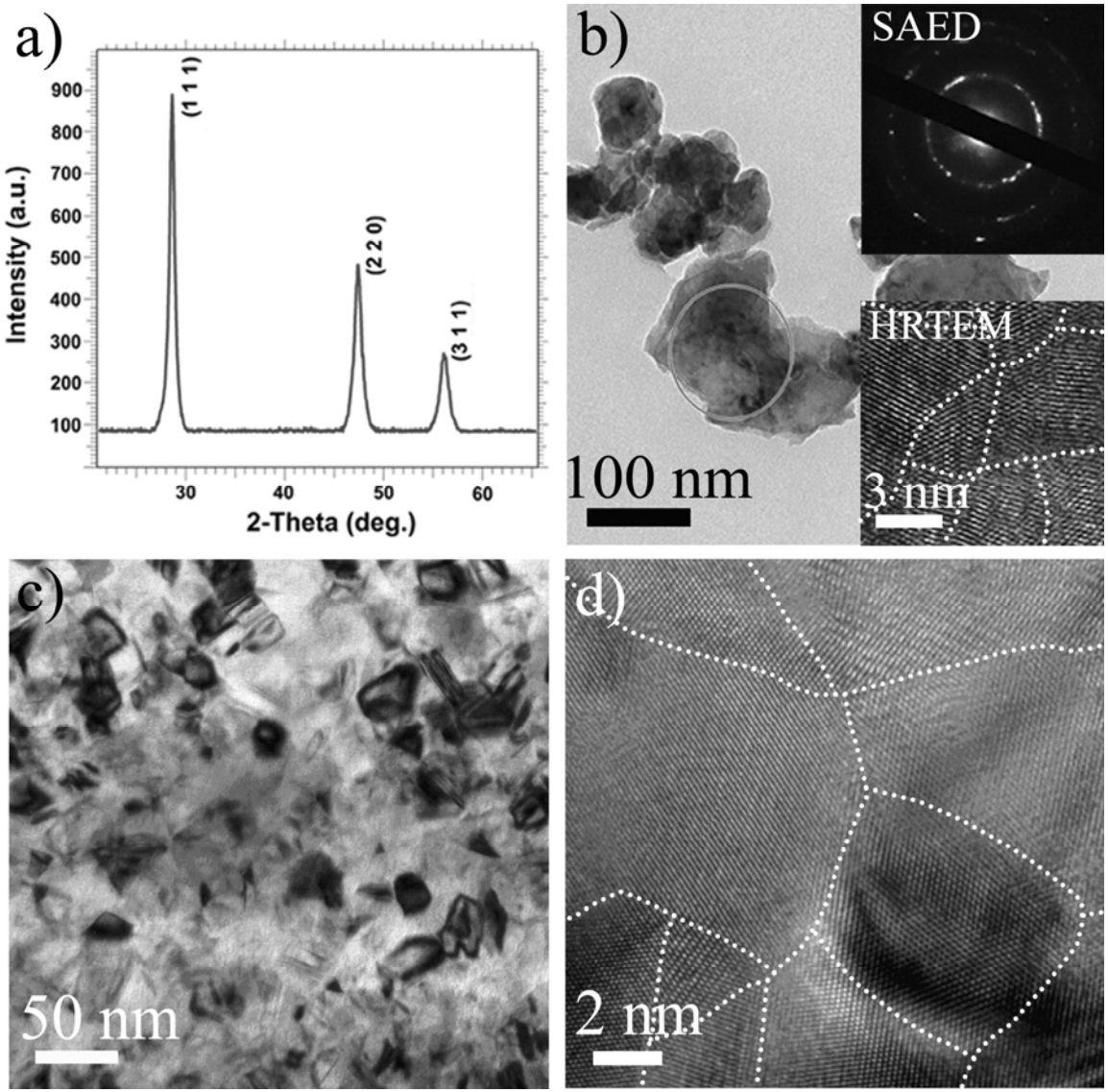
Poudel et al., *Science* **320**, 634 (2008)

MIT

The nanocomposite approach is applicable to many materials systems

Skutteridtes Yb_xCoSb_3	
$Si_{0.95}Ge_{0.05}$	ZT=0.95
p-type SiGe	ZT=0.95
n-type SiGe	ZT=1.3
p-type Bi_2Te_3	ZT=1.4
p-type Bi_2Te_3 chunks	ZT=1.3

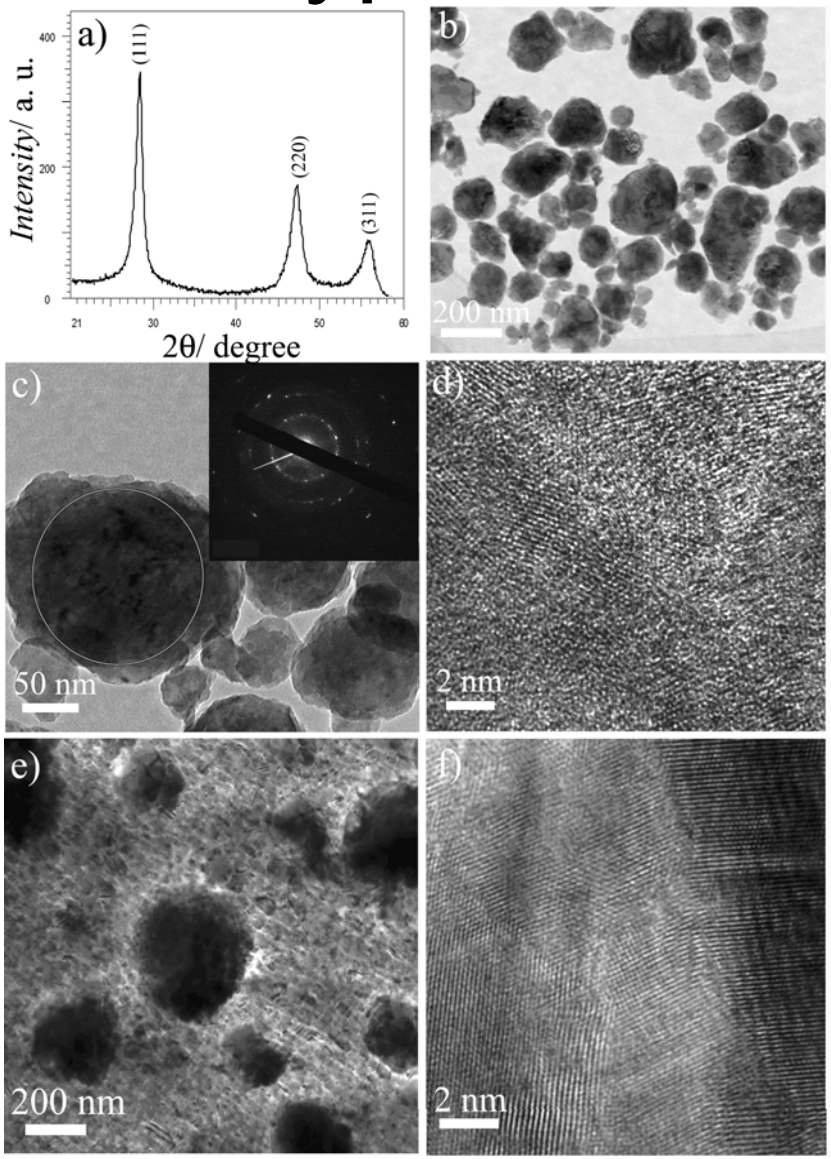
$Si_{0.95}Ge_{0.05}$



ZT=0.95

G. H. Zhu, H. Lee, Y. C. Lan, X. W. Wang, G. Joshi, D. Z. Wang, J. Yang, D. Vashaee, H. Guilbert, A. Pillitteri, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Phys. Rev. Lett.* **2009**, 102, 196803

P-Type SiGe



ZT=0.95

G. Joshi, H. Lee, Y. C. Lan, X. W. Wang, G. H. Zhu, D. Z. Wang, R. W. Gould, D. C. Cuff, M. Y. Tang, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Nano Lett.* **2008**, 8, 4670–4674.

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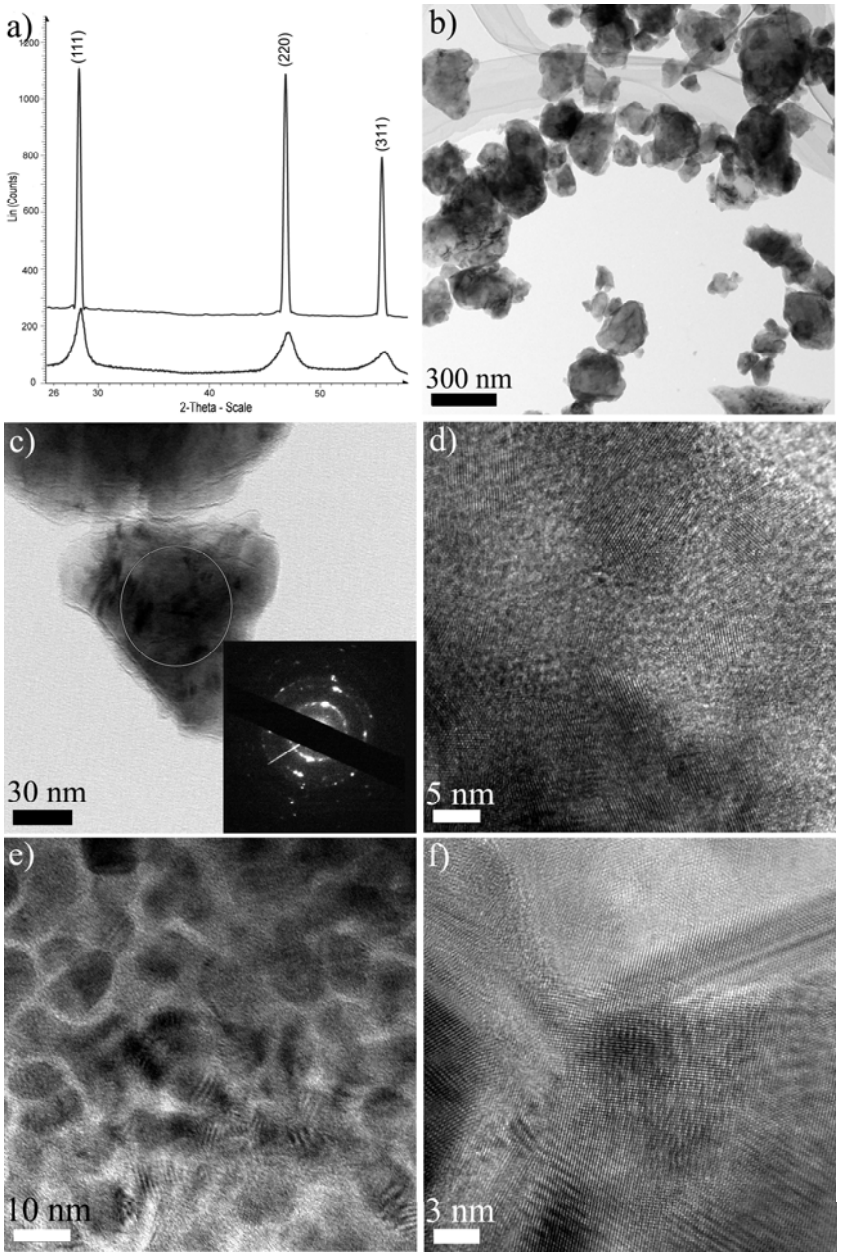
N-Type SiGe



ZT=1.3

X. W. Wang, H. Lee, Y. C. Lan, G. H. Zhu, G. Joshi, D. Z. Wang, J. Yang, A. J. Muto, M. Y. Tang, J. Klatsky, S. Song, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Appl. Phys. Lett.* **2008**, 93, 193121-1–193121-3.

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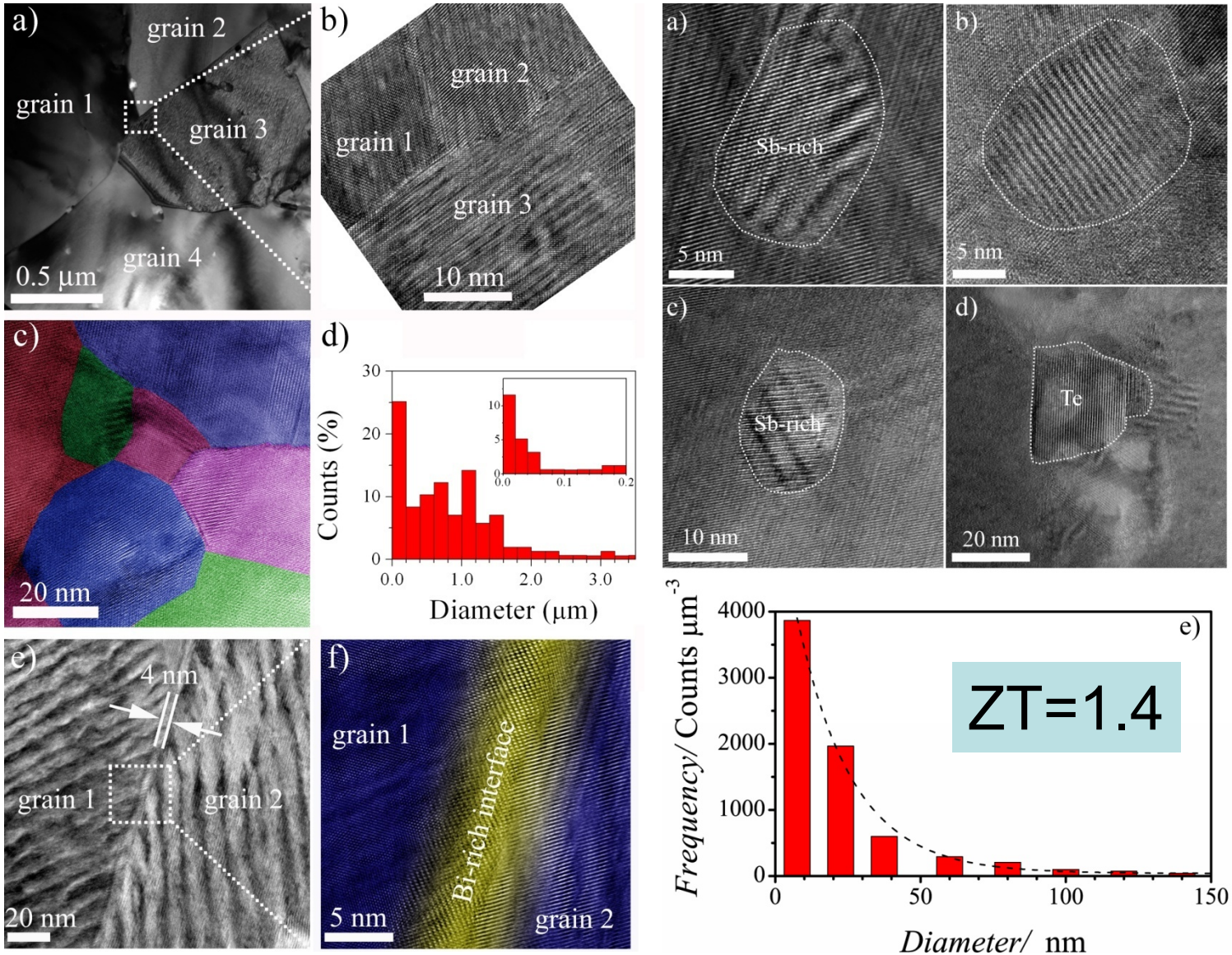
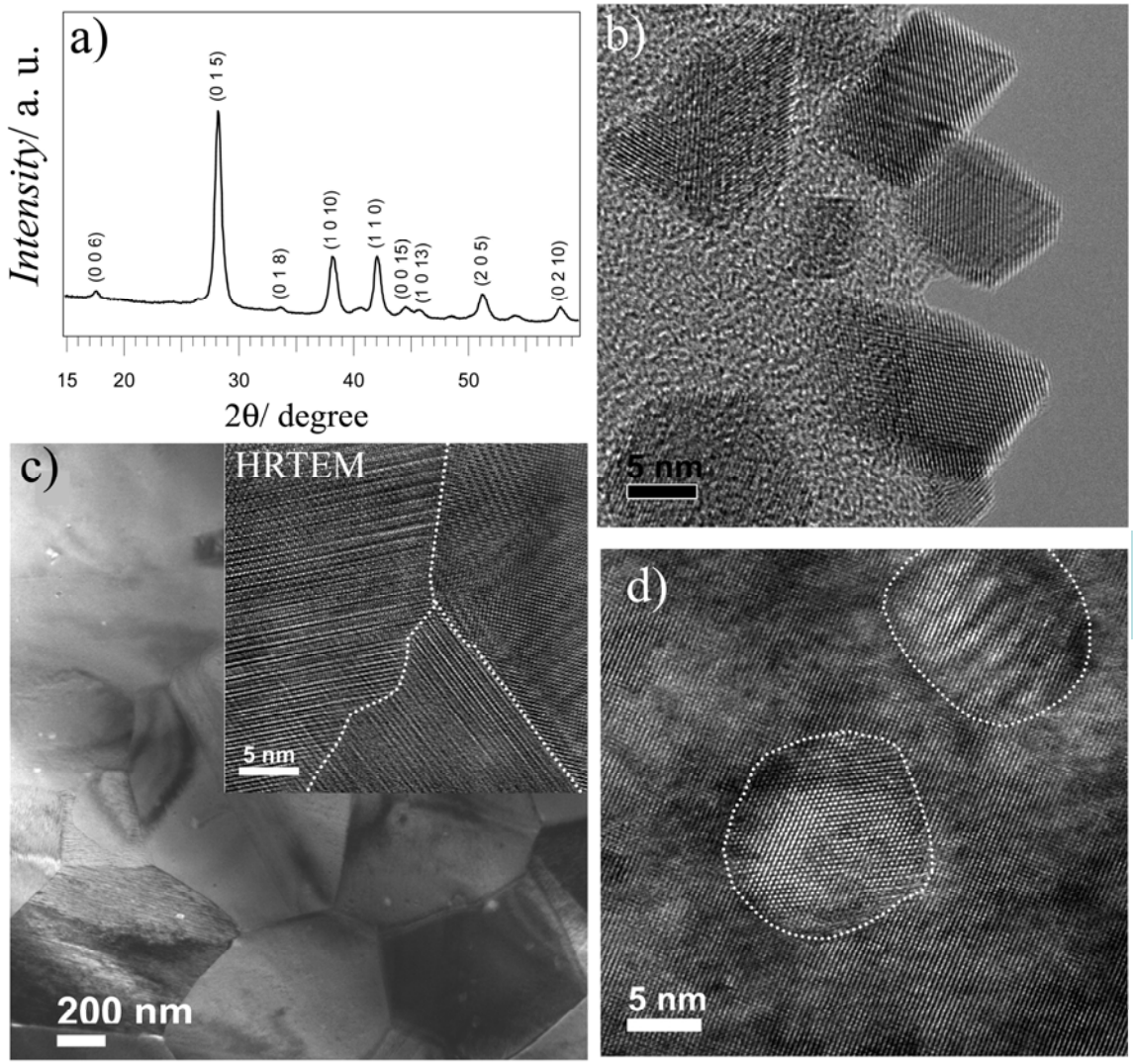
P-Type Bi_2Te_3



Y. C. Lan, B. Poudel, Y. Ma, D. Z. Wang, M. S. Dresselhaus, G. Chen, Z. F. Ren, *Nano Lett.* **2009**, 9, 1419–1422.

MIT

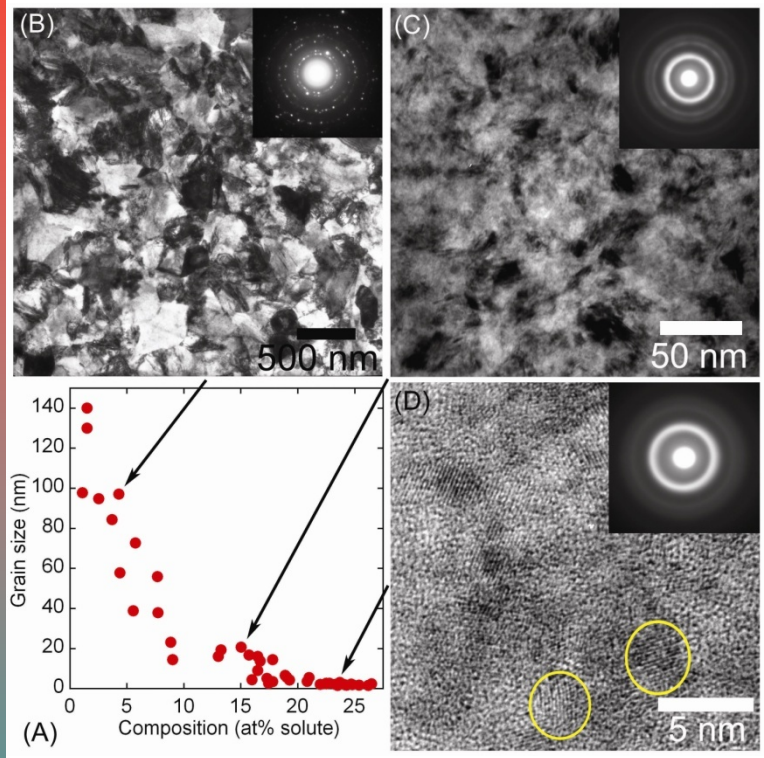
P-Type Bi_2Te_3 Chunks



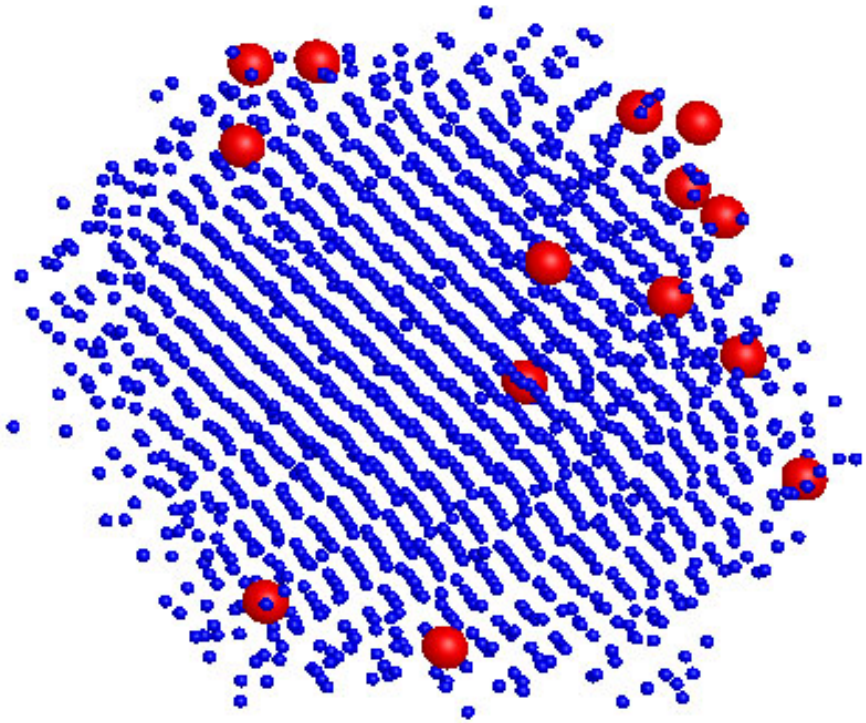
ZT=1.3

Y. Ma, Q. Hao, B. Poudel, Y. C. Lan, B. Yu, D. Z. Wang, G. Chen, Z. F. Ren, *Nano Lett.* **2008**, 8, 2580–2584.

Thermal Stability



Experimental Investigation of Thermal Stability



Computer Simulation

Perspectives on Recent Advances in Thermoelectric Materials Research

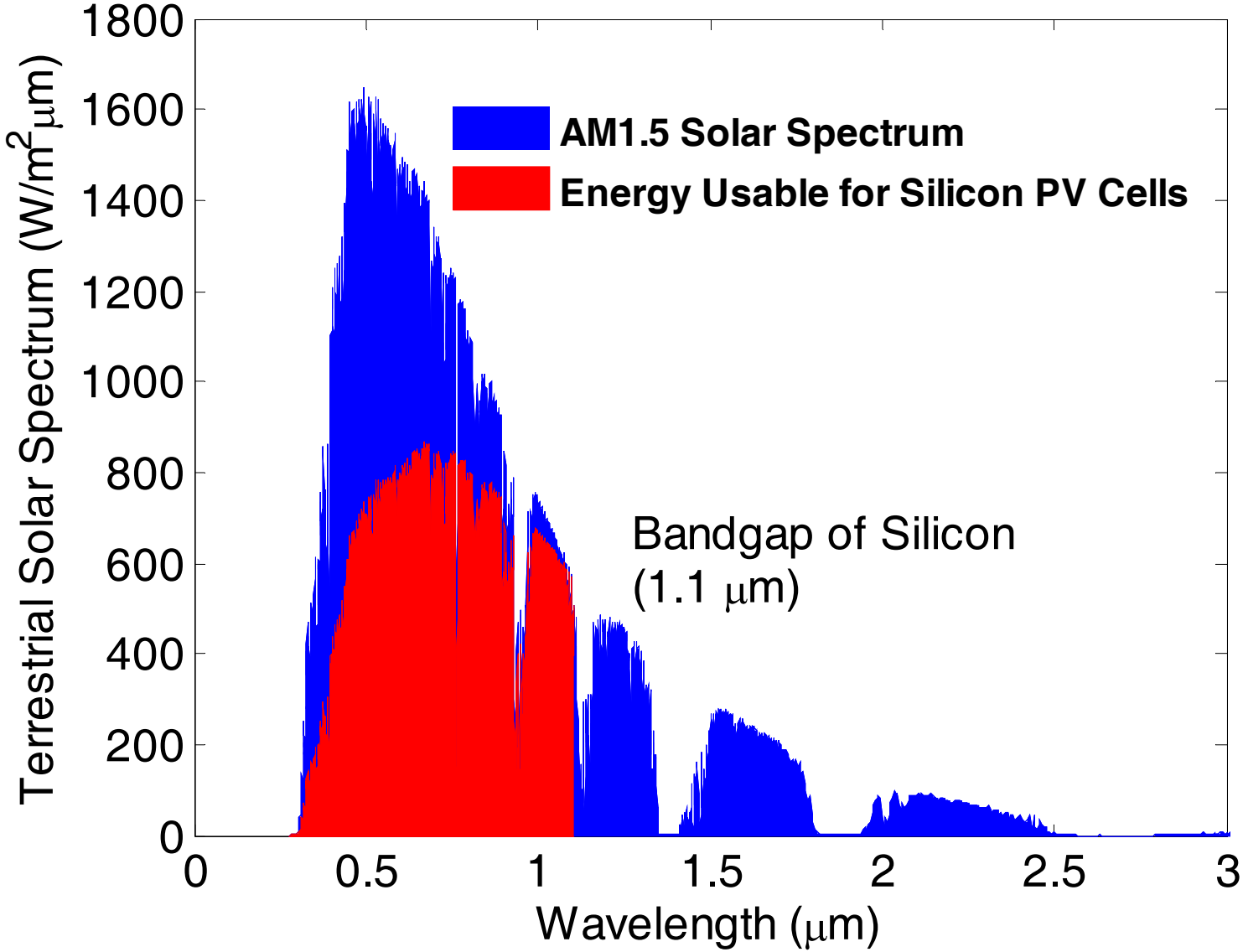
OUTLINE

- Some strategies for enhancing ZT through nanomaterials
- Some recent advances in thermoelectric materials research
- Looking to the future

Looking to the Future

- Materials Optimization by working together with Theoretical Modeling will yield further increases in ZT for many thermoelectric materials suitable for making thermoelectric modules
- Increased demand for thermoelectric products starting with car seats that cool passengers will create a market for thermoelectric modules with enhanced performance
- New large scale applications for thermoelectrics are likely to take off
  - automotive and buildings – to promote fuel efficiency
  - thermophotovoltaic – to exploit thermal solar energy conversion to electricity

Solar Spectrum



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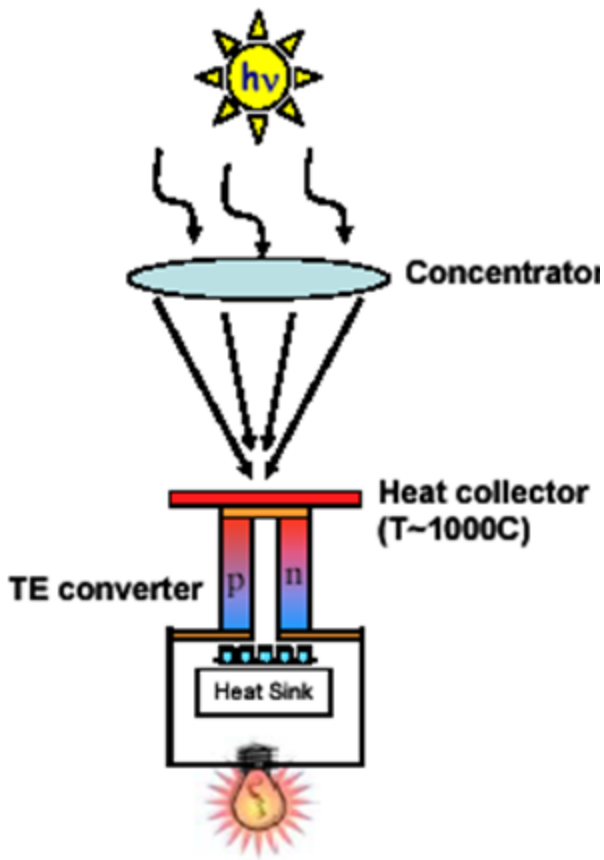
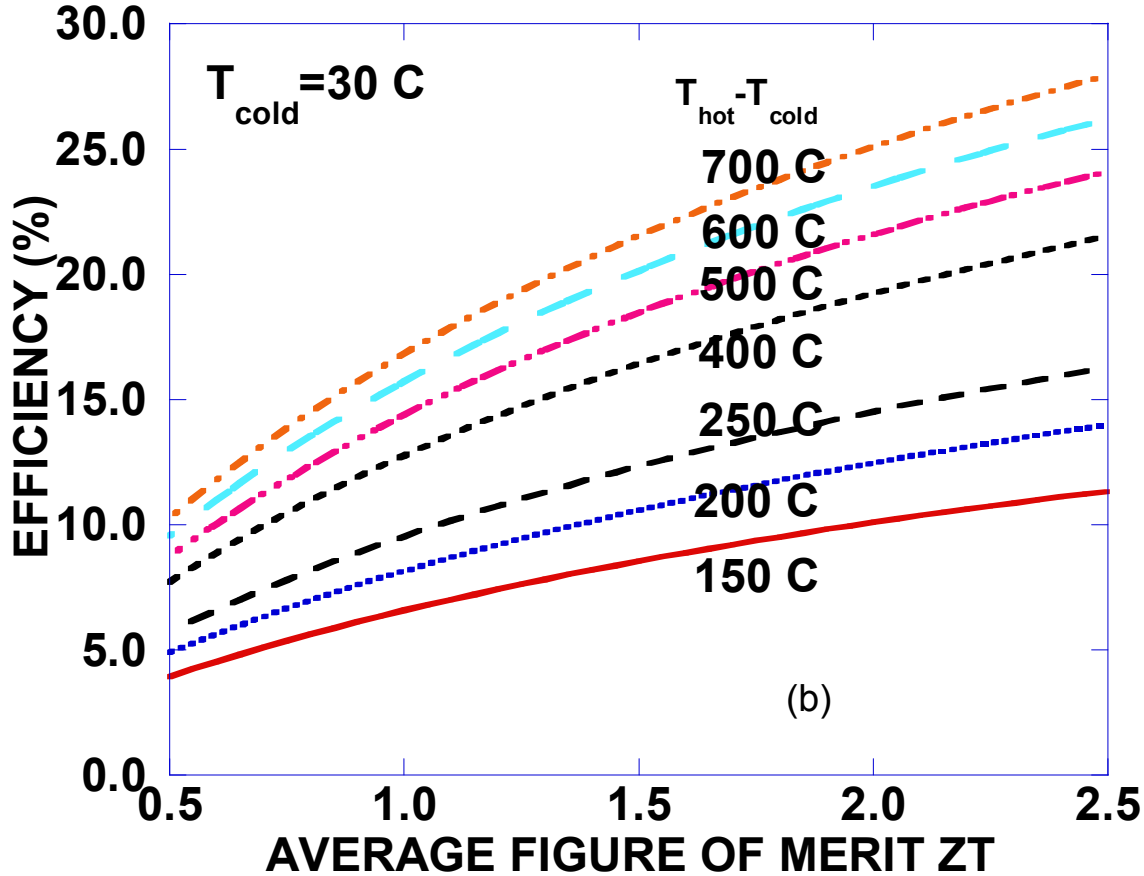
Solar Thermoelectrics





- **Low materials cost and low capital cost, potentially high efficiency.**
- **Key Challenges: Develop materials with high thermoelectric figure of merit; and selective surfaces that absorb solar radiation but do not re-radiative heat.**

MIT

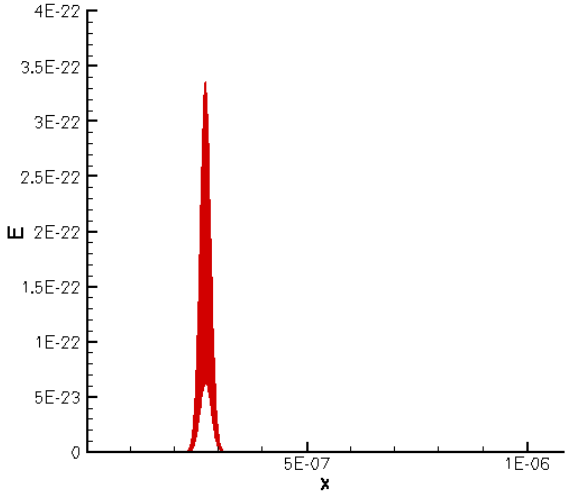
End

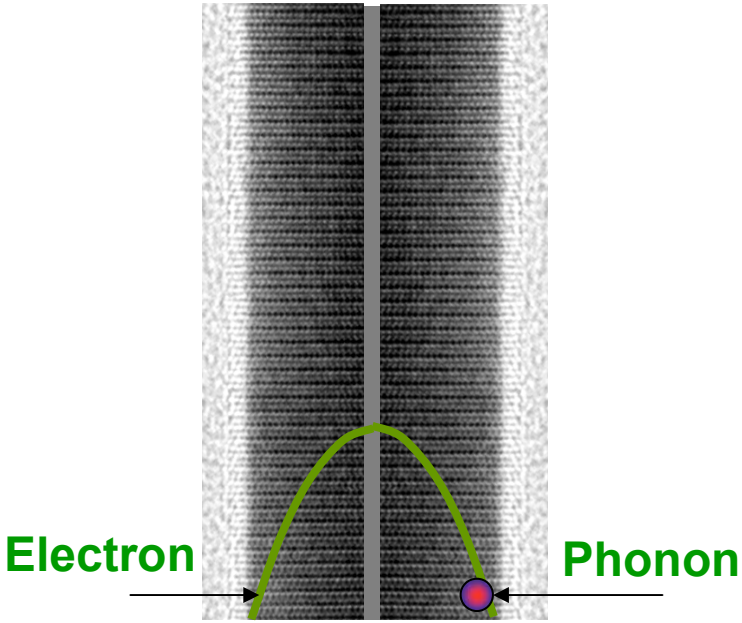
Nanoscale Effects for Thermoelectrics

Interfaces that Scatter Phonons but not Electrons

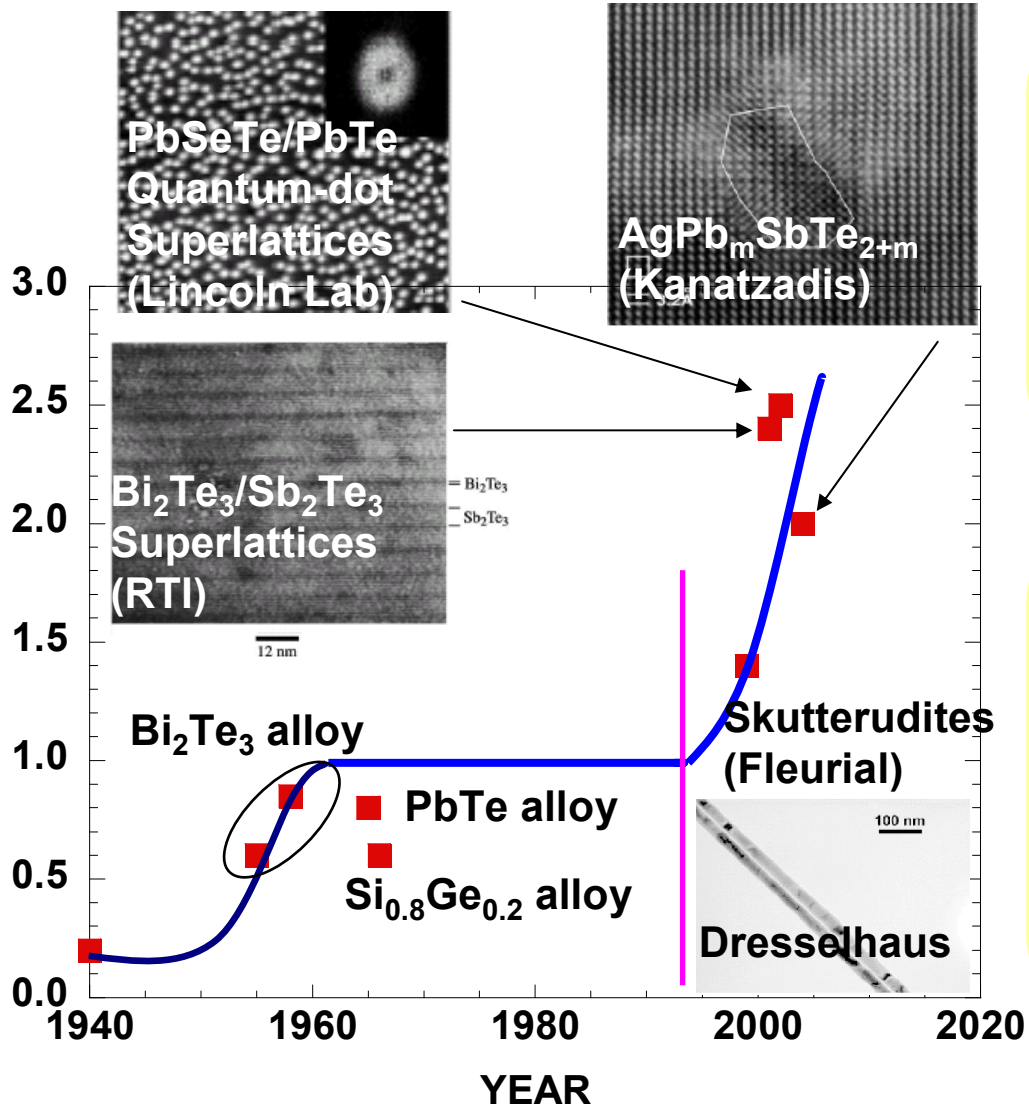
Electrons
Λ=10-100 nm
λ=10-50 nm

Phonons
Λ=10-100 nm
λ=1 nm





Advances in Thermoelectrics



PbTe/PbSeTe	Nano	Bulk
$S^2\sigma$ (μW/cmK^2)	32	28
k (W/mK)	0.6	2.5
ZT (T=300K)	1.6	0.3

Harman et al., Science, 2003

Bi_2Te_3/Sb_2Te_3	Nano	Bulk
$S^2\sigma$ (μW/cmK^2)	40	50.9
k (W/mK)	0.6	1.45
ZT (T=300K)	2.4	1.0

Venkatasubramanian et al., Nature, 2002.

MIT