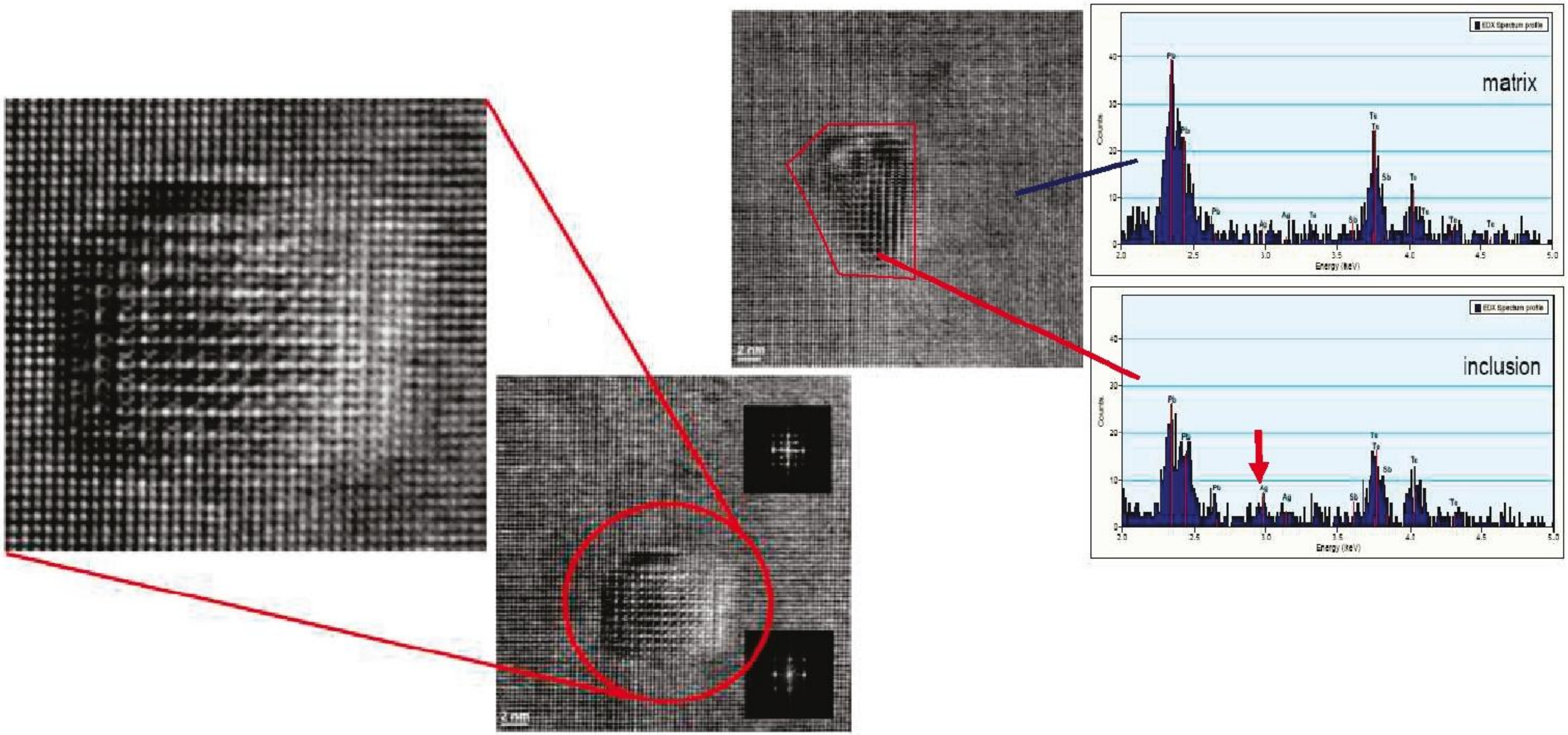
Nanostructured Thermoelectrics



Nathan George
MATRL 286G
May 28, 2010

Bruce A. Cook, Matthew J. Kramer, Joel L. Harringa, Mi-Kyung Han, Duck Young Chung, Mercouri G. Kanatzidis, Analysis of Nanostructuring in $Ag_{1-x}Pb_mSbTe_{2+m}$ High Figure-of-Merit Thermoelectric Materials, *Advanced Functional Materials*, **2009,** 19, 1254-1259.

Motivation

Heat Recovery

~90% of world's energy produced by heat energy (fossil fuels)

30-40% efficiency, lose 15 TW energy as waste heat

Refrigeration

Reduce CFC and HCFC release to atmosphere

Solid State Heating/Cooling

no moving parts

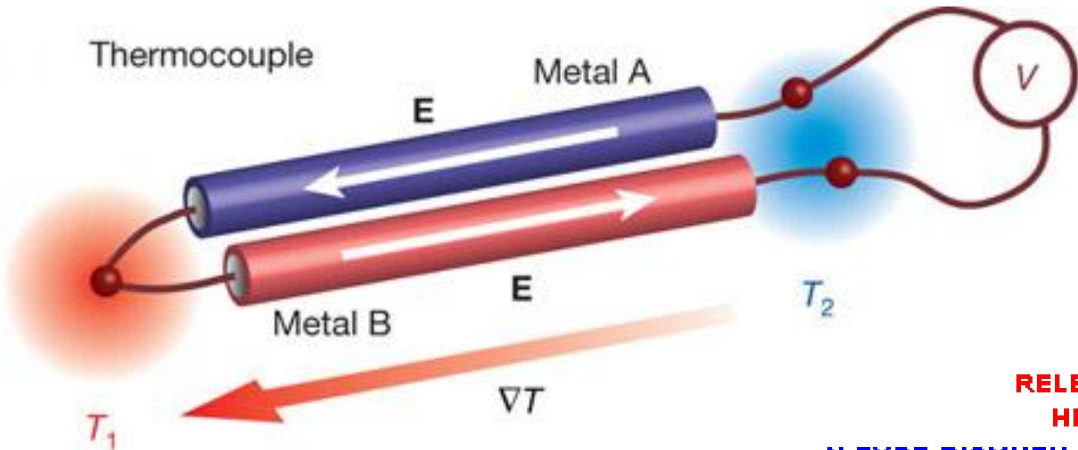
niche applications (car seat heater, cooling/heating in space)

Allon I. Hochbaum, Renkun Chen, Raul Diaz Delgado, Wenjie Liang, Erik C. Garnett, Mark Najarian, Arun Majumdar & Peidong Yang, Enhanced thermoelectric performance of rough silicon nanowires. *Nature,* **2008**, 451, 163–167.

Electricity $\longleftrightarrow$ ΔT

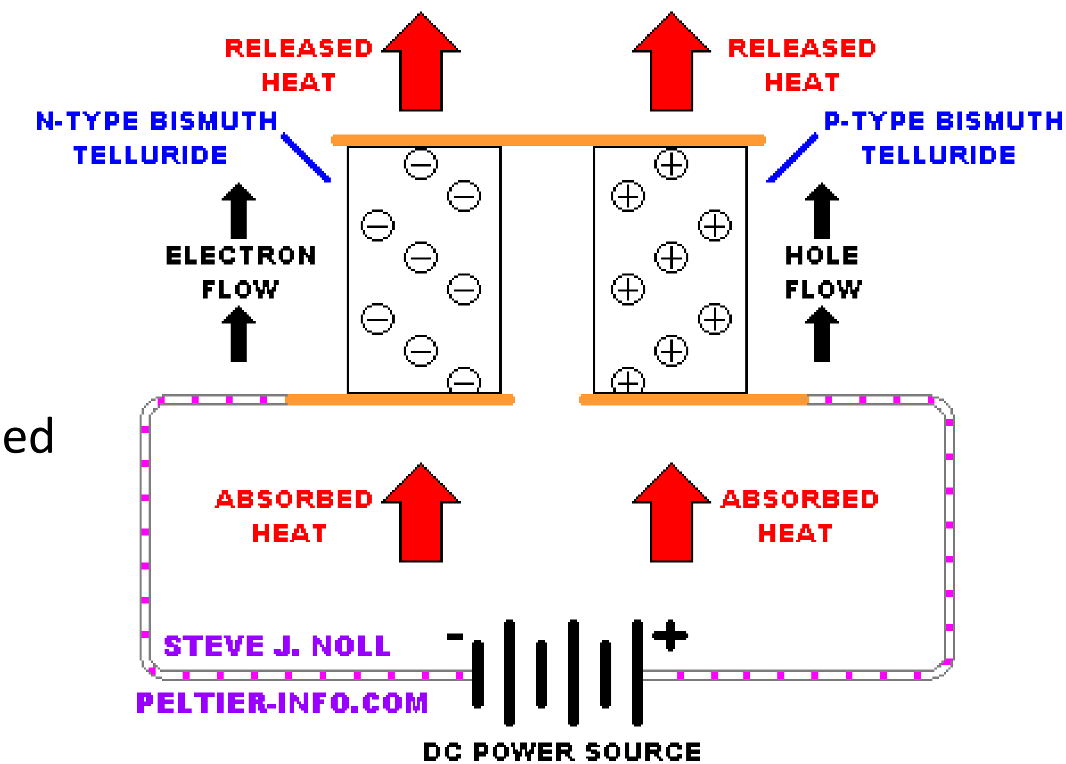
Seebeck effect

Voltage caused by temperature gradient



Peltier effect

Temperature gradient caused by application of voltage



http://www.spintronics-info.com/spin-seebeck-effect

http://www.peltier-info.com/photos.html

Thermoelectric Figure of Merit

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

$$\kappa = \kappa_{el} + \kappa_{latt}$$

$$S = \frac{\Delta T}{\Delta V}$$

$$\kappa_{latt} = \frac{1}{3} C_v l v_s$$

S= Seebeck coefficient	[μV/K]
σ = electrical conductivity	[S/cm]
κ = thermal conductivity	[W/m*K]
C_v = specific heat	[W/kg*K]
l = mean free phonon path	[nm]
v_s = average velocity of sound	[m/s]

σS^2 = power factor	[$\mu W/K^2 cm$]

Joseph R. Sootsman, Duck Young Chung, Mercouri G. Kanatzidis, New and Old Concepts in Thermoelectric Materials, *Angewandte Chemie International Edition*, **2009**, 48, 8616-8639.

Maximum attainable Z

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

γ = degeneracy of band extrema
m_i = effective mass of carriers in i-th direction
τ_z = relaxation time of the carriers moving
along the transport direction (usually z)
r = scattering parameter
κ_{latt} = lattice thermal conductivity

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Strategies for improving ZT by lowering κ_{latt}

Alloys

- Bi_2Te_3 system, $Bi_{2-x}Sb_xTe_3$ $BiTe_{3-x}Se_x$
- "Alloy limit"-minimum κ_{latt} at some composition
- Can deteriorate carrier mobility

Phonon-glass-electron crystal (PGEC)

- Large rattling atoms in cages or tunnels
- Not proven, other factors affect κ

Nanostructuring

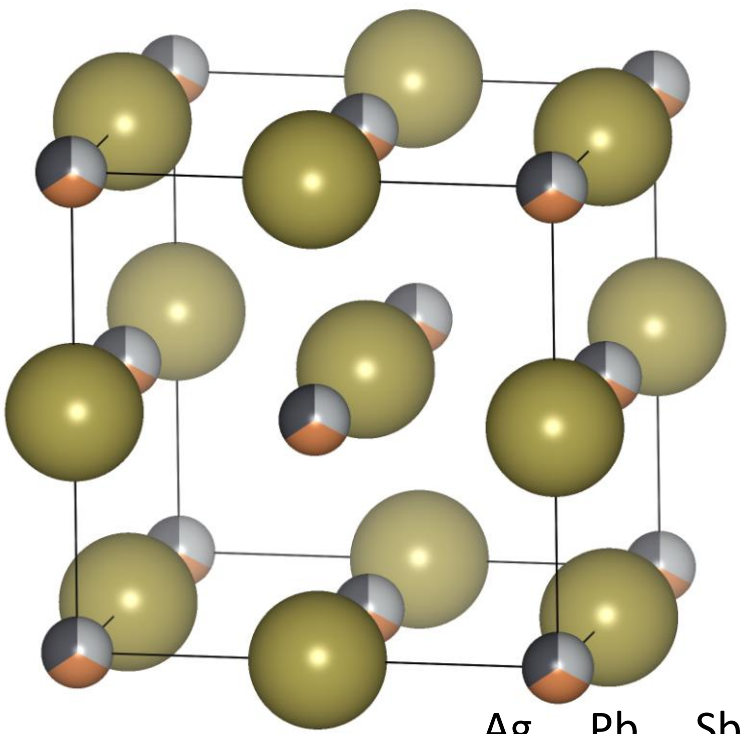
- Self-formed inhomogenieties driven by phase segregation
- Nanocomposites (spark plasma sintering, hot pressing, etc.)
- Liquid encapsulation (PbTe-PbS)

Mercouri G. Kanatzidis, Nanostructured Thermoelectrics: The New Paradigm?, *Chemistry of Materials*, **2010**, 22, 648-659.

$AgPb_mSbTe_{2+m}$ (LAST-*m*)

PbTe

- 600-800 K range
- NaCl structure (SG Fm-3m #225)
- 0.32 eV band gap, can be doped p- or n-type
- Max ZT 0.8-1.0 at ~650 K
- κ_{latt}~2.2 W/(m*K) at 293 K, falls off at higher temp as 1/T



$Ag_{1.33}Pb_{1.33}Sb_{1.33}Te_4$

$AgPb_mSbTe_{2+m}$ $((AgSbTe_2)_{1-x}(PbTe)_x)$

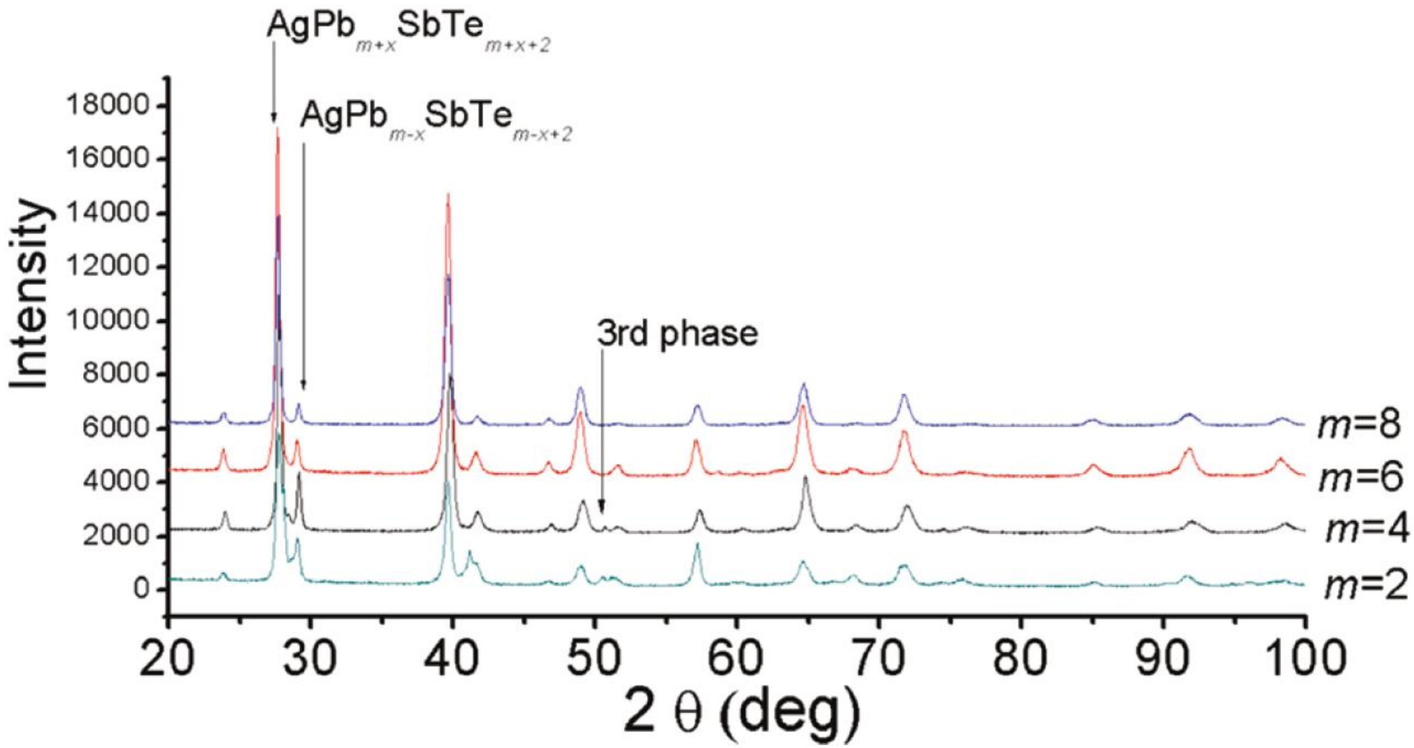
- m<10 results in phase segregation
- m>10 appear to follow Vegard's law
- Not solid solution; nanostructuring occurs

Mercouri G. Kanatzidis, Nanostructured Thermoelectrics: The New Paradigm?, *Chemistry of Materials*, **2010**, 22, 648-659.

$AgPb_mSbTe_{2+m}$ (LAST-*m*) Synthesis

m<10

- $AgSbTe_2$ and PbTe Melted (>1200 °C)
- Quench or slowly cool below 500 °C, single phase observed
- Anneal at ~400 °C (if quenched)
- Microscopic phase separation results
- κ_{latt}~1 W/(m*K)



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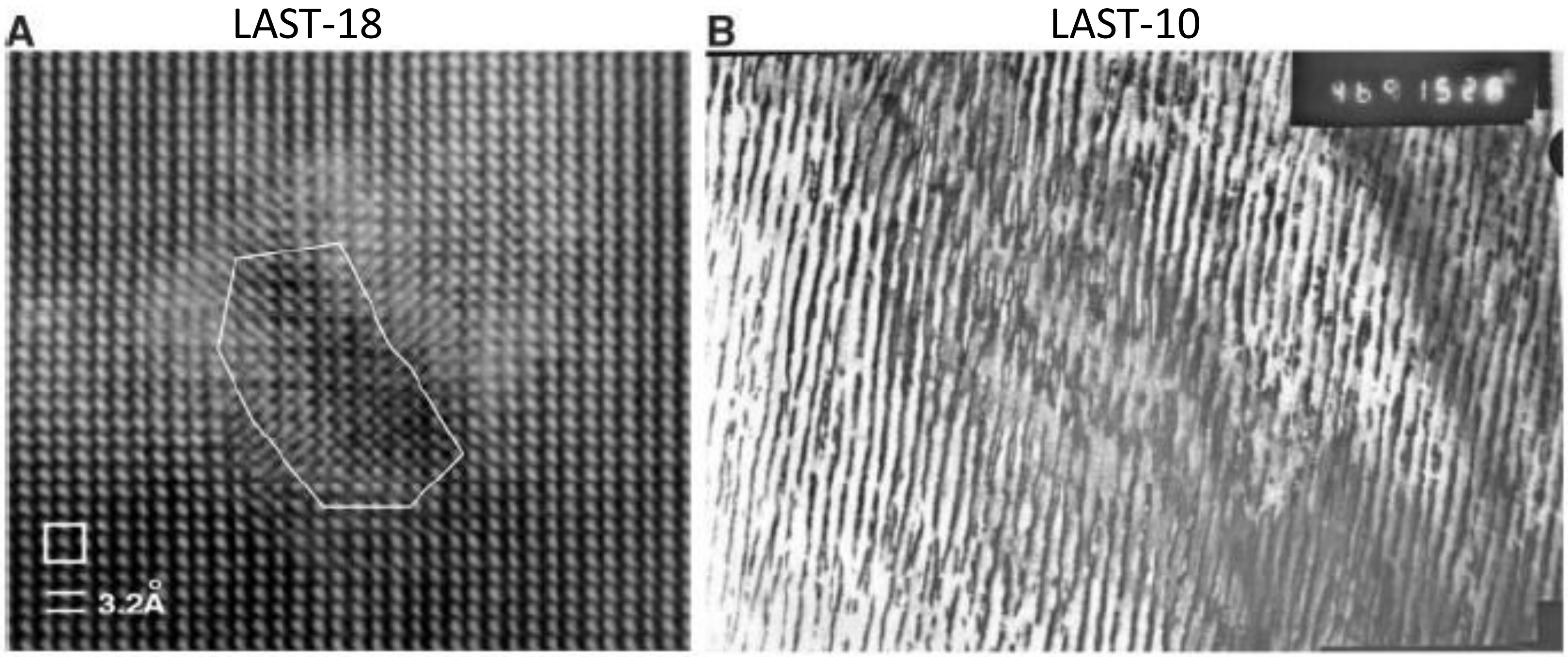

Nanoscale phase segregation from nucleation and growth (3-20 nm)
Nanoscale inclusions disrupt medium/long range phonons (change l)
Anisotropy (10-20 nm spacing) from periodic conc. changes effective carrier masses
LAST-18 -- κ_{latt}~ 1W/(m*K), σ~200 S/cm, ZT~2.2, at 800 K, σ~1800 S/cm at 300K

Kuei Fang Hsu, Sim Loo, Fu Guo, Wei Chen, Jeffrey S. Dyck, Ctirad Uher, Tim Hogan, E. K. Polychroniadis, and Mercouri G. Kanatzidis, Cubic $AgPb_mSbTe_{2+m}$: Bulk Thermoelectric Materials with High Figure of Merit, *Science,* **2004**, 303 (5659), 818.

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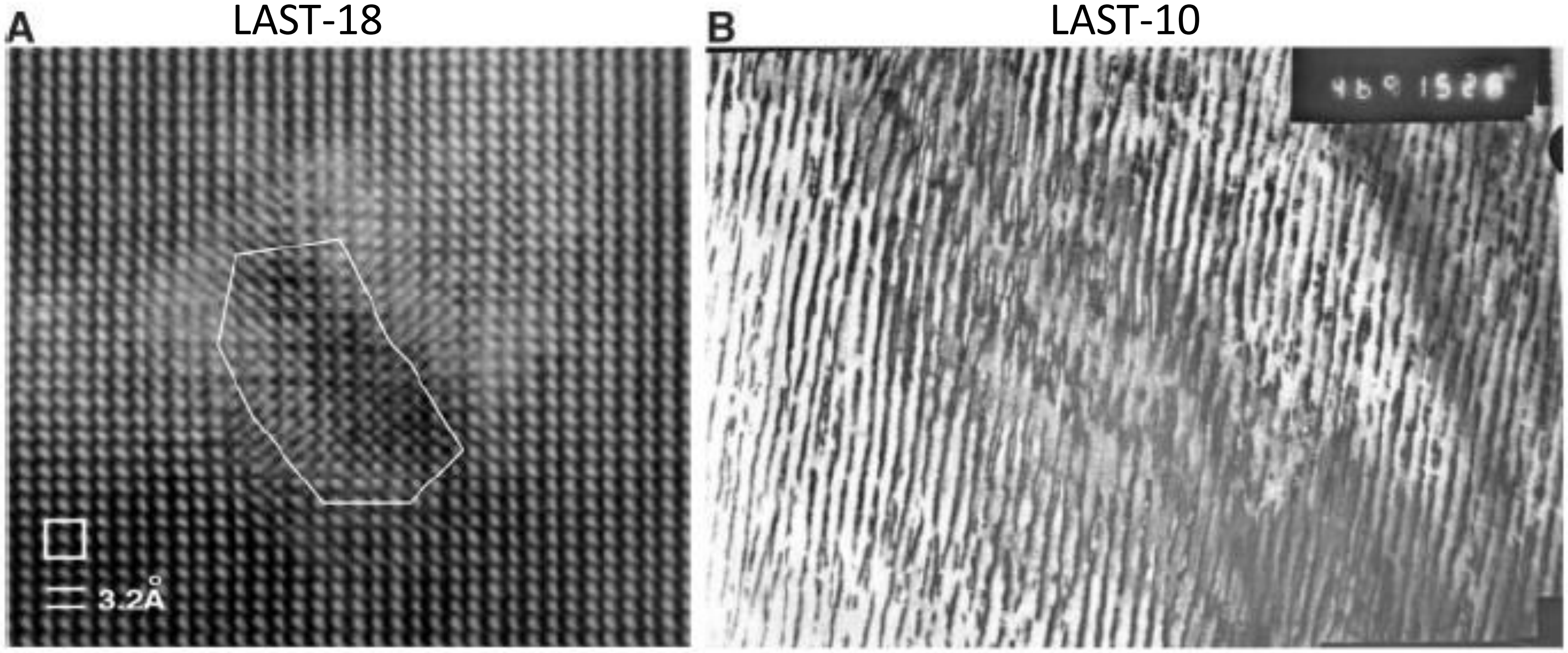

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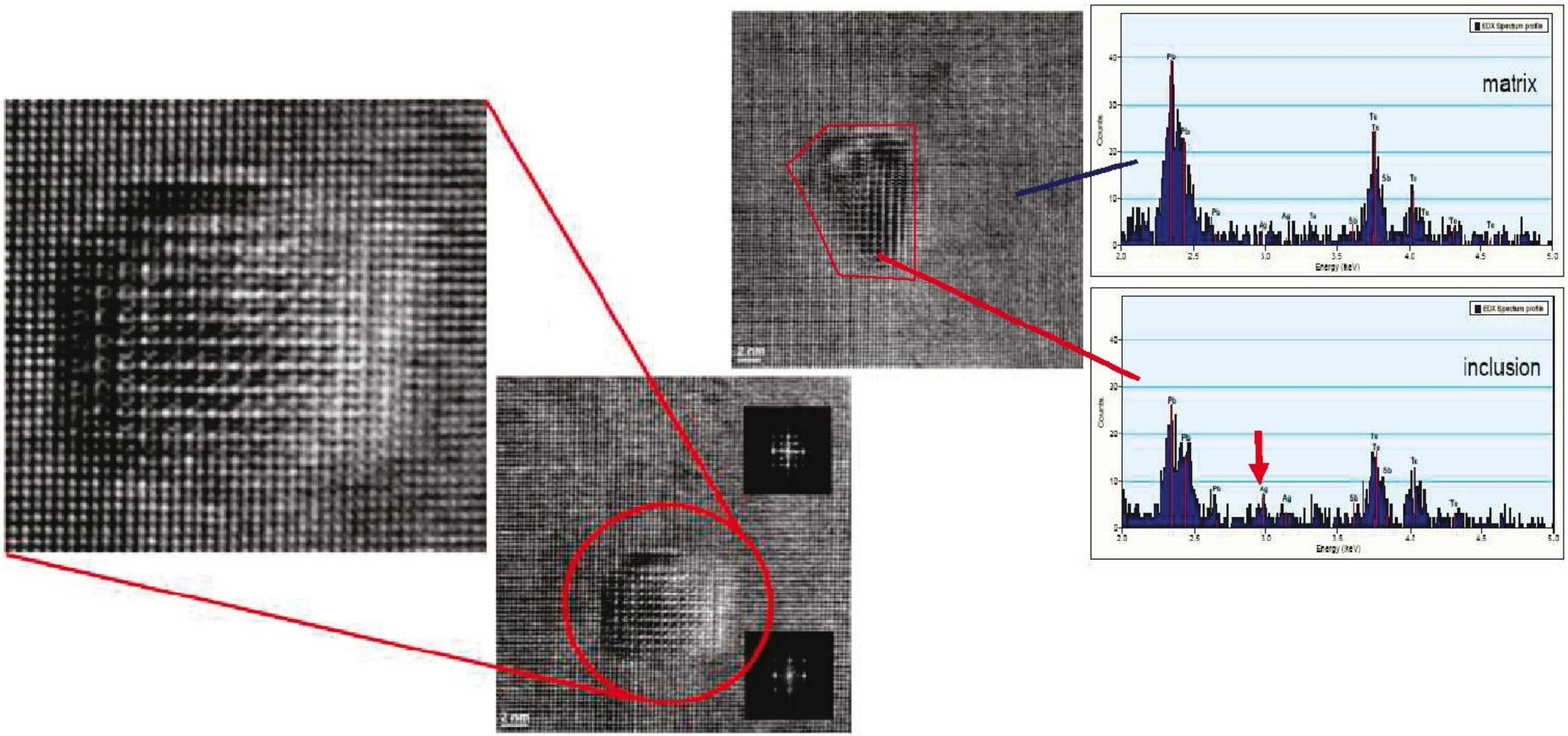
$AgPb_mSbTe_{2+m}$ (LAST-*m*) nanostructuring

TEM of nanoscale phase segregation (~20 nm diameter particle)
Surrounding area is Ag/Sb poor, cell parameter ~PbTe (6.44 Å)
EDS shows the nanoscale inclusion is Ag-rich



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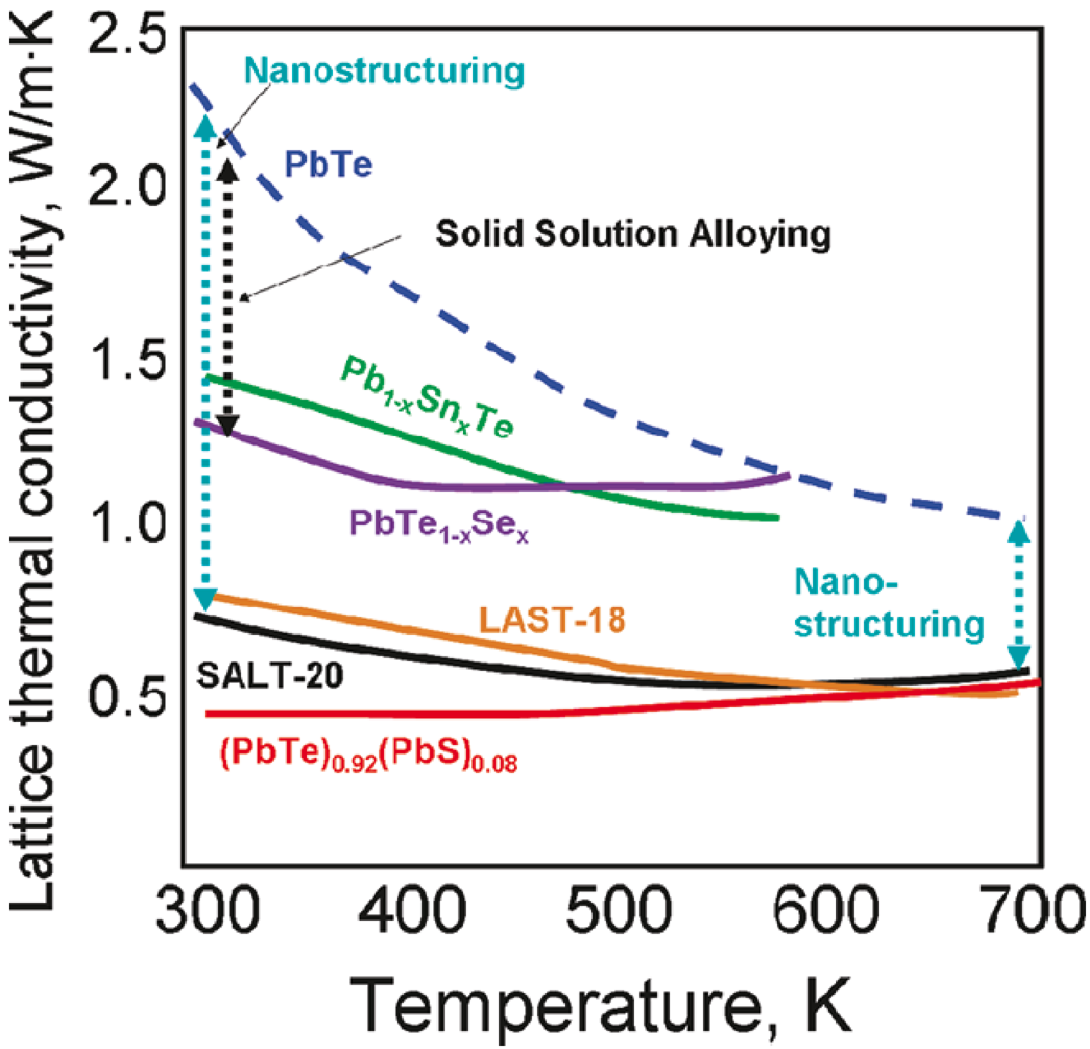
Nanostructuring enables new lows of κ_{latt}



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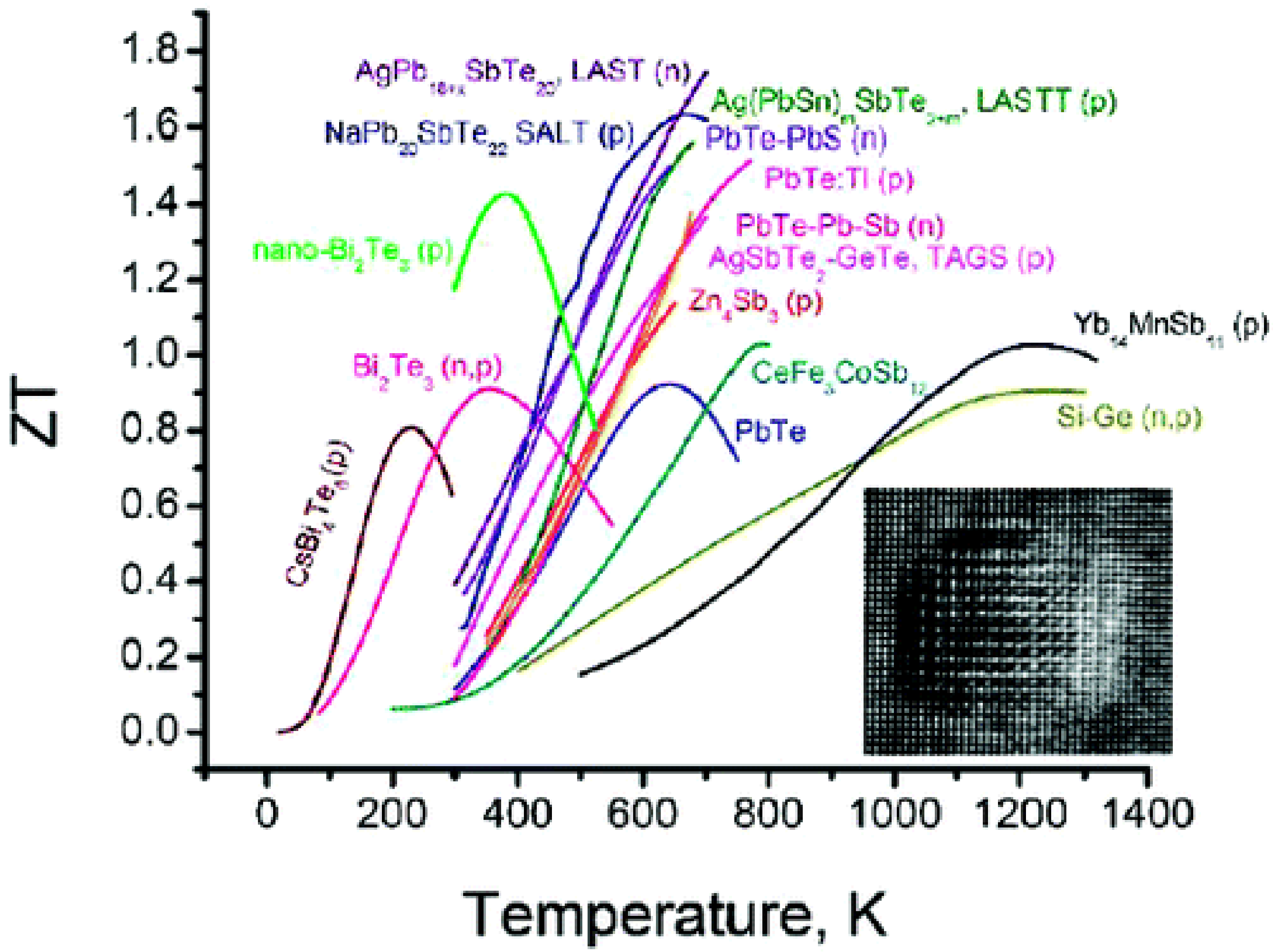
ZT doubled by nanostructuring

Efficiencies up from 5-6% to 11-15%



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Kanatzidis's Opinion

"It is evident that the field of thermoelectrics now needs new bold theoretical guidance on how the power factor can be enhanced by 2--4-fold in the existing leading materials, especially enhancements that derive from the thermopower. Theorists in the field are urged to take risks."

Mercouri G. Kanatzidis, Nanostructured Thermoelectrics: The New Paradigm?, *Chemistry of Materials*, **2010**, 22, 648-659.