NSLS Users' Meeting
May 24, 2010

Understanding and Controlling Nanoscale Fluctuations in Thermoelectric Materials

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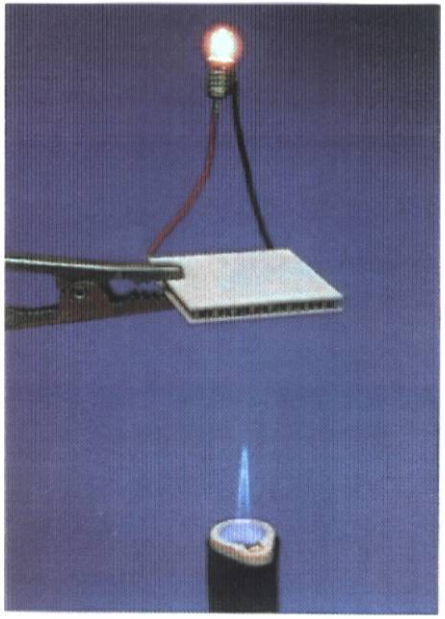
EFRC: *Revolutionary Materials for Solid State Energy Conversion*

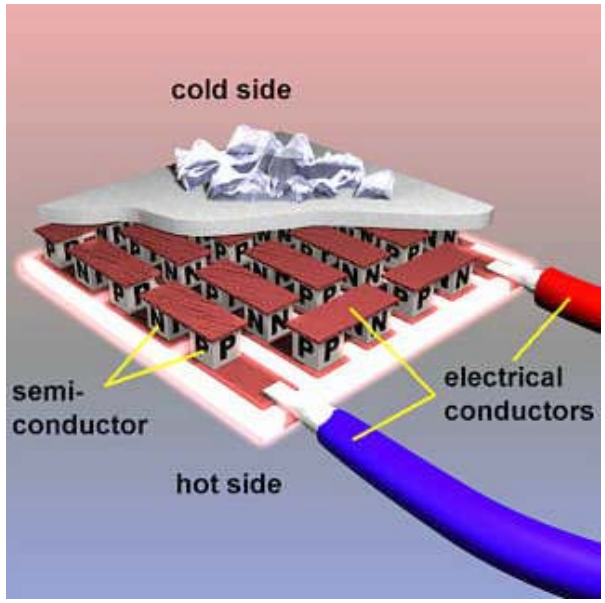
Michigan State University, Northwestern University

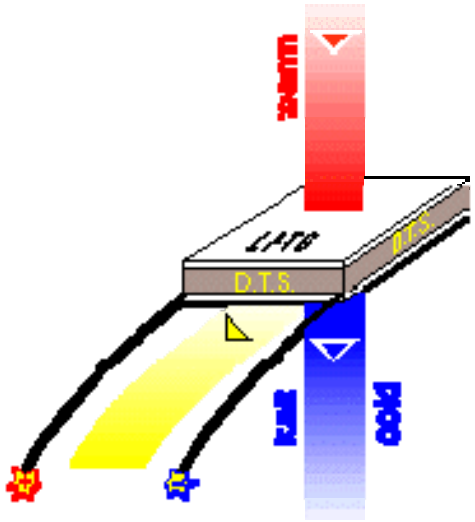
Heat to Electrical Energy Directly

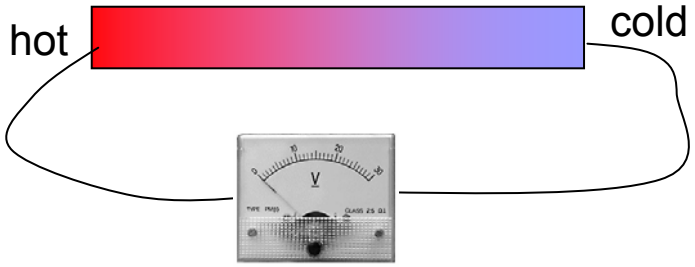
Up to 20% conversion efficiency with right materials



Electrical
Power Generation







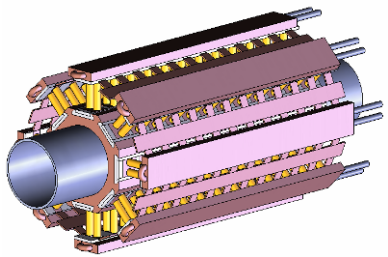
Thermopower $S = \Delta V/\Delta T$

TE devices have <u>no moving parts, no noise, reliable</u>

http://www.dts-generator.com/

Thermoelectric applications

- Waste heat recovery
  - Automobiles
  - Over the road trucks
  - Utilities
  - Chemical plants



- Space power
- Remote Power Generation
- Solar energy
- Geothermal power generation
- Direct nuclear to electrical

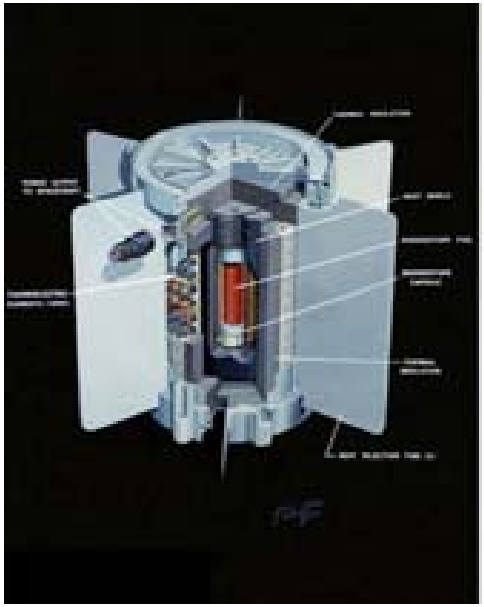
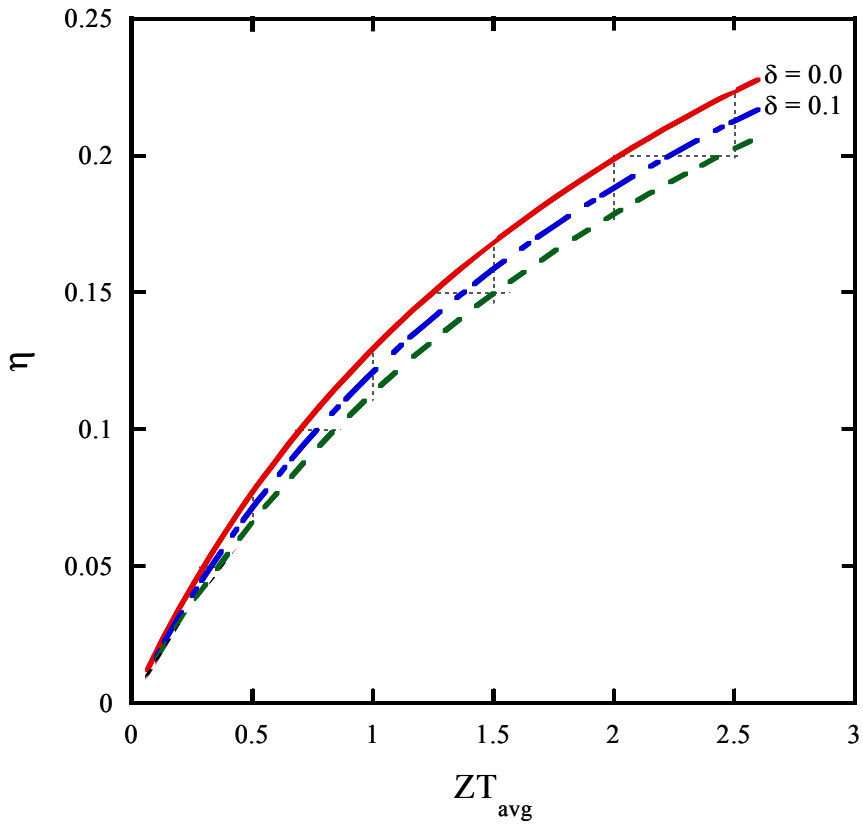


Figure of Merit

$$\eta = \frac{T_h - T_c}{T_h} \cdot \frac{\sqrt{1+z\bar{T}} - 1}{\sqrt{1+z\bar{T}} + T_c / T_h}$$

Carnot efficiency



electrical conductivity

thermopower

$$ZT = \frac{\sigma \cdot S^2}{\kappa_{total}} \bullet T$$

Total thermal conductivity

Power factor

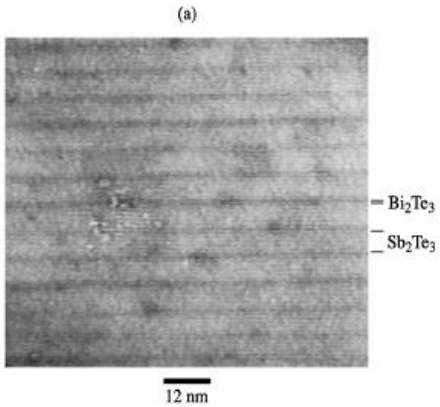
$$\sigma \cdot S^2$$

$\delta = R_c/R$

For T_h = 800K
T_c = 300K

Today's situation

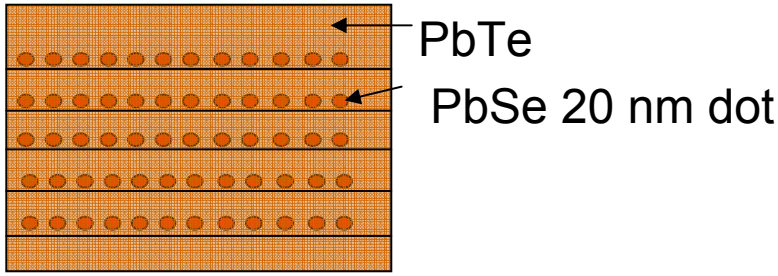
- The most efficient materials today for power generation:
- PbTe: ZT~0.8 at 800 K (n-type)
- TAGS: ZT~1.2 700 K (p-type)
- $Bi_2Te_{3-x}Se_x$: ZT~1 at 300 K
- Further improvements are needed.
- New materials emerging with breakthrough properties



ZT~2.4: 10Å/50Å Bi2Te3/Sb2Te3 superlattice structures

Venkatasubramanian R, Siivola E, Colpitts T et al. Nature, 2001, 413: 597

- Quantum Dot Layers in thin MBE-grown PbSe/PbTe superlattices (Harman *et al*, ZT~3)



Harman T C, Taylor P J, Walsh M P et al. Science, 2002, 297: 2229

Thermoelectrics

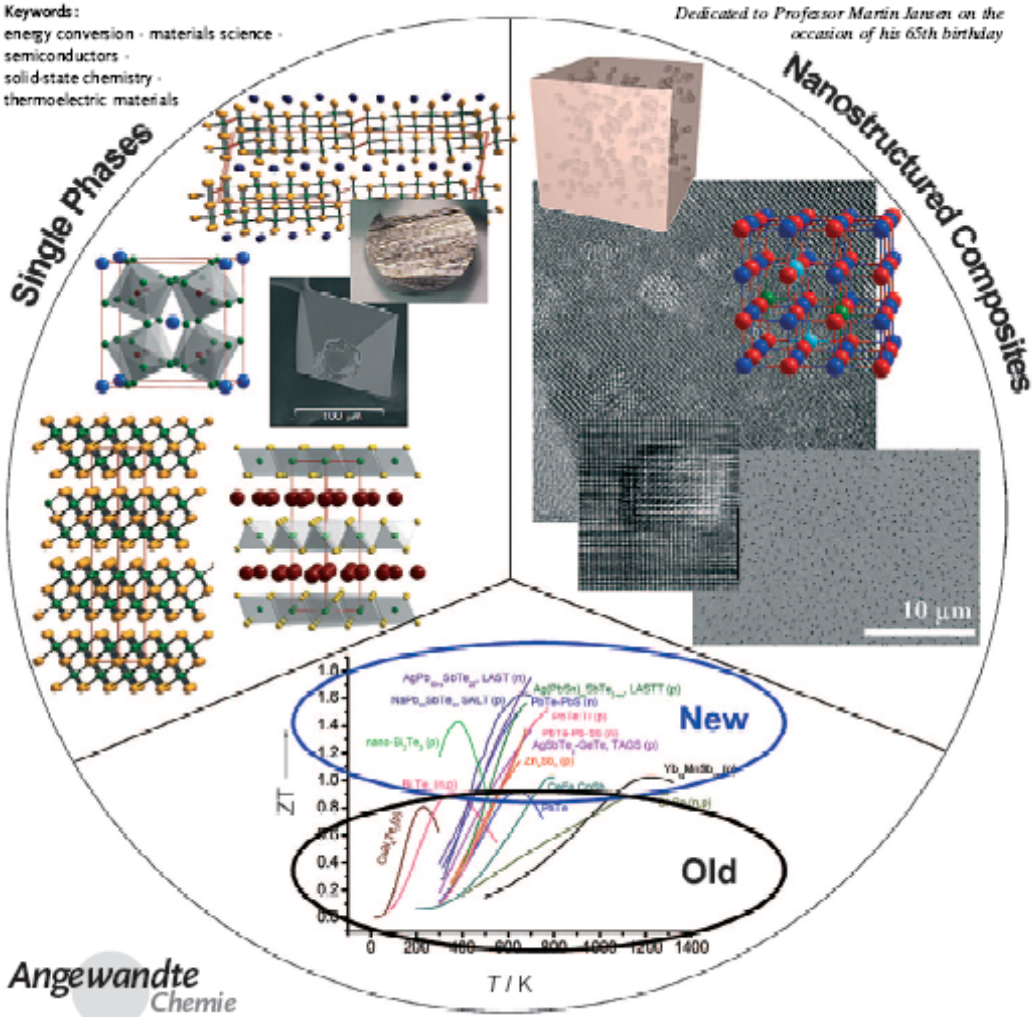
DOI: 10.1002/anie.200900598

New and Old Concepts in Thermoelectric Materials

*Joseph R. Sootsman, Duck Young Chung, and Mercouri G. Kanatzidis**

Keywords:
energy conversion · materials science · semiconductors · solid-state chemistry · thermoelectric materials

Dedicated to Professor Martin Jansen on the occasion of his 65th birthday



Angewandte Chemie

2009

ZT and Electronic Structure

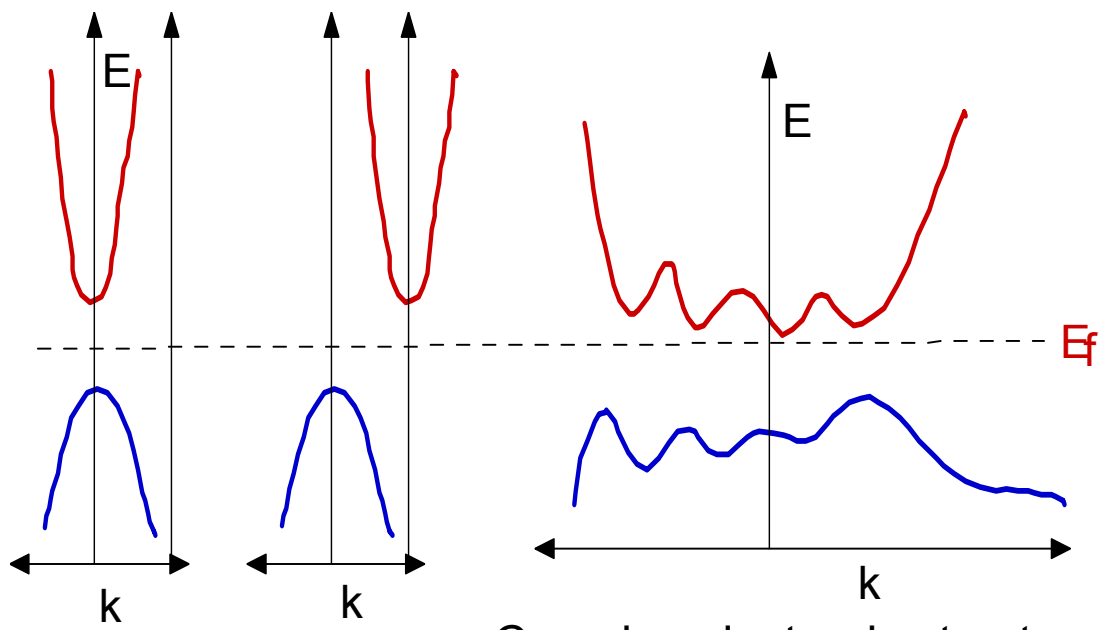
Isotropic structure

Anisotropic structure

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

For acoustic phonon scattering
r=-1/2

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



Complex electronic structure

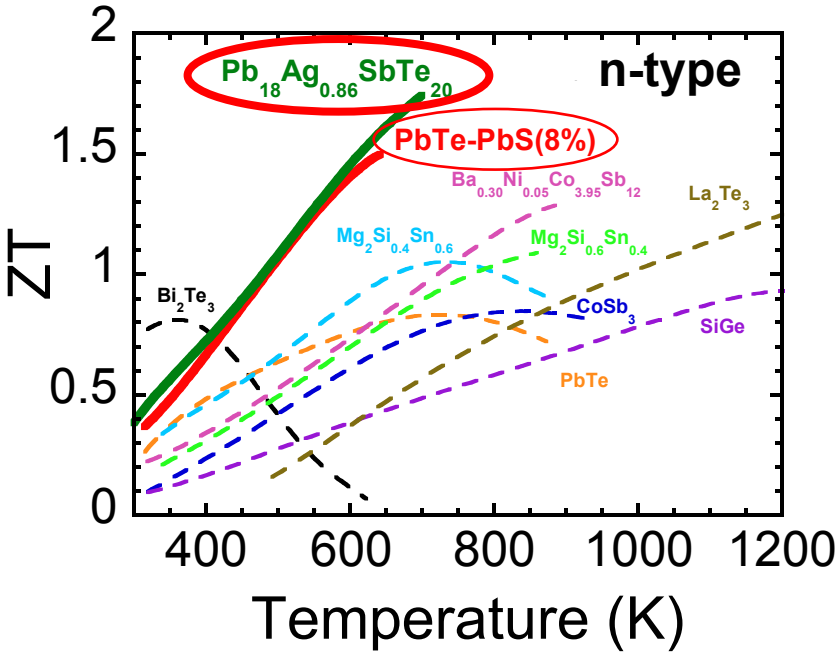
Large γ comes with
(a) high symmetry e.g. rhombohedral, cubic
(b) off-center band extrema

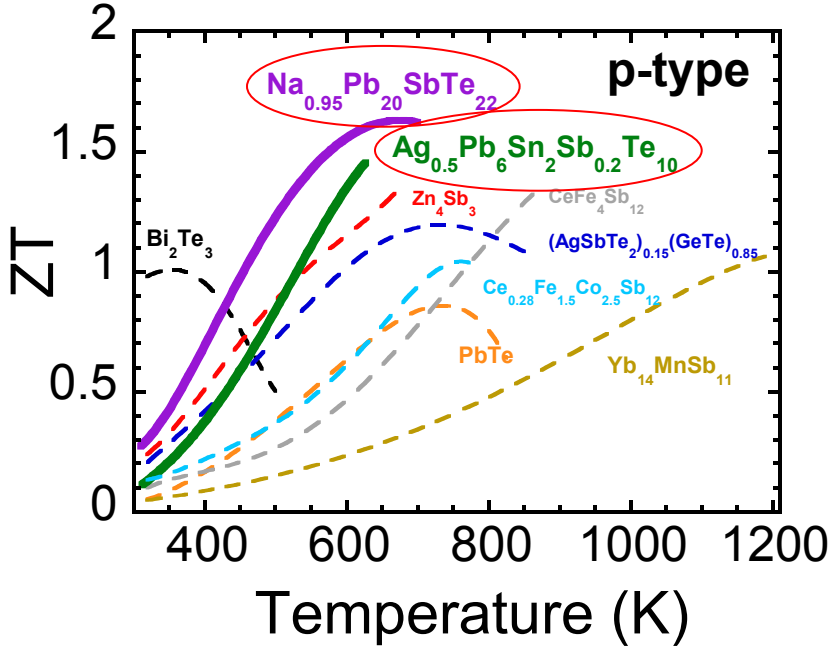
Best thermoelectric materials

Developed new *bulk* thermoelectric materials with record ZT_{max}

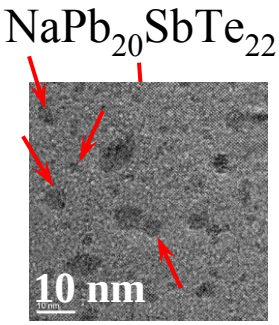
n-type: ZT_{max} ~1.7 at 700K - 100% improvement over state-of-the-art

p-type: ZT_{max} ~1.6 at 700K - 33% improvement over state-of-the-art



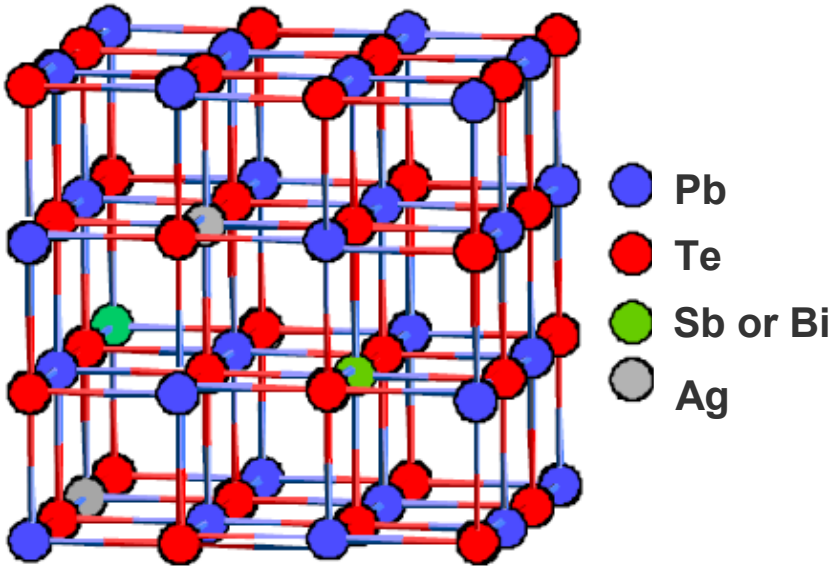


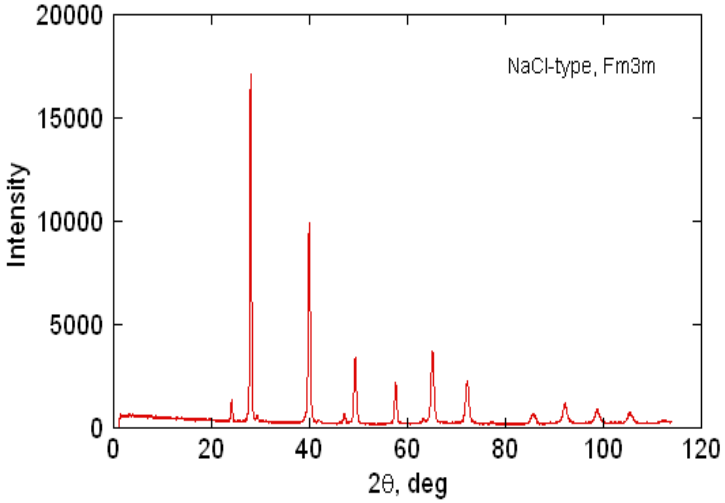
Major discovery: Unanticipated self-assembled nanodots in *bulk* materials responsible for record ZT's



LAST(T)-m: $Ag(Pb,Sn)_mSbTe_{2+m}$

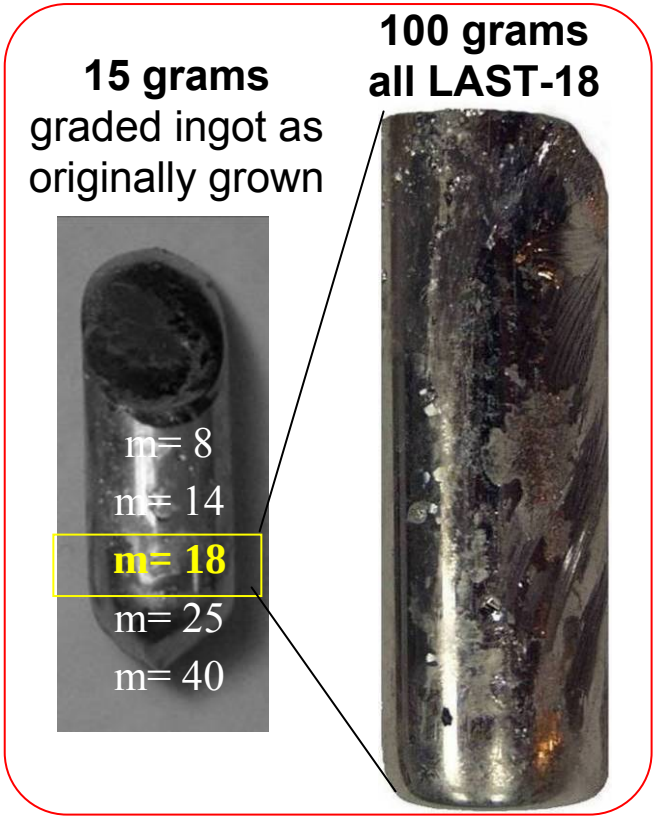
- Average structure cubic Fm-3m
- No phase transitions to melting point
- Solid solutions, but..
- Nanostructured
  - → Spinodal decomposition
  - → Nucleation growth
- Nanostructure and properties very sensitive to cooling and growth conditions
- Doping through non-stoichiometry: $Ag_{1-x}Pb_{18}SbTe_{20}$

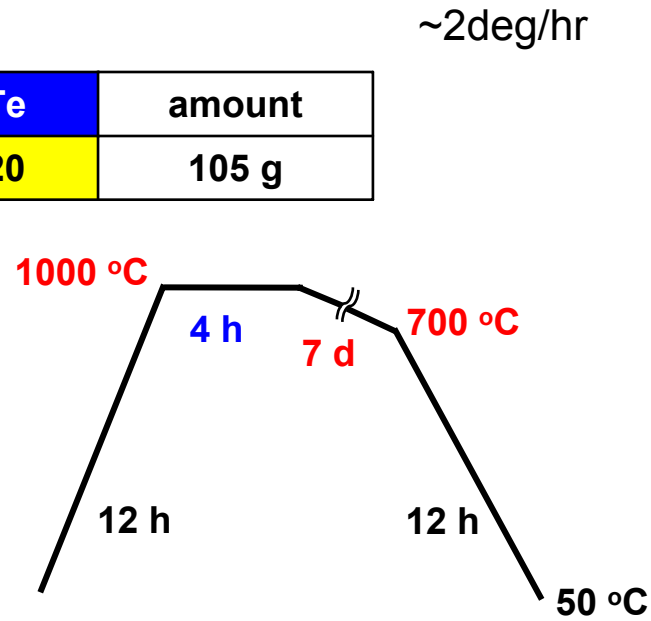




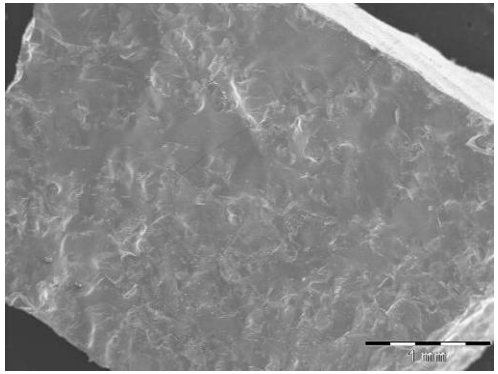
LAST-18: Synthesis with Slow Cooling

Ag	Sb	Pb	Te	amount
0.86	1	19	20	105 g

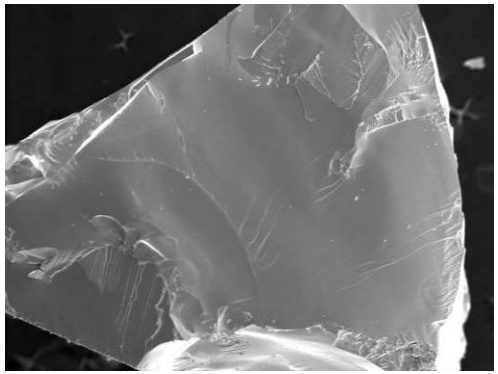




ETN125	σ (S/cm)	S (μV/K)	PF (μW/cm•K²)
A	535	-121	7.8
B	959	-128	15.7
C	1026	-158	25.6
D	1341	-180	43.4



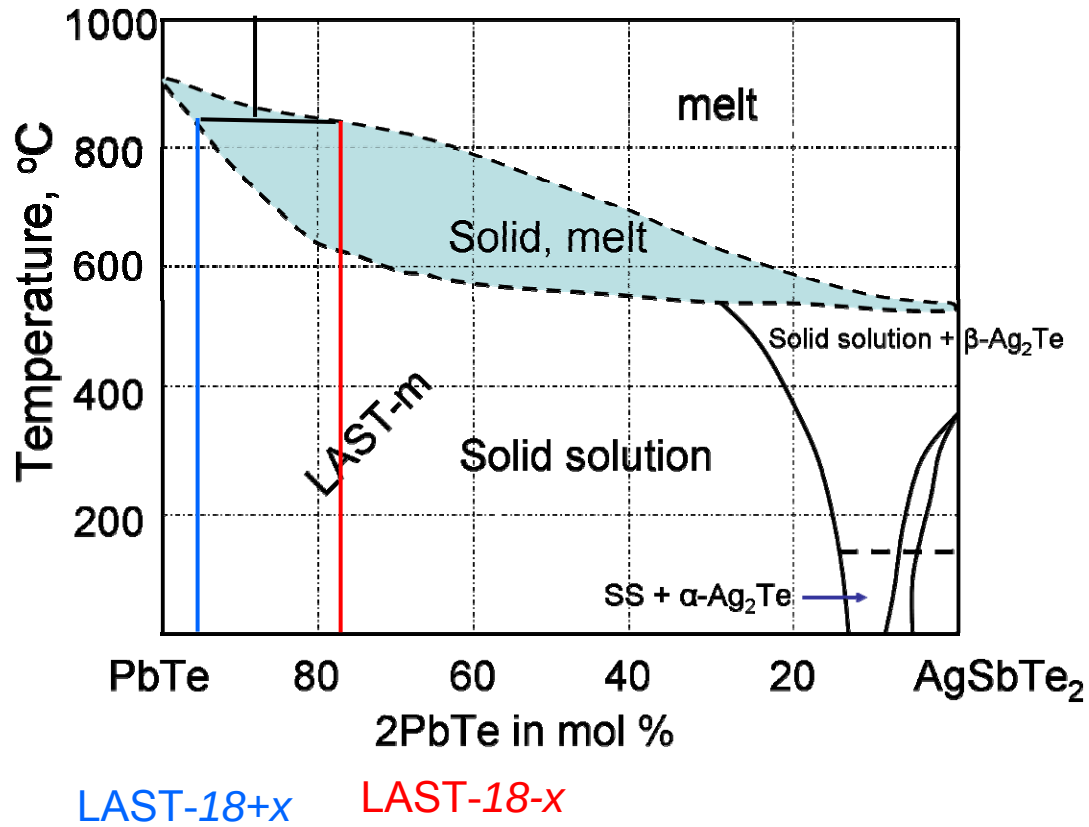
fast cooled sample



slow cooled sample

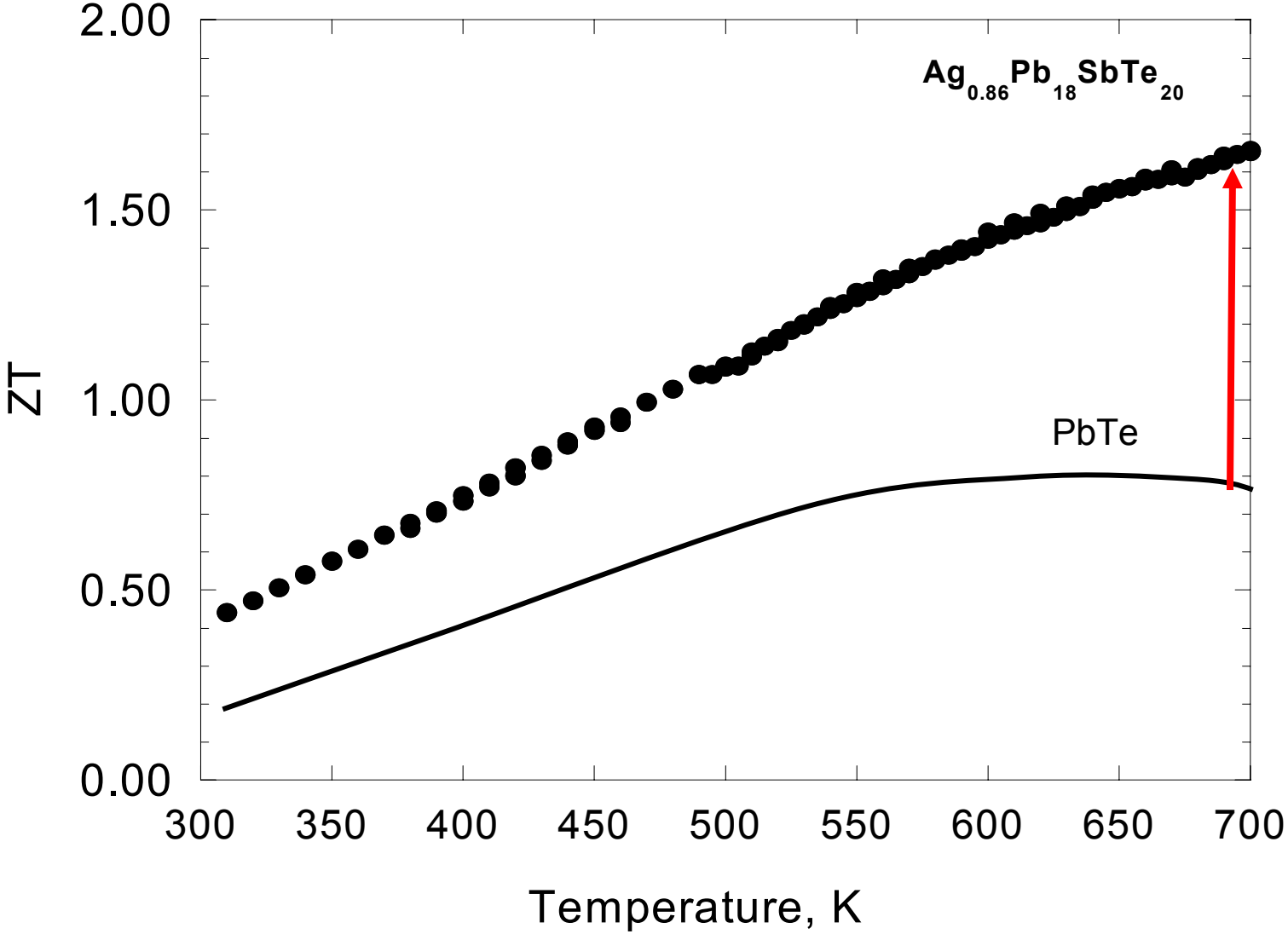
Chemical implications of non-stoichiometry $Ag_{1-x}Pb_{18}SbTe_{20}$

- No vacancies in Na sites of NaCl lattice
- $(AgPb_{18}SbTe_{20})_{1-x}(Sb)_x$
- This predicts Sb phase might be present
- The "$AgPb_{18}SbTe_{20}$" part may be a combination of solid solution and nanostructured.
- Even other phases may be present complicating the picture (e.g. Ag_2Te or Sb_2Te_3)

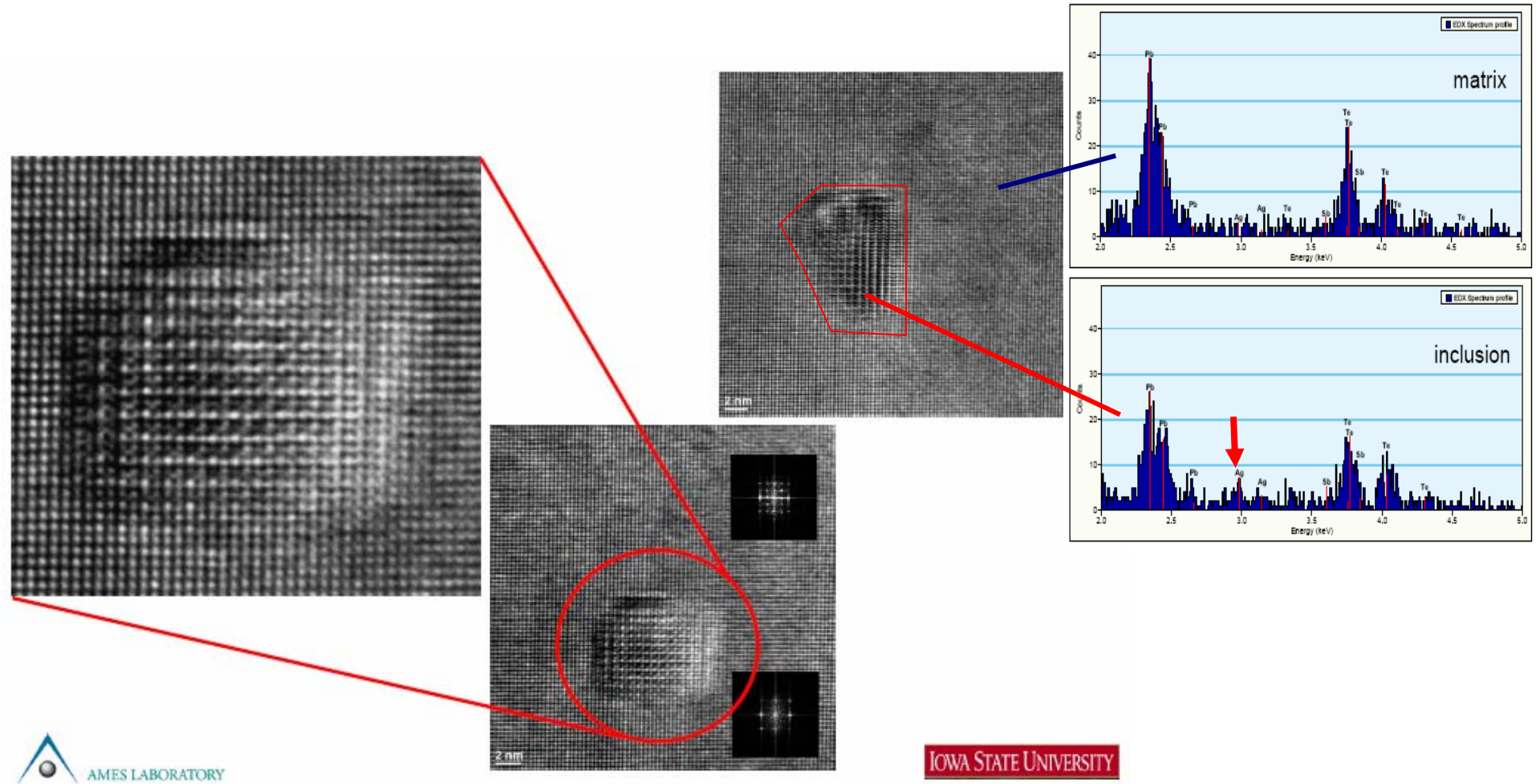


R. G. Maier *Z. Metallkunde* 1963, 311

Lattice thermal conductivity



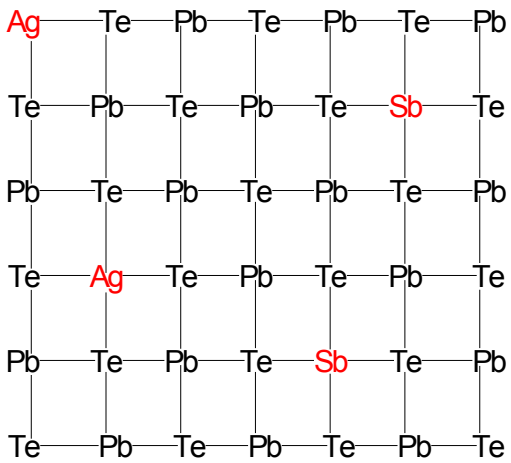
What is the dot made of?



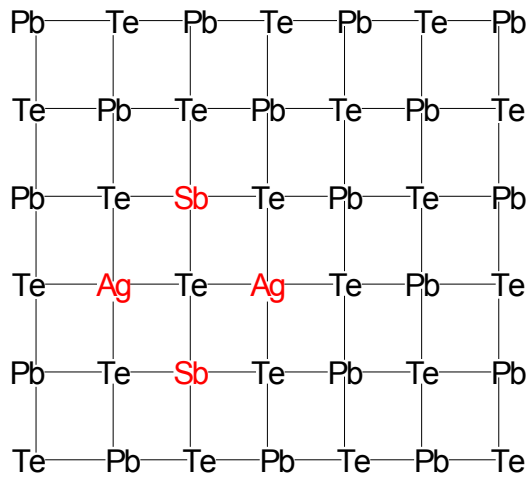
Cook, Kramer, Harringa, Han, Chung, Kanatzidis *Advanced Functional Materials*, 2009, *19*, 1-6

Why do the LAST materials nanostructure?

Driving force for segregation Ag^{+}/Sb^{3+} pair: thermodynamics



Dissociated state..unstable



Associated state..stable

Any +1/+3 pair

$AgPb_mSbTe_{m+2} = (AgSbTe_2)(PbTe)_m$

$a=6.079(1)Å$

S.G. $Fm\bar{3}m$

$a=6.460(1)Å$

S.G. $Fm\bar{3}m$

Lattice mismatch

$6.08Å < a < 6.46Å$?

S.G. $Fm\bar{3}m$?

Are nanostructures thermally stable?

Yes! Nanostructures are still present after annealing at 600°C for 3 months

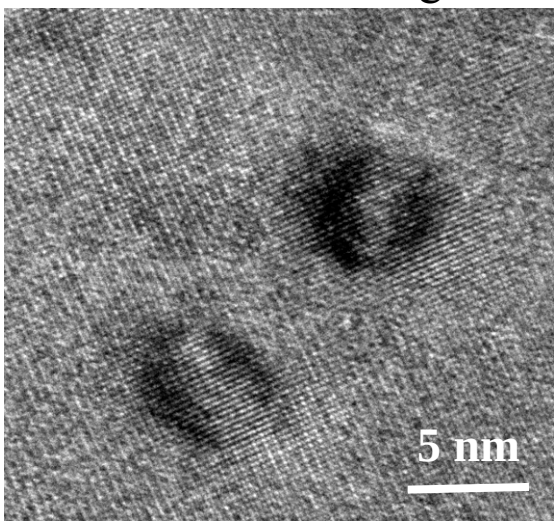
Thermal conductivity slightly decreases (5%)

Seebeck remains unchanged, while electrical conductivity remains improves slightly (~5-10%)

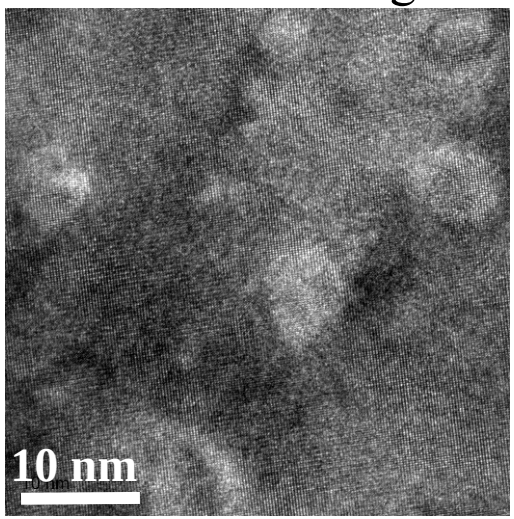
$Ag_{0.86}Pb_{19}SbTe_{20}$

600°C, 3 mos., vacuum (sealed silica tube)

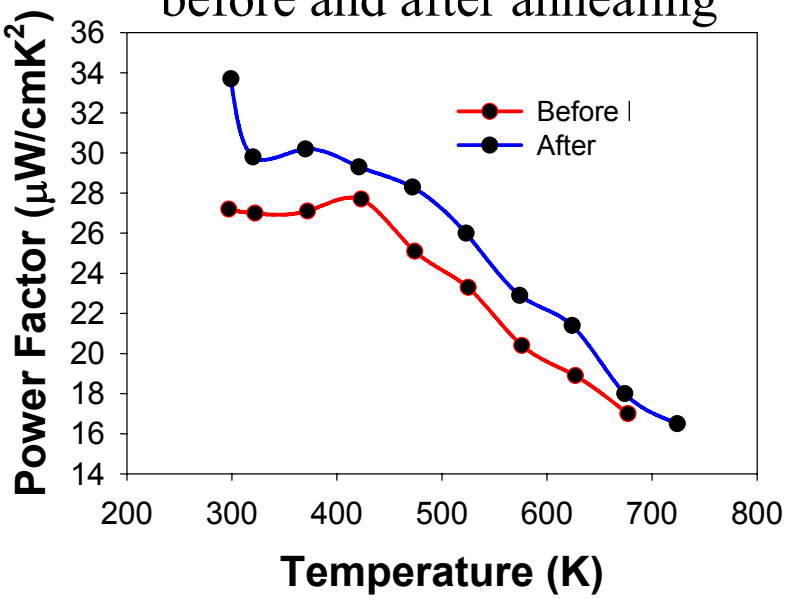
Before annealing



After annealing



Power factor measurements before and after annealing



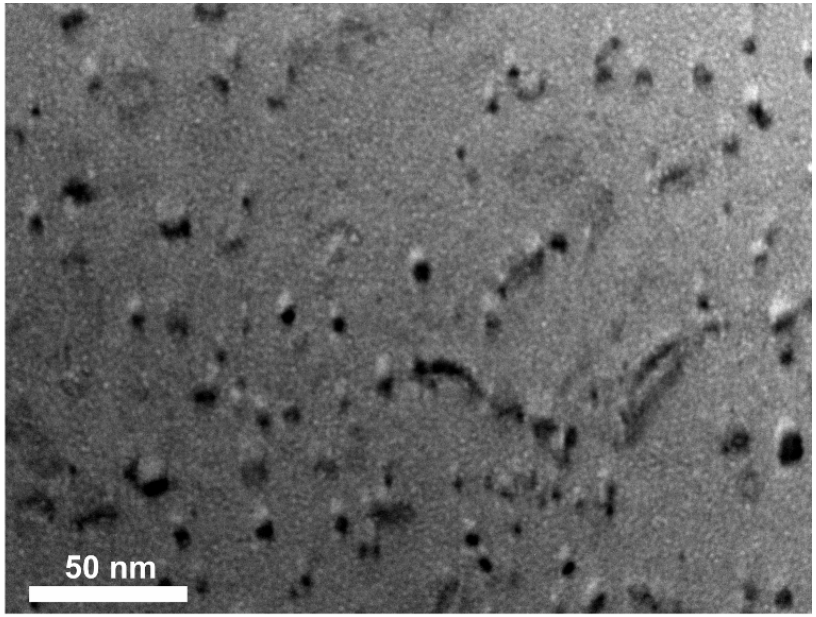
Note: images from the same material run, but not the same sample

Na-based materials (SALT-m)

$Na_{1-x}Pb_mSbTe_{2+m}$

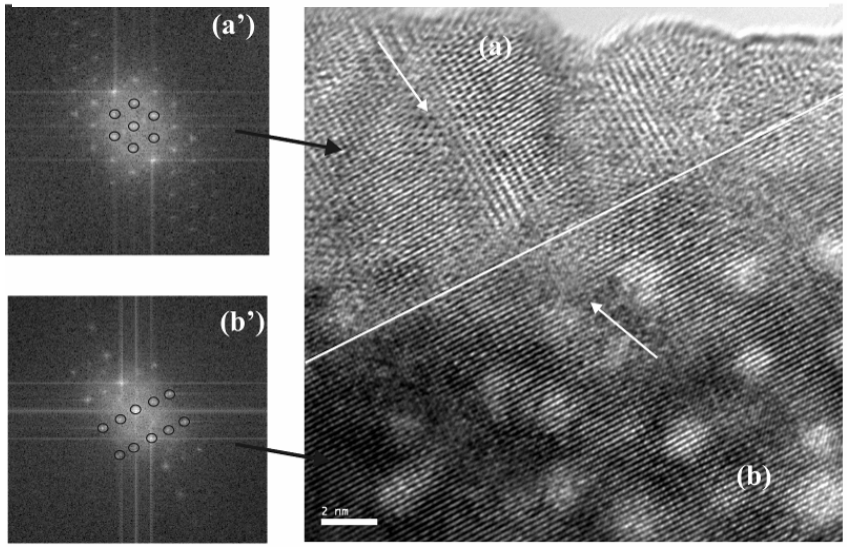
m~19-21

p-type
ZT~1.6 670 K



Energy bad gaps

SALT-18	0.37 eV
LAST-18	0.29 eV

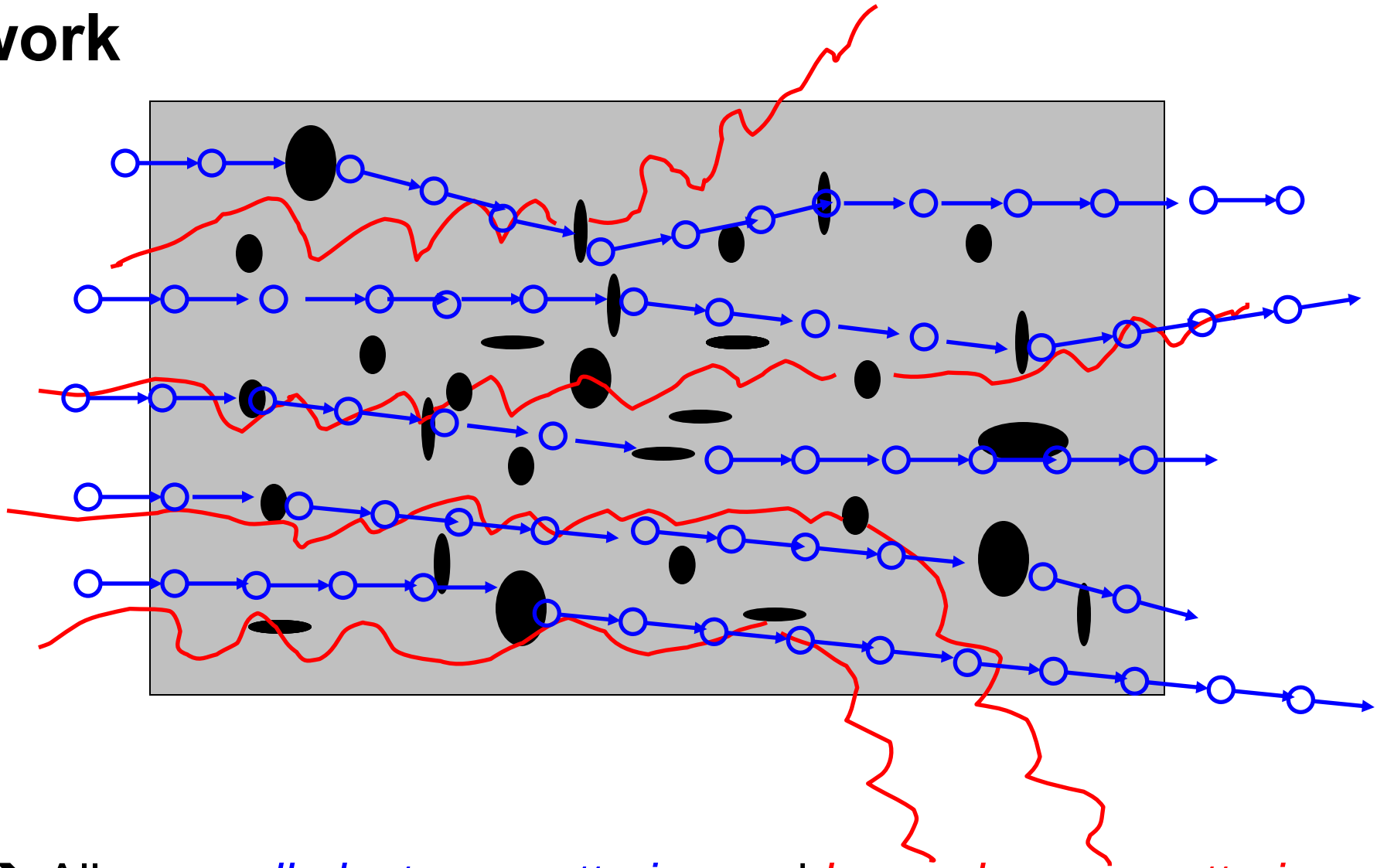


2 nm (B)

SALT κ_{latt} < LAST κ_{latt}

0.5 W/mk

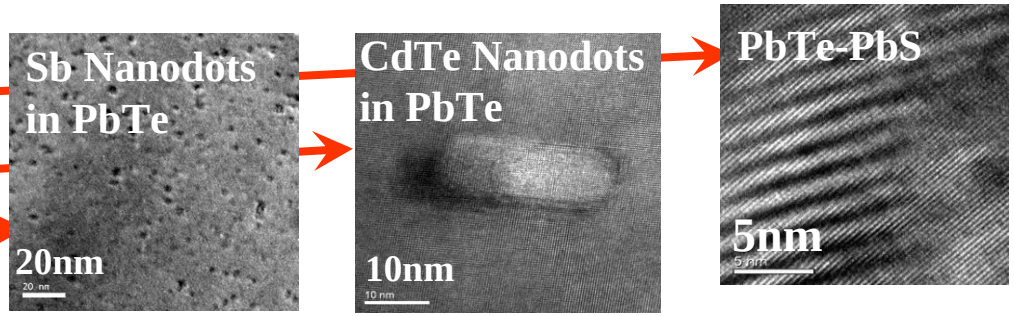
How *Nanostructured* Thermoelectrics work



➔ Allow *small electron scattering* and *large phonon scattering*

Major insights going forward

- New means of introducing nanostructures in bulk materials
  - Spinodal decomposition
  - Nucleation and growth
  - Liquid encapsulation

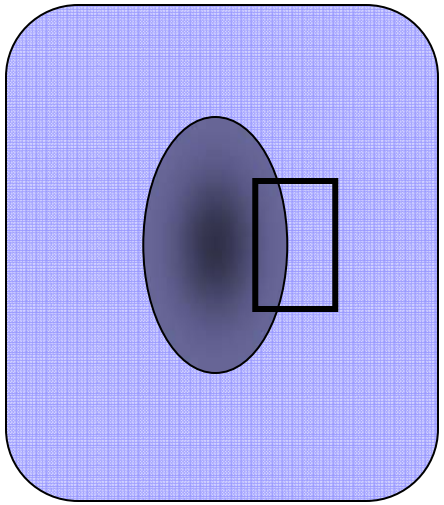


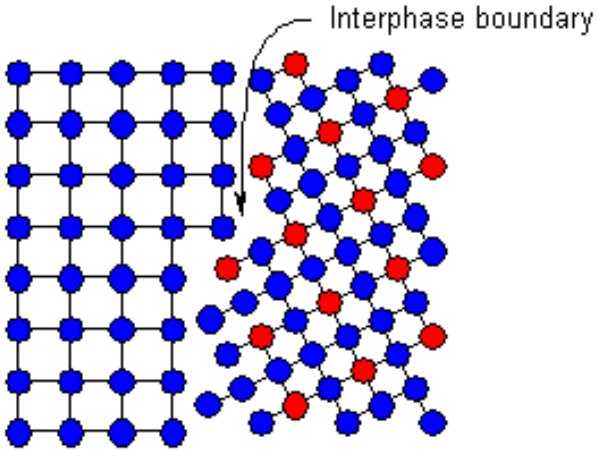
- Resonance states may be introduced in the band structure of PbTe to enhance power factor by adding substitutional dopands (Cd) or nanoparticles (Pb, Sb)

Interfaces:

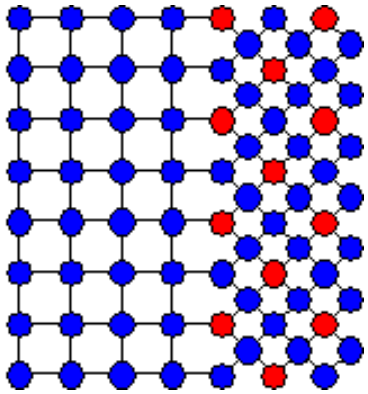
God is in the details!

- ➔ **Localized and delocalized strain accommodation**
- ➔ **Chemical interdiffusion**
- ➔ **High temperature behavior**
- ➔ **3-D distribution**
- ➔ ***Spatial variation across length-scales: atomic to microscale***

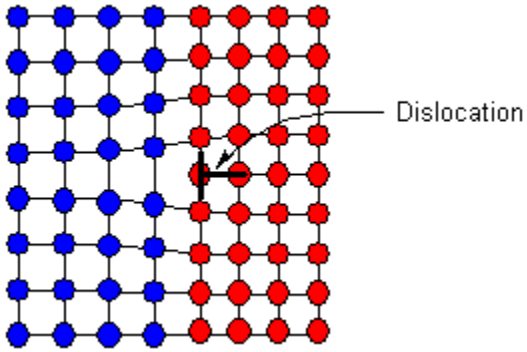




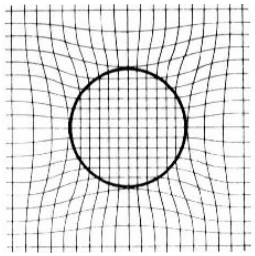
Incoherent interface

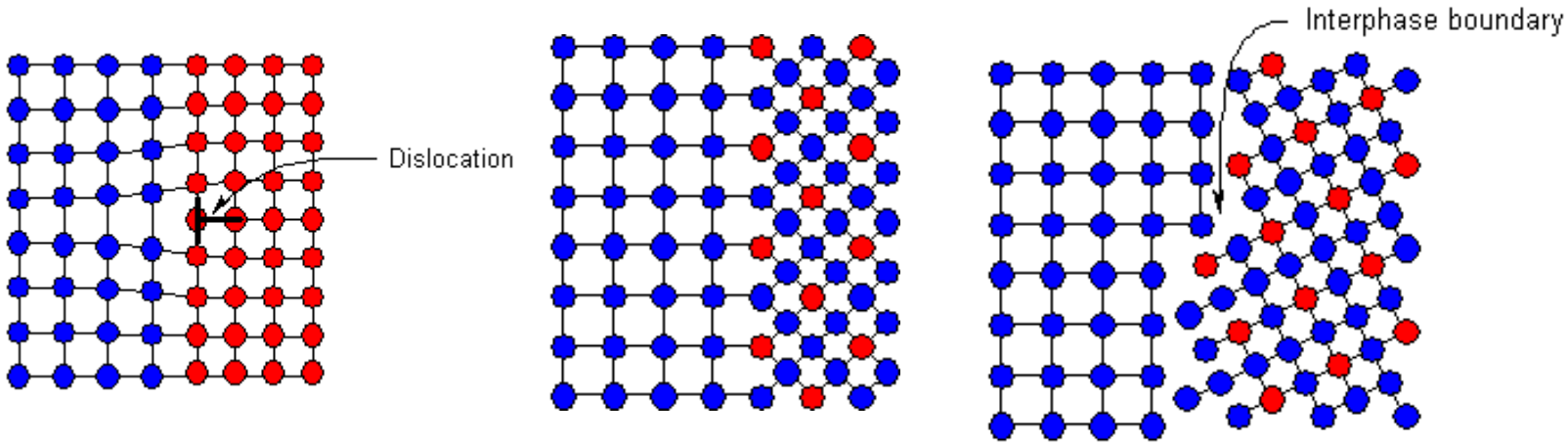


Coherent (strained) interface



Semi-coherent interface



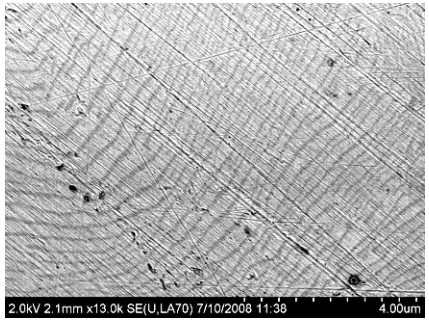

Dislocation
Interphase boundary

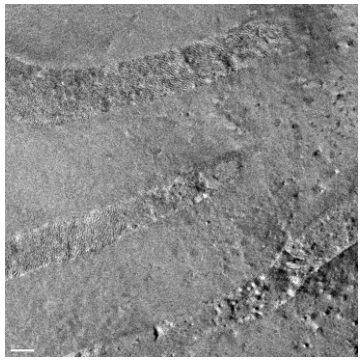
Controlling nanostructuring

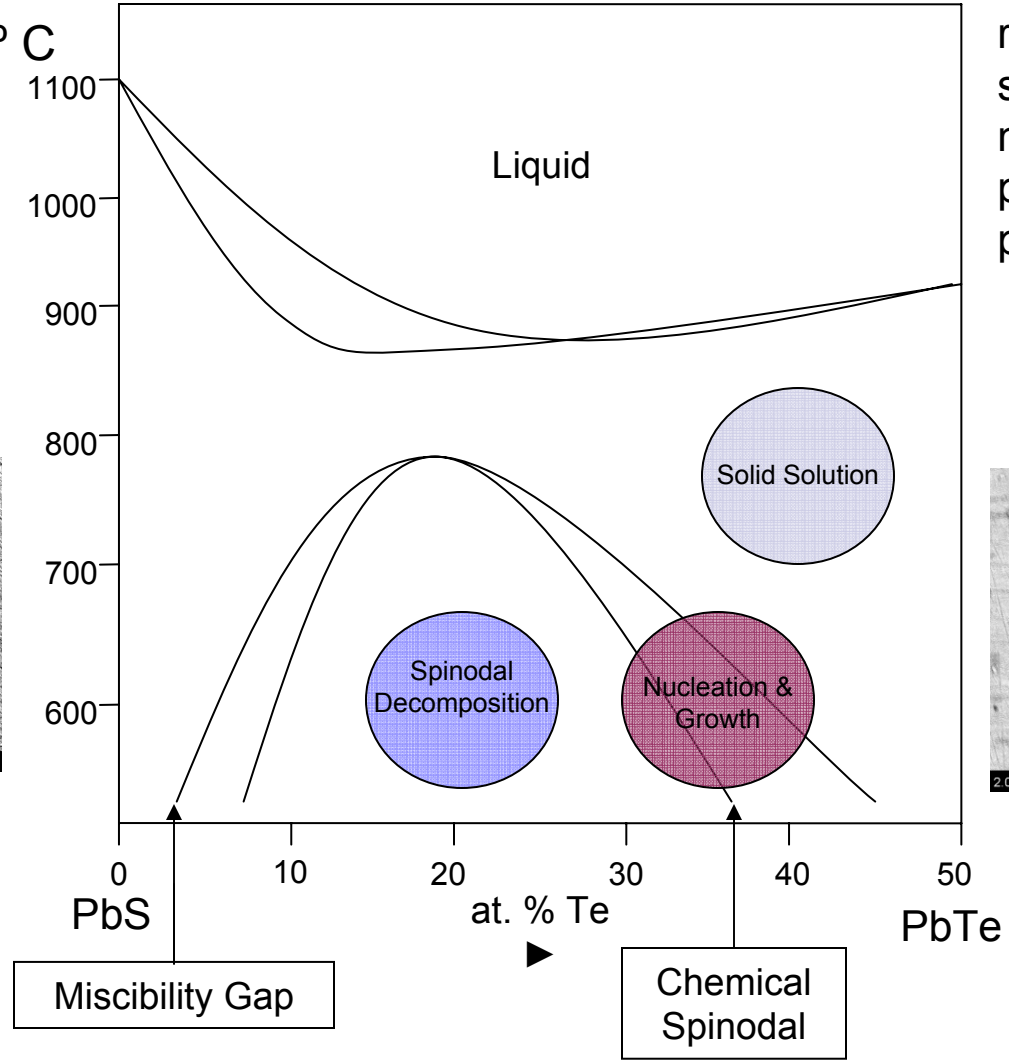
- Spinodal decomposition
- Nucleation and growth
- Liquid encapsulation

PbTe – PbS system – nanostructuring phenomena.

- **Spinodal decomposition** results in phase segregation by compositional fluctuations that begin at a very small scale.
  - Segregation of PbTe- and PbS- rich bands 20 – 200 nm in width



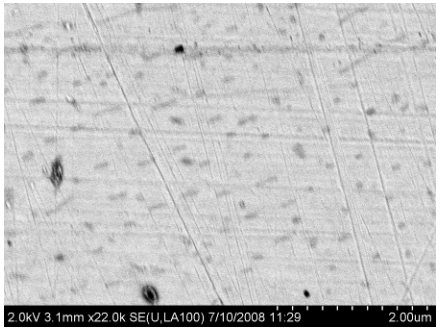


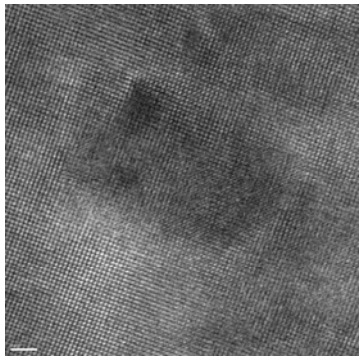


Nucleation and growth

results in phase segregation by nucleation of particles of the minor phase.

- Spherical nanoparticles 2 – 500 nm in diameter.

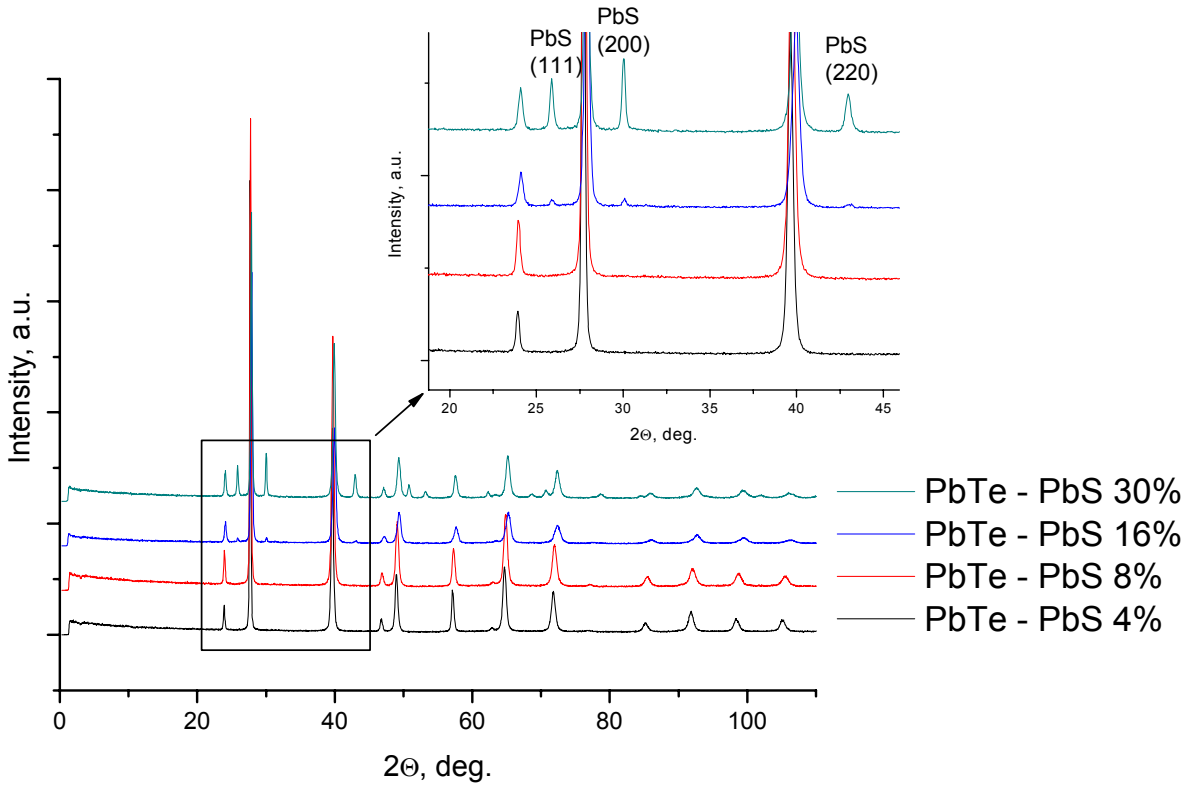




Androulakis, J. et al., *JACS* 2007, *129*, 9780-9788.

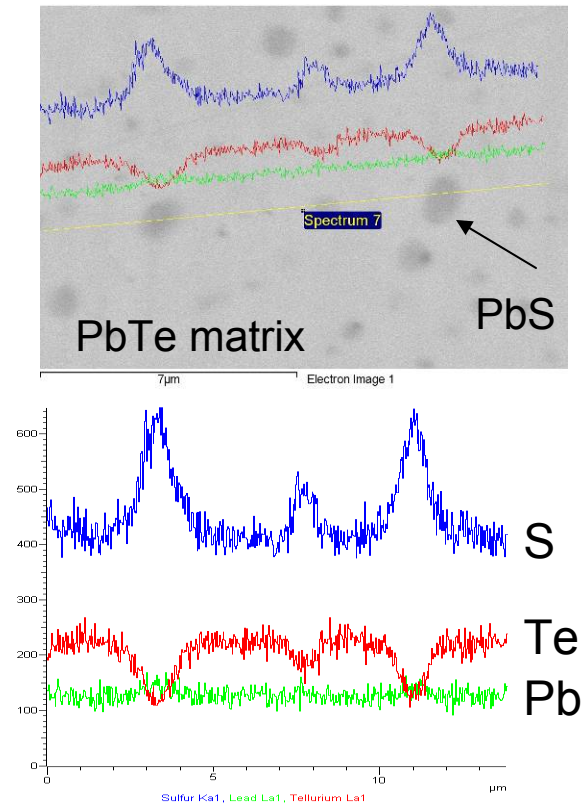
Powder X-Ray diffraction and EDS analysis

Powder X-Ray diffraction patterns



For compositions of PbTe – PbS > 8%, a large second phase of PbS is detected by PXRD.

Energy dispersive spectroscopy (EDS) in SEM

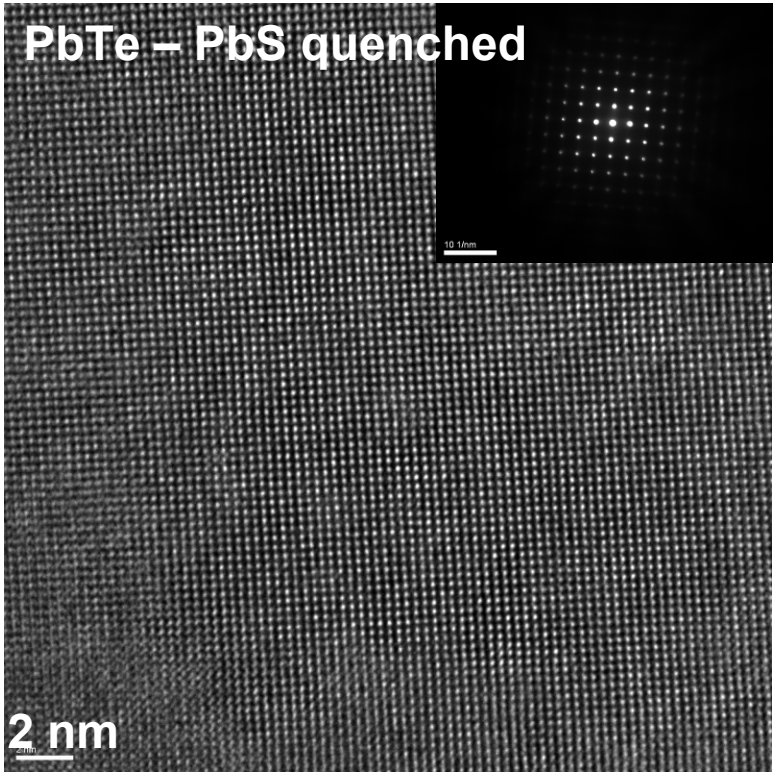


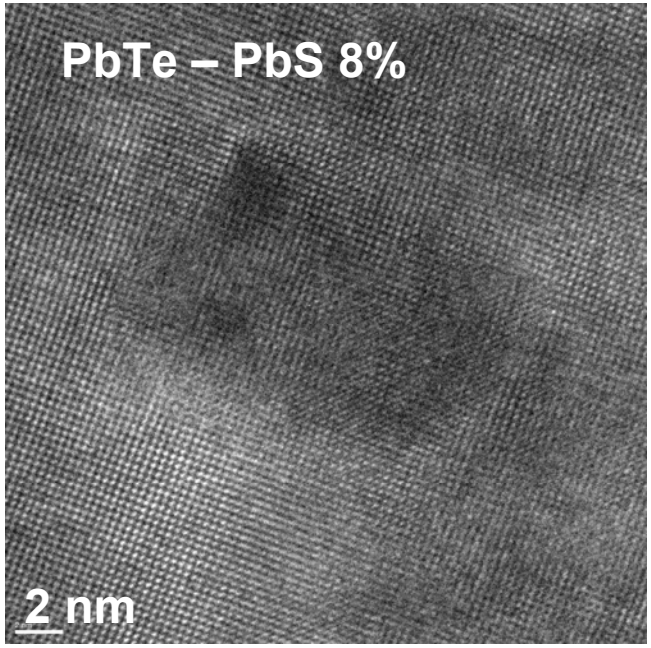
EDS line scans show presence of PbS particles within the PbTe matrix.

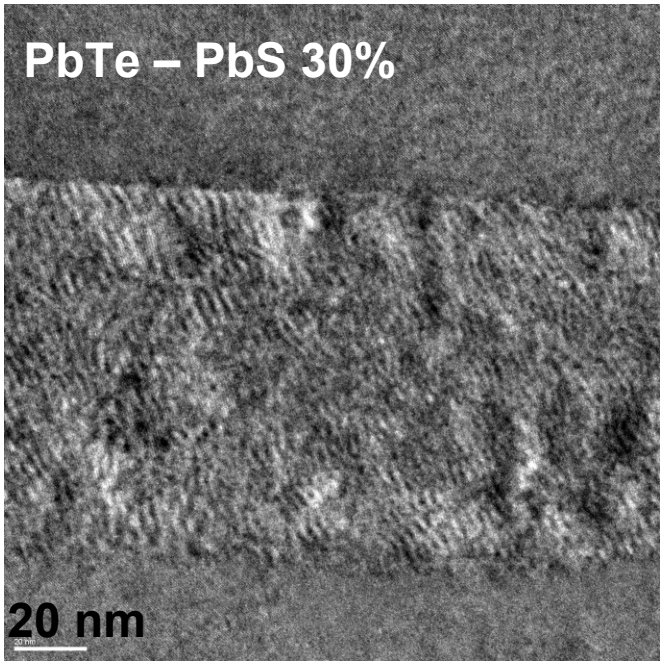
Androulakis, J. et al., *JACS* 2007, *129*, 9780-9788.

Steven Girard

Quenched vs. Annealed samples



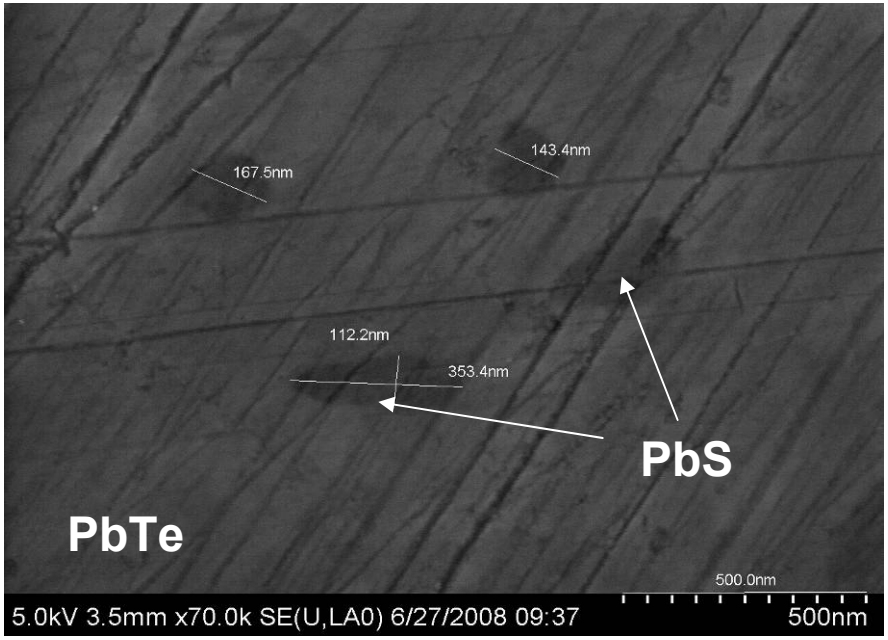


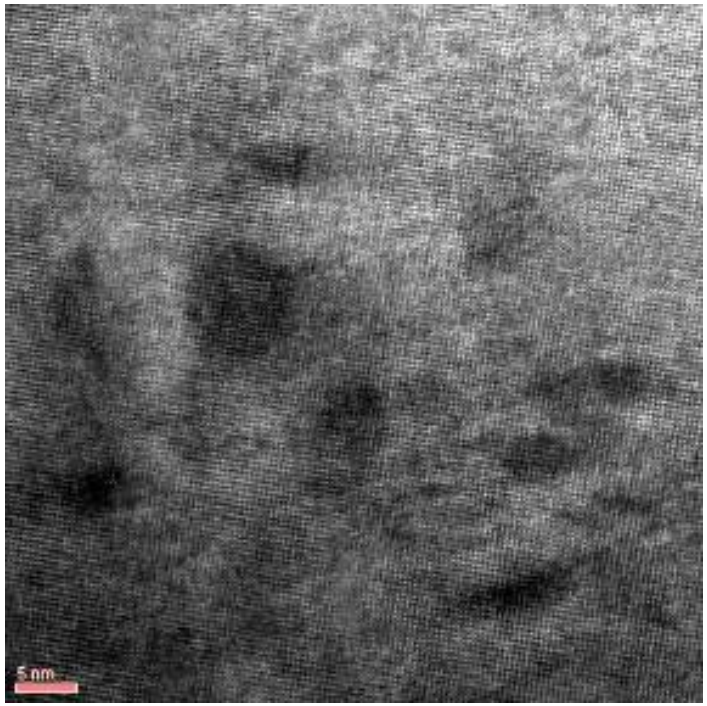


Annealing of samples allows for coherent PbS nanostructures to precipitate from the PbTe matrix.

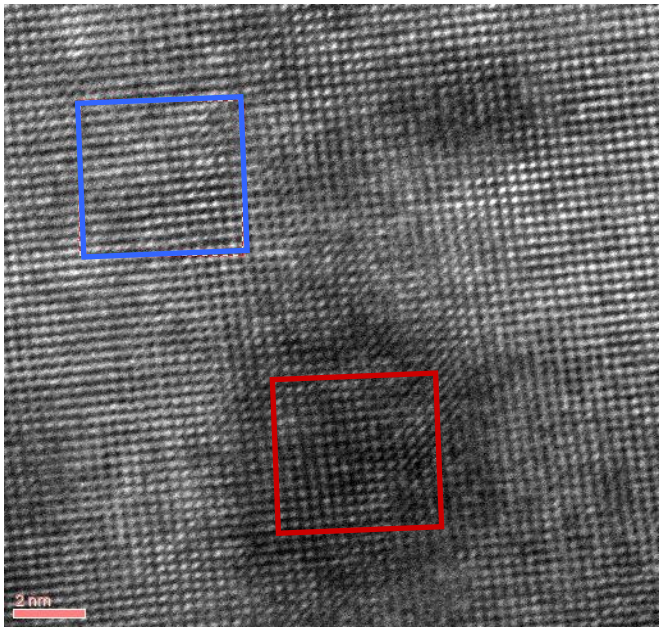
Jiaqing He, Vinayak Dravid

PbTe-PbS8% sample

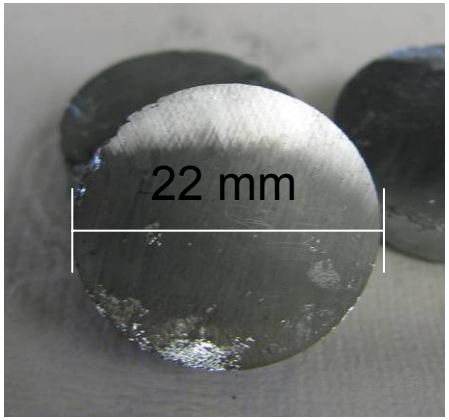


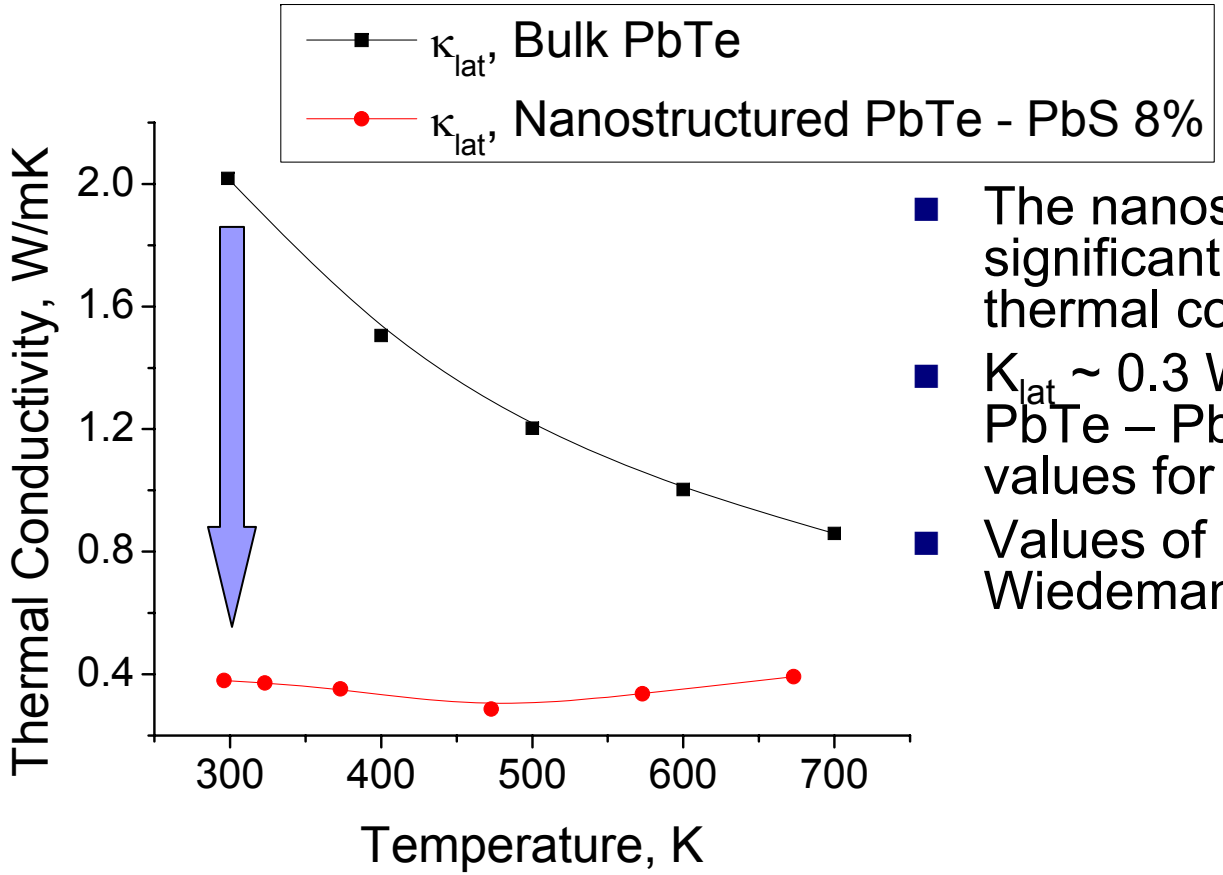


Two types of precipitates:
- large one by SEM image
- small precipitate with smaller lattice parameters.



Thermal conductivity





- The nanostructures help to significantly reduce lattice thermal conductivity.
- K_{lat} ~ 0.3 W/mK observed for PbTe – PbS 8%, among lowest values for a bulk system.
- Values of K_{lat} calculated using Wiedemann-Franz law.

Large-scale synthesis of PbTe – PbS 8%

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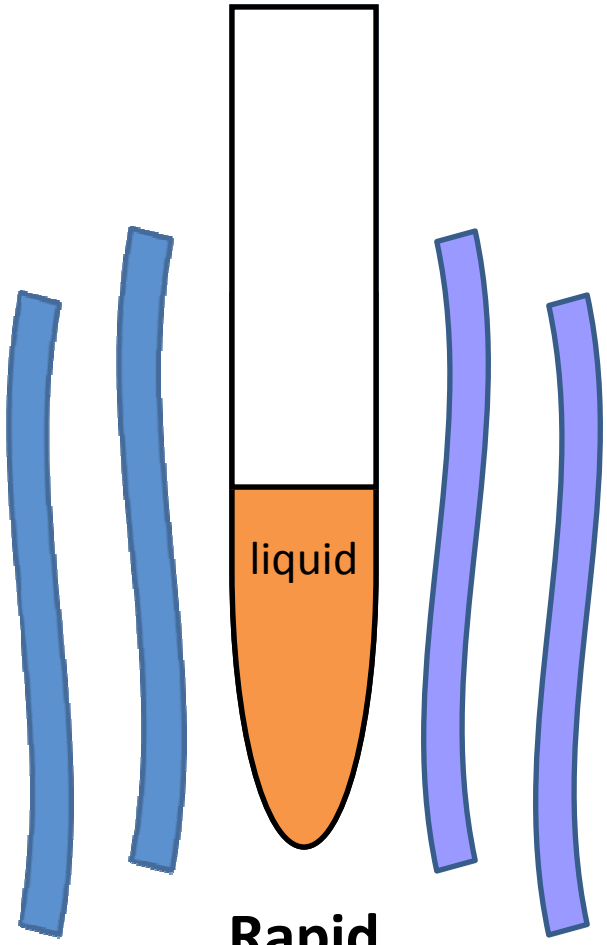
Creating a solid solution alloy of $PbS_{0.08}Te_{0.92}$



Rapid cooling

(in air)

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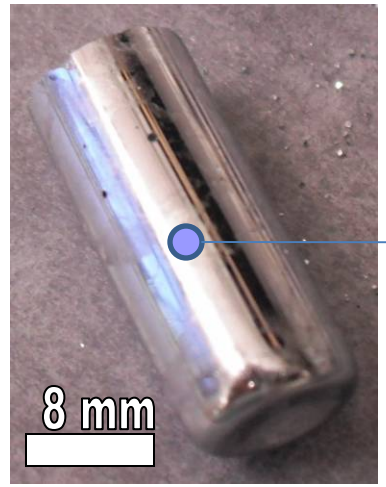
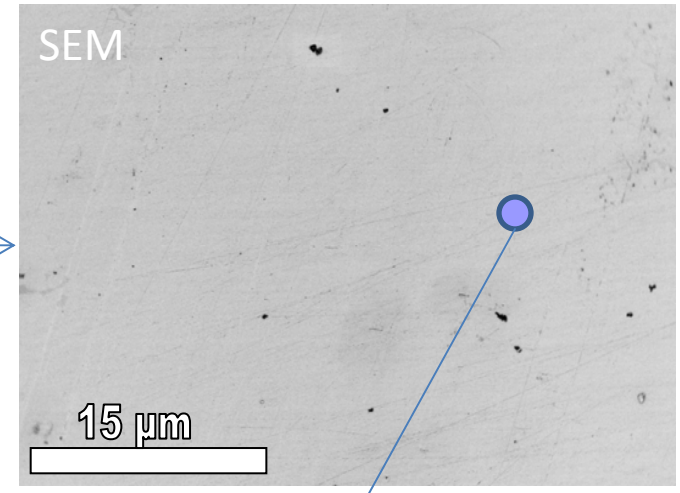


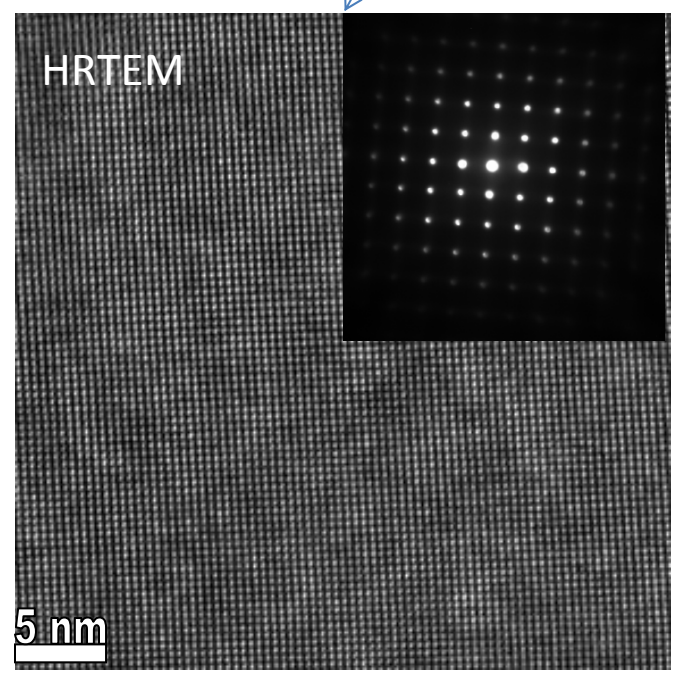
As-prepared ingot

We can confirm the rapidly cooled ingot is a solid solution alloy of $PbS_{0.08}Te_{0.92}$.

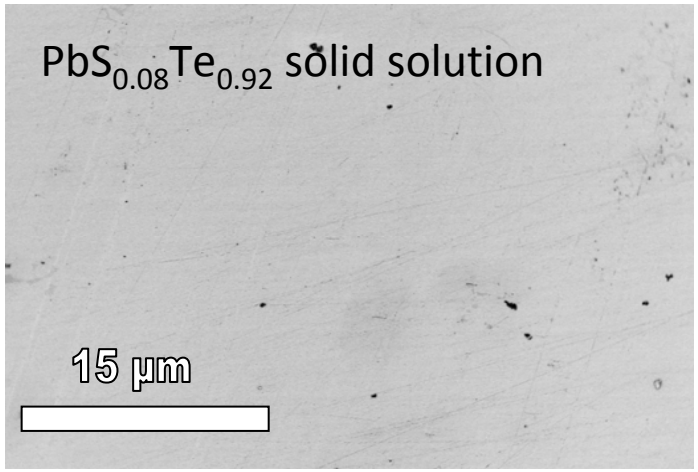
There is no presence of PbS particles.

Solid solution alloy of $PbS_{0.08}Te_{0.92}$



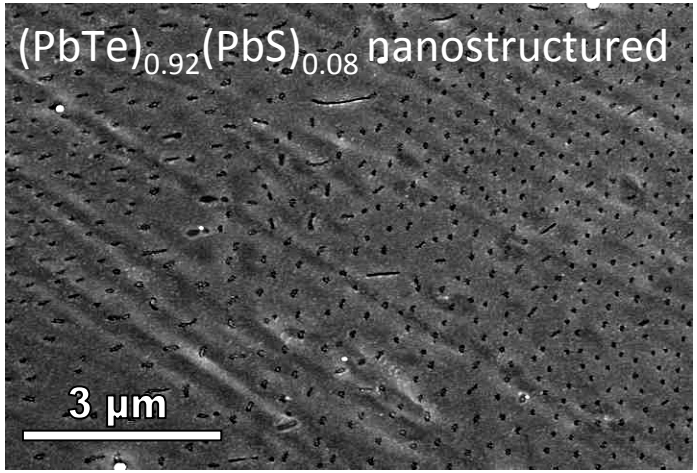


Inducing precipitation of PbS: $PbS_{0.08}Te_{0.92}$ to $(PbTe)_{0.92}(PbS)_{0.08}$

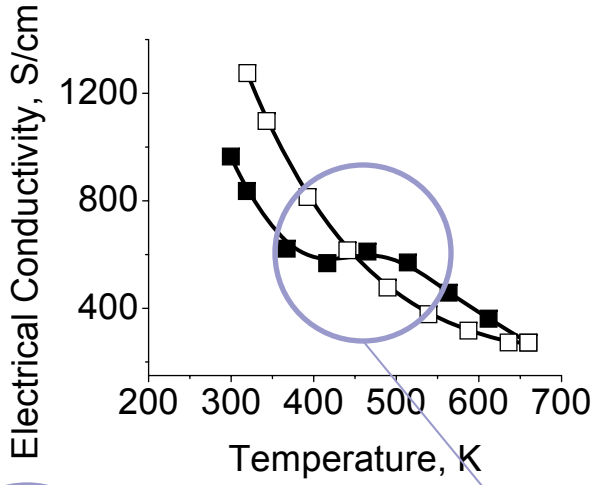


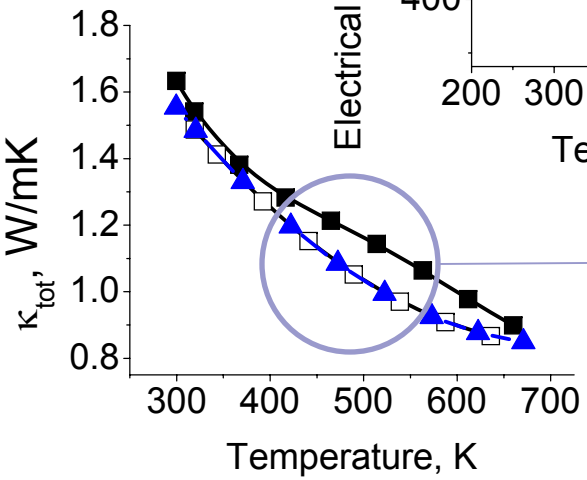
High-temperature measurement

Induces precipitation of PbS

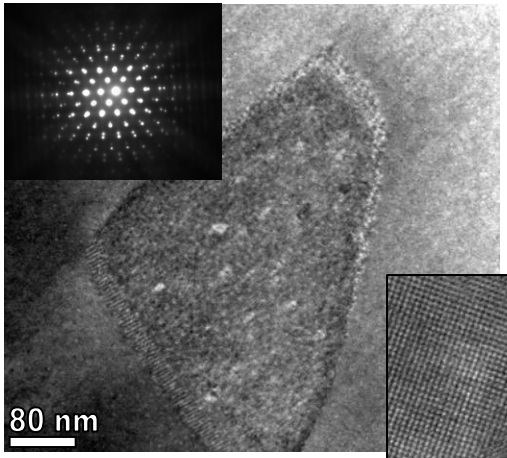


Precipitation is observed in TE measurements.



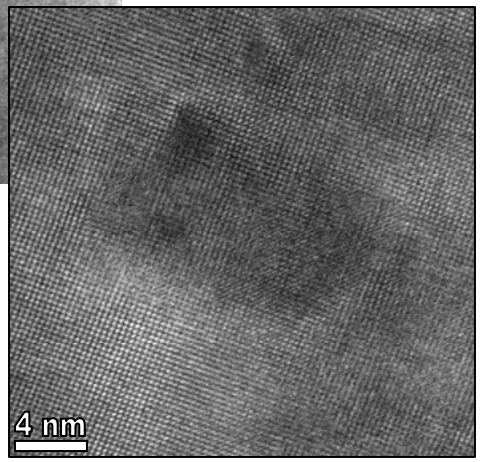


Precipitation occurs

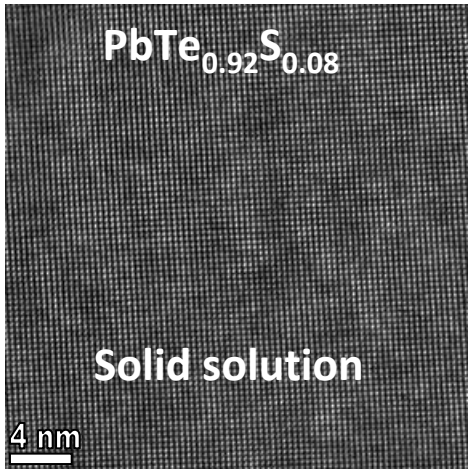


Particle size range 200 – 2 nm

Particles are PbS rich.



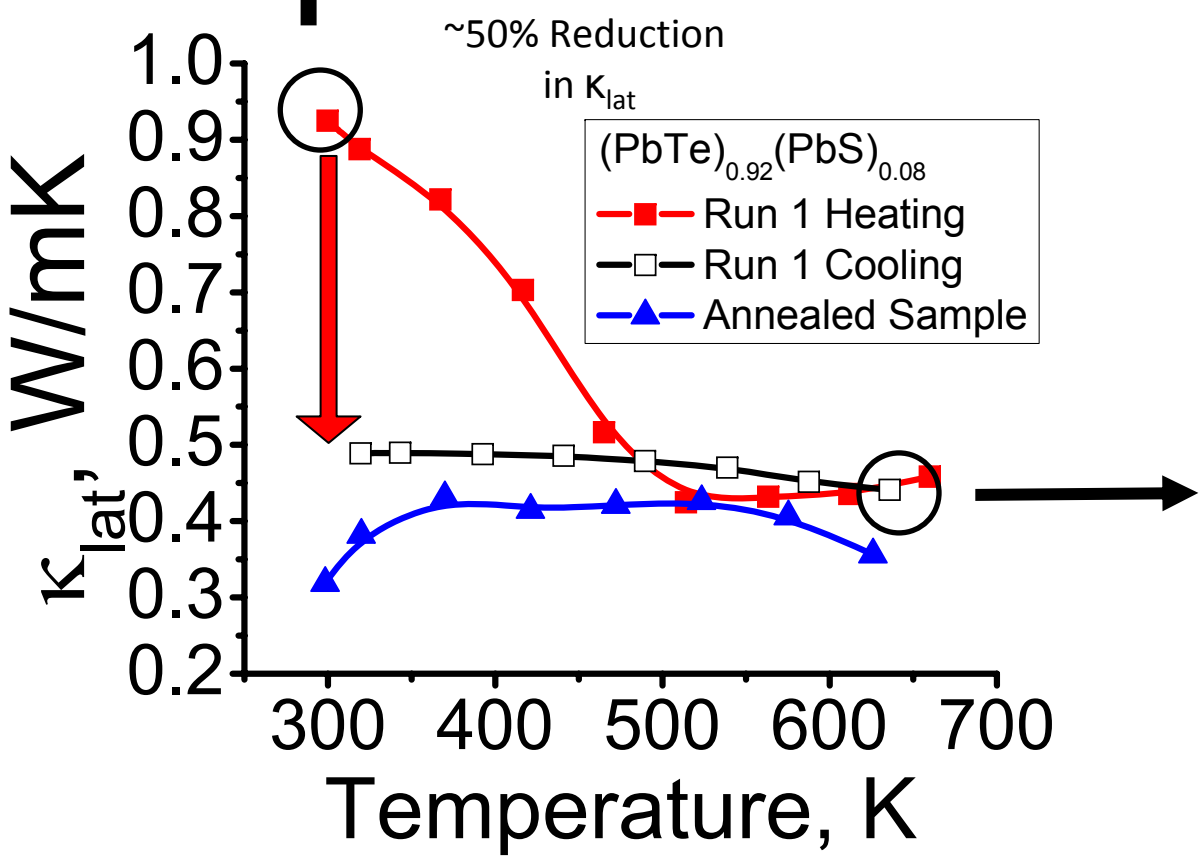
Significant reduction in κ_{lat}

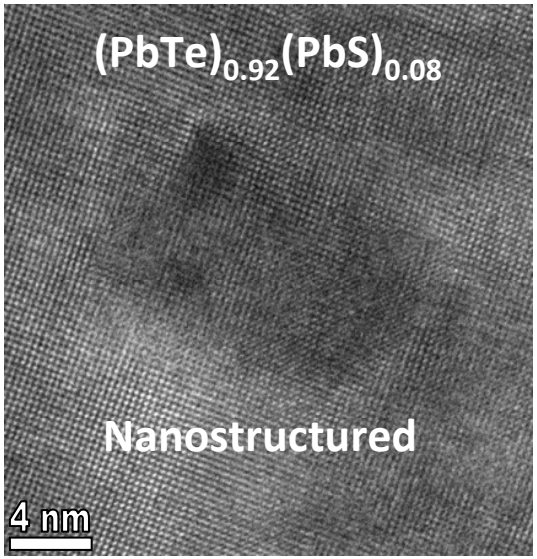


$$PbTe_{0.92}S_{0.08} \xrightarrow{heat} (PbTe)_{0.92}(PbS)_{0.08}$$

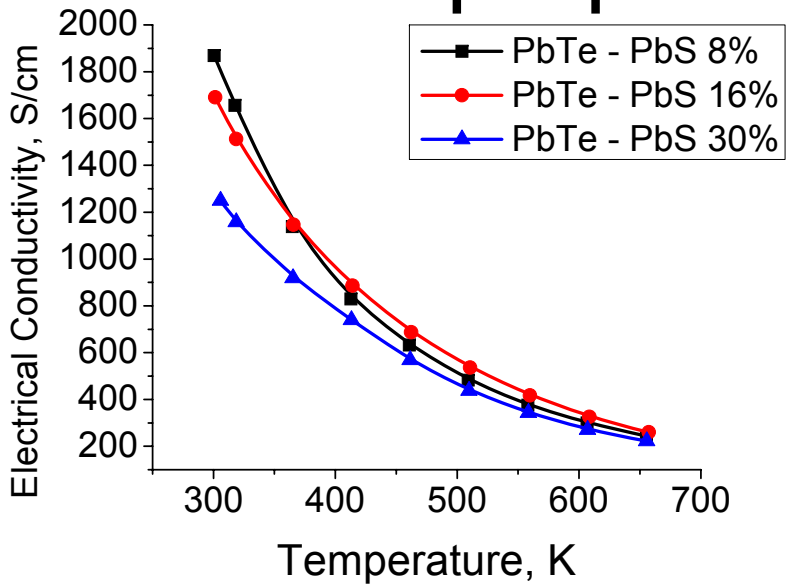
Solid solution — Nanostructured

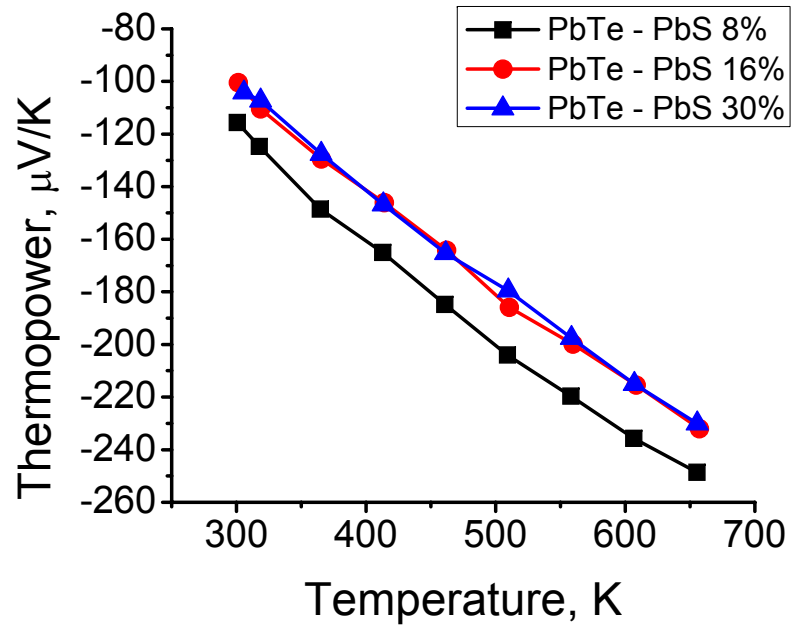
We can see the effect of nanoscale precipitation of PbS *in situ* on the lattice thermal conductivity.

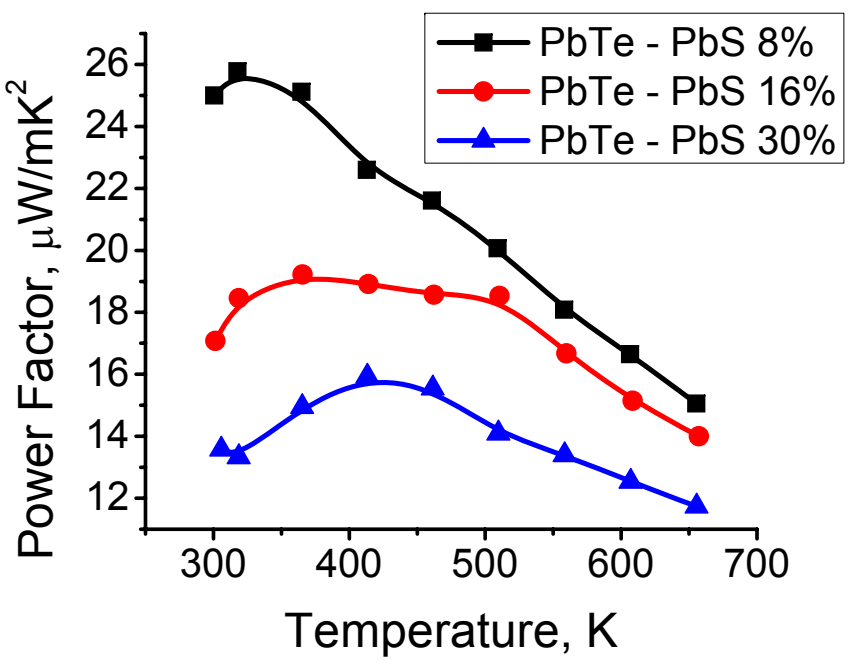




Electrical properties







All samples doped n-type with PbI_2.

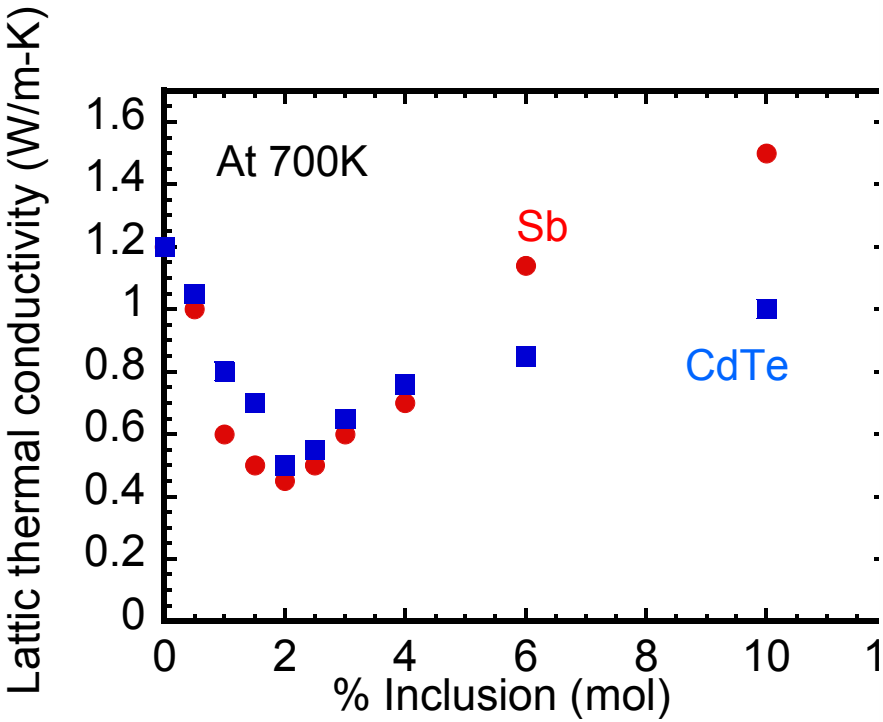
Even with nanostructures embedded throughout matrix, electrical transport is very similar to doped PbTe.

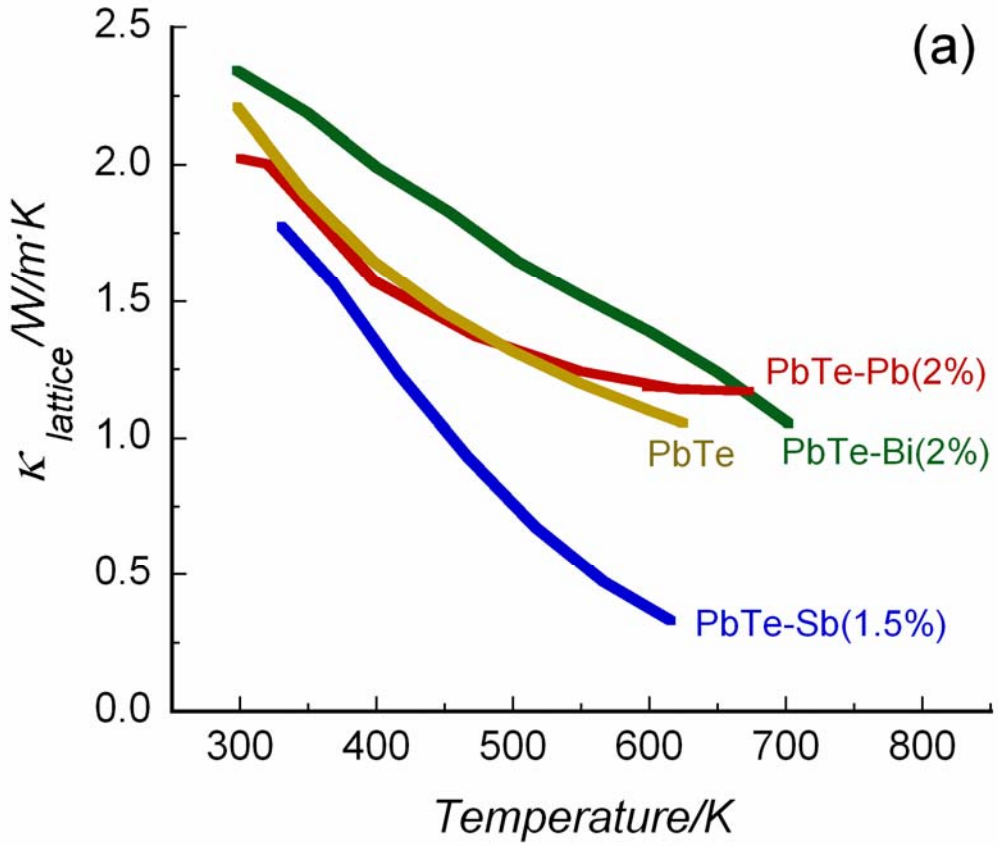
Power factor is optimized for PbTe – PbS 8%.

Steven Girard

Nanostructuring PbTe with inclusions

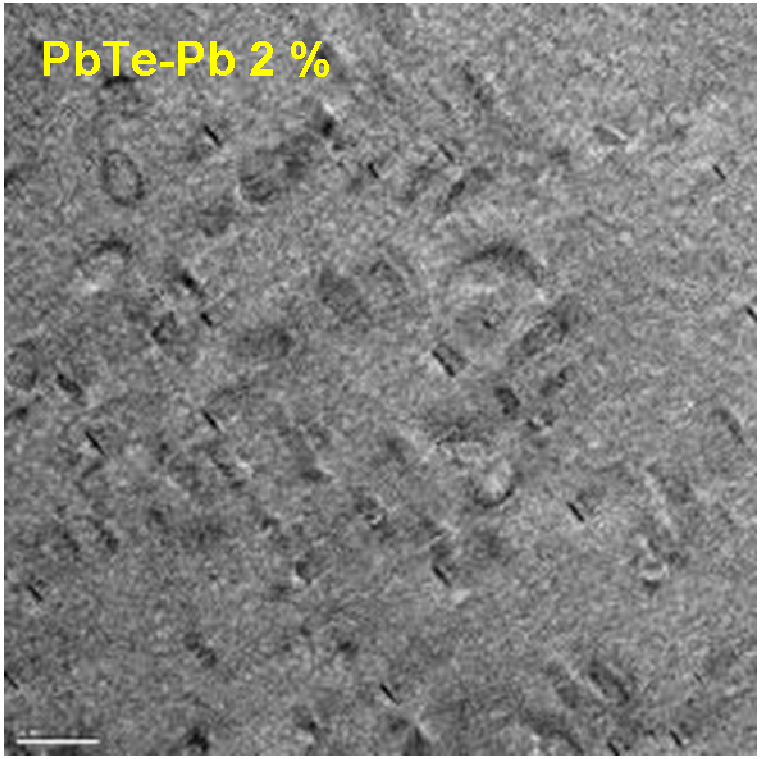
Liquid encapsulation technique

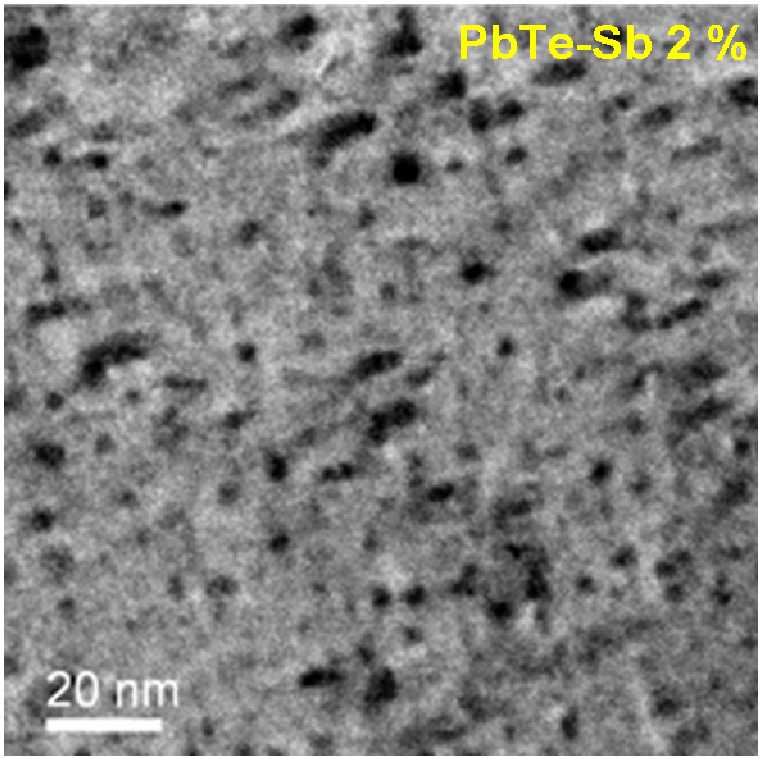




Joe Sootsman, Kyunghan Ahn

TEM diffraction contrast and Phase contrast (HREM) imaging/analysis

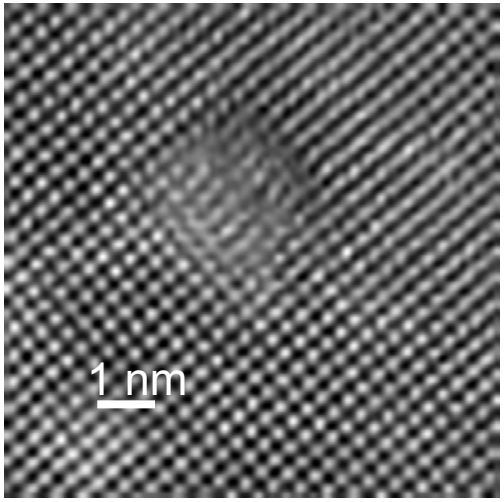


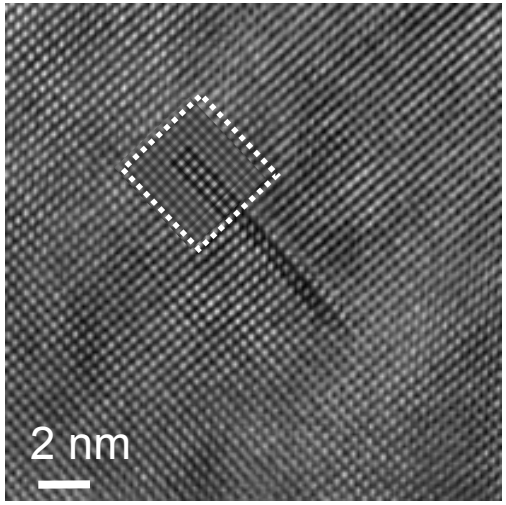


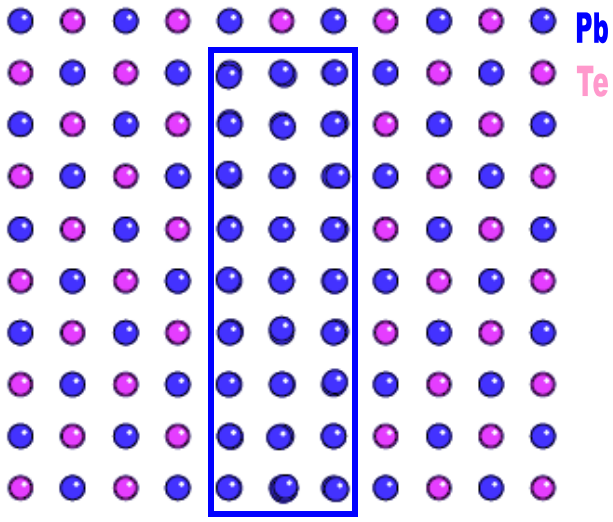
PbTe-Pb 2 % **PbTe-Sb 2 %**

Jiaqing He

[001] **[010]**



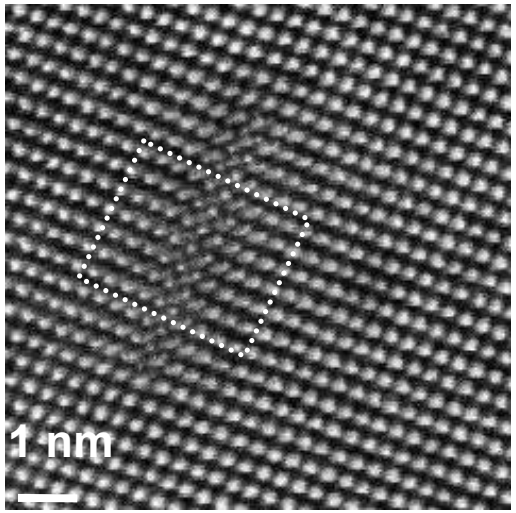


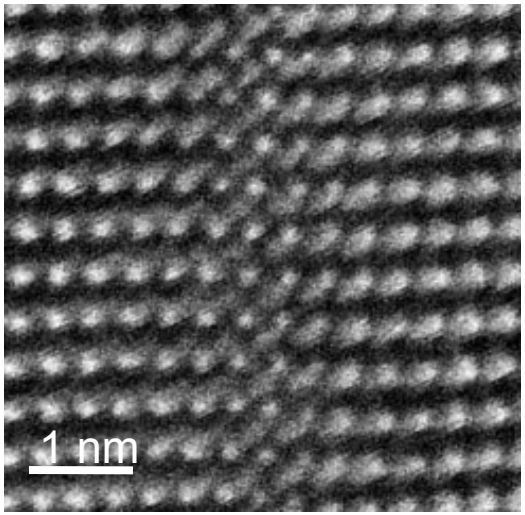


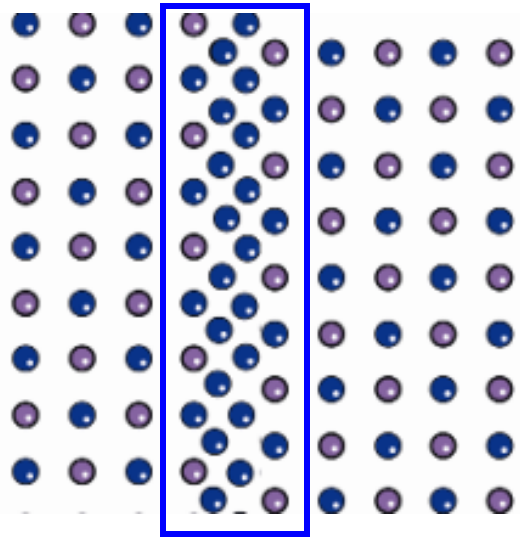
PbTe-Pb 2%

Not all defects are alike

Pb-rich Defects



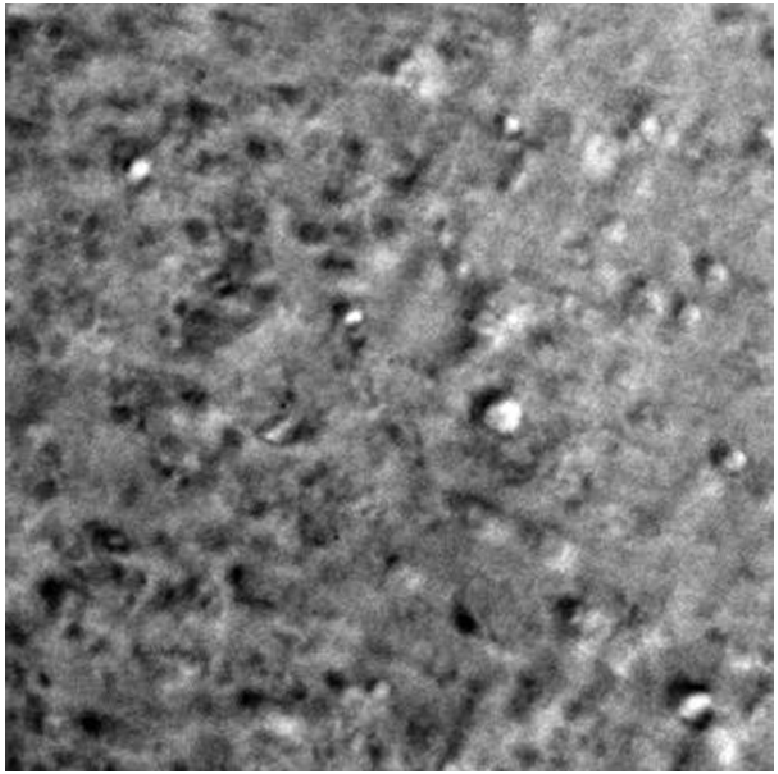


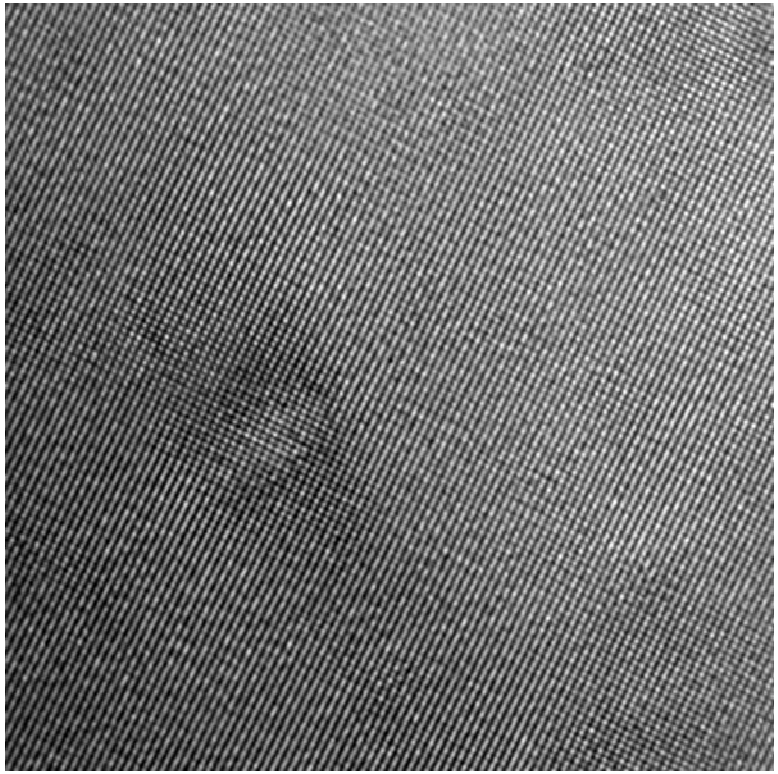


STEM HAADF

TEM of PbTe-Sb(1.5%)

- Small precipitates at RT





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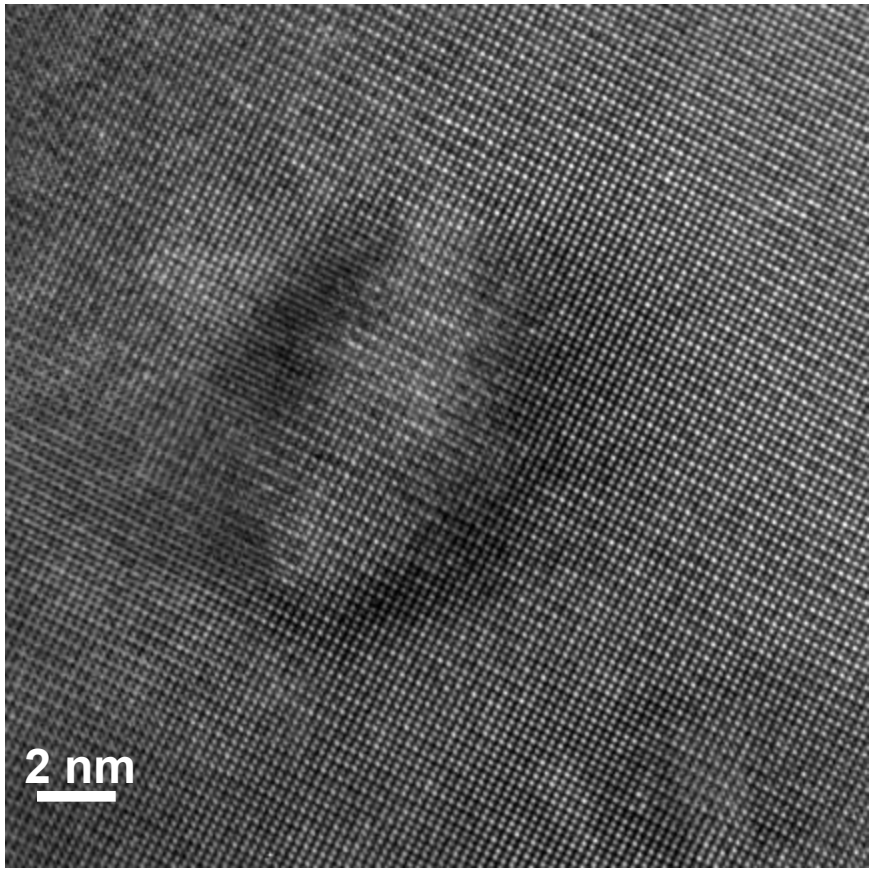
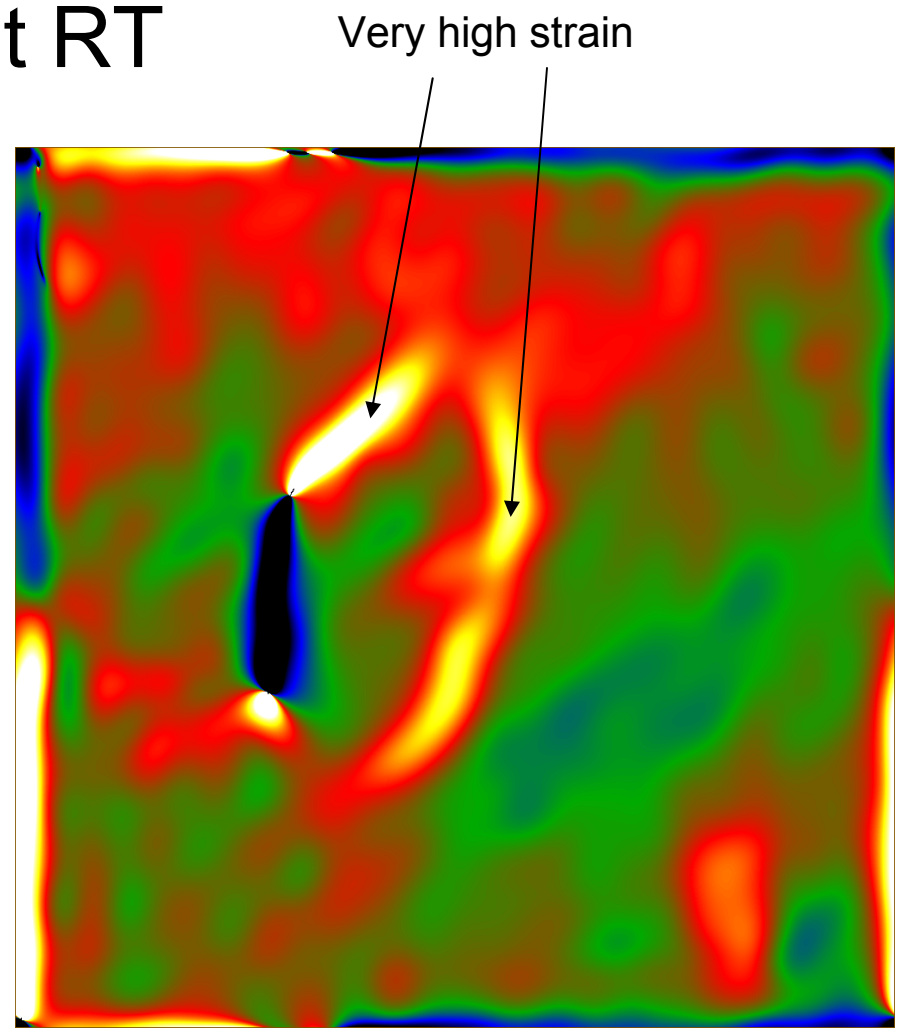
TEM of PbTe-Sb(1.5%)

- Small precipitates at RT





Strain Analysis

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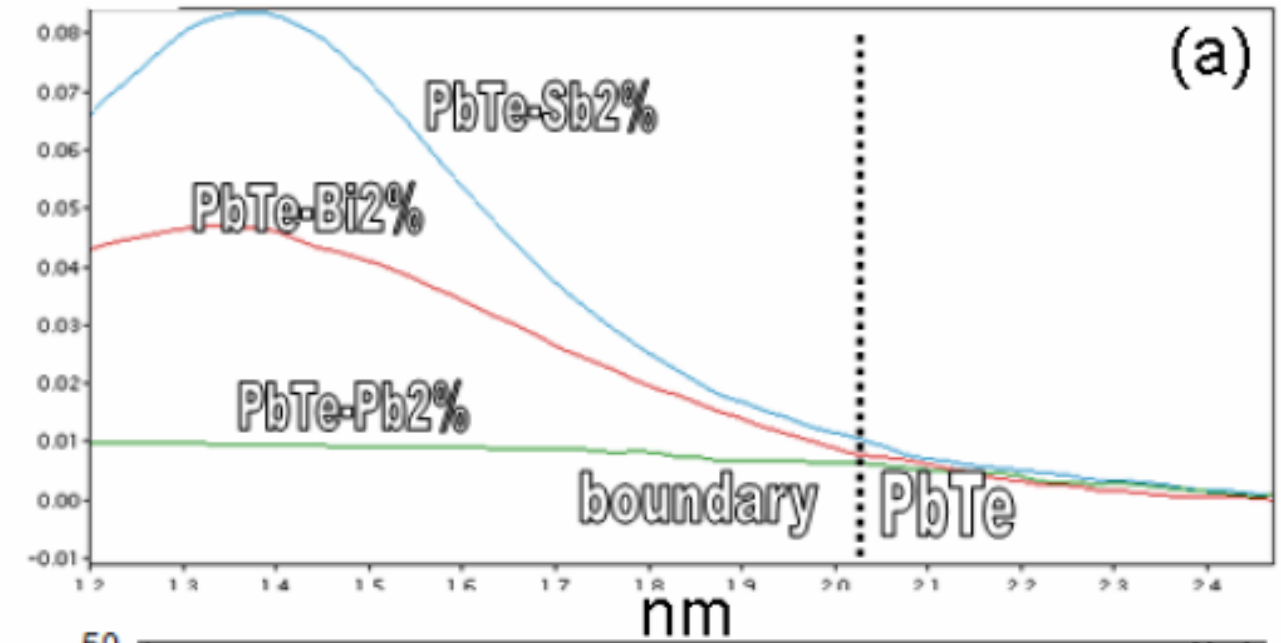
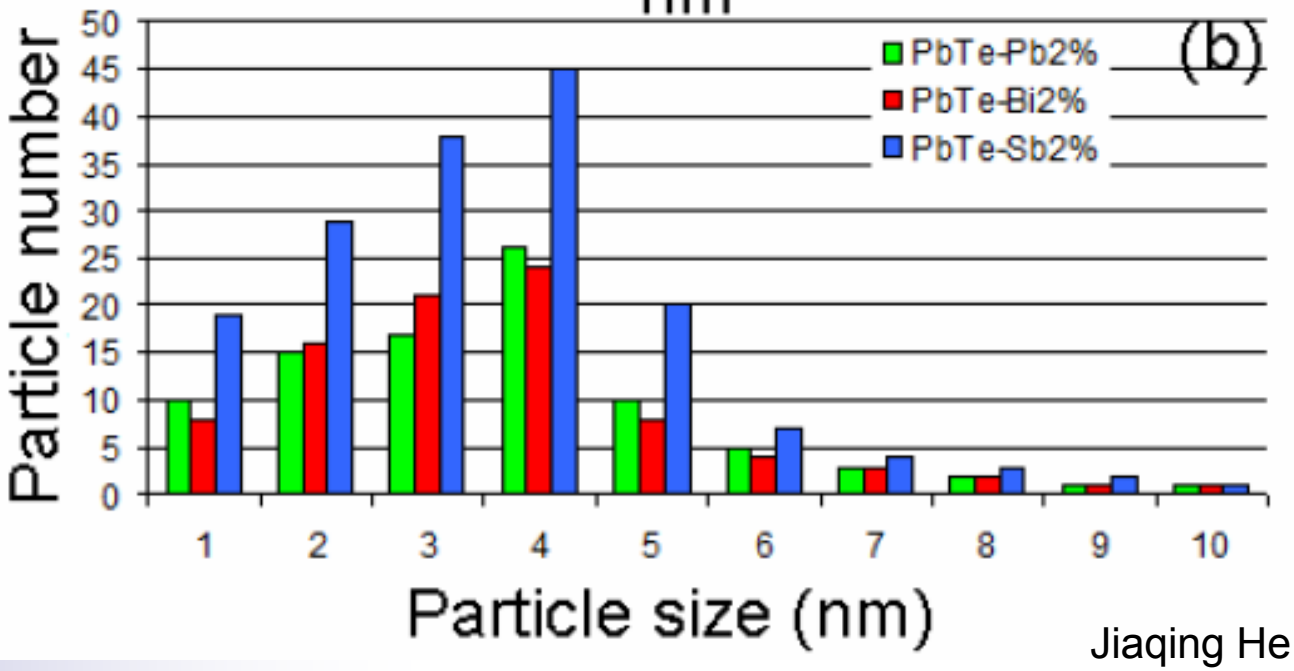
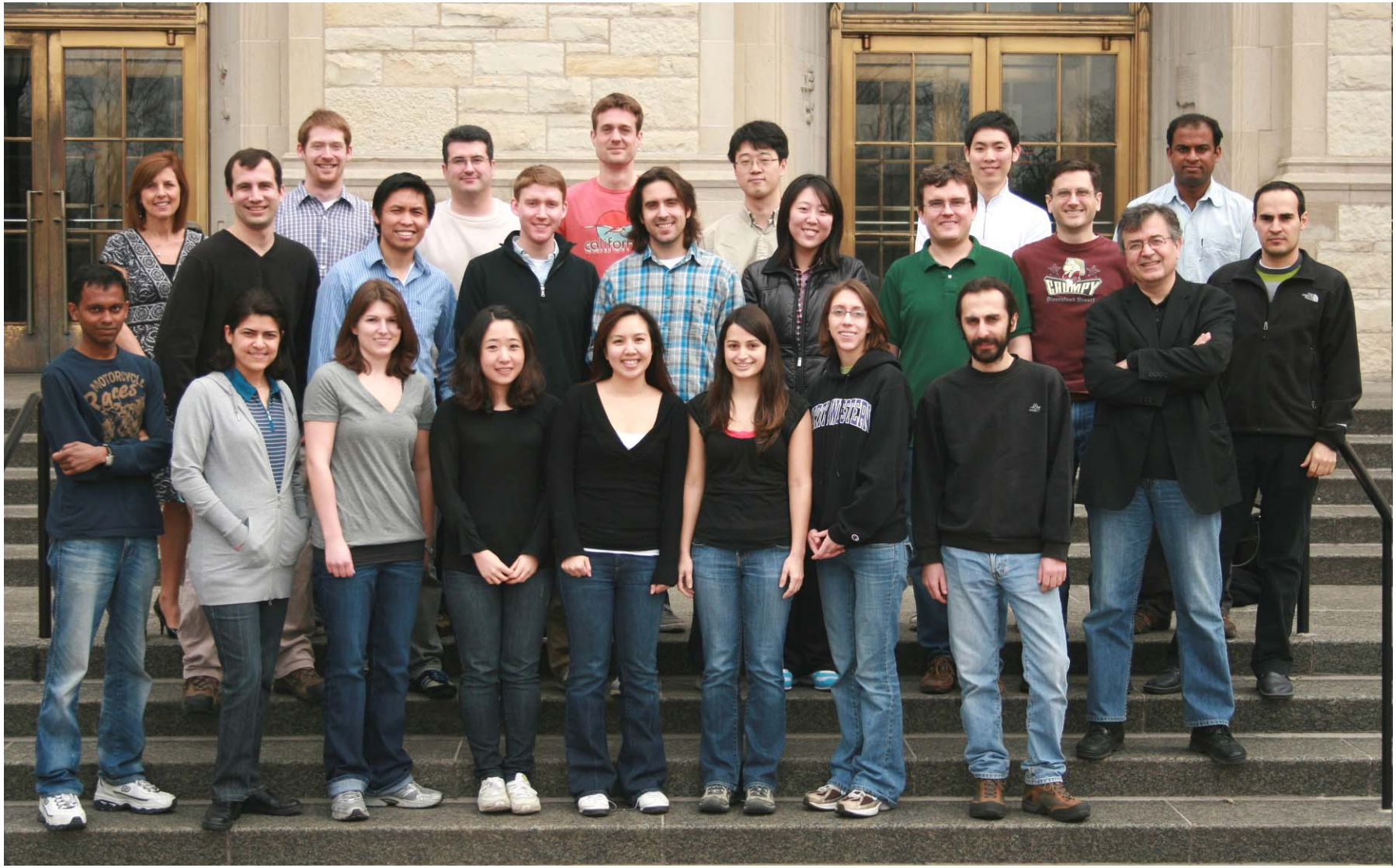

(a)
PbTe-Sb2%
PbTe-Bi2%
PbTe-Pb2%
boundary
PbTe
nm


(b)
PbTe-Pb2%
PbTe-Bi2%
PbTe-Sb2%
Particle number
Particle size (nm)

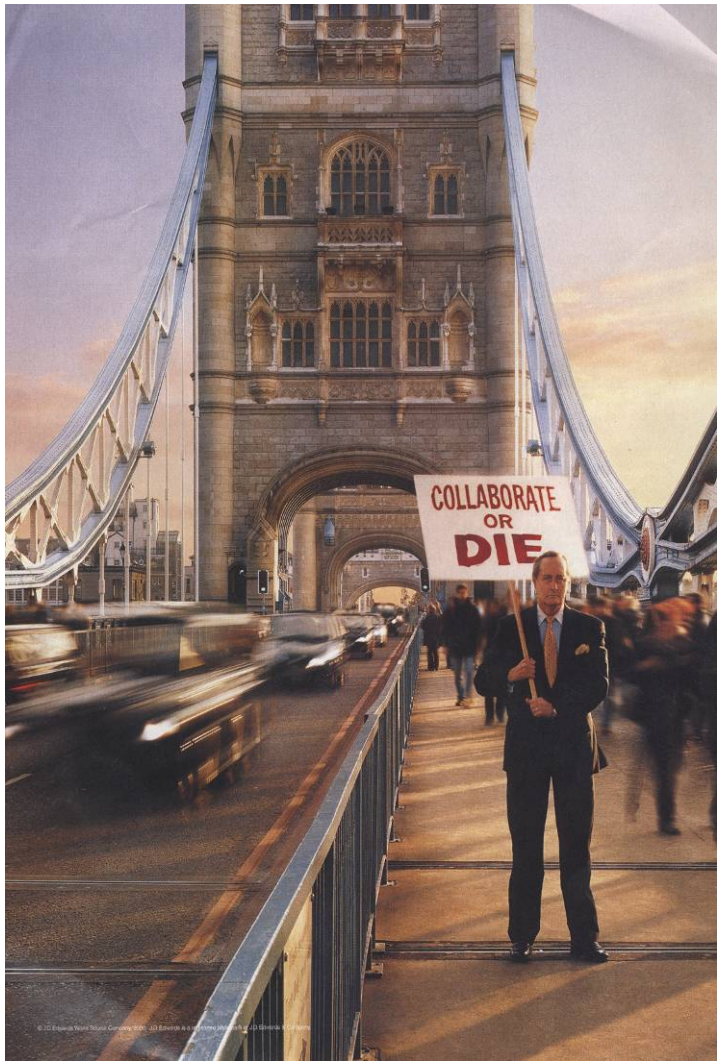
Jiaqing He

Conclusions

- LAST, SALT: promising thermoelectric materials for power generation modules.
- PbTe-PbS system as good as LAST
- Properties very sensitive to synthesis conditions. Built-in inhomogeneity. Slow cooling is important.
- Nanostructures reduce the lattice thermal conductivity to 0.6-0.4 W/mK at 700K.
- 0.4 W/mK probably a minimum in PbTe
- Nanostructure stability is high but more studies needed.
- Co-nanostructuring PbTe produces PF enhancements



2010

Collaborators

- Tim Hogan, MSU
- S. D. (Bhanu) Mahanti, MSU
- Ctirad Uher, Michigan
- Simon Billinge, Columbia
- Eldon Case, MSU
- Vinayak Dravid, NU
- Art Freeman, NU
- David Seidman, NU
- SonBinh Nguyen, NU
- Chris Wolverton, NU
- Ray Osborn, Argonne
- Stephane Rosenkranz, Argonne
- Ken Gray, Argonne
- John Mitchell, Argonne
- Duck Young Chung, Argonne
- Gerasimos Armatas, U Crete