Spring 2008 ACS National Meeting
Sunday, April 6 — Thursday, April 10, 2008
New Orleans

Growing nanocrystals inside crystals for thermodynamically stable advanced thermoelectrics

Mercouri Kanatzidis, Northwestern University

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KANATZIDIS
NU, CHEMISTRY
Solid State Chemistry
Synthesis, Discovery

↔

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CTIRAD UHER
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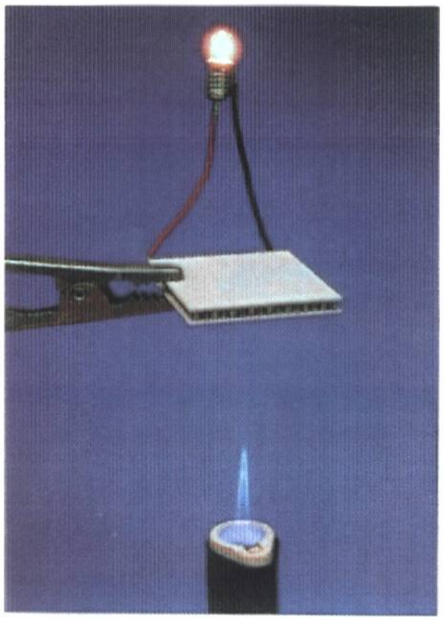
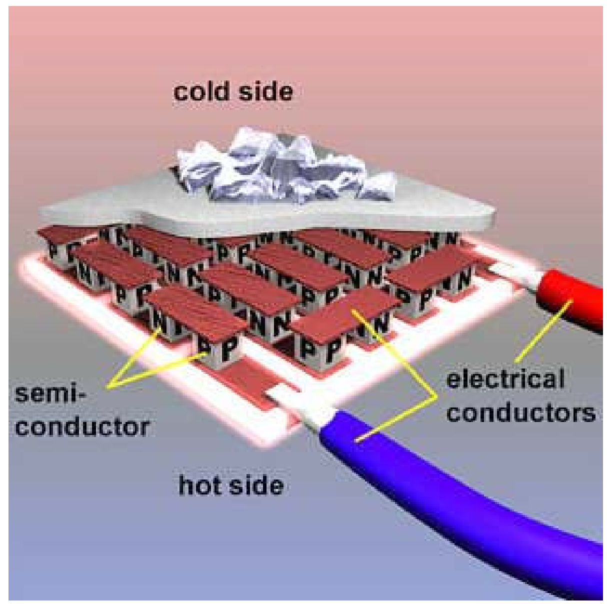
Physics
Measurements

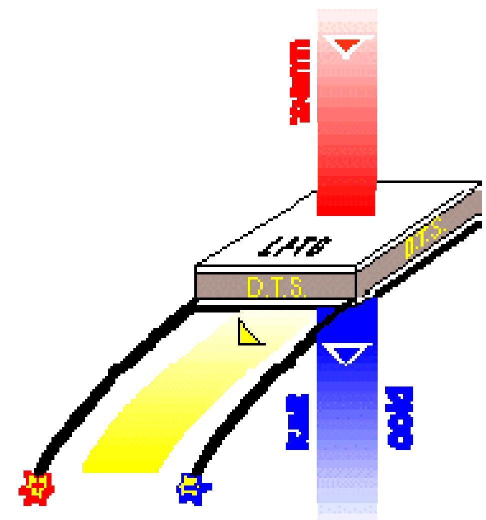
Heat to Electrical Energy Directly

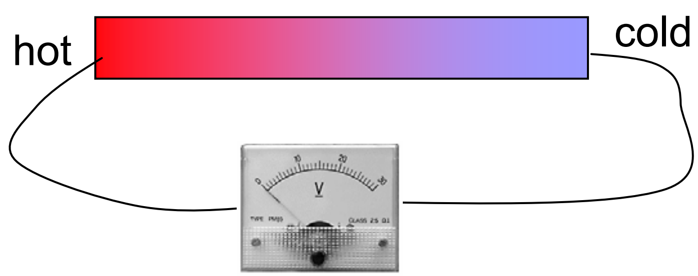
Up to 20% conversion efficiency with right materials



Electrical
Power Generation







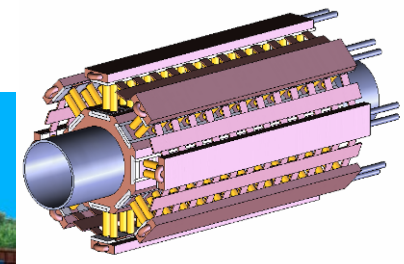
Thermopower $S = \Delta V / \Delta T$

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

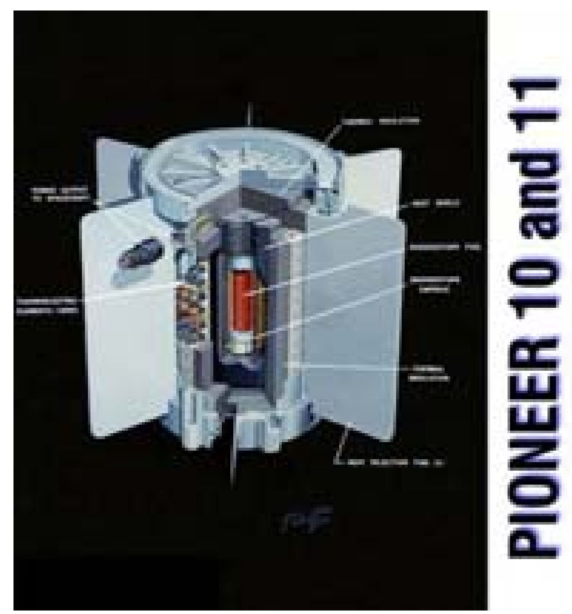
http://www.dts-generator.com/

Thermoelectric applications

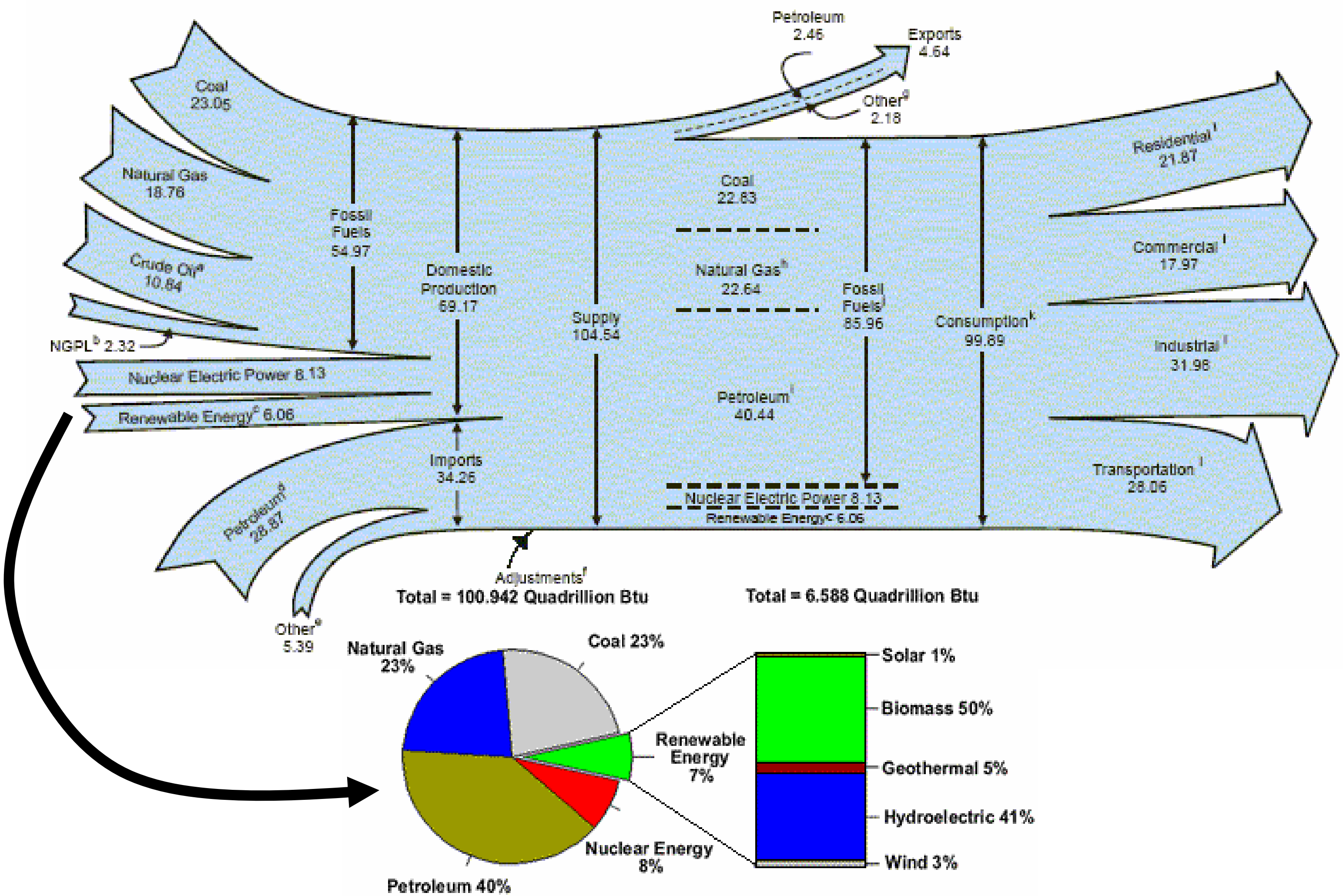
- Waste heat recovery
  - Automobiles
  - Over the road trucks
  - Utilities
  - Chemical plants



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



U.S. Energy Flow, 2006



http://www.eia.doe.gov/emeu/aer/

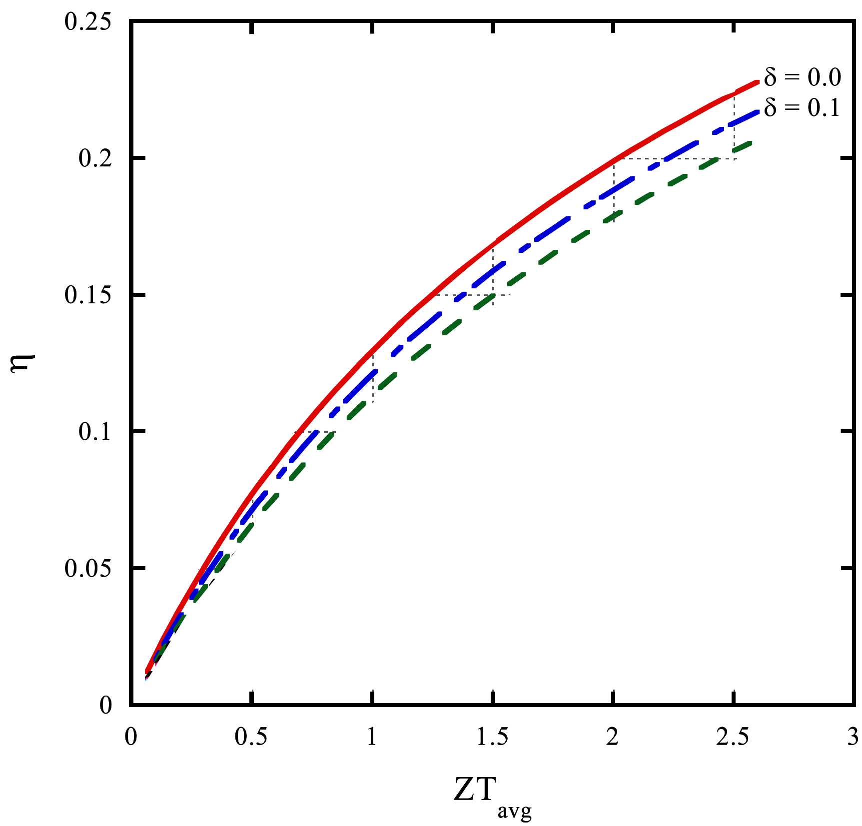
~65% of energy becomes waste heat,

~10% conversion to useful forms can have huge impact on overall energy utilization

Figure of Merit

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

Carnot efficiency



electrical conductivity

thermopower

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

Total thermal conductivity

Power factor

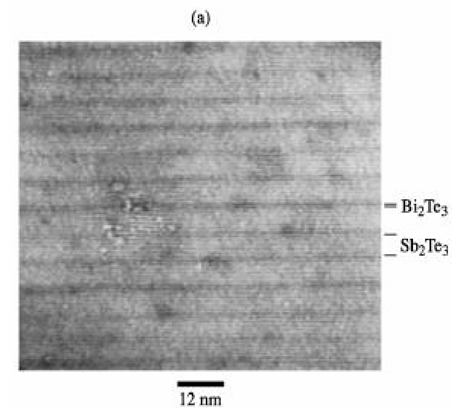
$$\sigma \cdot S^2$$

δ=R_c/R

For T_h = 800K
T_c = 300K

Diamond ~ 1600 W/mK
Cu ~ 300 W/mK
Bi2Te3 ~ 1.5 W/mK
PbTe ~ 2.2 W/mK
Wood ~ 0.2 W/mK

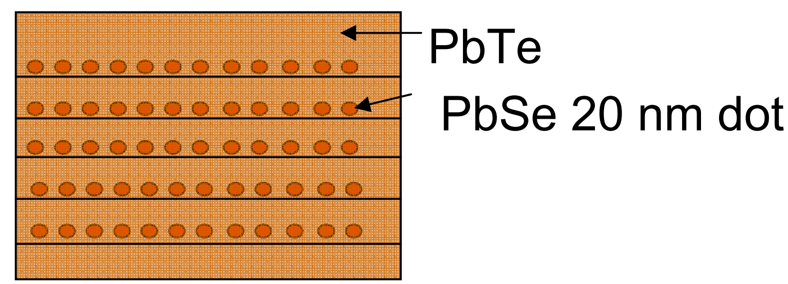
- The most efficient commercial materials today for power generation:
- PbTe: ZT~0.8 at 800 K (n-type)
- TAGS: ZT~1.2 700 K (p-type)
- $Bi_2Te_{3-x}Se_x$: ZT~1 at 300 K
- Further improvements are needed.
- New materials emerging



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)

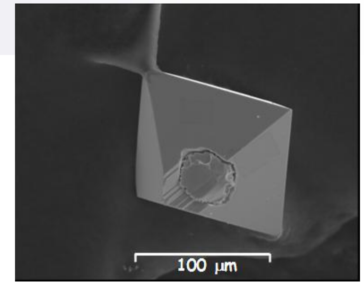


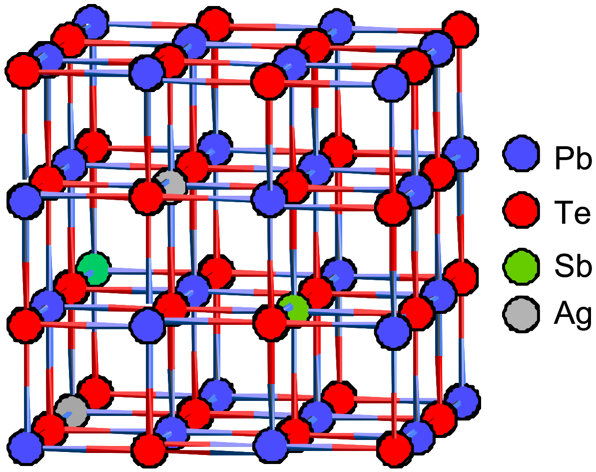
Harman T C, Taylor P J, Walsh M P et al. Science, 2002, 297: 2229

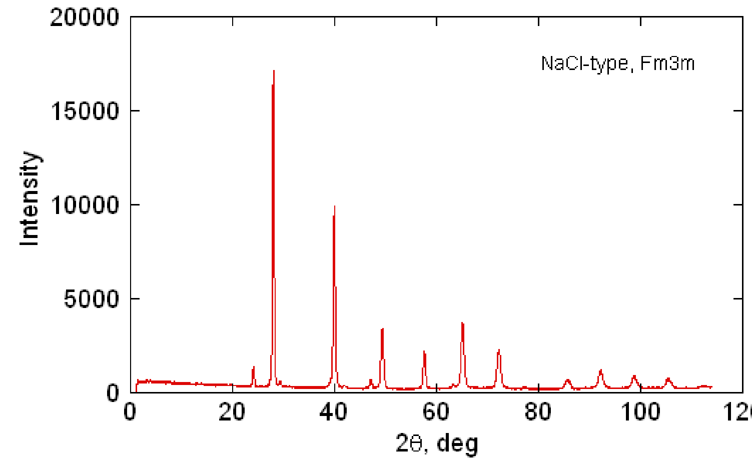
Some promising systems under investigation

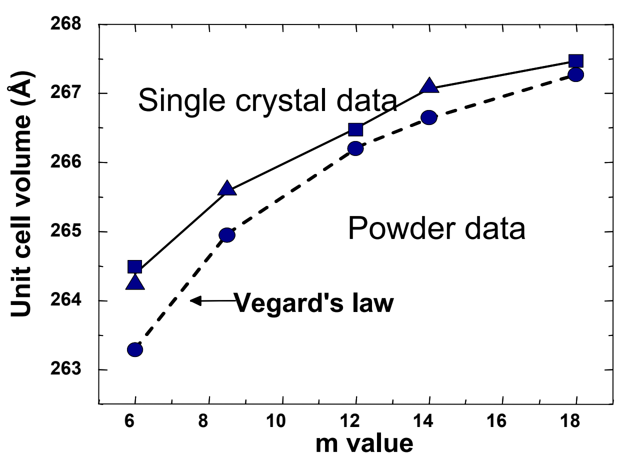
- half-Heusler alloys (ZrNiSn)
- Zn_4Sb_3
- Clathrates
- Skutterudites ($CoSb_3$)
- $Yb_{14}MnSb_{11}$
- Bulk nanocomposites based on PbTe
- Bulk nanocomposites based on Si-Ge
- $AgSbTe_2$/PbTe, $NaSbTe_2$/PbTe

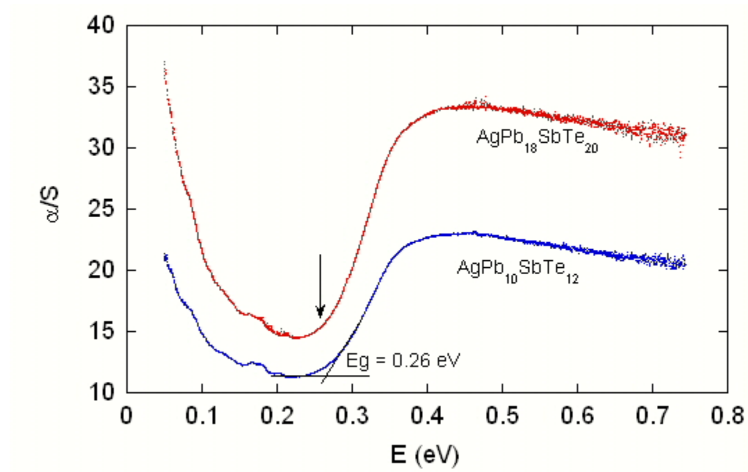
$AgPb_mSbTe_{2+m}$ (LAST-*m*)
$NaPb_mSbTe_{2+m}$ (SALT-*m*)











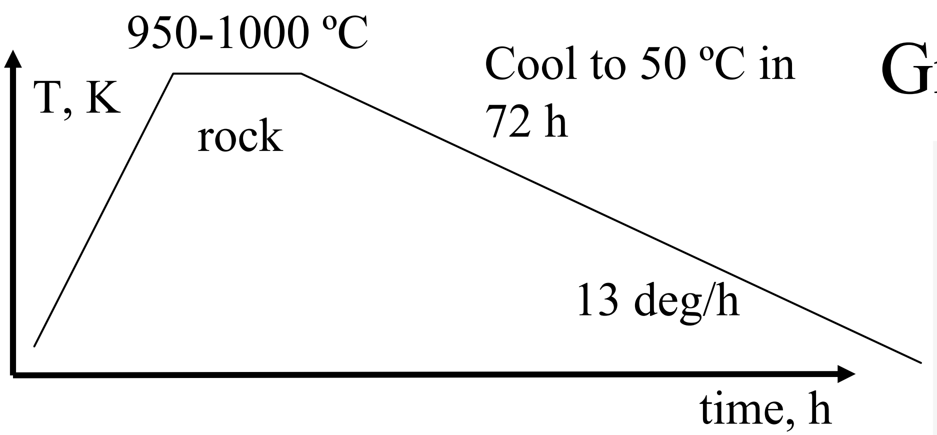
(1) (a) Rodot, H. *Compt. Rend.* **1959**, *249*, 1872-4.
(2) (a) Rosi, F. D.; Hockings, E. S.; Lindenblad, N. E. *Adv. Energy Convers.* **1961**, *1*, 151.

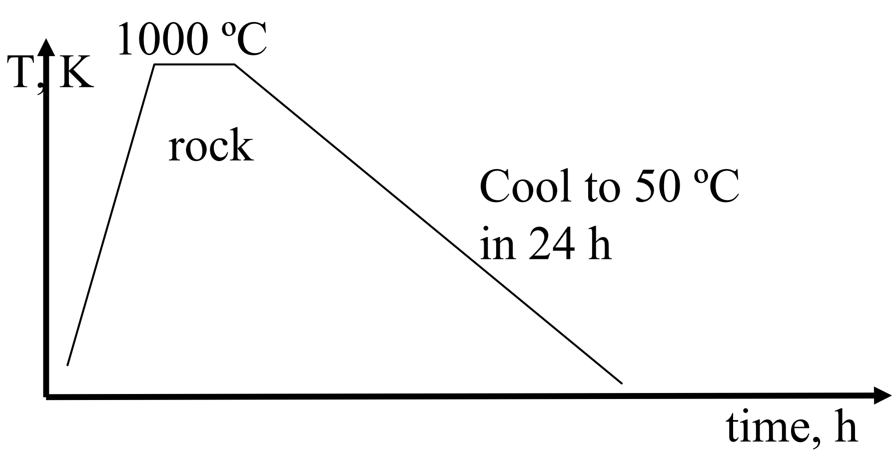
- No phase transitions to melting point

Synthesis

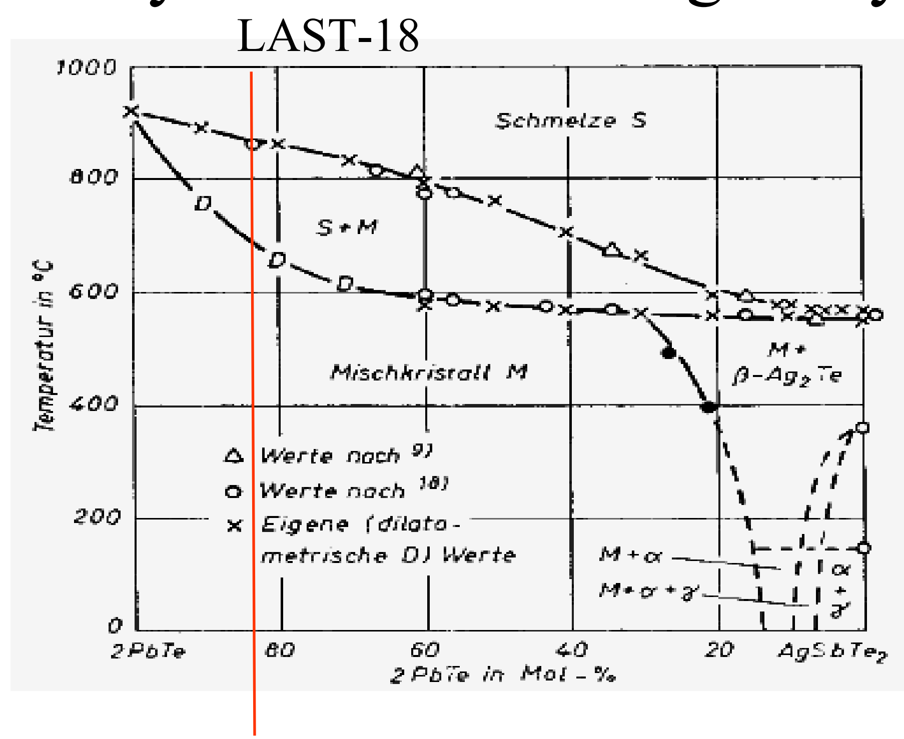
Ag + *m*Pb + Sb + (2+*m*)Te

Ingot properties very sensitive to cooling profile





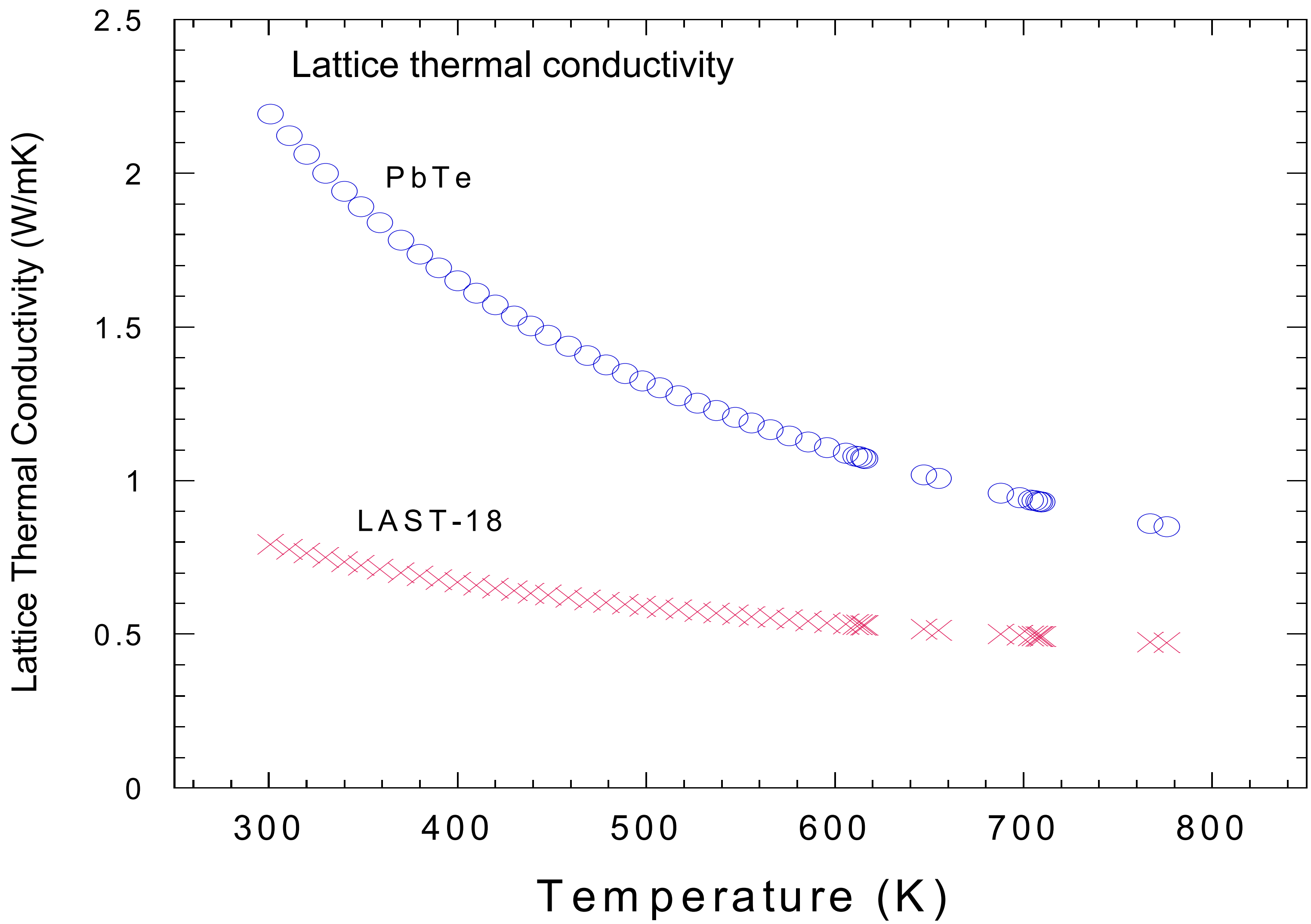
Gravity induced inhomogeneity



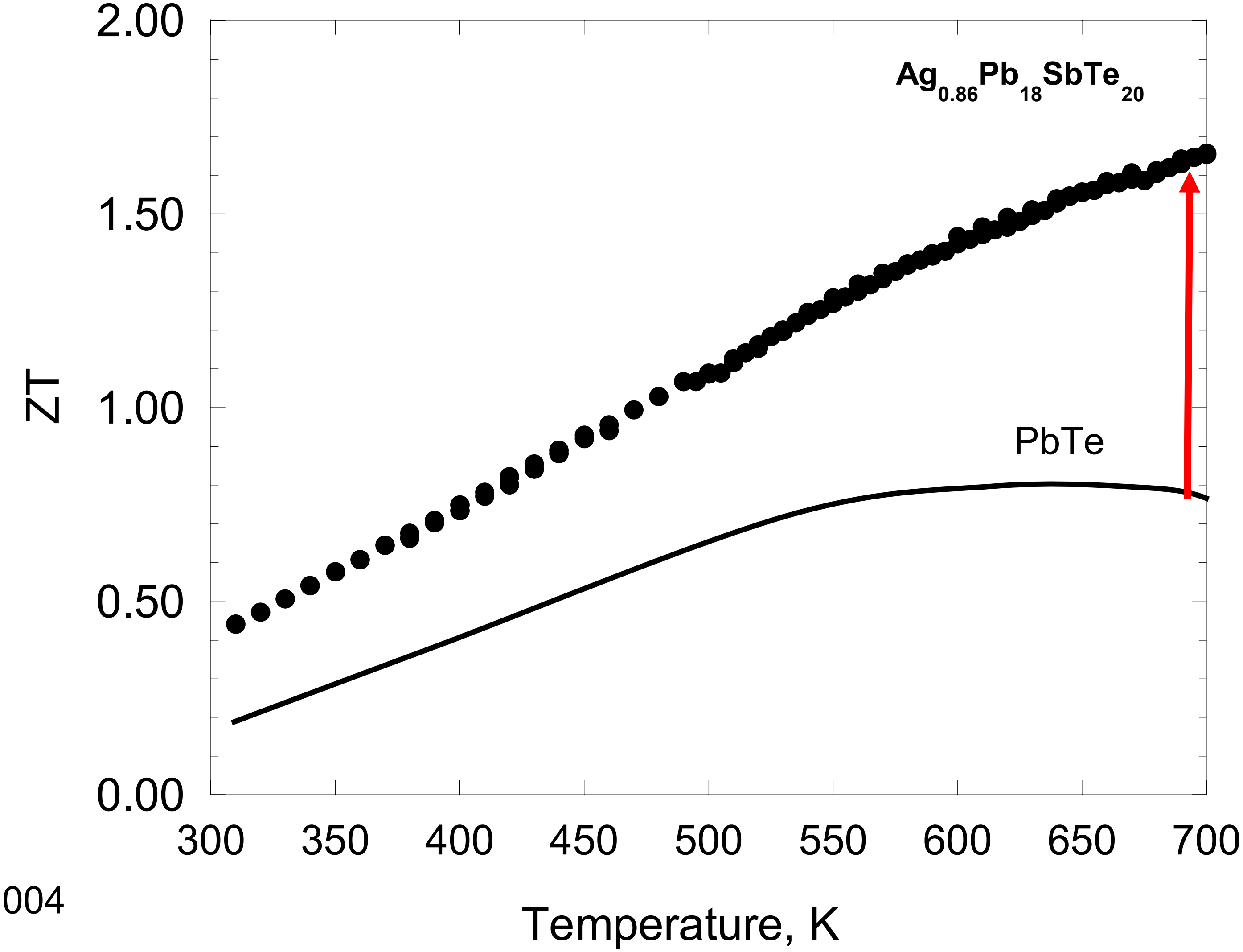
Wernick, J. H.. *Metallurg. Soc. Conf. Proc.* (1960), 5 69-87.

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

Properties of $Ag_{1-x}Pb_{18}SbTe_{20}$

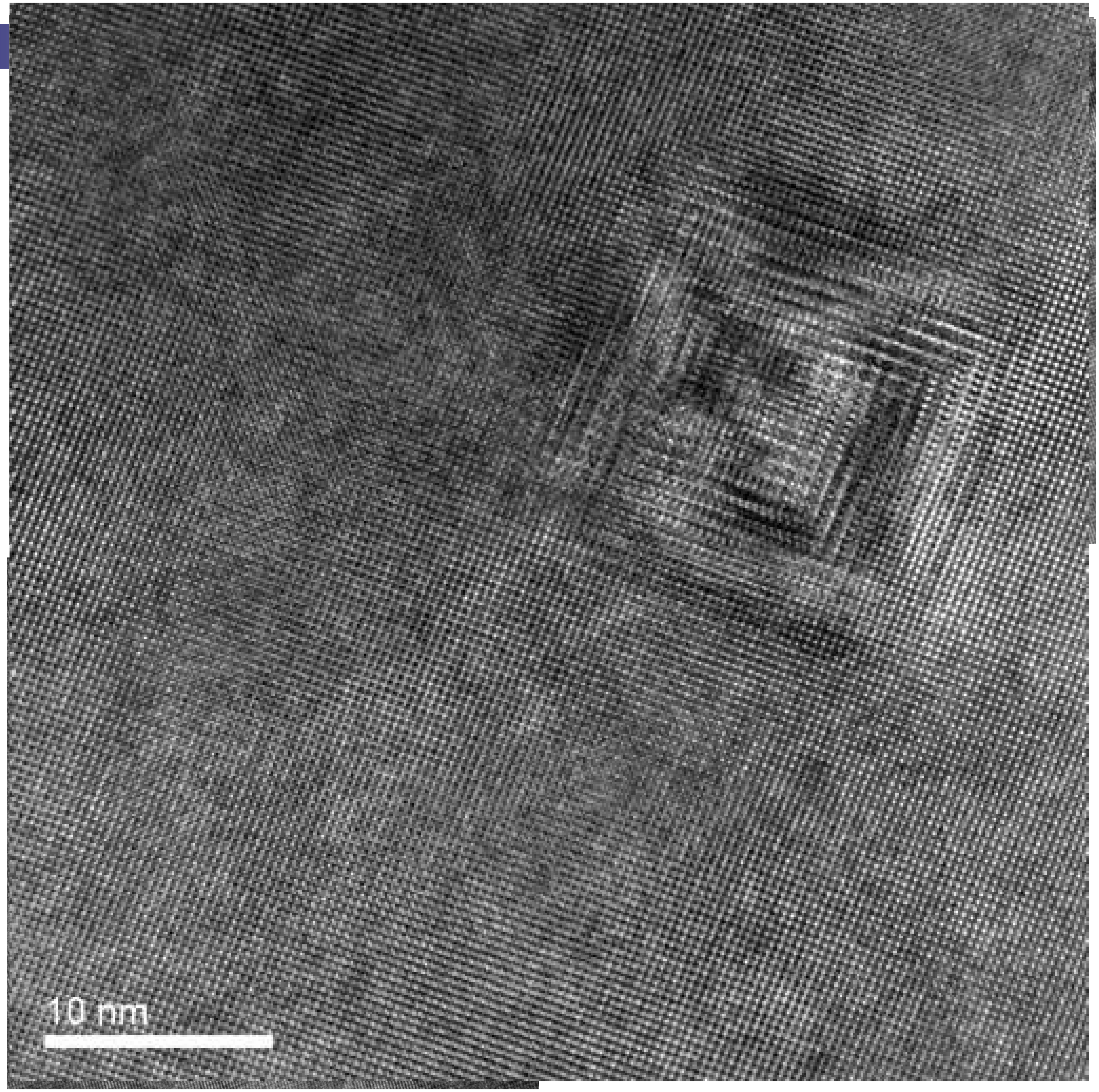


LAST-18 ZT~1.6

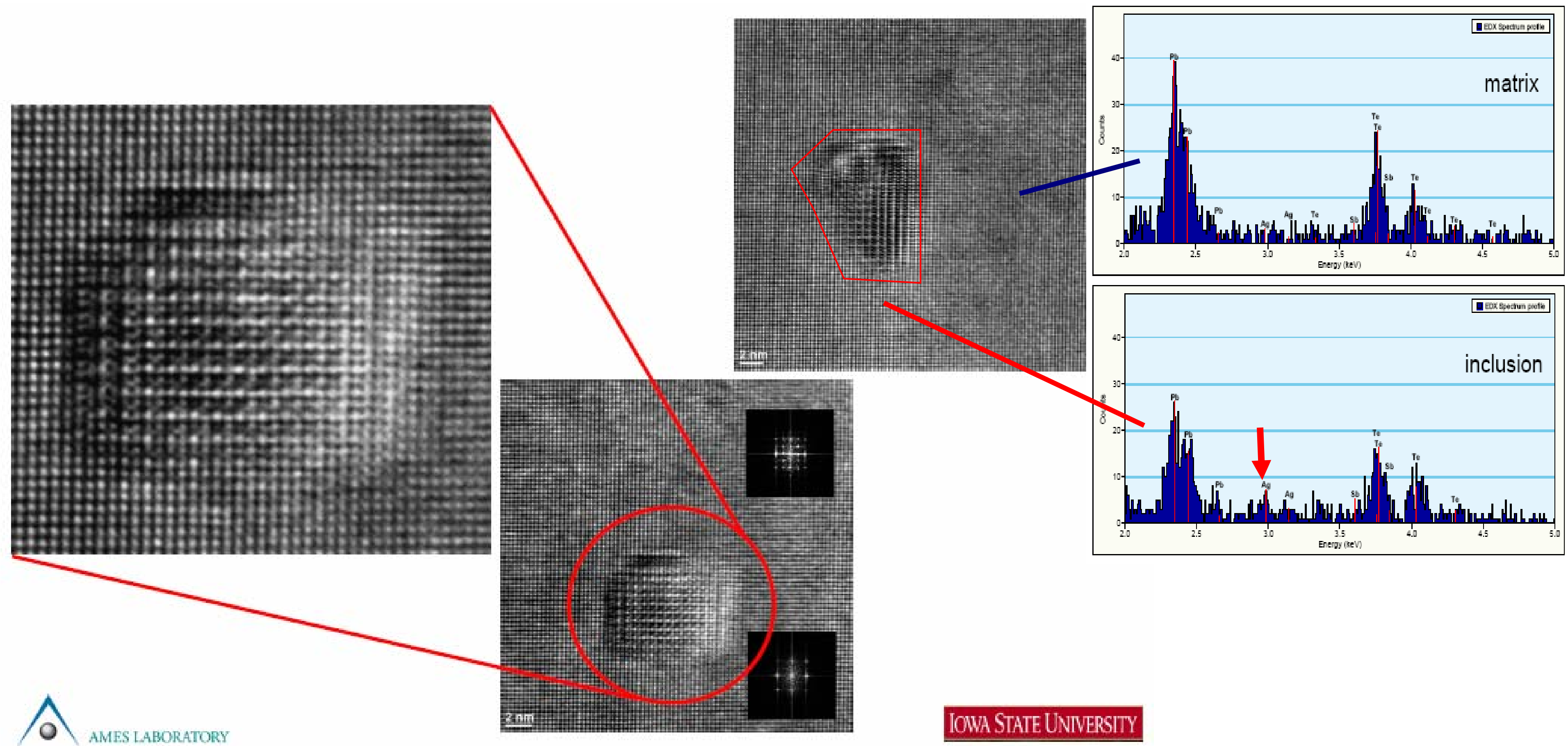


Science 2004

HRTEM of LAST-18

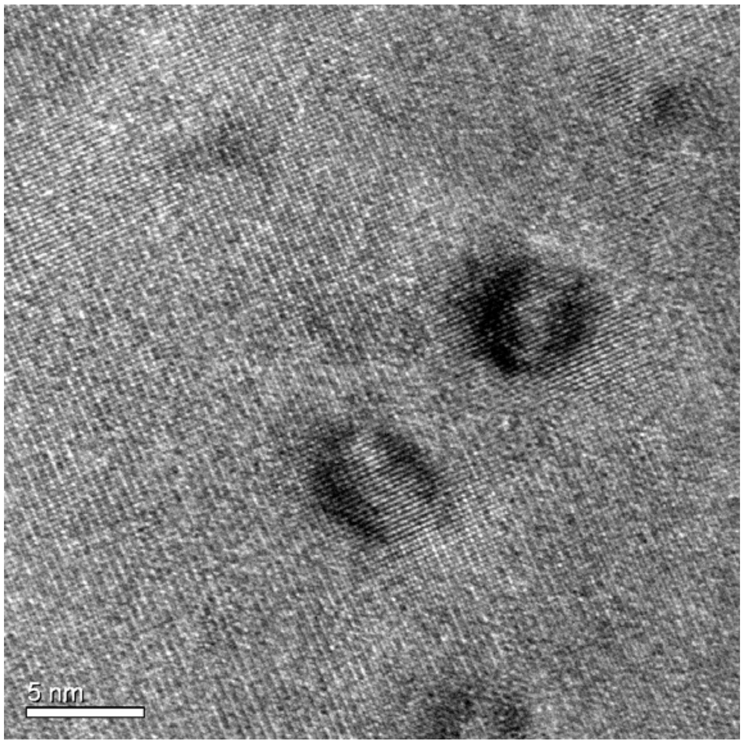


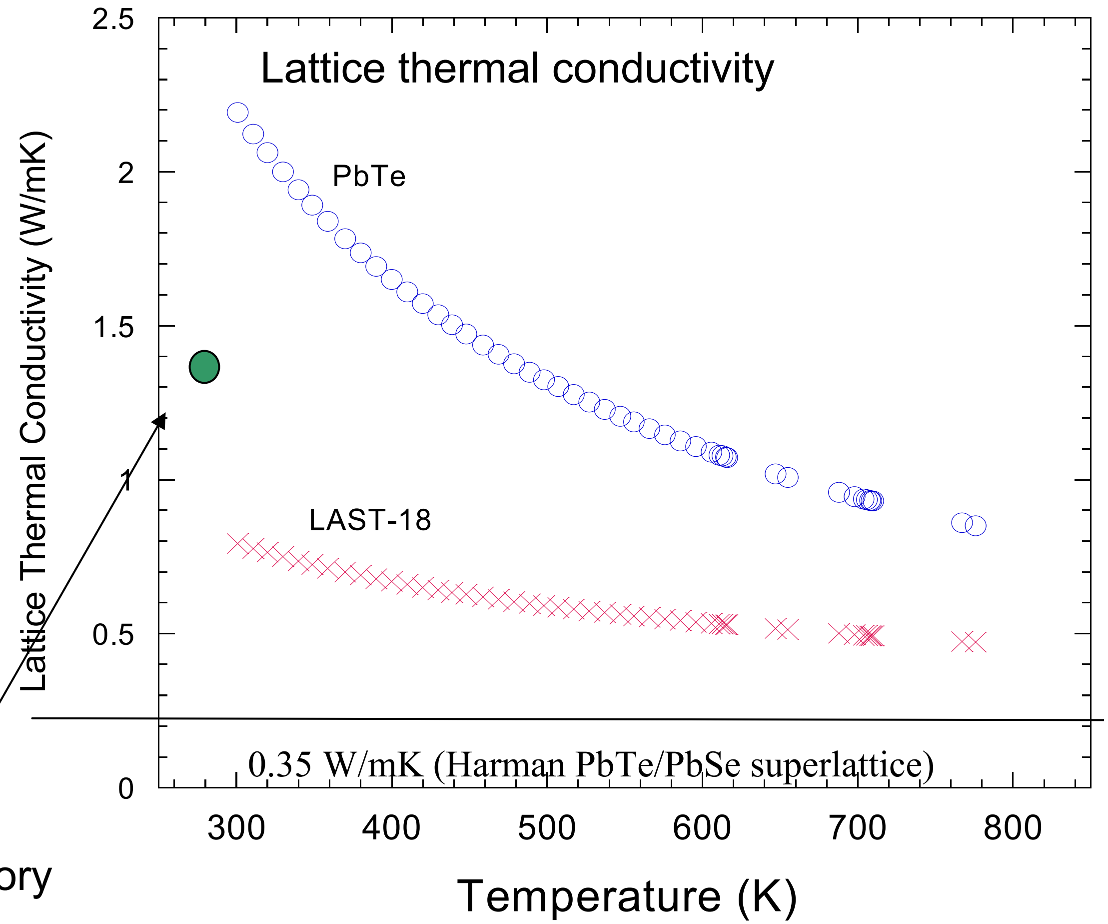
What is the dot made of?



Cook, Kramer
Ames Lab

Nanostructures reduce the lattice thermal conductivity





Clemens-Drabble theory

Recent Reports for $Ag_{0.8}Pb_{18+x}SbTe_{20}$, ZT ~ 1.5 at 680 K

APPLIED PHYSICS LETTERS **88**, 092104 (2006)

High-performance $Ag_{0.8}Pb_{18+x}SbTe_{20}$ thermoelectric bulk materials fabricated by mechanical alloying and spark plasma sintering

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State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Weishu Liu and Bo-Ping Zhang
School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, People's Republic of China

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ARTICLES
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Nanostructured $AgPb_mSbTe_{m+2}$ System Bulk Materials with Enhanced Thermoelectric Performance

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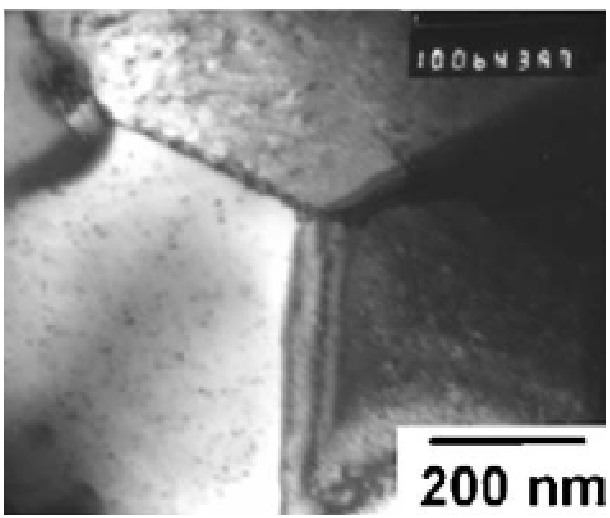
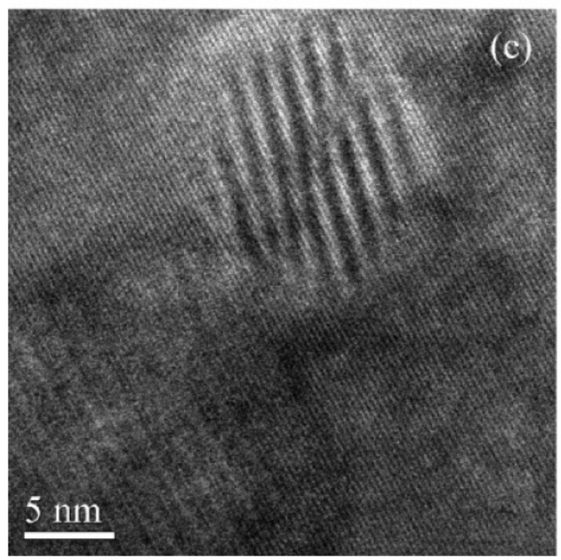
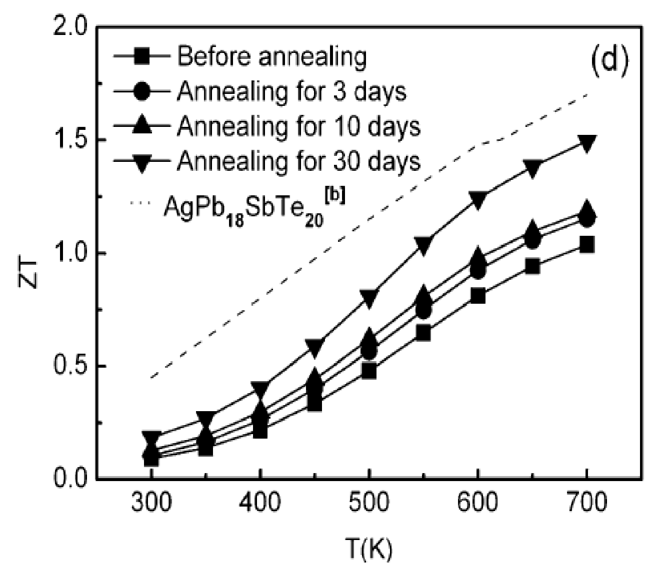
State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing, 100084, China and Material Engineering Division III, Vehicle Engineering Group, Higashifuji Technical Center, Toyota Motor Corporation, 1200, Mishuku, Susono, Shizuoka, 410-1193, Japan

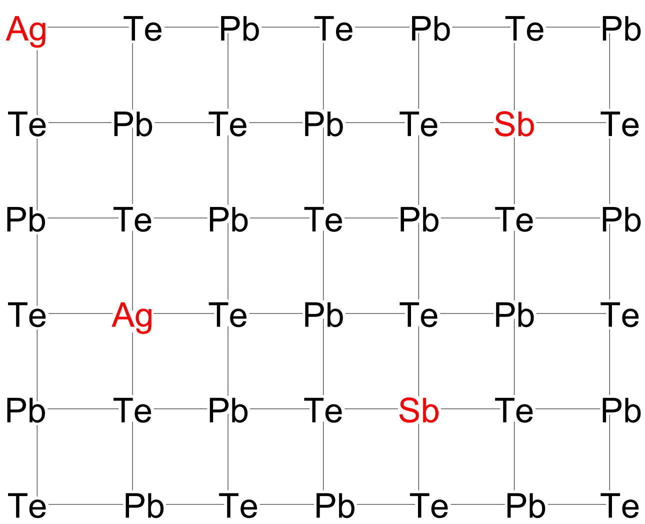




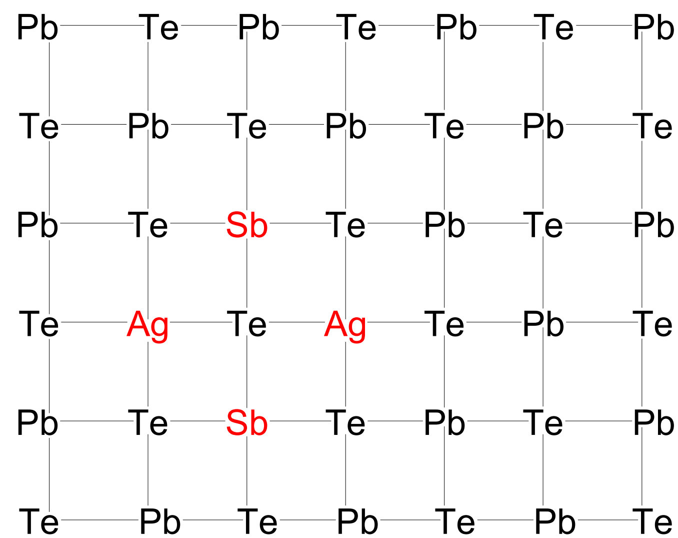


Why do the LAST materials nanostructure?

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

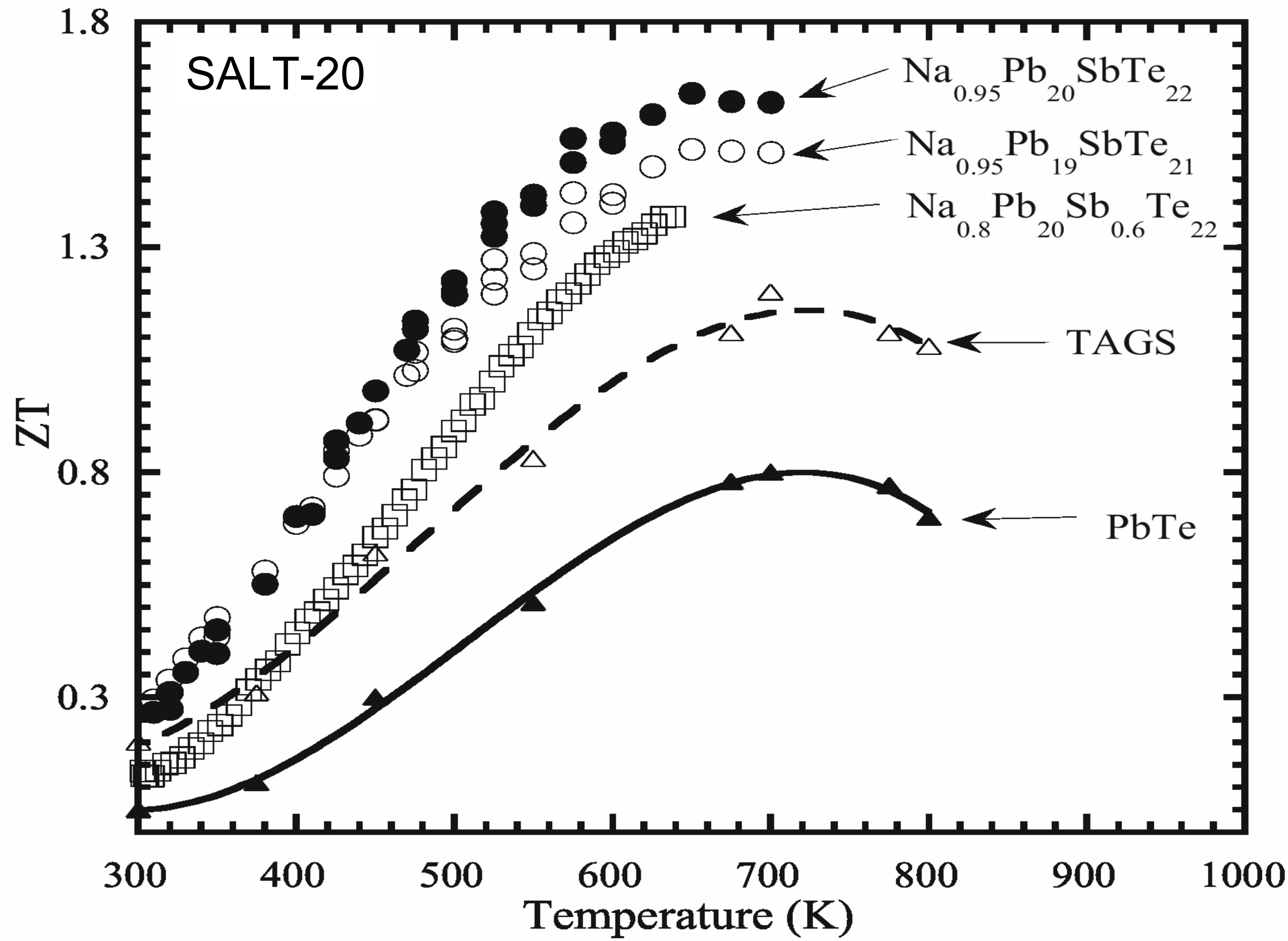


Dissociated state..unstable

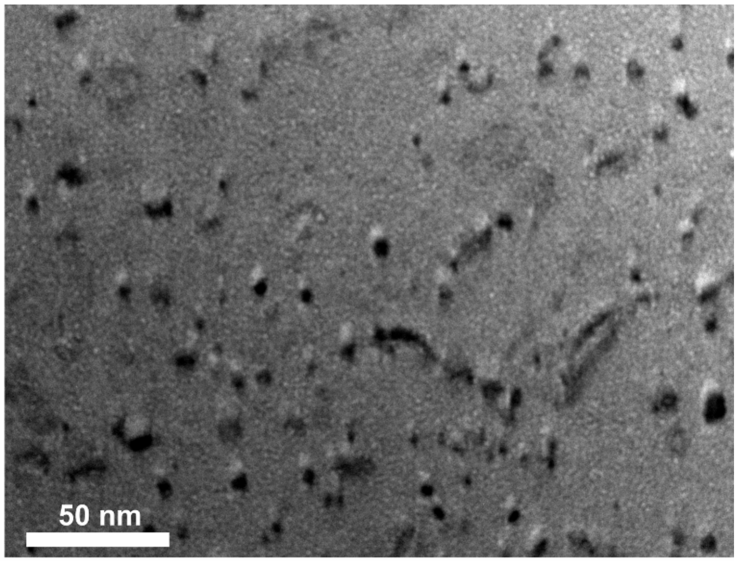


Associated state..stable

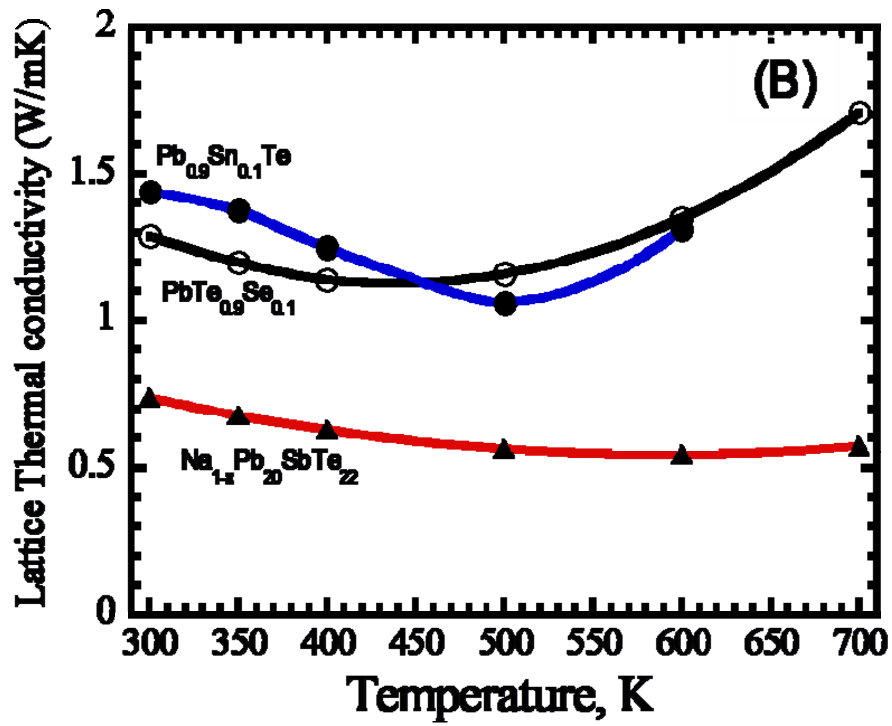
Any +1/+3 pair


SALT-20
$Na_{0.95}Pb_{20}SbTe_{22}$
$Na_{0.95}Pb_{19}SbTe_{21}$
$Na_{0.8}Pb_{20}Sb_{0.6}Te_{22}$
TAGS
PbTe
ZT
1.8
1.3
0.8
0.3
300
400
500
600
700
800
900
1000
Temperature (K)

What is nanostructuring worth?

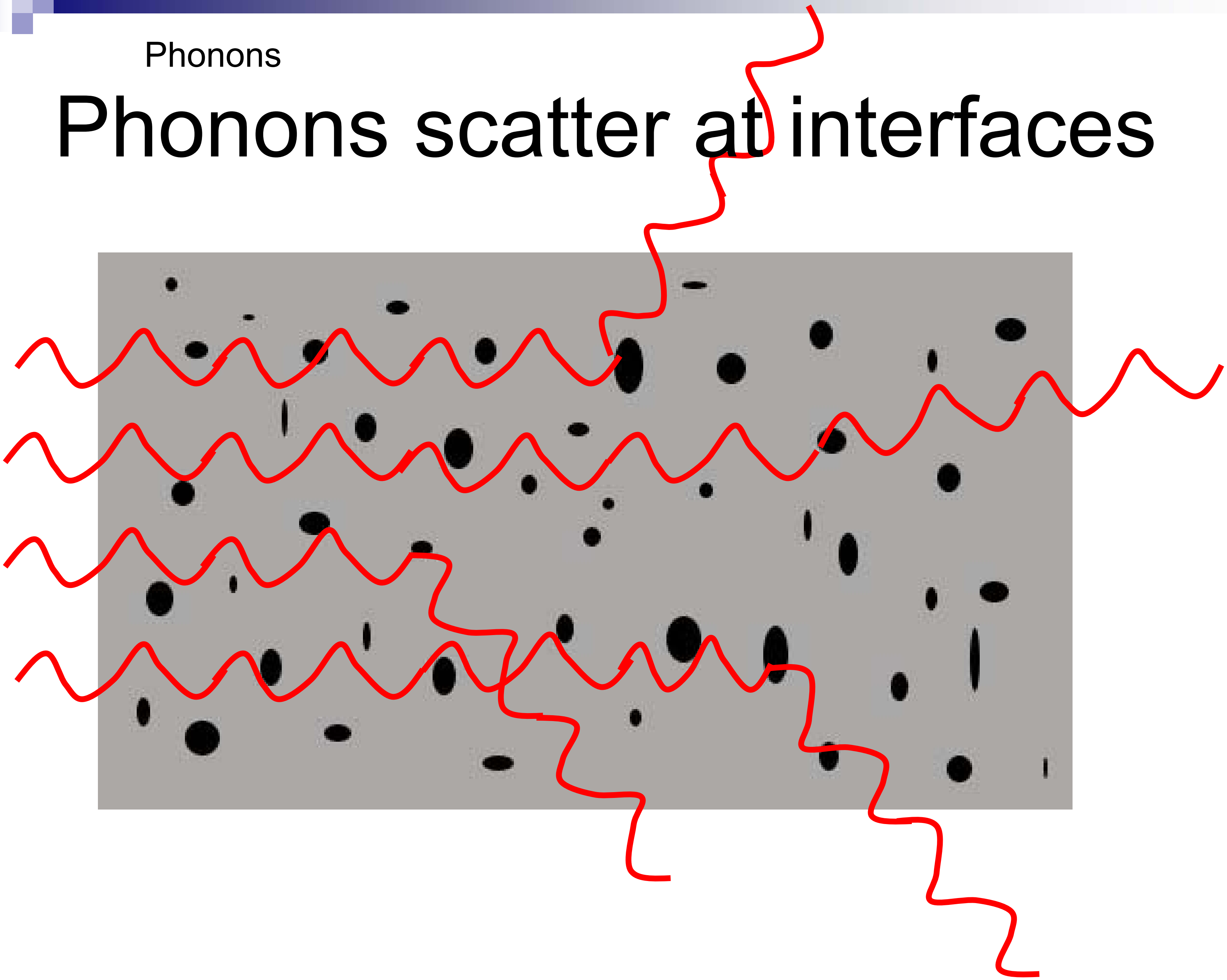


Pb	Te	Pb	Te	Pb	Te	Pb
Te	Pb	Te	Pb	Te	Pb	Te
Pb	Te	Sb	Te	Pb	Te	Pb
Te	Na	Te	Na	Te	Pb	Te
Pb	Te	Sb	Te	Pb	Te	Pb
Te	Pb	Te	Pb	Te	Pb	Te

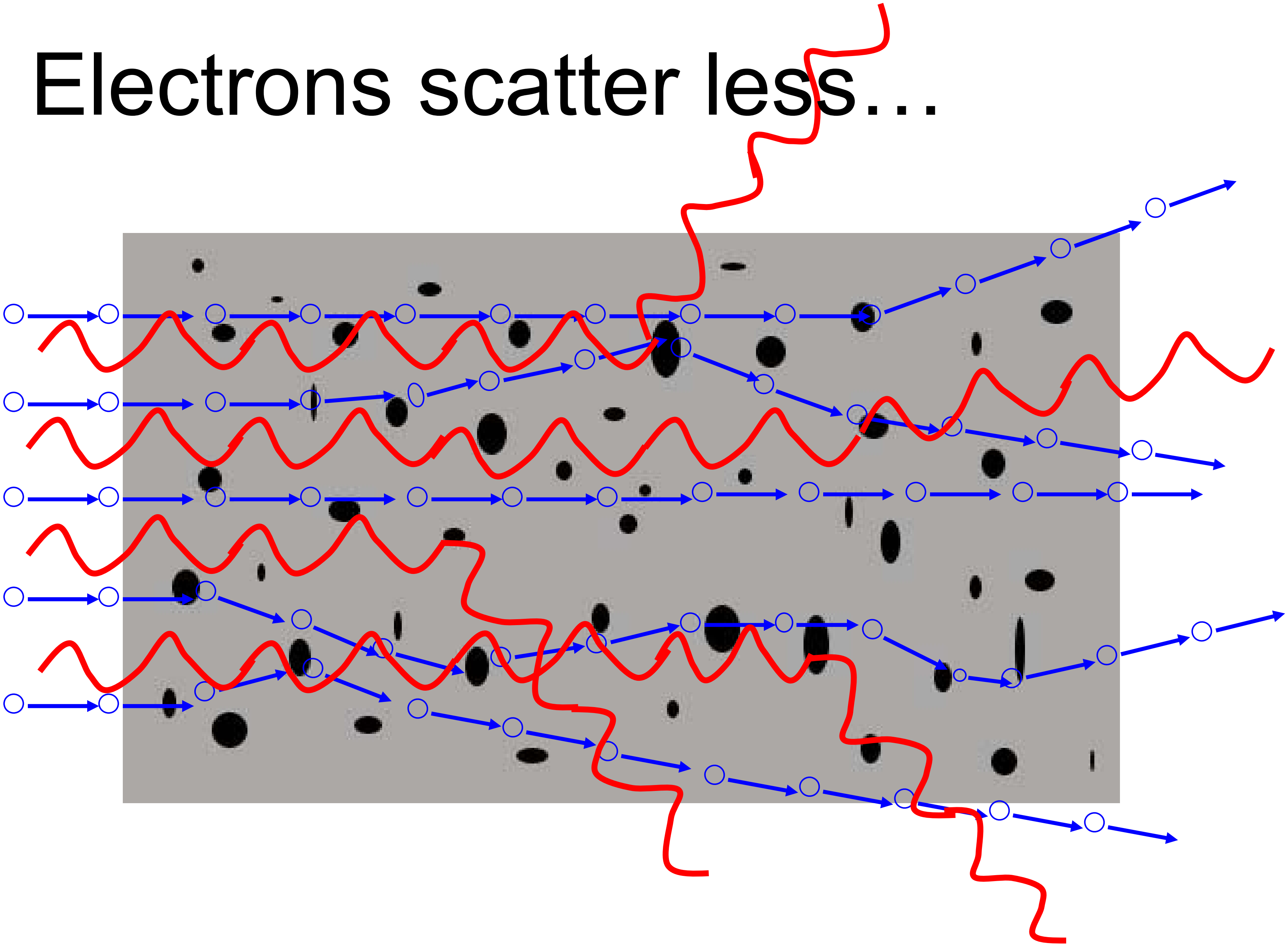


P. F. P. Poudeu, J. D'Angelo, A. D. Downey, J. L. Short,
T. P. Hogan, M. G. Kanatzidis, *Angew. Chem. Int. Ed.* **2006**, 45, 1

Phonons scatter at interfaces



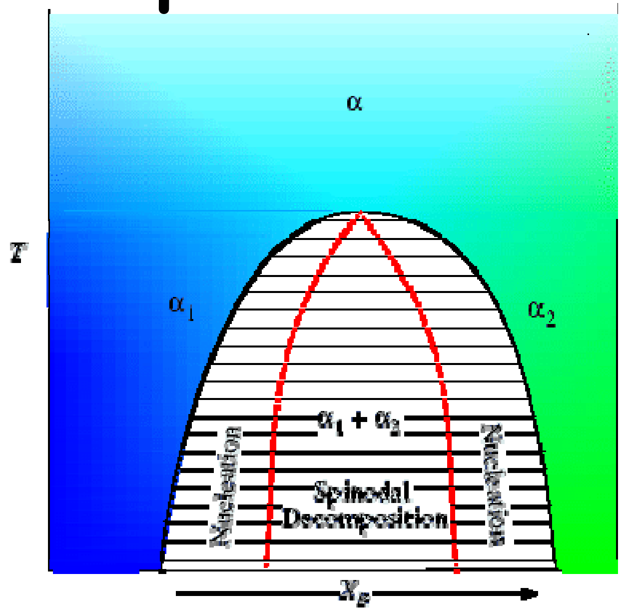
Electrons scatter less…

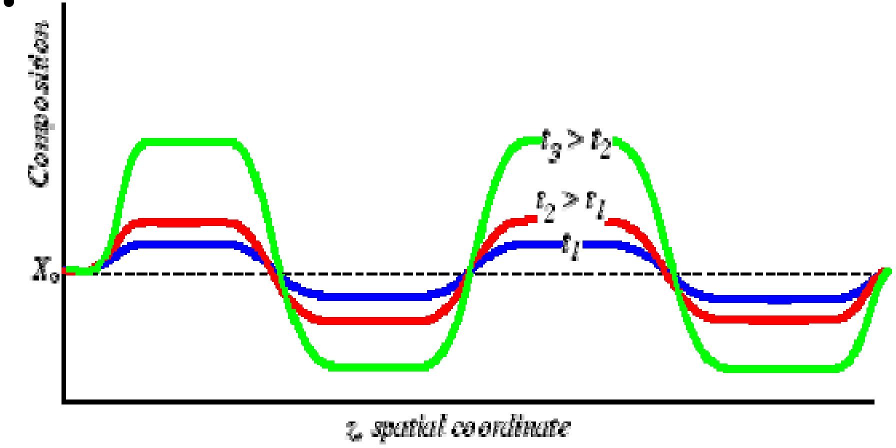


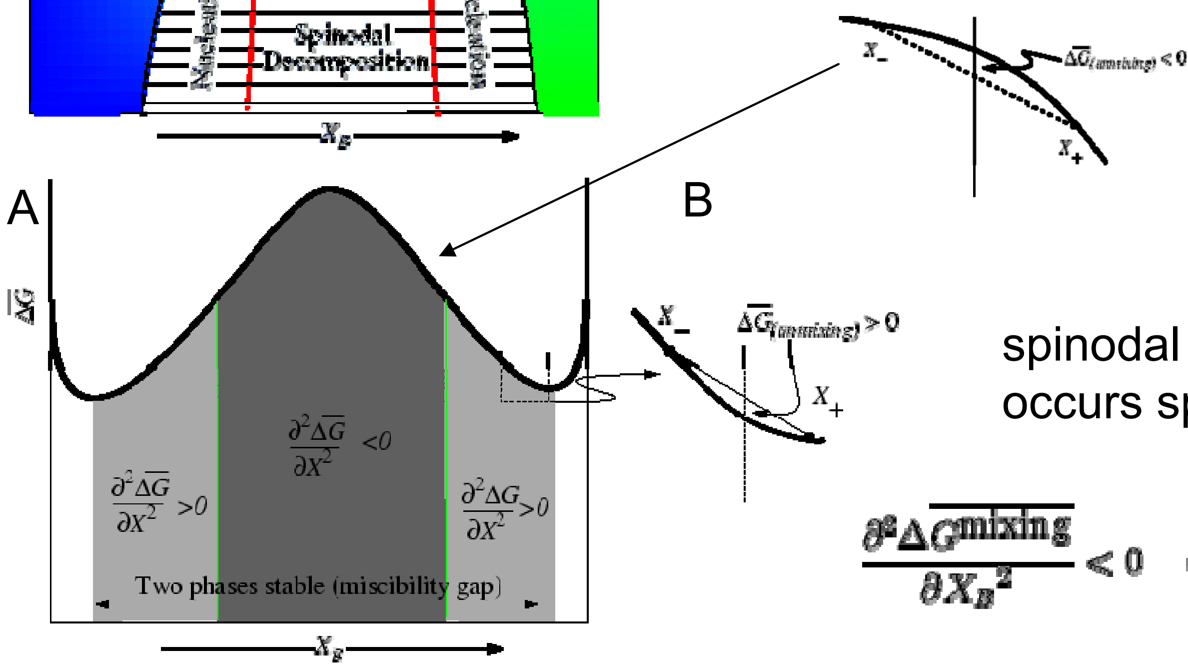
Methods to Produce Nanostructured PbTe

- Precipitation and Growth (PbTe-CdTe, LAST, PbTe-PbS)
  - Supersaturated solution decomposition
- Spinodal Decomposition (LAST, PbTe-PbS)
  - Solid immiscibility
- Matrix Encapsulation
  - Low melting, nonreactive phase kinetically trapped in solid matrix

Spinodal Decomposition



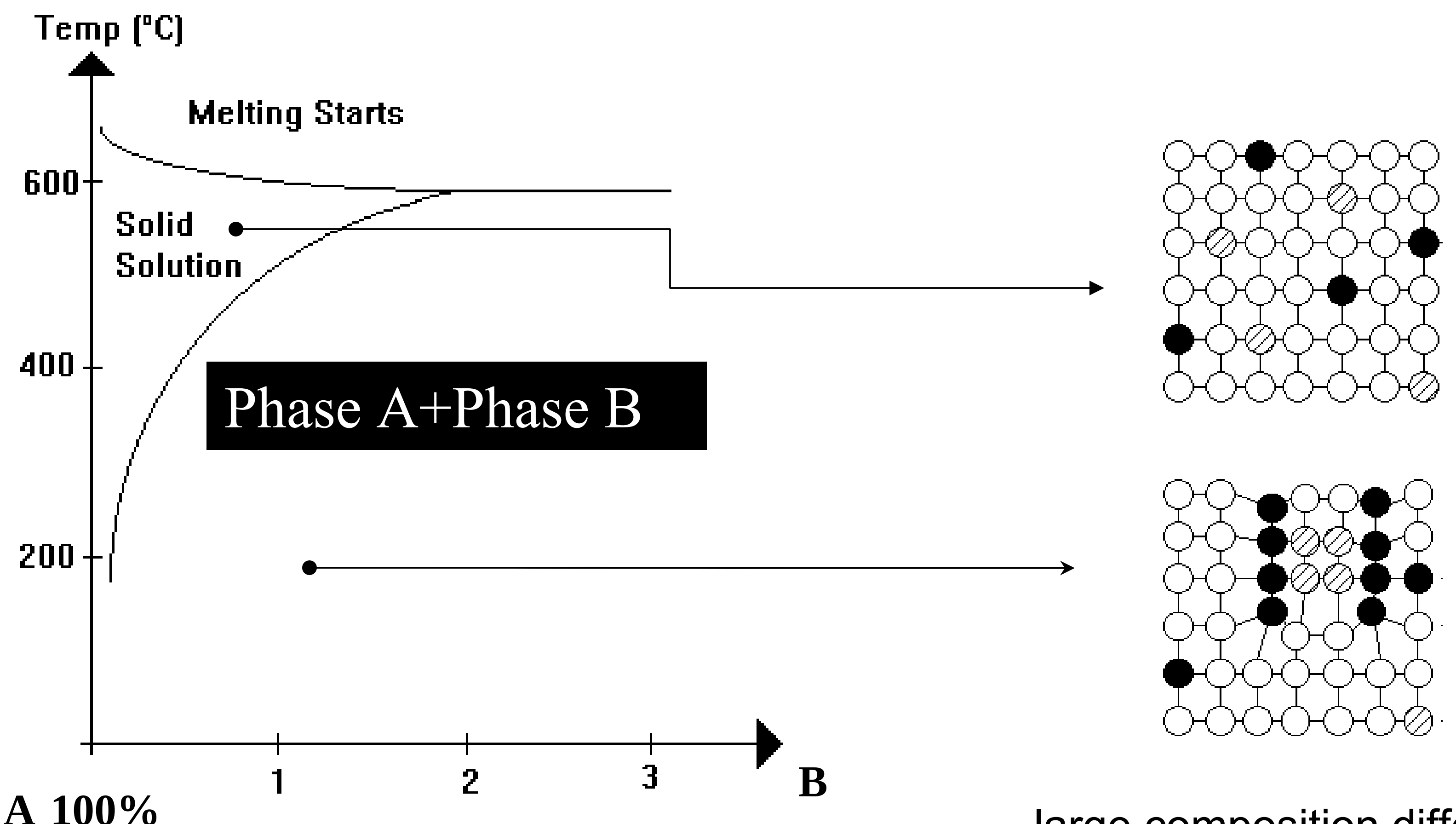




spinodal decomposition and it occurs spontaneously when

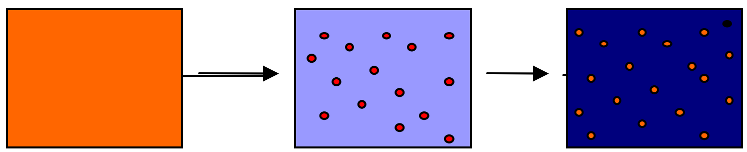
$$\frac{\partial^2 \Delta \overline{G^{\text{mixing}}}}{\partial X_B{}^2} < 0 \quad \text{(condition for spinodal decomposition)}$$

Nucleation and growth



large composition difference

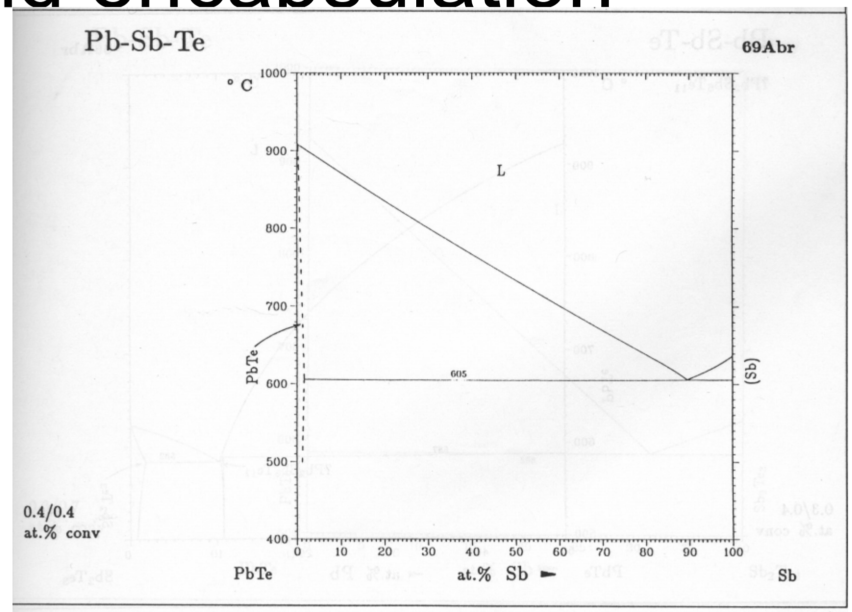
Nanostructures via Liquid encapsulation



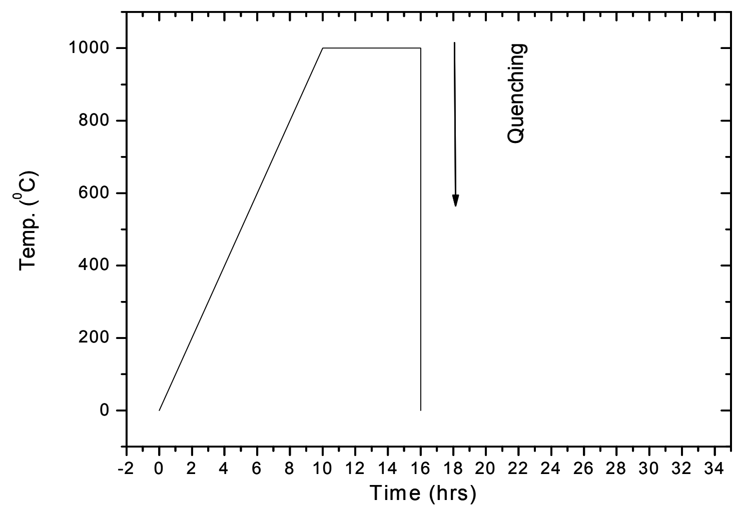
1000° C
Melt

900-600° C
Solid PbTe
Molten Sb

< 600° C
Solid PbTe
Solid Sb

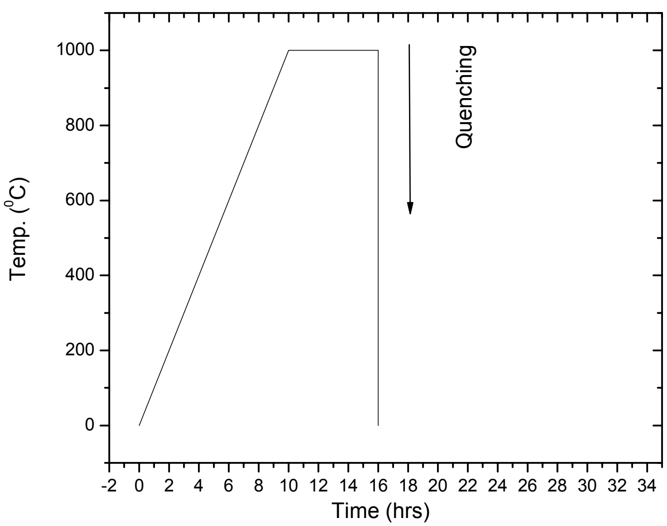


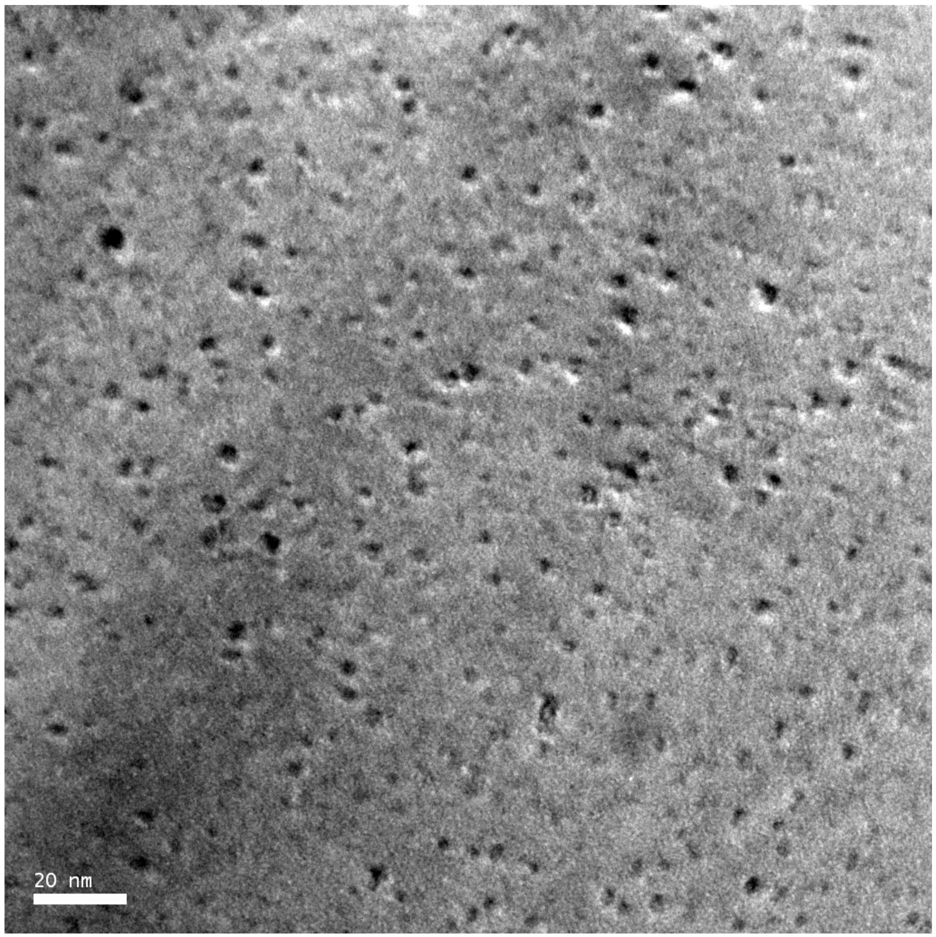
- X = Sb, Bi, InSb, other **low melting** inclusion with **little solubility** in the matrix
- Sample is cut and characterized using
  - Electron Microscopy (SEM / TEM)
  - Powder X-ray diffraction
  - Electrical and Thermal Transport



J.R. Sootsman *et. al. Chem. Mater.* 18, 4993-4995, (2006)

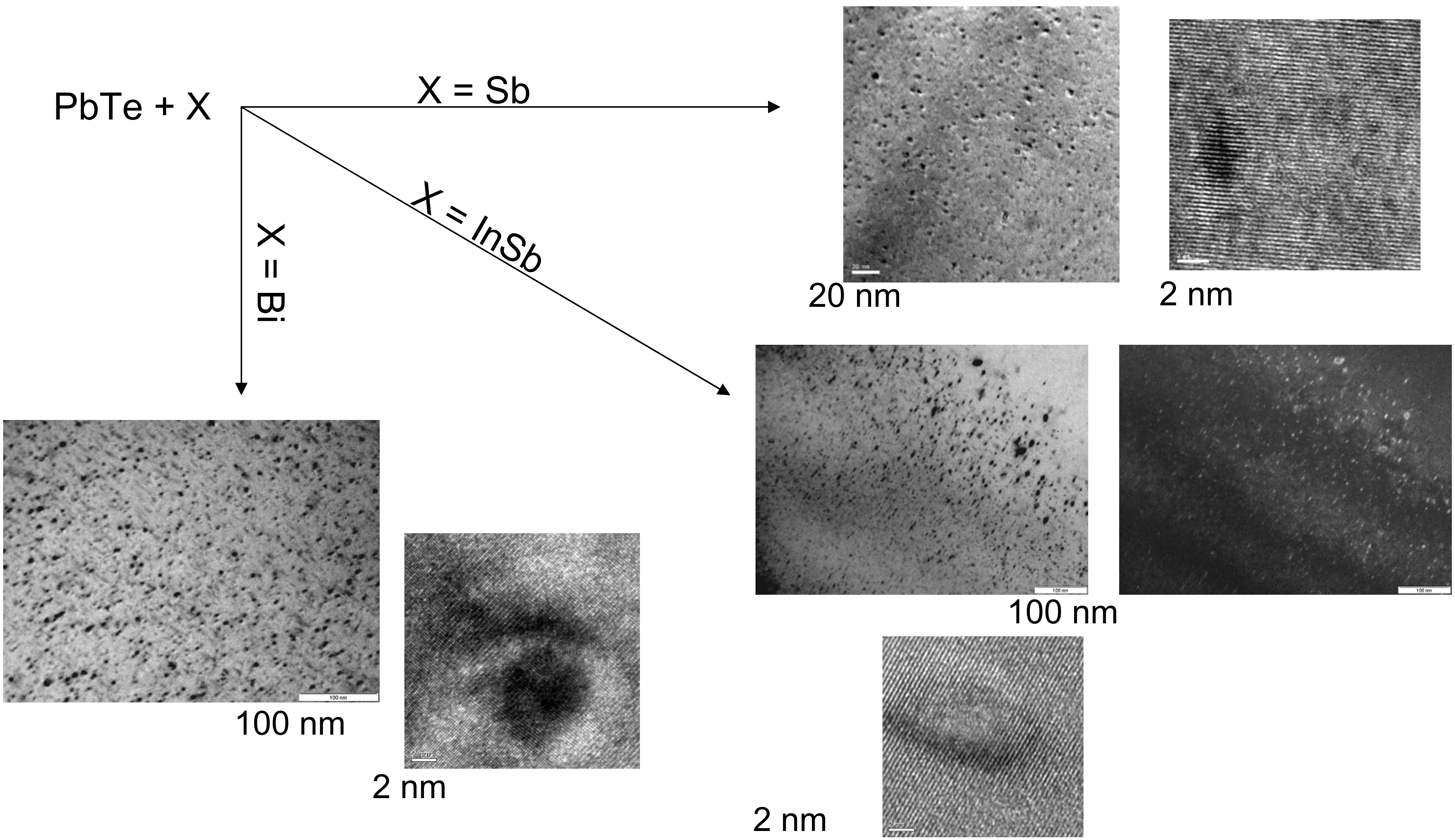
Nanocrystals of Sb in PbTe



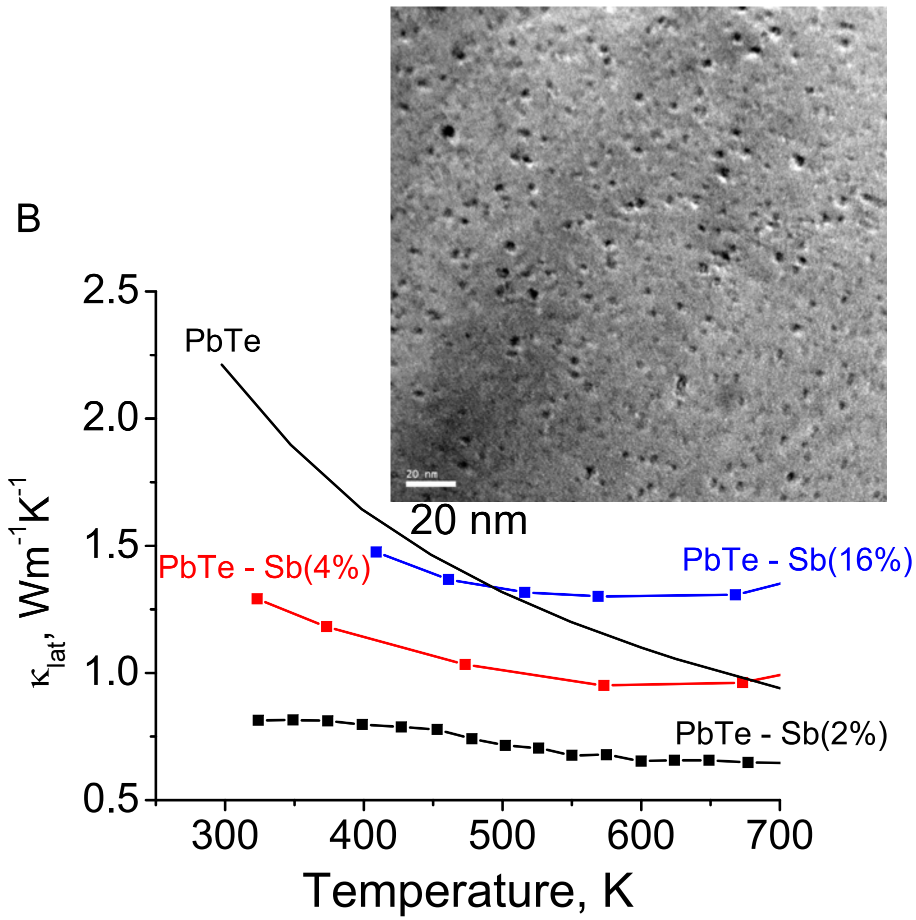


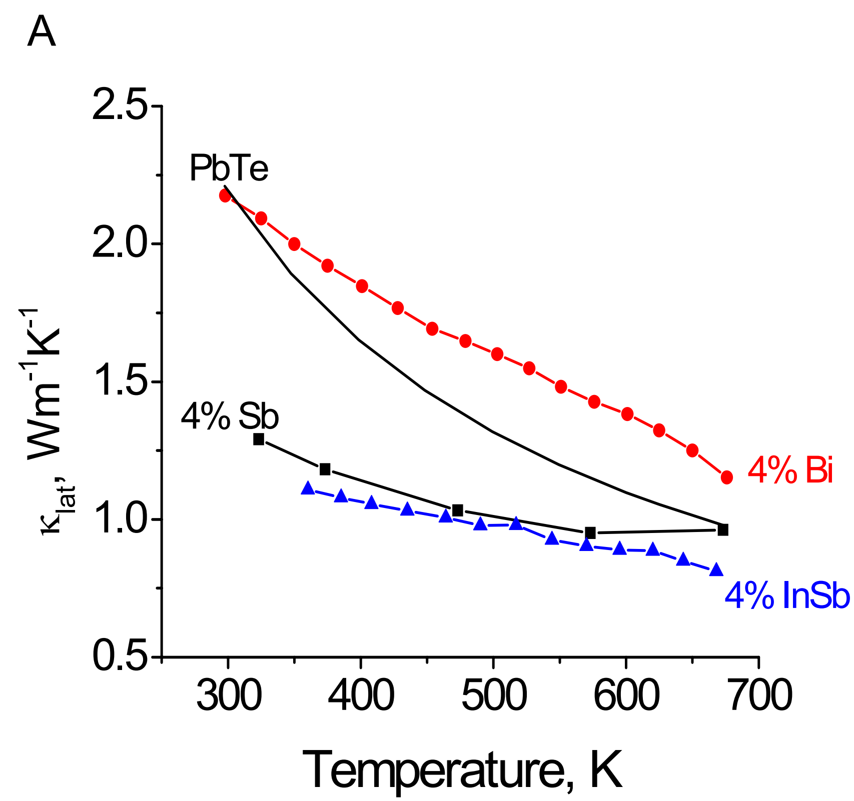
J. R. Sootsman, R. J. Pcionek, H. Kong, C. Uher, and M. G. Kanatzidis, *Chem. Mater*. **2006**, *18*, 4993-4995.

Matrix Encapsulation as a Route to Nanostructured PbTe



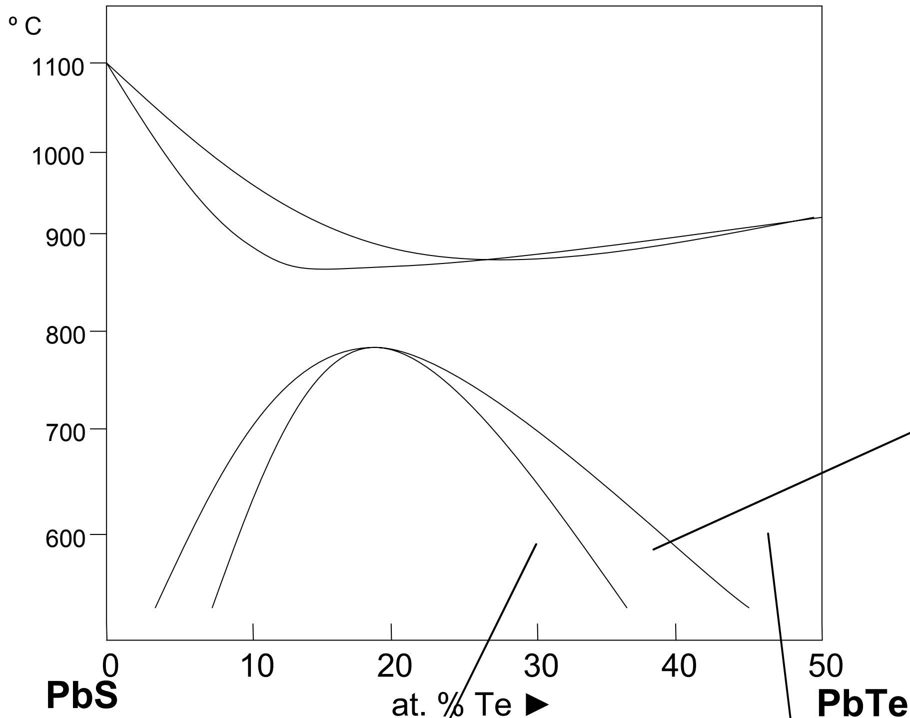
Nanocrystals of Sb in PbTe

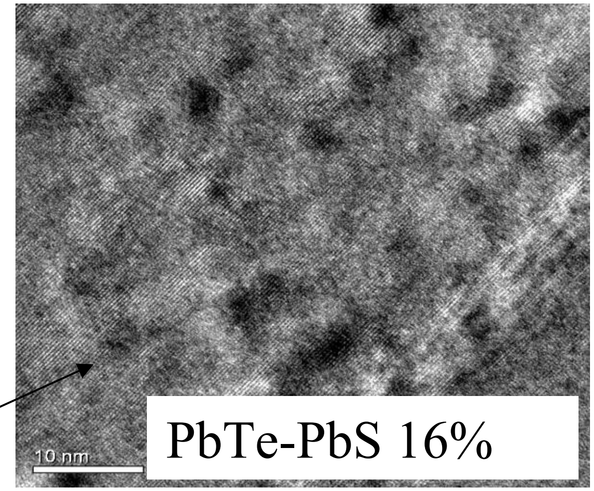




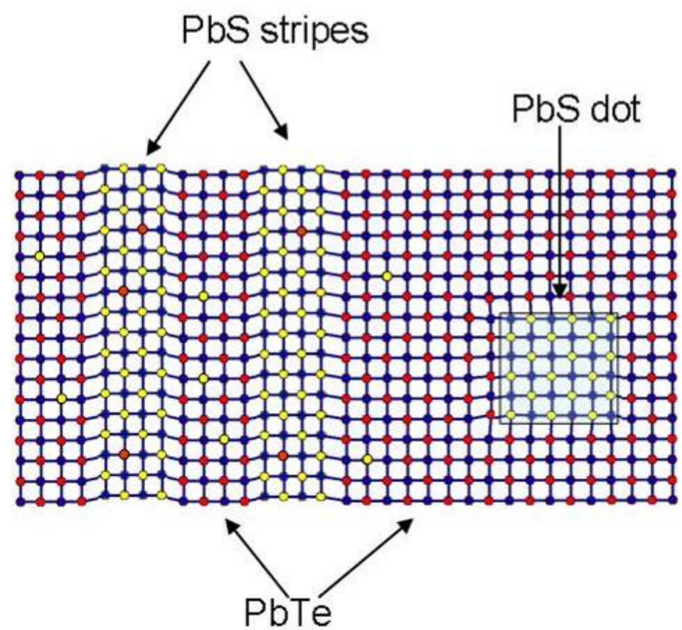
- An optimum concentration of nanoscale second phase is necessary
- Mass fluctuations play a role in thermal conductivity reduction
- Lattice thermal conductivity reduced, however ZT low due to small Seebeck

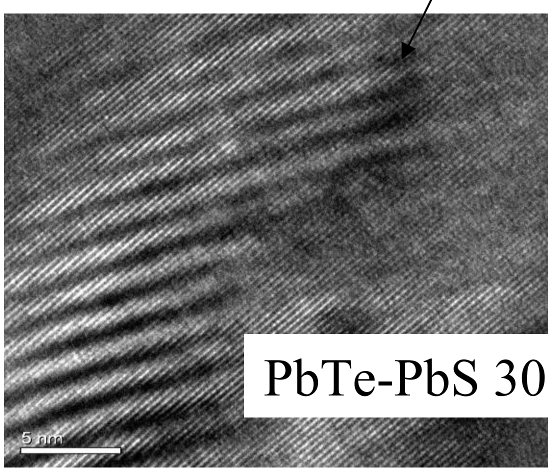
PbTe-PbS





PbTe-PbS 16%



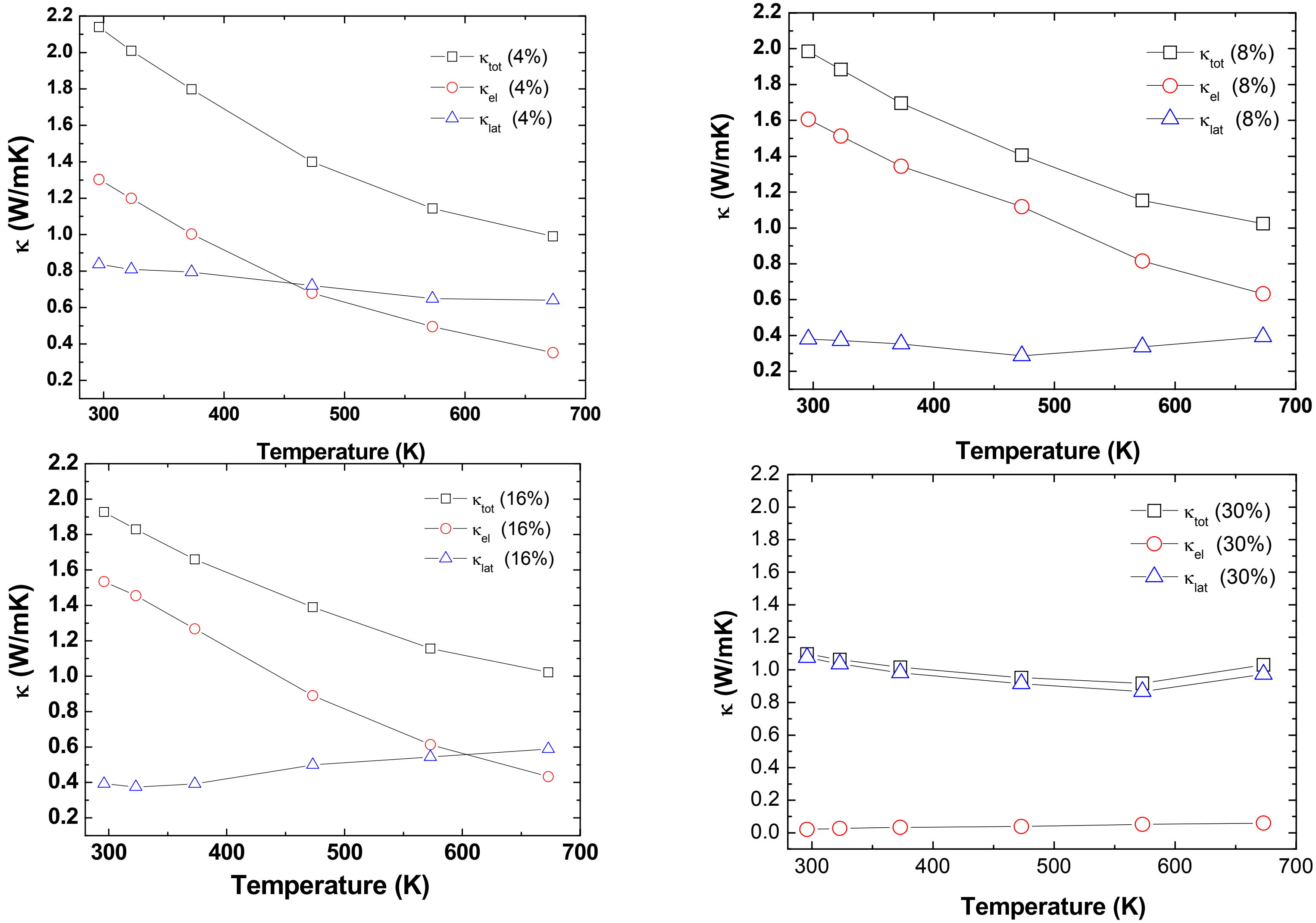


PbTe-PbS 30%

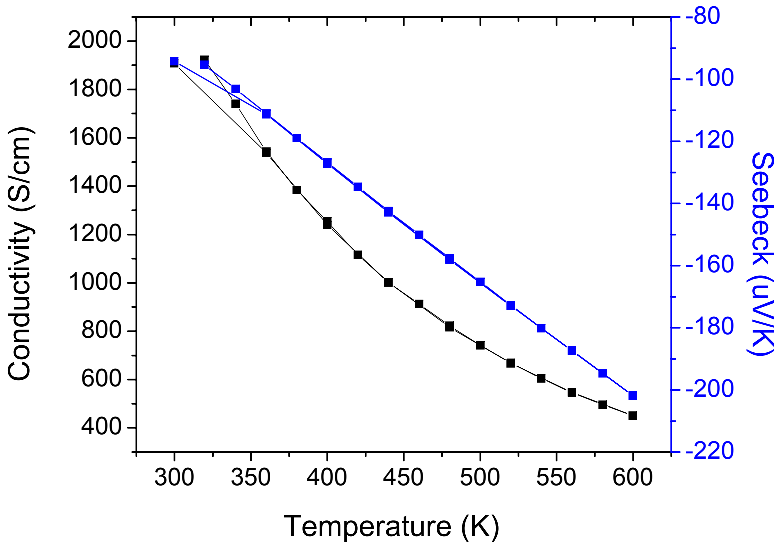
PbTe-PbS 4%: solid solution

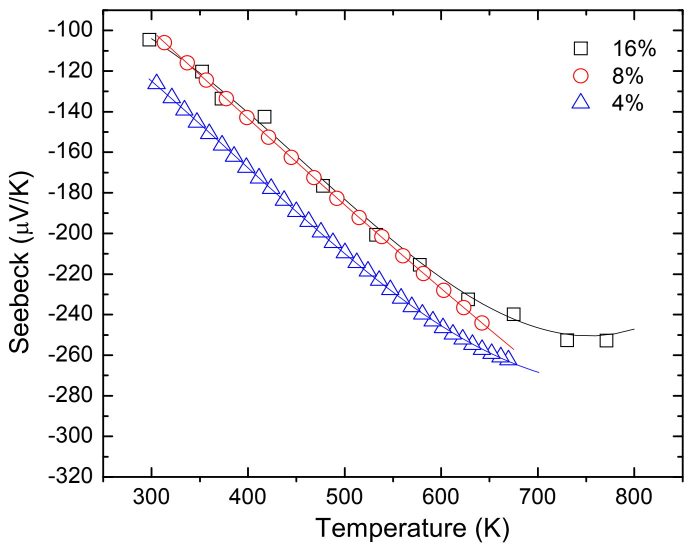
Androulakis, J.; Lin, C.-H.; Kong, H.-J.; Uher, C.; Wu, C.-I.; Hogan, T.; Cook, B. A.; Caillat, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**; 129(31); 9780-9788.

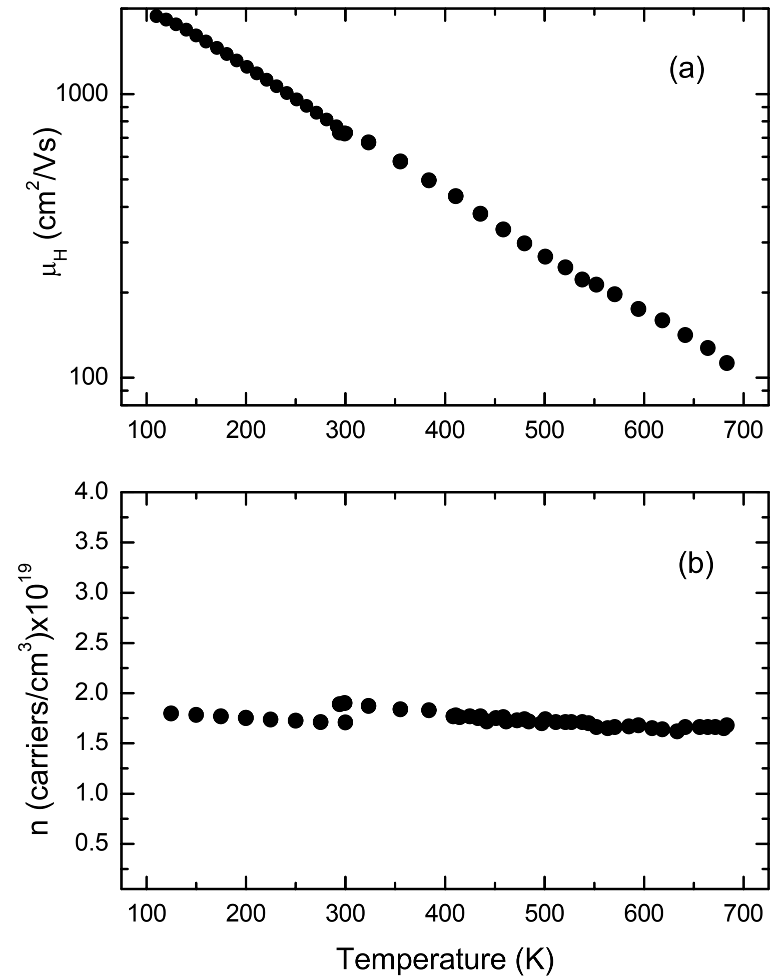
Thermal conductivity in PbTe-PbS



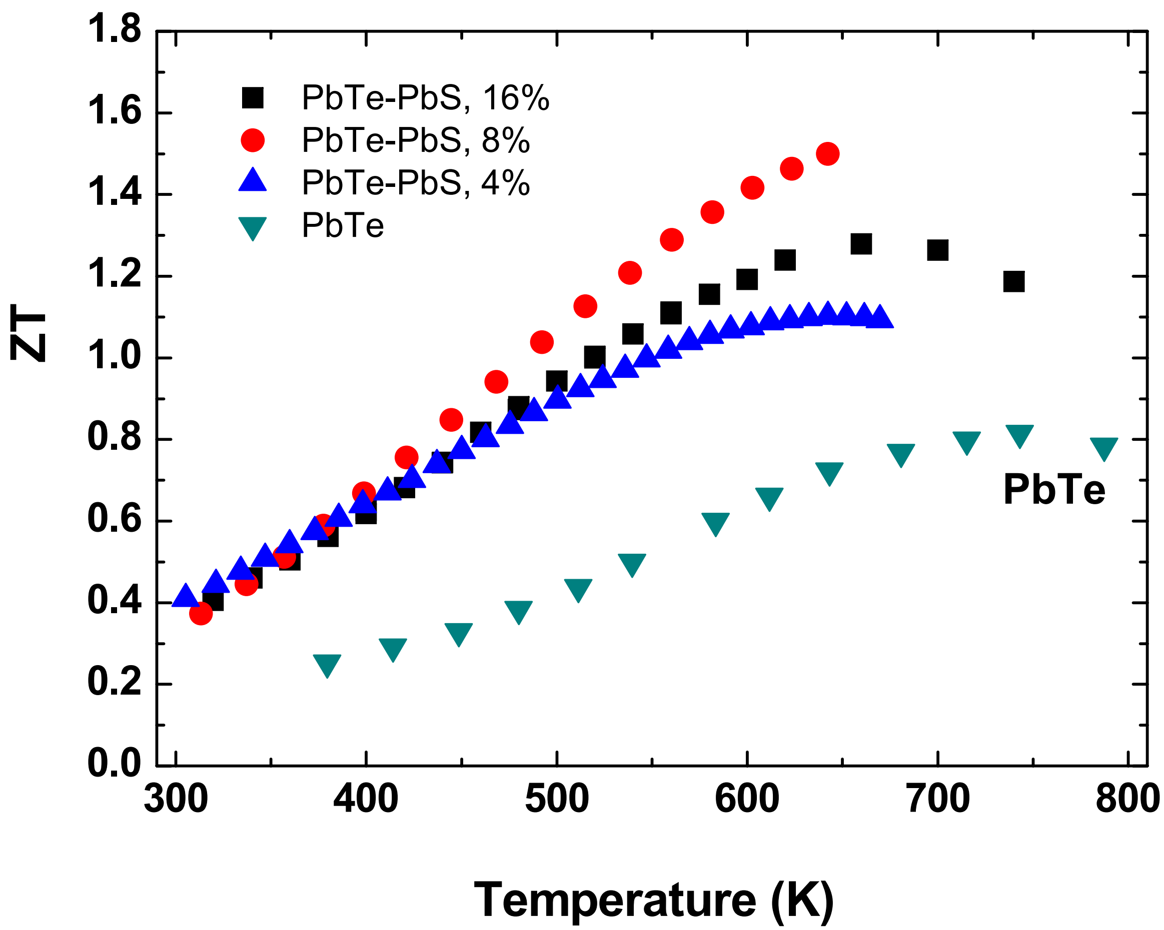
$Pb_{0.95}Sn_{0.05}Te$-PbS 16% Transport Data







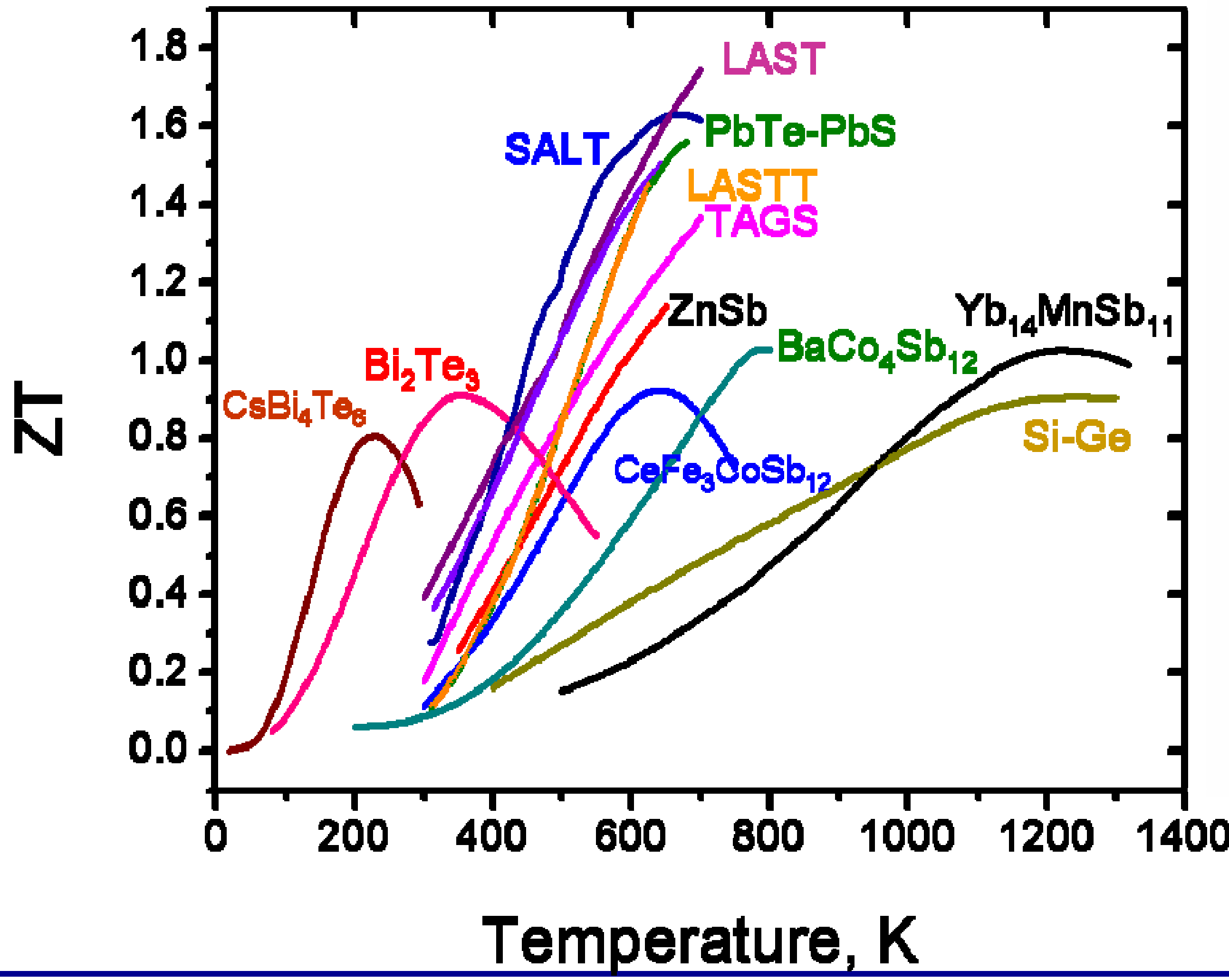
ZT enhancements: PbTe-PbS



A Ag-free system with as good properties as LAST-18.

Androulakis, J.; Lin, C.-H.; Kong, H.-J.; Uher, C.; Wu, C.-I.; Hogan, T.; Cook, B. A.; Caillat, T.; Paraskevopoulos, K. M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**; 129(31); 9780-9788.

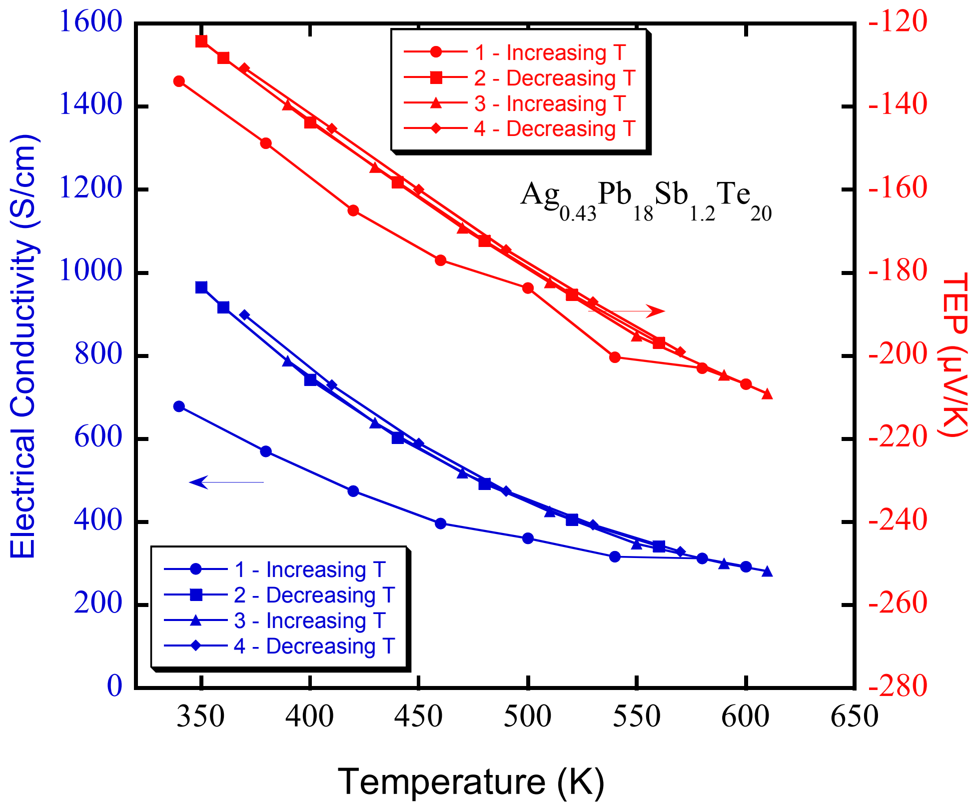
Best ZT Materials



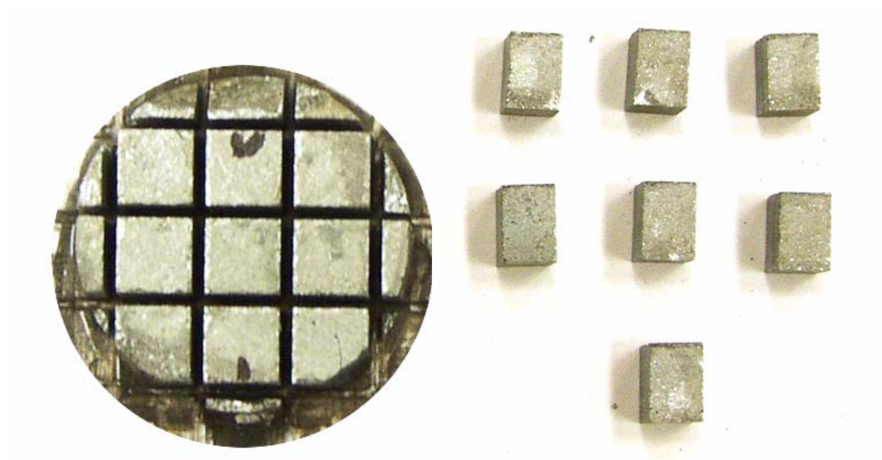
Schock

Completed and Processed Ingot

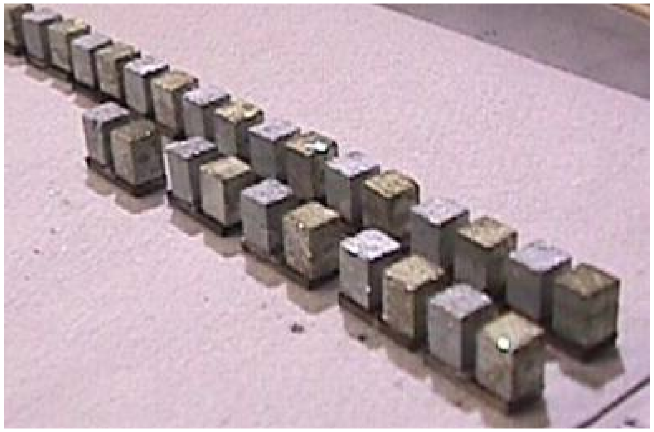
Composition: $Ag_{0.43}Pb_{18}Sb_{1.2}Te_{20}$ Weight: 200 grams

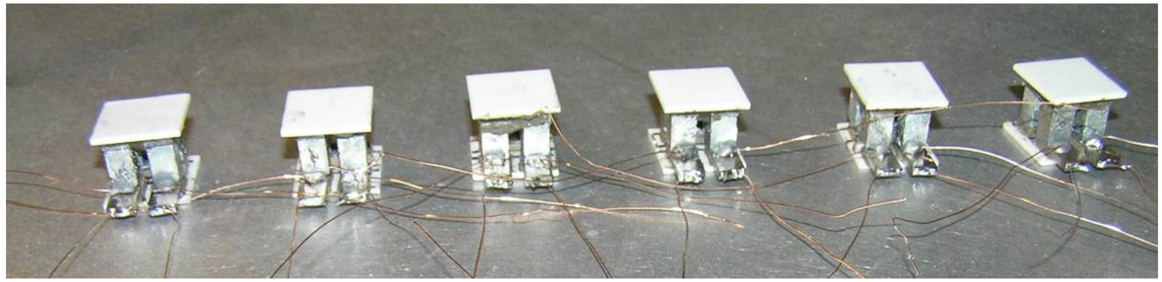


Temperature cyclability

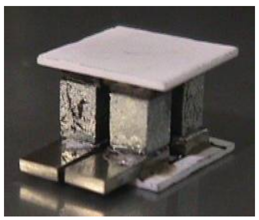


Module Fabrication

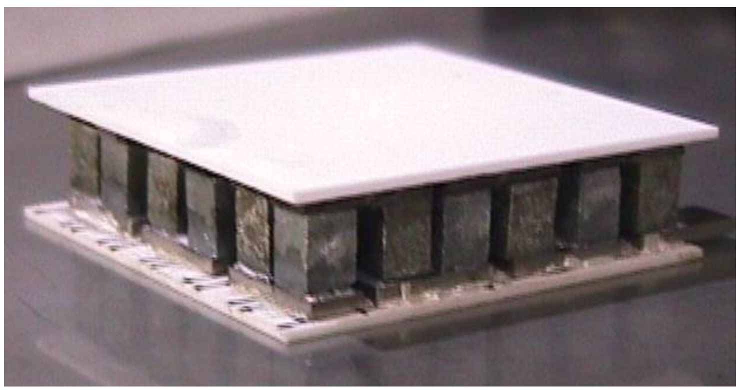


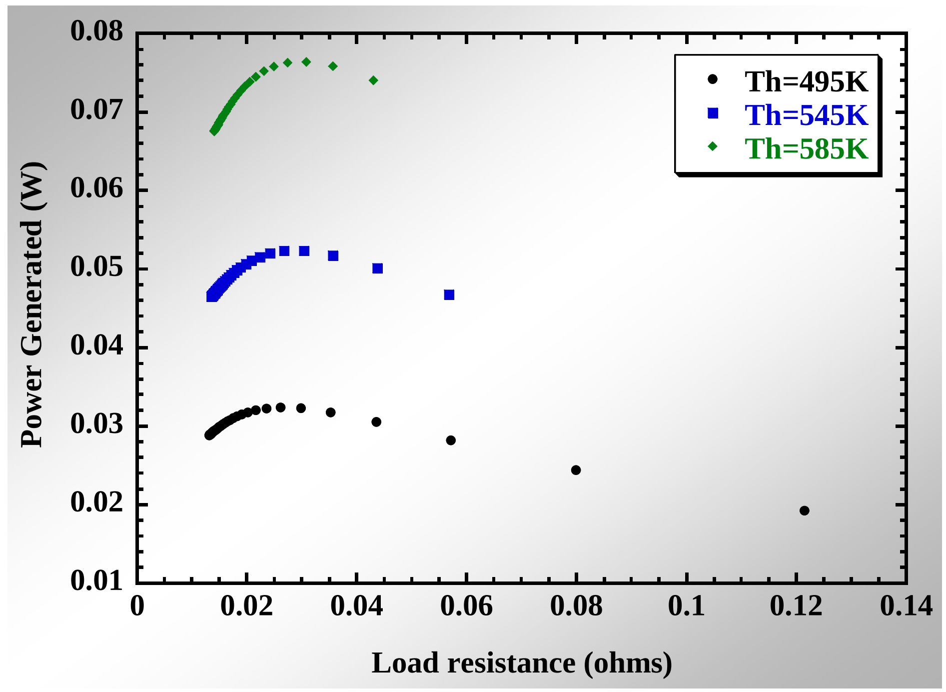


- Hot side diffusion contacts, and cold side solder contacts with <10 μW·cm2 have been achieved.



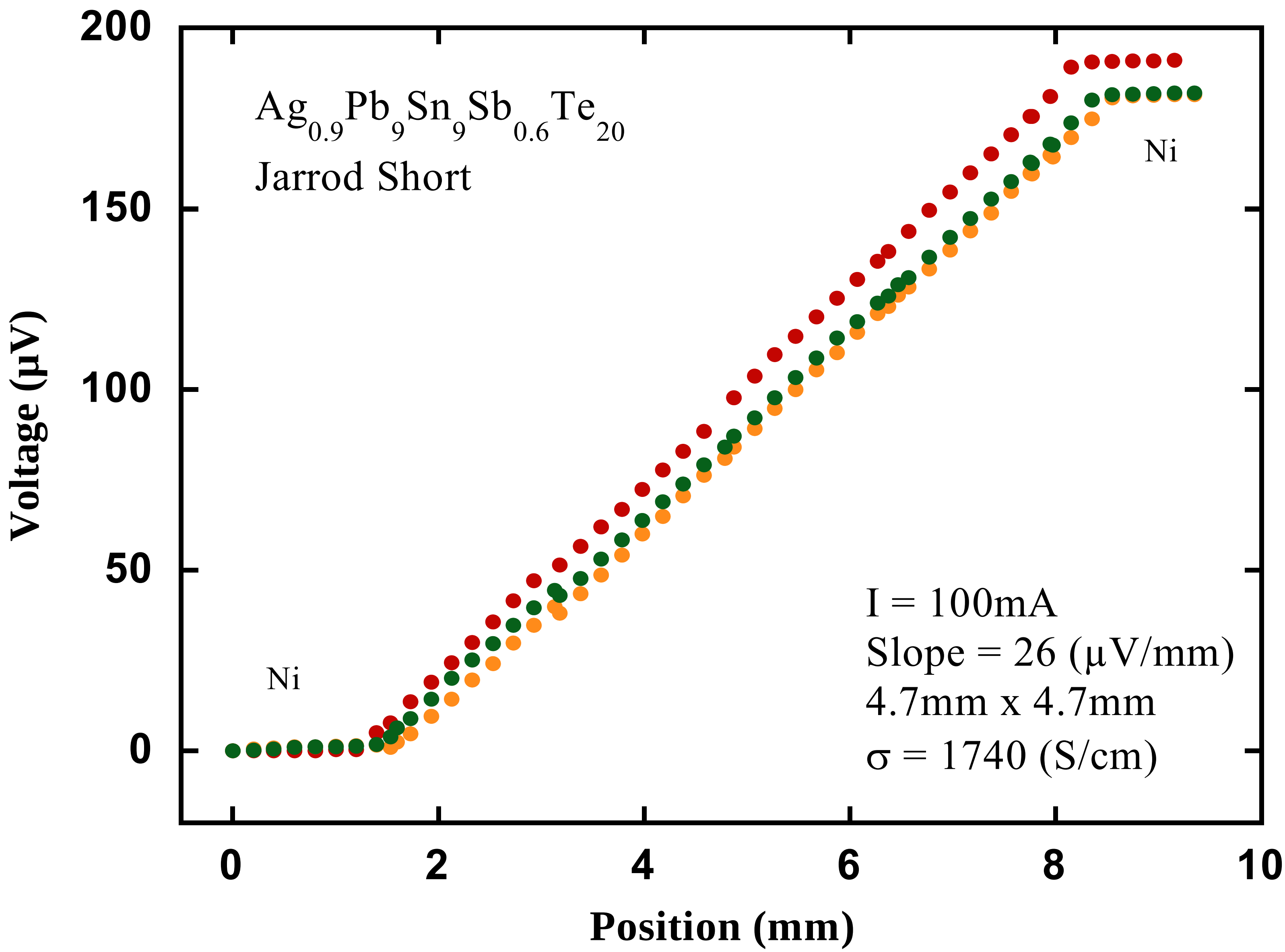
1.78mΩ total → 16.0μΩ·cm²





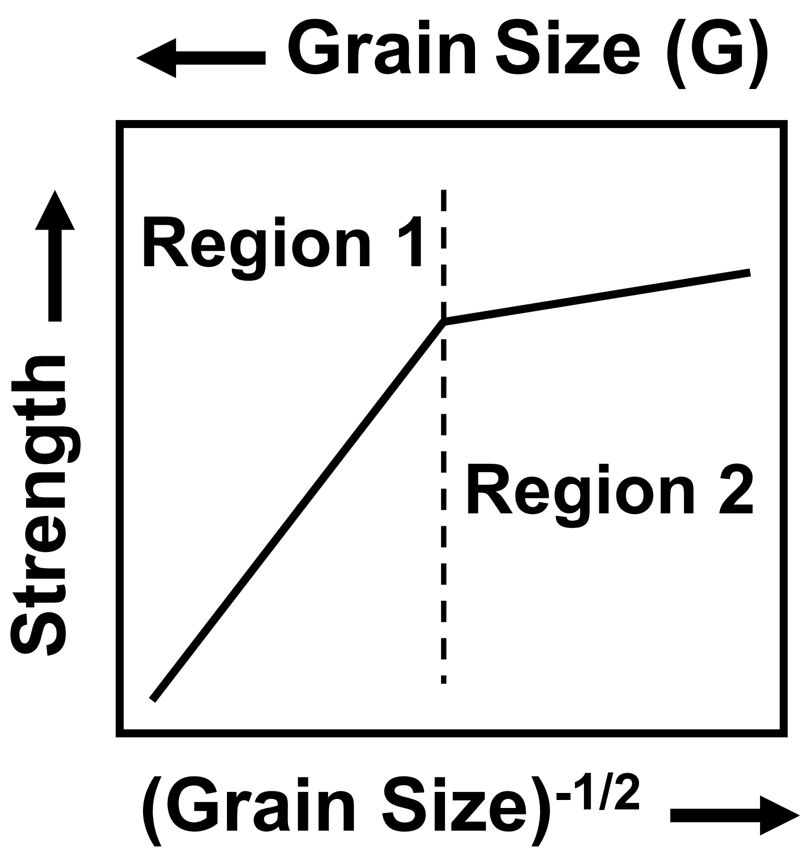
Scanning Probe Results

Ni electrode on LASTT

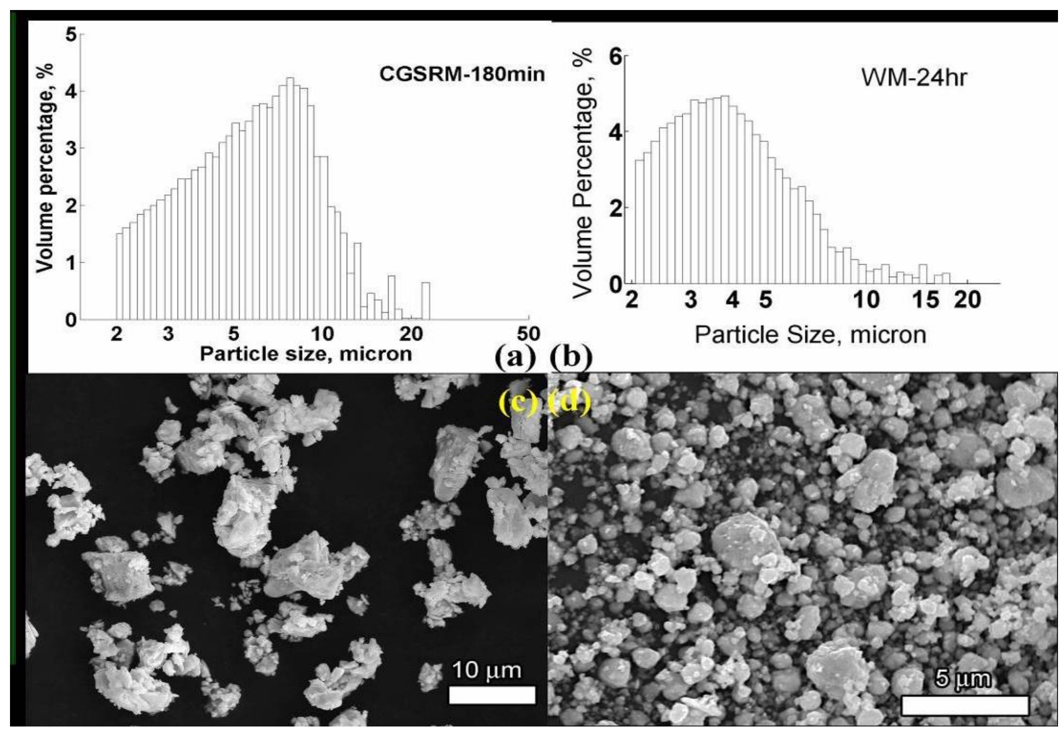


Making brittle materials strong

Eldon Case



For brittle materials in general, the fracture strength is a function of the reciprocal square root of grain size.

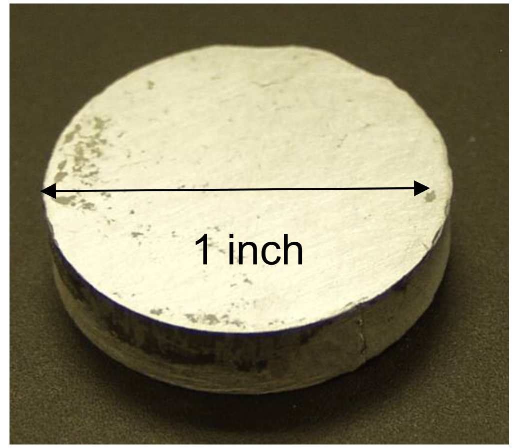


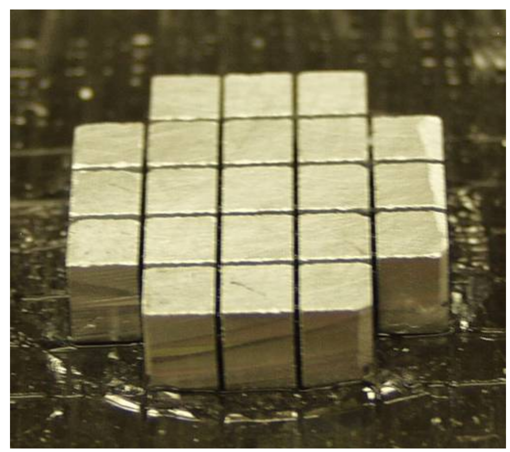
Powder processing
Hot pressing

Hot Press Billets

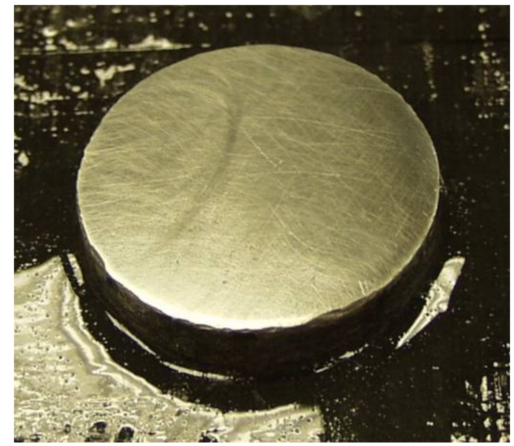
Schock, Case

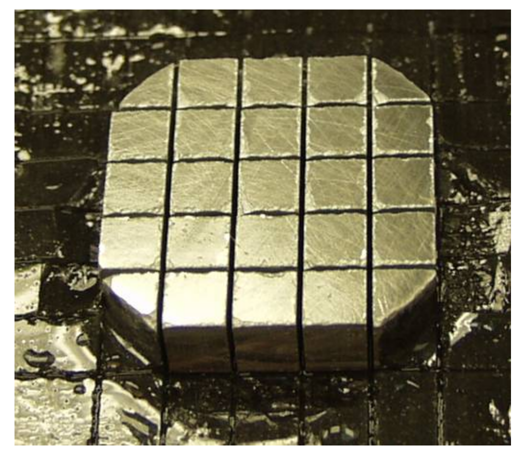
HPMSU-01





HPMSU-02





Conclusions

- LAST, LASTT and SALT: promising thermoelectric materials for next generation power generation modules. (expected device efficiency ~14%)
- Nanostructures strongly reduce thermal conductivity (the new paradigm…).
- Scale up successful in producing large quantities but material is brittle and contains microcracks.
- Hot pressing and powder processing yield 3x improvement in strength.
- Higher average ZT (>2) needed to reach 20% efficiency.
- Can nanostructures increase the power factor?

Students and postdocs

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- Jarrod Short, Electrical Engineering
- Jonathan D'Angelo, Electrical Engineering
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- Chris Malliakas, Chemistry
- Khang Hoang, Physics
- Ahmed Salameh, Physics
- Mayank Mittal, Mech. Engineering
- Aurelie Guegen, Chemistry

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- Ed Timm, Mechanical Engineering
- Robert Pcionek, Chemistry
- Chun-I Wu, E. Engineering
- Mi Kyung Han, Chemistry
- Chia-Her Lin, Chemistry
- Kyunghan Ahn, Chemistry

Undergraduates

- Adam Pilchak, Materials Science
- Teresa Rhodes, Chemistry
- Jason Johnson, Materials Science

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