2007 International Institute for Nanotechnology Symposium

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Hotel Orrington, Evanston, IL

From Heat to Electricity: How "nano" Saved Thermoelectrics

Mercouri Kanatzidis, Northwestern University

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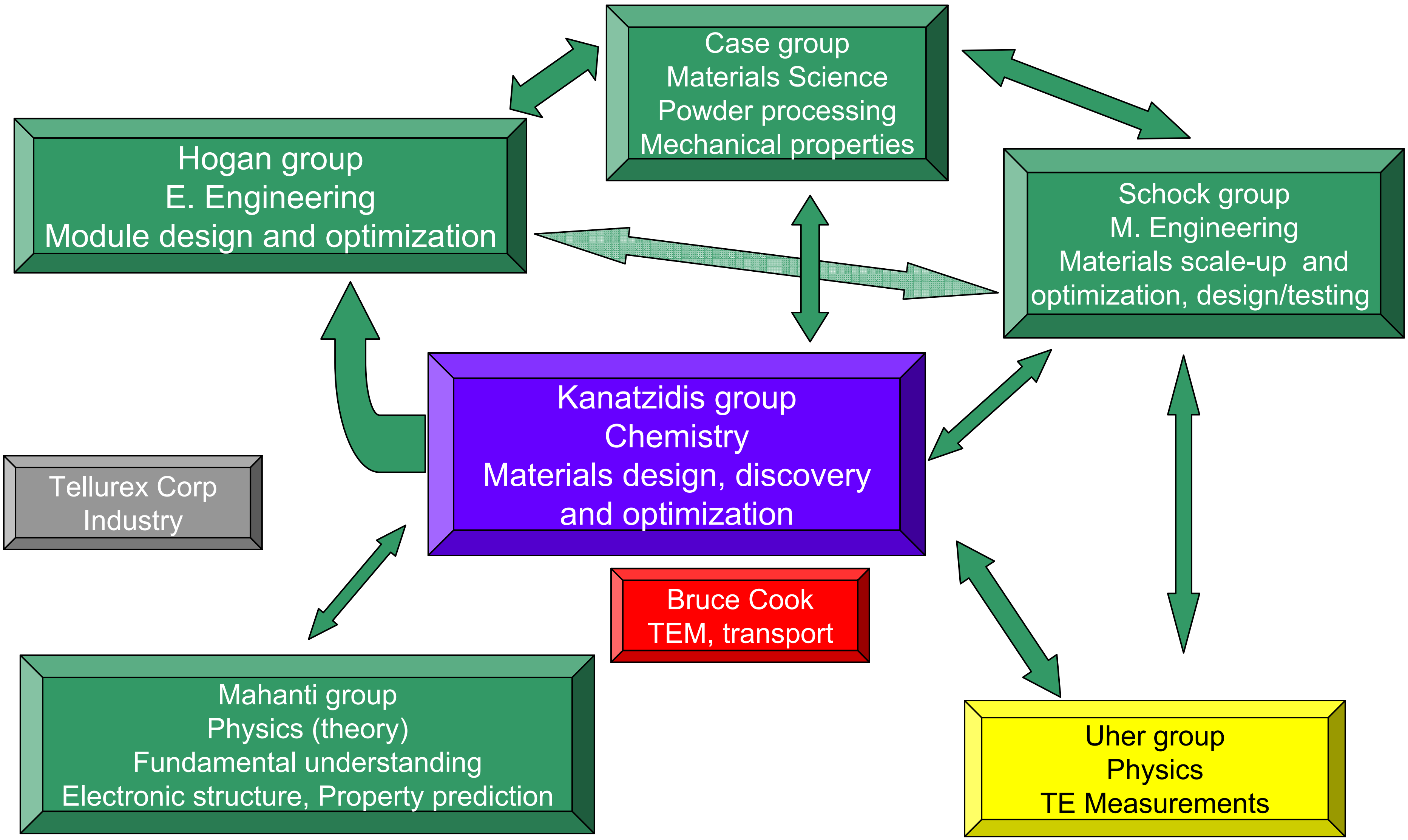
Collaborating Team interactions

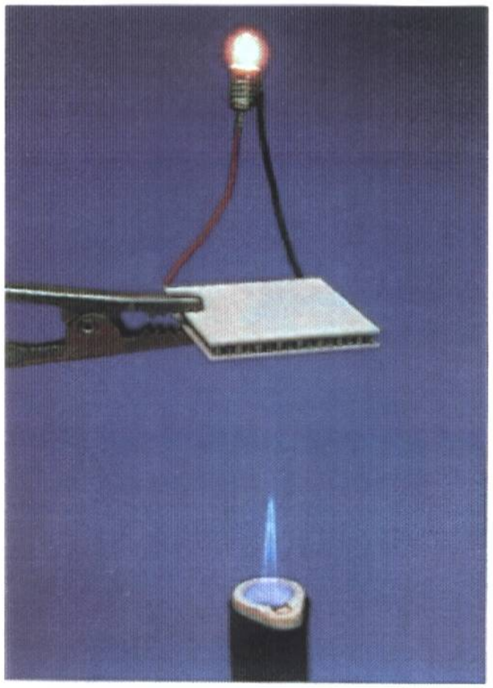


Outline

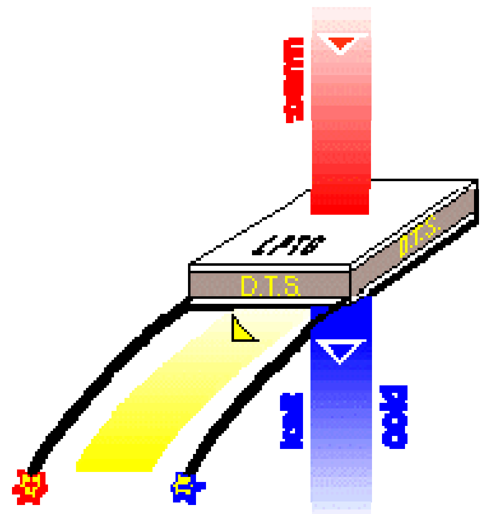
- Introduction
- Materials under investigation
- Synthesis (successes and challenges)
- TEM characterization and nanostructuring
- Structure property relationships- Nanostructures reduce the lattice thermal conductivity
- Materials scale up and optimization
- Module Fabrication Progress, low resistance contacts
- Making brittle materials strong
- Conclusions

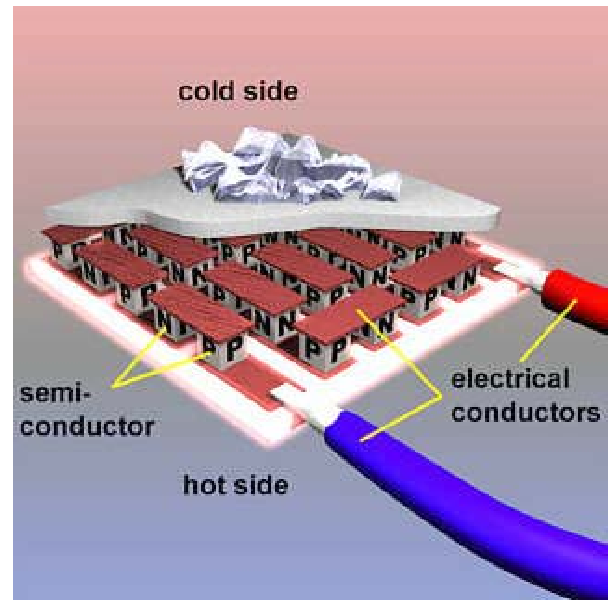
Heat to Electrical Energy Directly

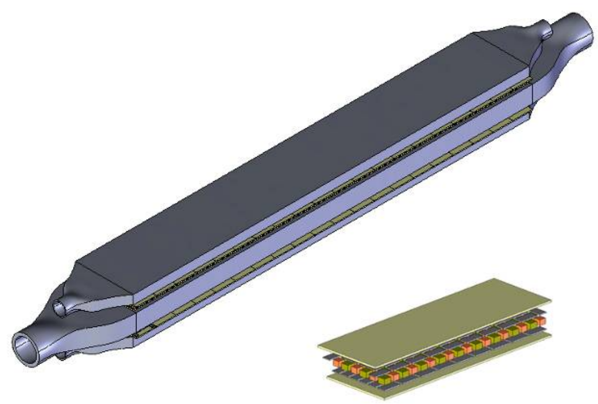
Up to 20% conversion efficiency with right materials



Electrical
Power Generation





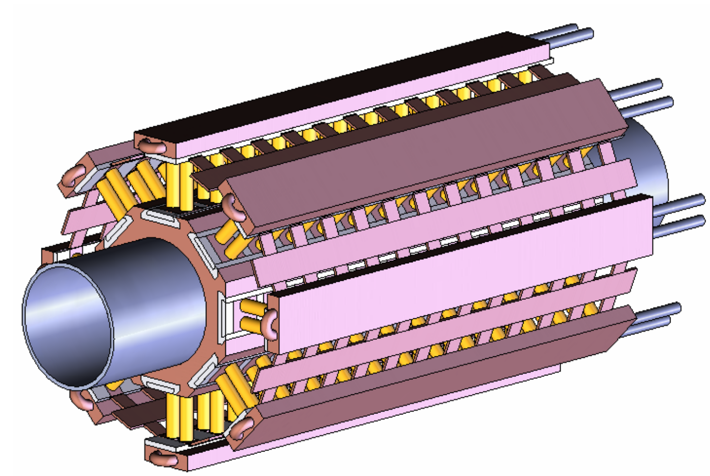


TE devices have <u>no moving parts, no noise, reliable</u>

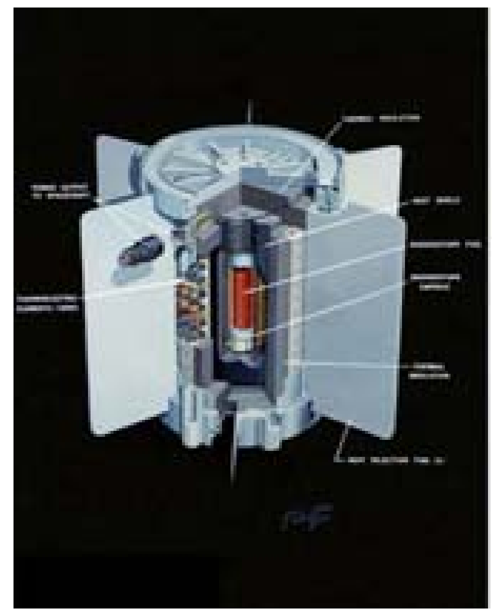
http://www.dts-generator.com/

Thermoelectric applications

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

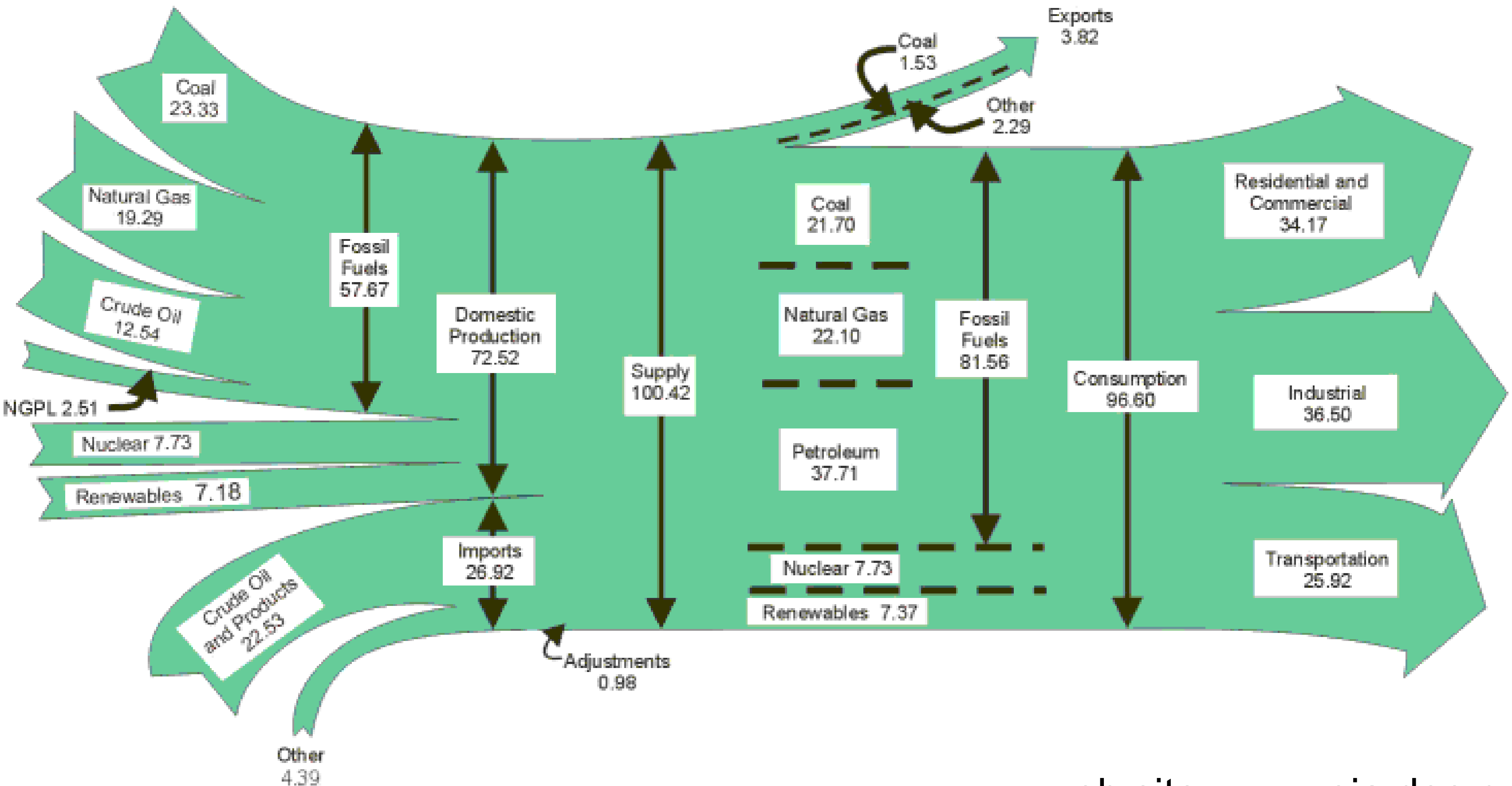


- Space power
- Remote Power Generation
- Solar energy
- Geothermal power generation
- Direct nuclear to electrical



PIONEER 10 and 11

U.S. Energy Flow, 1999



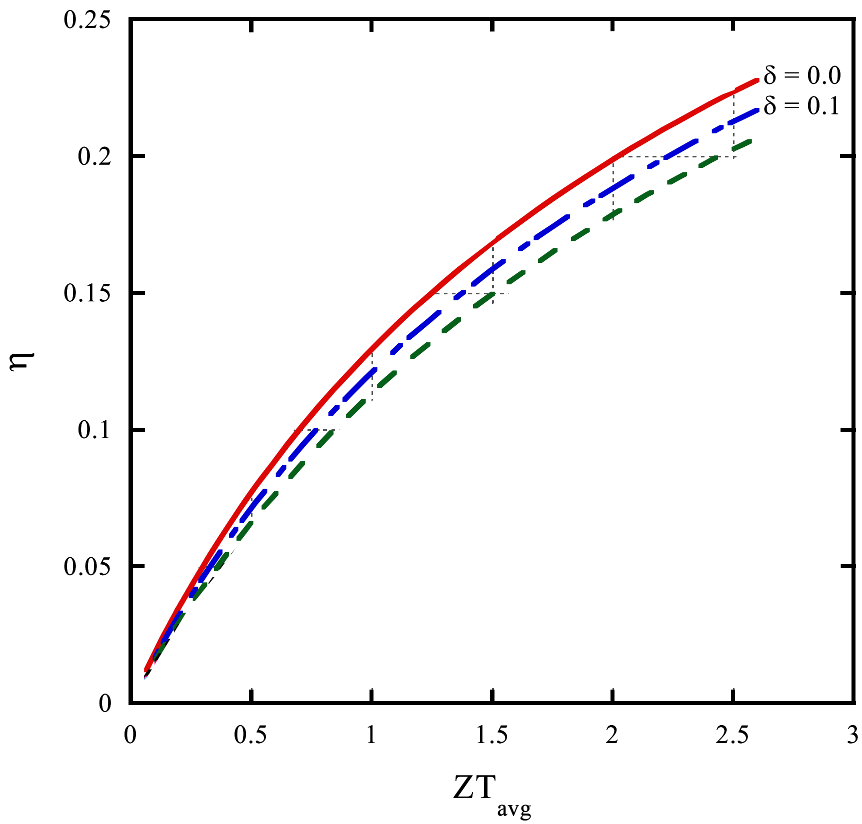
web site: www.eia.doe.gov

Given that ~60% of energy becomes waste heat, even a 10% capture and 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

$$\sigma \cdot S^2$$

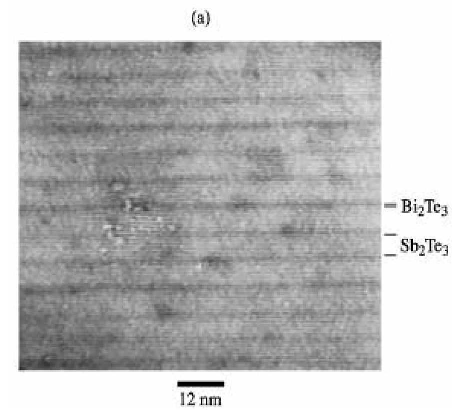
$\delta = R_c/R$

For T_h = 800K

T_c = 300K

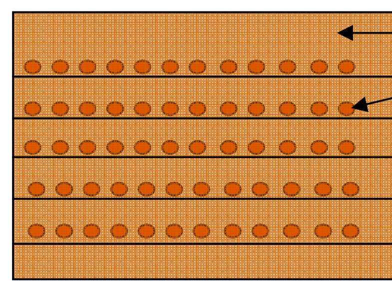
Today’s situation

- 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



10Å/50Å Bi2Te3/Sb2Te3 superlattice structures

- 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

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

Recent Developments in Bulk Thermoelectric Materials

George S. Nolas, Joe Poon, and Mercouri Kanatzidis

Abstract

Good thermoelectric materials possess low thermal conductivity while maximizing electric carrier transport. This article looks at various classes of materials to understand their behavior and determine methods to modify or "tune" them to optimize their thermoelectric properties. Whether it is the use of "rattlers" in cage structures such as skutterudites, or mixed-lattice atoms such as the complex half-Heusler alloys, the ability to manipulate the thermal conductivity of a material is essential in optimizing its properties for thermoelectric applications.

Keywords: *alloy, compound, thermal conductivity, thermoelectricity.*

scattering centers, thus greatly reducing the lattice thermal conductivity of these compounds, has resulted in improvements in the TE properties of skutterudites.[1,2] The smaller and heavier the ion in the voids, the larger the disorder that is produced and thus the larger the reduction in the lattice thermal conductivity. Skutterudite antimonides possess the largest voids and are therefore of particular interest for TE applications. Results from Sales et al.[4] and Fleurial et al.[5] show high *ZT* values (the common figure of merit for comparing different TE materials) at elevated temperatures in $LaFe_3CoSb_{12}$ and $CeFe_3CoSb_{12}$ for both *p*-type and *n*-type specimens. *ZT* values approaching 1.4 above 900°C for these materials have been reported,[5] indicating their successful optimization for TE power-conversion applications.

It should be noted, however, that a small concentration of void-fillers results in a large reduction in thermal conductivity. Five percent of La[6] or Ce,[7] for example, in the voids of $CoSb_3$ results in a thermal-conductivity reduction of ~50%, as compared with $CoSb_3$. In certain cases, higher power factors have also been obtained with partial filling, as compared with more fully filled, charge-compensated compositions. The aim in investigating partially filled skutterudites is realizing an optimum electron concentration while re-

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ZT and Electronic Structure

Isotropic structure

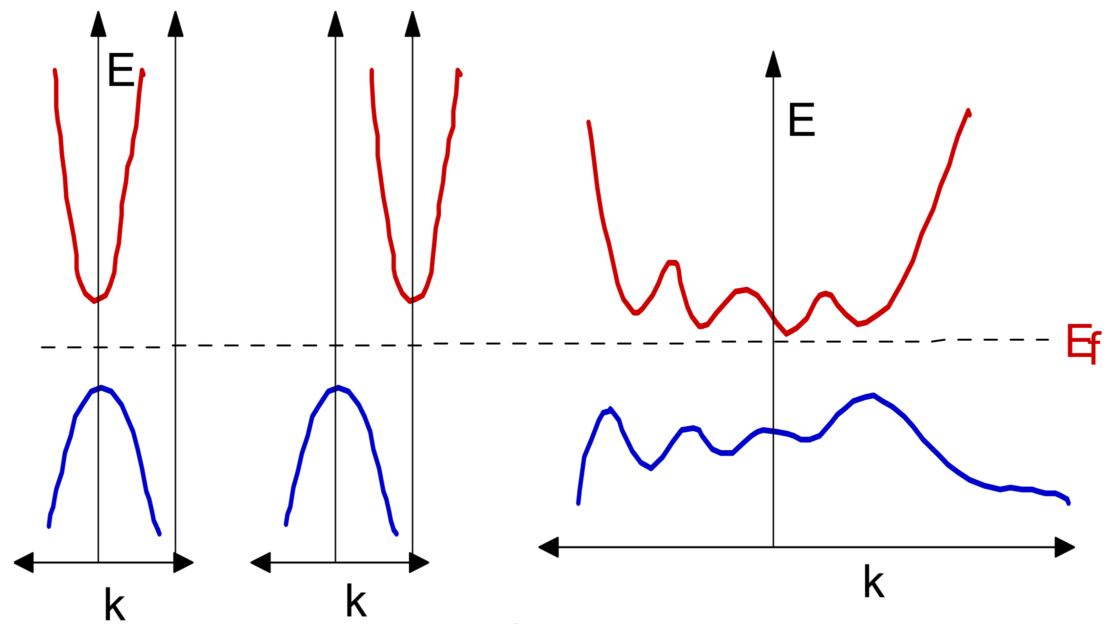
Anisotropic structure

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

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

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



Complex electronic structure

Selection criteria for candidate materials

- Narrow band-gap semiconductors
- Heavy elements
  - High μ, low κ
- Large unit cell, complex structure
  - low κ
- Highly anisotropic or highly symmetric…
- Complex compositions
  - low κ, complex electronic structure

Investigating the A/Bi/Q system

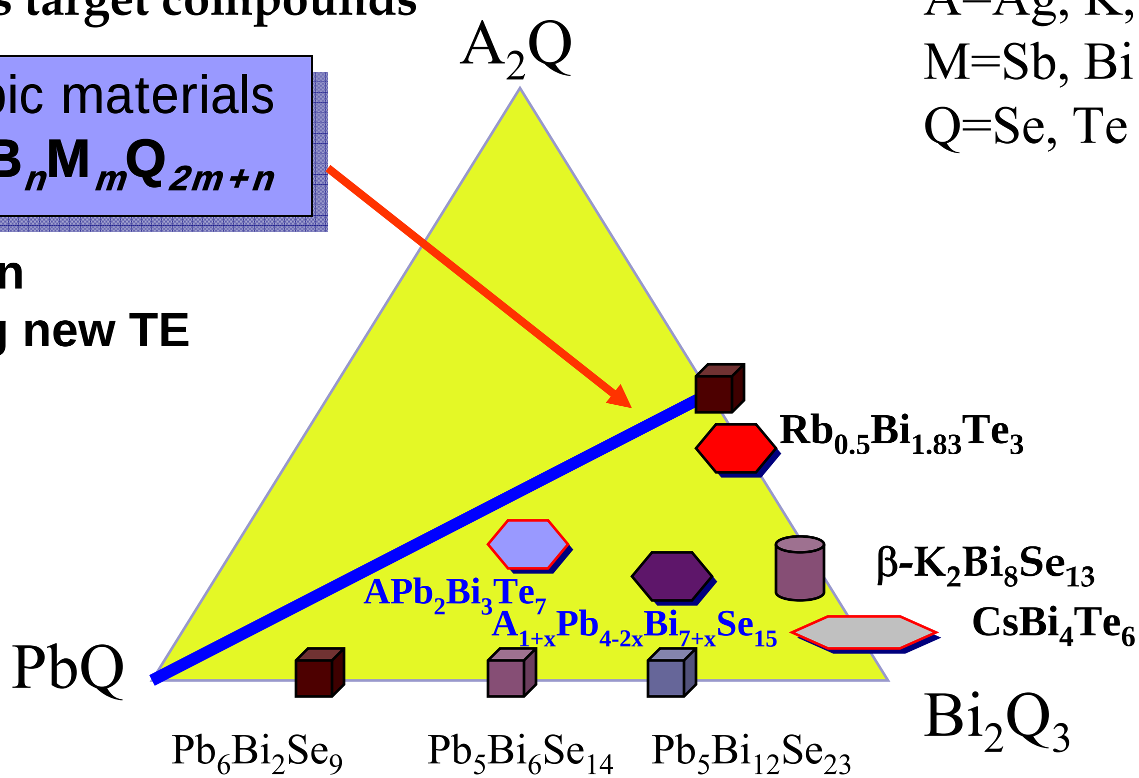
$A_2Q + PbQ + M_2Q_3$ ------> $(A_2Q)_n(PbQ)_m(M_2Q_3)_p$

Map generates target compounds

A=Ag, K, Rb, Cs
M=Sb, Bi
Q=Se, Te

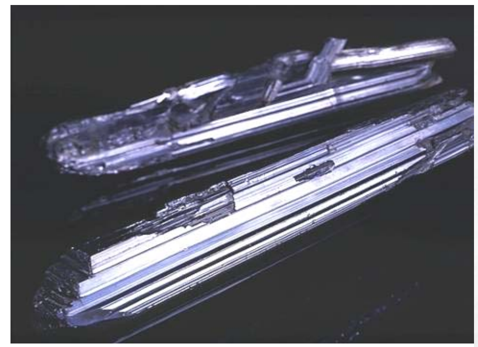
Cubic materials
$A_mB_nM_mQ_{2m+n}$

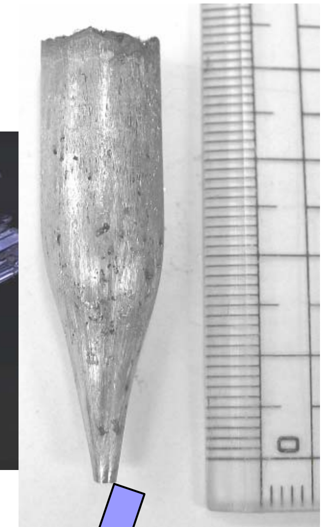
Phases shown are promising new TE materials

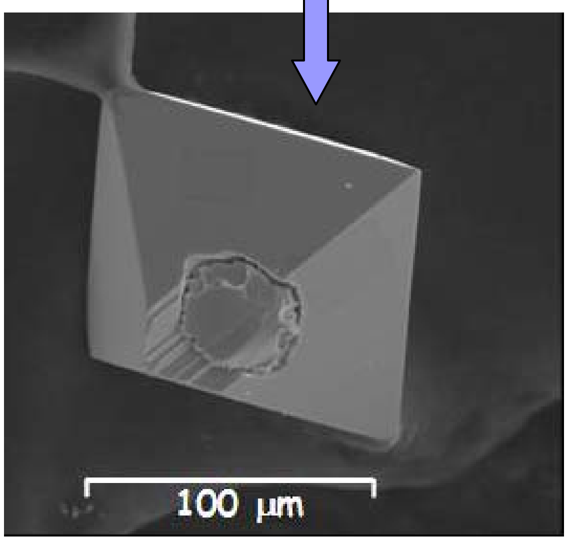


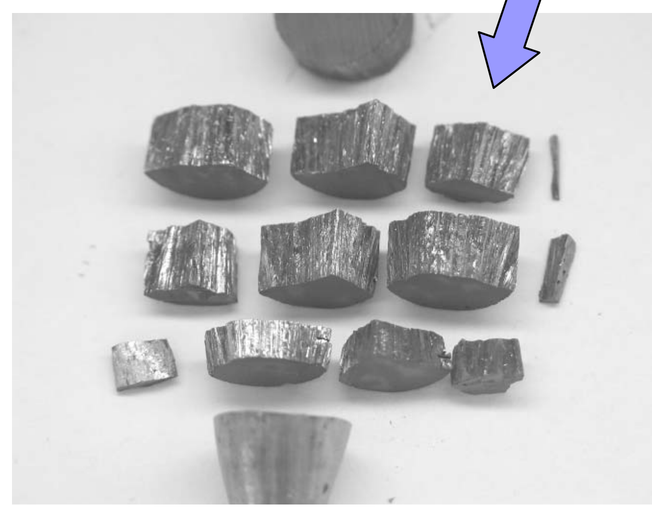
Compounds discovered

- $K_2Bi_8Se_{13}$, $KPbBi_9Se_{13}$, $KPb_4Sb_7Se_{15}$
- $Cs_{1-x}Pb_{5-x}Bi_{10+x}Se_{21}$
- $CsPbBi_3Te_6$, $CsPb_2Bi_3Te_7$, $RbPbBi_3Te_6$, $RbPb_2Bi_3Te_7$, $RbPb_3Bi_3Te_8$,
- $KPbBiSe_3$, $K_2PbBi_2Se_5$
- $AgPb1_0SbTe_{12}$, $NaPb_{20}SbTe_{22}$

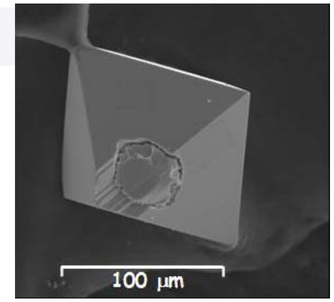


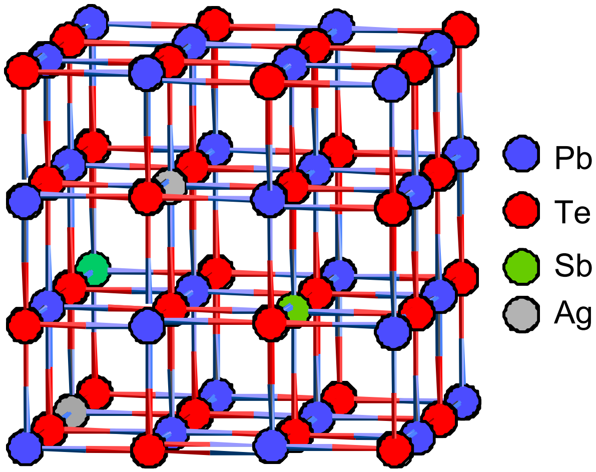


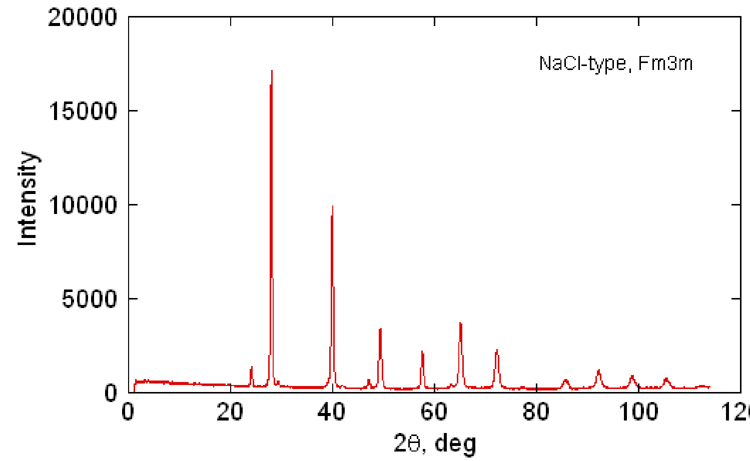


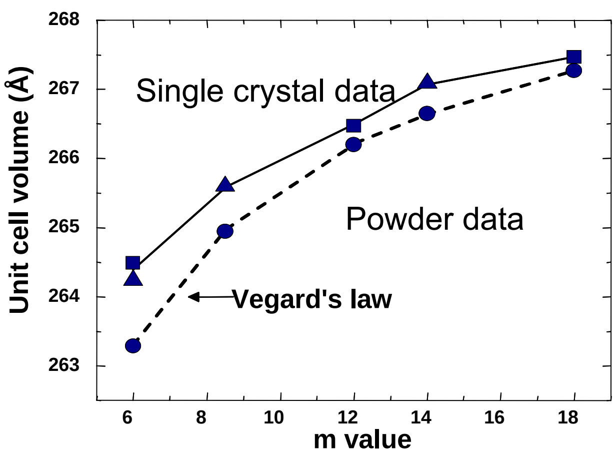


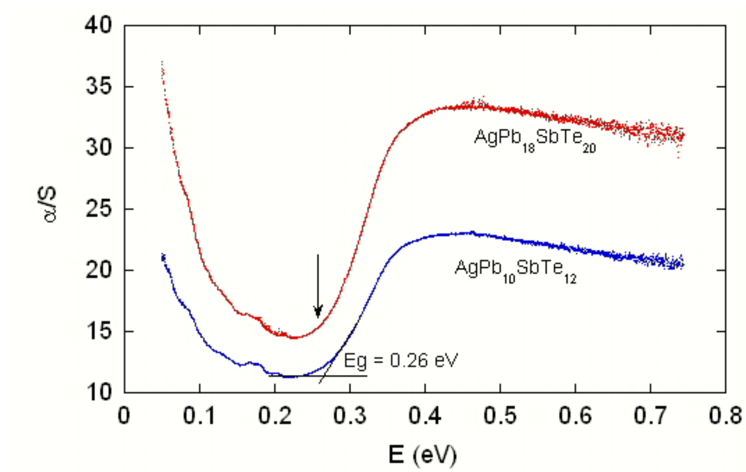
$AgPb_mSbTe_{2+m}$ (LAST-*m*)
$NaPb_mSbTe_{2+m}$ (SALT-*m*)







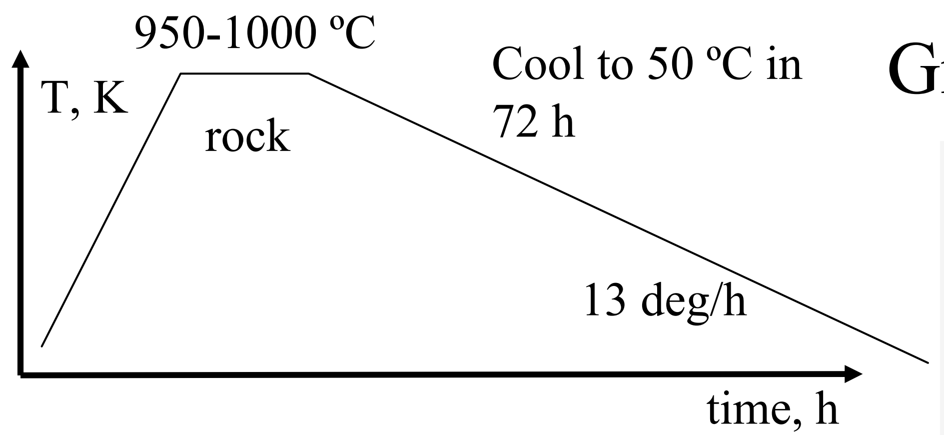


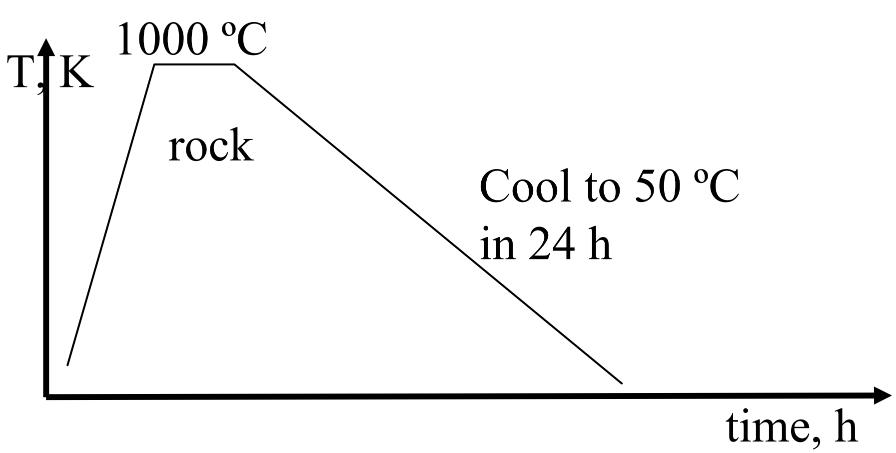


- No phase transitions to melting point

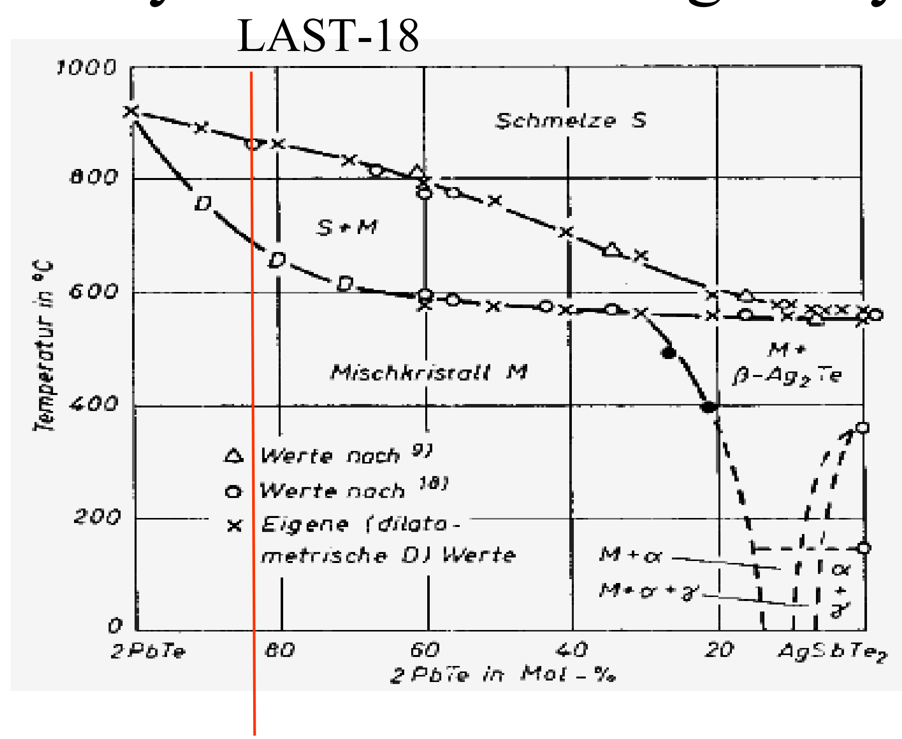
Synthesis

Ingot properties very sensitive to cooling profile





Gravity induced inhomogeneity

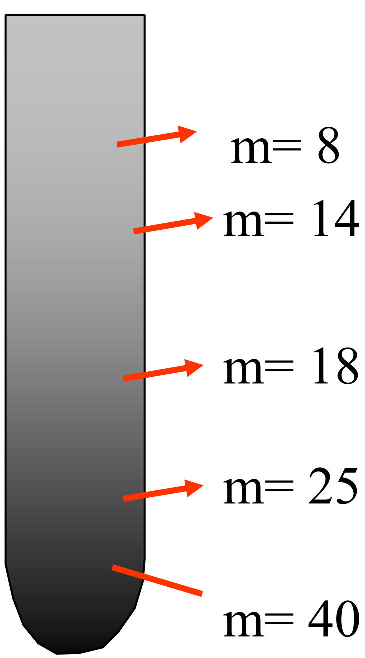


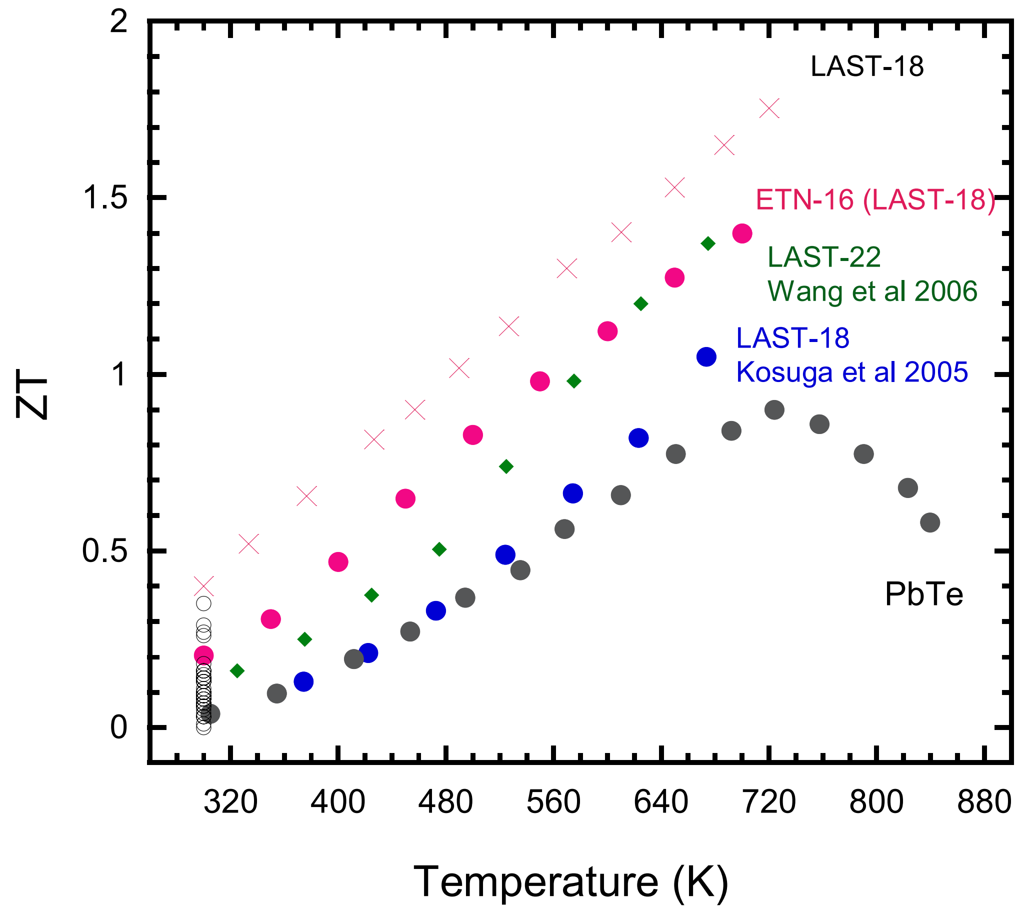
Wernick, J. H.. *Metallurg. Soc. Conf. Proc.* (1960), 5 69-87.

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

Large scale LAST-18 (n-type)

Strong composition grading along ingot





Deviations from the $AgPb_{18}SbTe_{20}$ composition
Best samples are Te-deficient

Kosuga et al *J. Alloys Compnds*, 2005, *391*, 288

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

ETN125 A	Ag	Sb	Pb	Te
	1.65	1.26	46.92	50.17
	1.60	1.39	47.27	49.75
	1.70	1.47	47.18	49.65
	1.42	1.44	47.43	49.71
Average	1.59	1.39	47.20	49.82

ETN125 B	Ag	Sb	Pb	Te
	1.19	1.21	47.63	49.98
	1.61	1.26	48.18	48.94
	1.82	1.45	47.65	49.08
	1.18	1.76	47.36	49.70
	2.04	1.47	46.98	49.51
Average	1.57	1.43	47.56	49.44

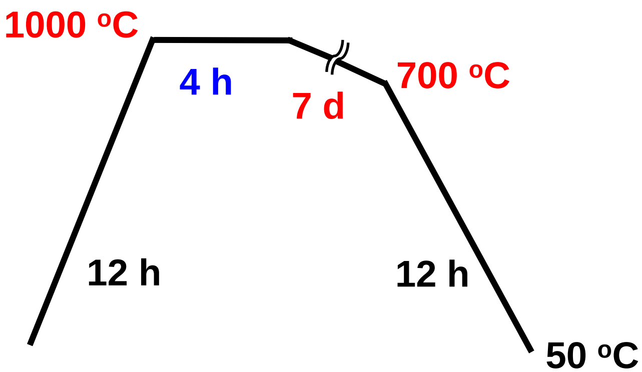
ETN125 C	Ag	Sb	Pb	Te
	1.49	1.60	47.04	49.87
	1.74	1.11	47.35	49.80
	0.73	1.72	48.05	49.50
	0.89	1.79	47.35	49.96
Average	1.21	1.56	47.45	49.78

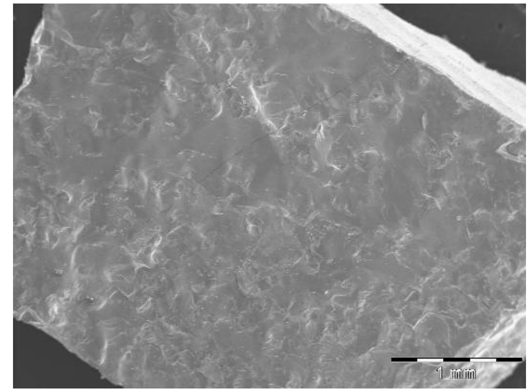
ETN125 D	Ag	Sb	Pb	Te
	1.55	0.85	48.19	49.92
	1.02	1.39	48.02	49.56
	1.45	1.24	47.70	49.61
	2.65	1.36	47.06	48.92
	1.12	1.18	47.73	49.97
Average	1.50	1.13	47.89	49.53

LAST-18: Synthesis with Slow Cooling

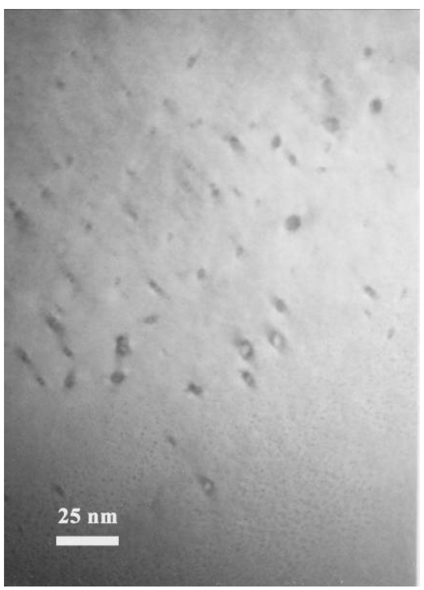
~2deg/hr

Ag	Sb	Pb	Te	amount
0.86	1	19	20	105 g

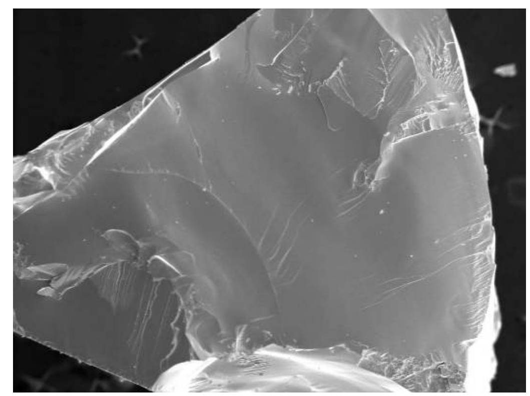




fast cooled sample

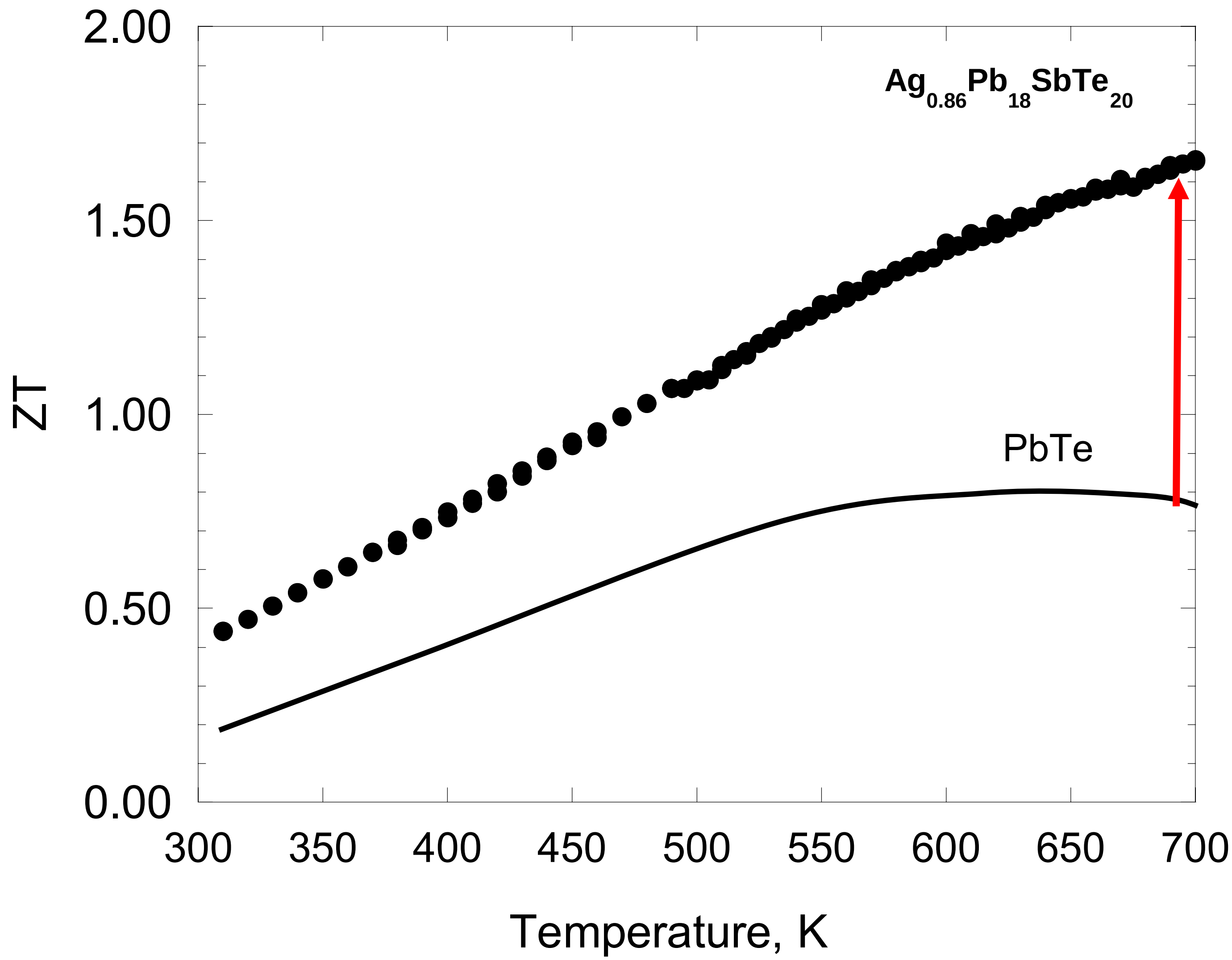


ETN125	σ (S/cm)	S (μV/K)	PF (μW/cm•K²)
A	535	-121	7.8
B	959	-128	15.7
C	1026	-158	25.6
D	1341	-180	43.4



slow cooled sample

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



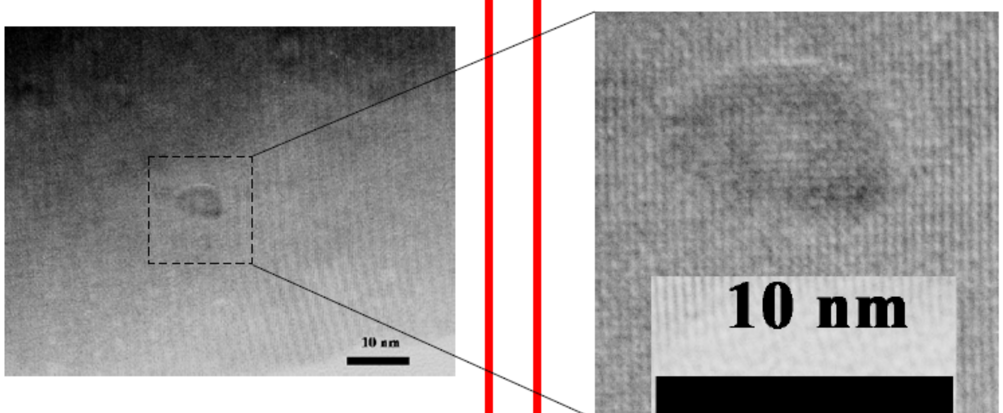
TEM investigation on nanostructuring: LAST-18 (Cook)

MSU DY-92062 quenched and annealed (450°C 2 days)
$Ag_{0.53}Pb_{18}Sb_{1.2}Te_{20}$

Sample was thinned, dimpled, ion-milled, and carbon coated (~ 10 nm/side) prior to examination

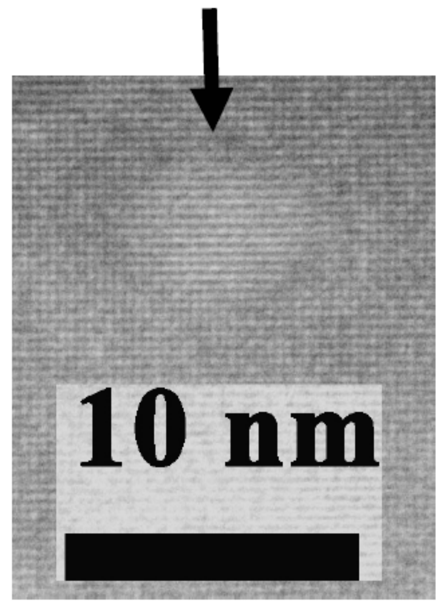
Near edge of foil – note semi-coherent feature (dark contrast) and high density of fully-coherent regions (light contrast)

Semi-coherent phase near edge of foil:



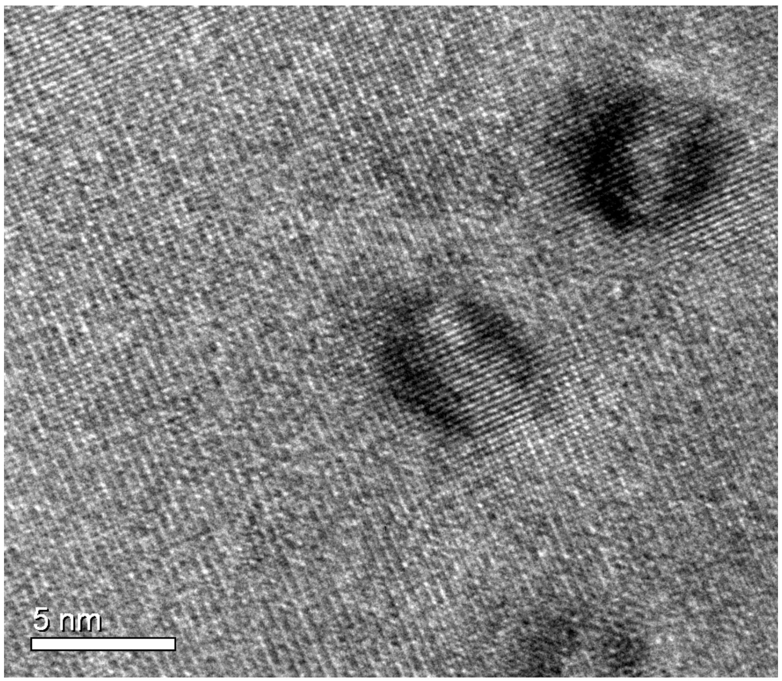
Example of coherent phase

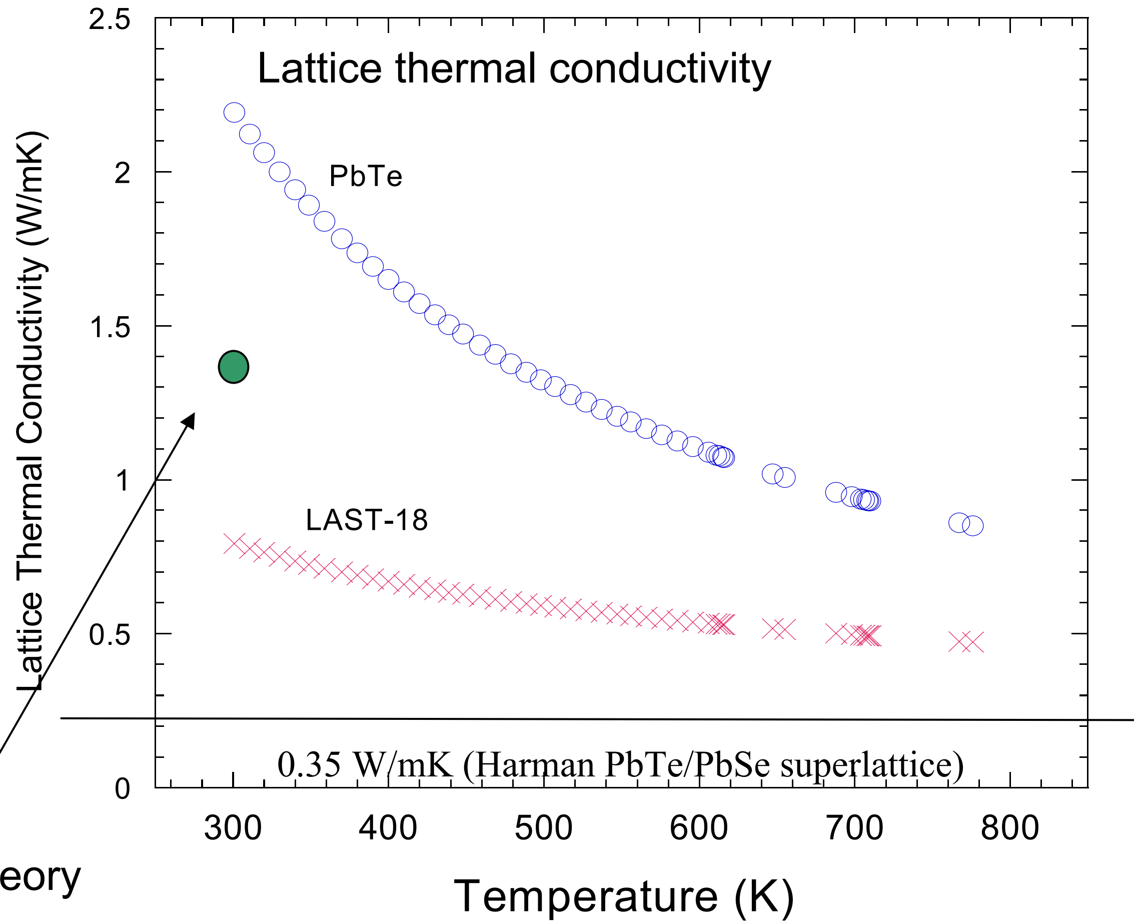
Note: strain field surrounds the region



Annealing may promote nucleation and growth of nanoscale phases. Coherent features appear to be intrinsic, not a result of sample preparation

Nanostructures reduce the lattice thermal conductivity





Clemens-Drabble theory

Recent Report for Sintered Pellet $Ag_{0.8}Pb_{22}SbTe_{20}$, ZT ~ 1.4 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

Heng Wang, Jing-Feng Li,[a] Ce-Wen Nan, and Min Zhou
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
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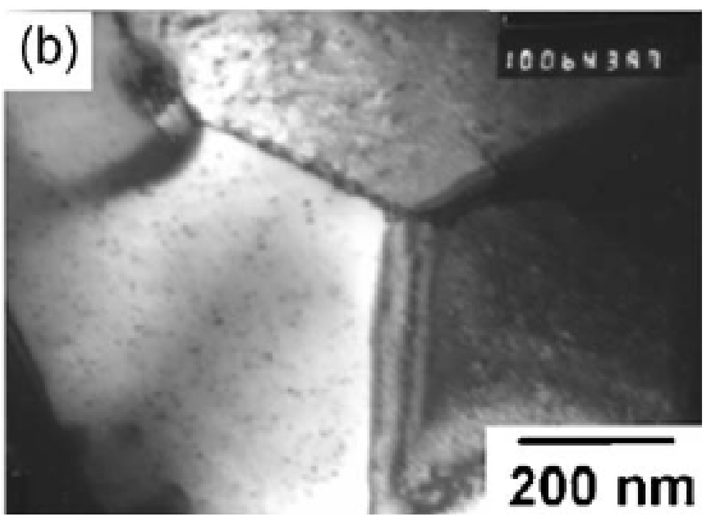
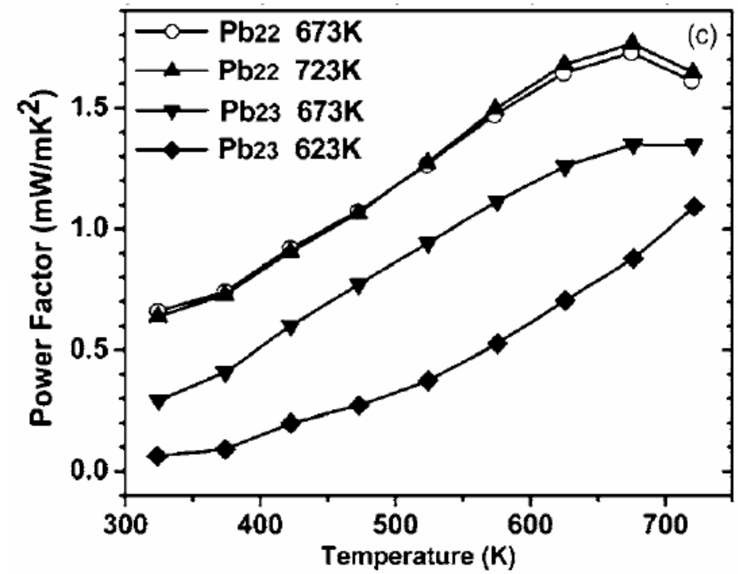
(Received 7 December 2005; accepted 7 February 2006; published online 28 February 2006)





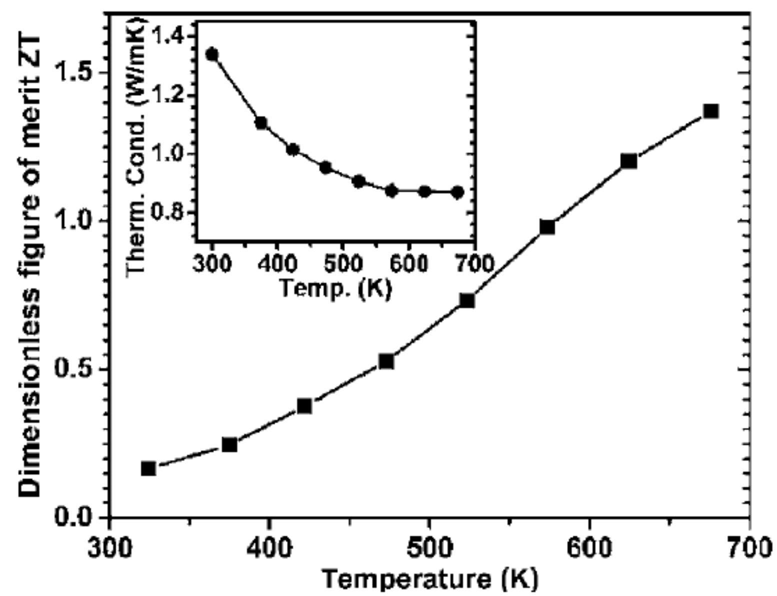
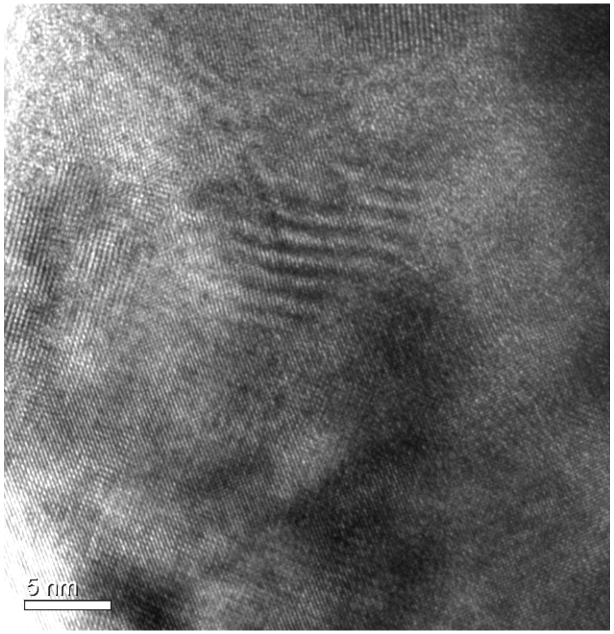
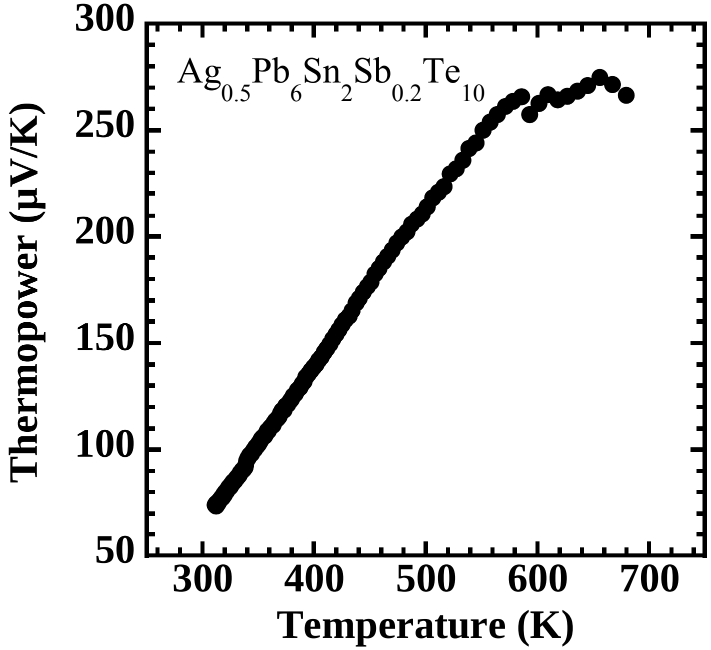


FIG. 4. *ZT* value and thermal conductivity (upper left corner) of $Ag_{0.8}Pb_{22}SbTe_{20}$ sample at different temperatures.

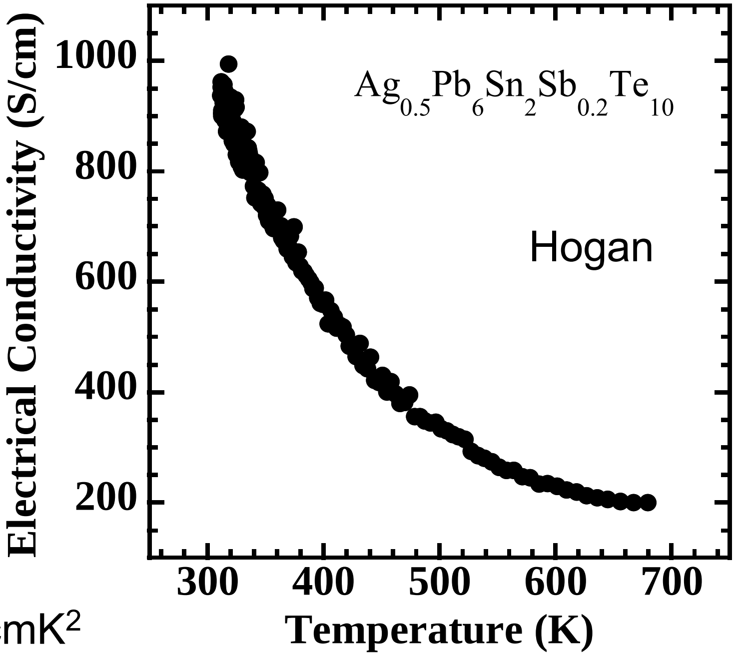
P-type materials, LASTT

- (LASTT-m) $Ag(Pb_{1-x}Sn_x)_mSbTe_{2+m}$
- Sn atoms act as acceptors
- Ag atoms act as acceptors
- Sb atoms act as donors
- e.g $AgPb_{10}Sn_8SbTe_{20}$, $Ag_xPb_7Sn_3Sb_yTe_{12}$, $Ag_{1-x}SnSb_{1+x}Te_3$, etc
- Very low lattice thermal conductivity
- Good homogeneity





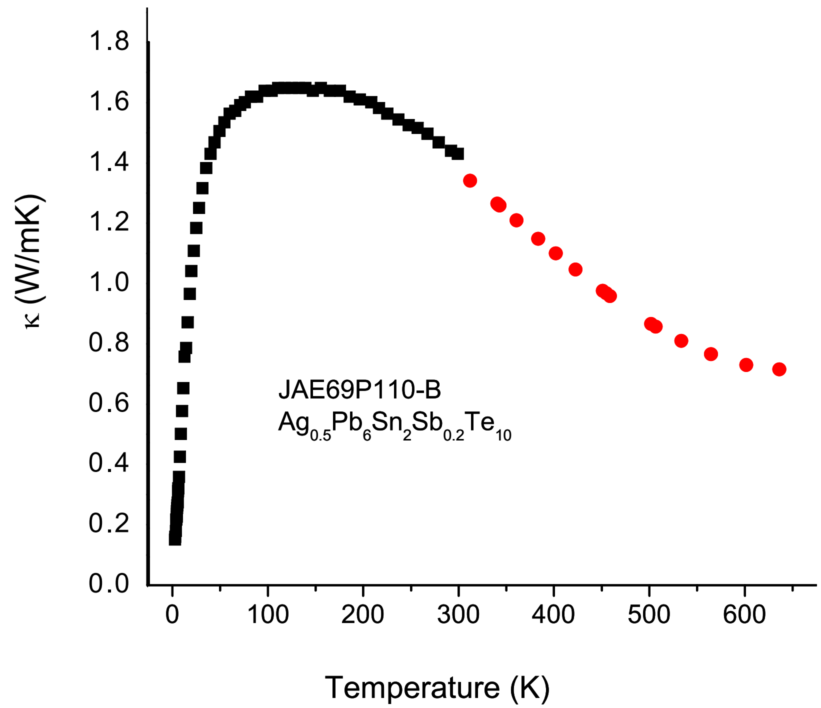
PF~17-18 μW/cmK^2

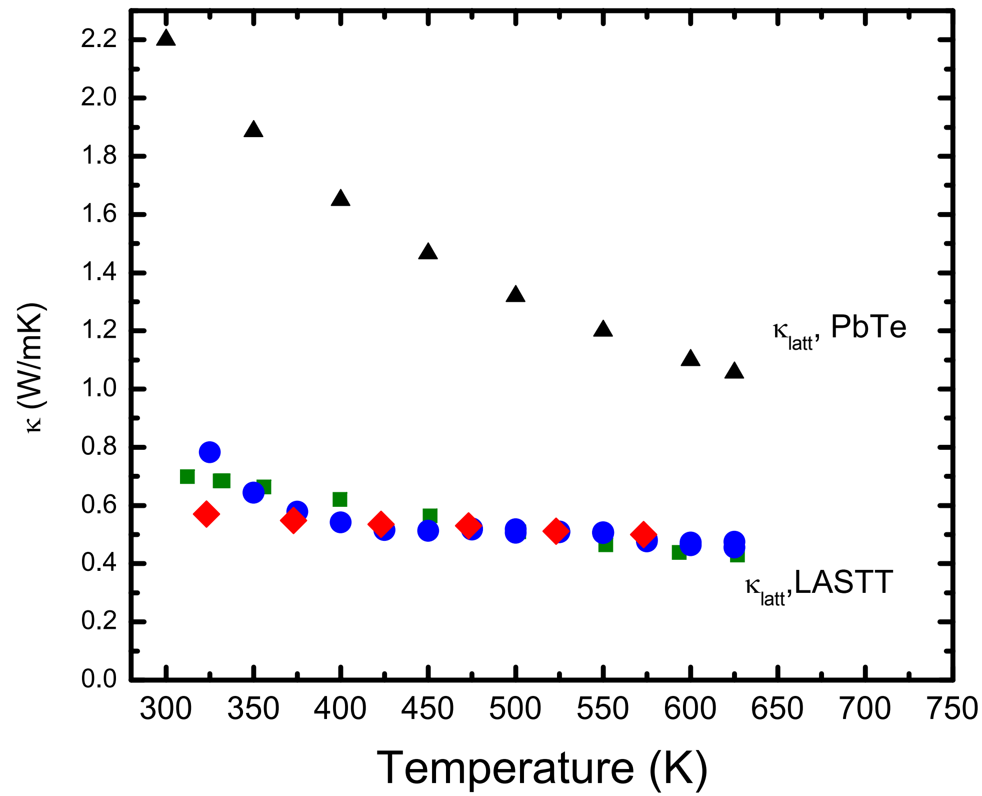


LASTT: Very low lattice thermal conductivity

LASTT-16: $AgPb_{14}Sn_4Sb_{0.4}Te_{20}$

LASTT-10: $AgPb_{10}Sn_{10}Sb_{0.7}Te_{22}$

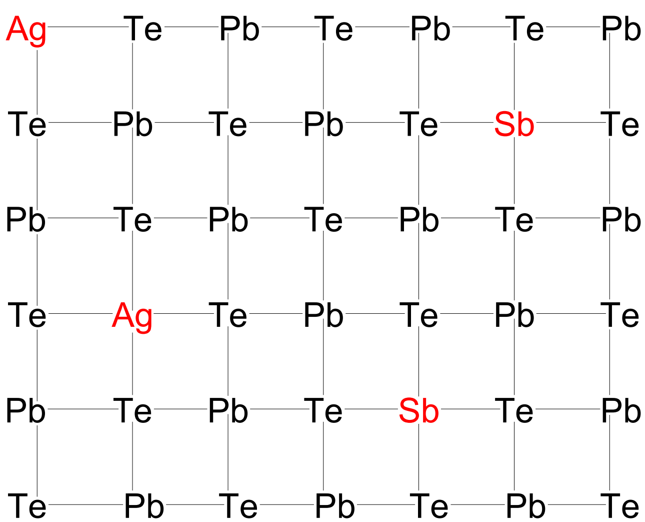




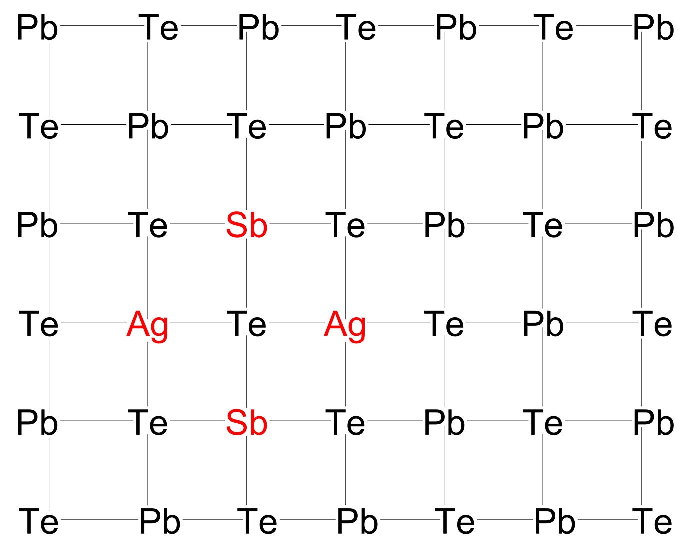
J. Androulakis, K. F. Hsu, R. Pcionek, H. Kong, C. Uher, J. J. D'Angelo,
A. Downey, T. Hogan, M. G. Kanatzidis, *Advanced Materials* **2006**, 18, 1170

Why do the LAST materials nanostructure?

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



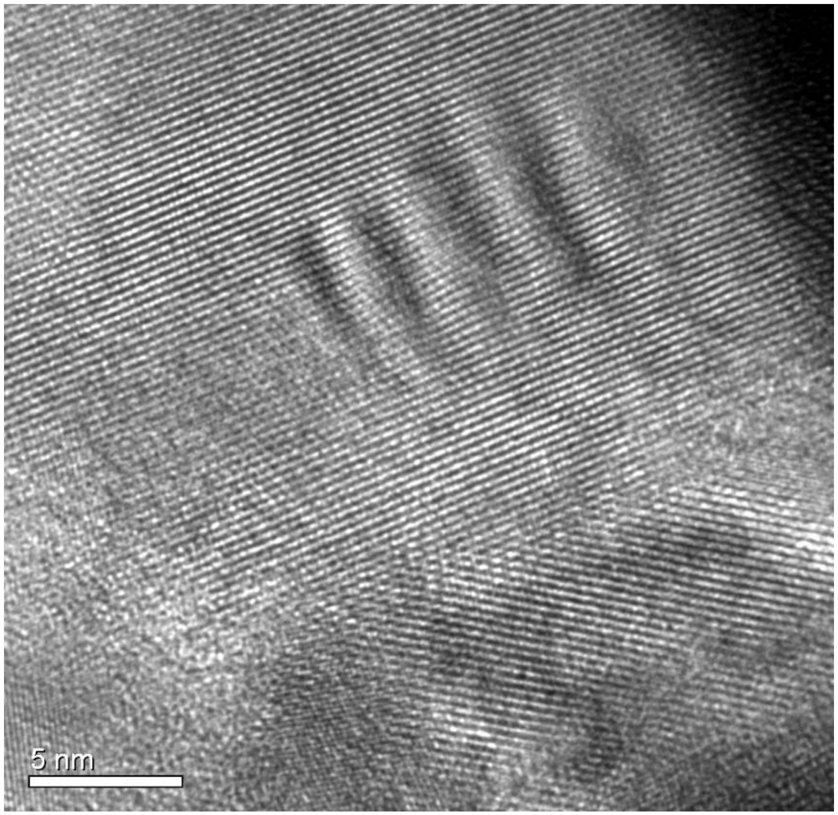
Dissociated state..unstable

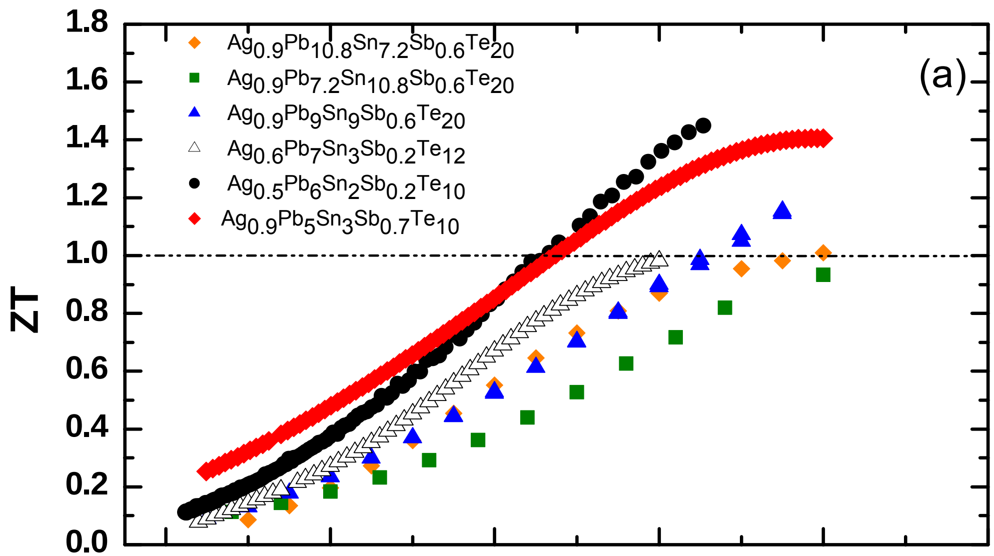


Associated state..stable

Any +1/+3 pair

Figure of Merit LASTT (p-type)

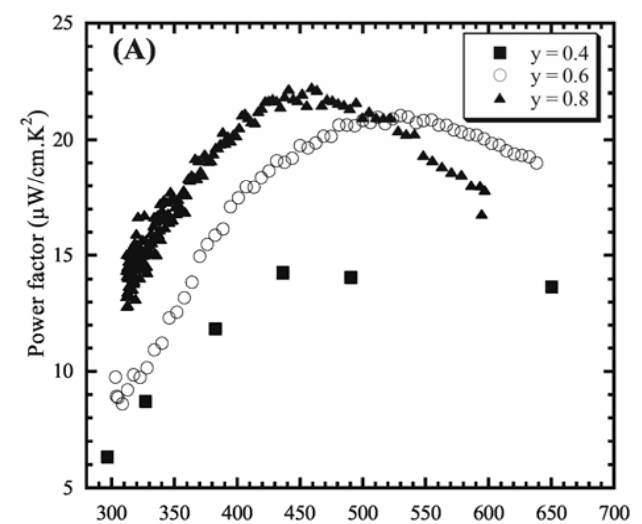


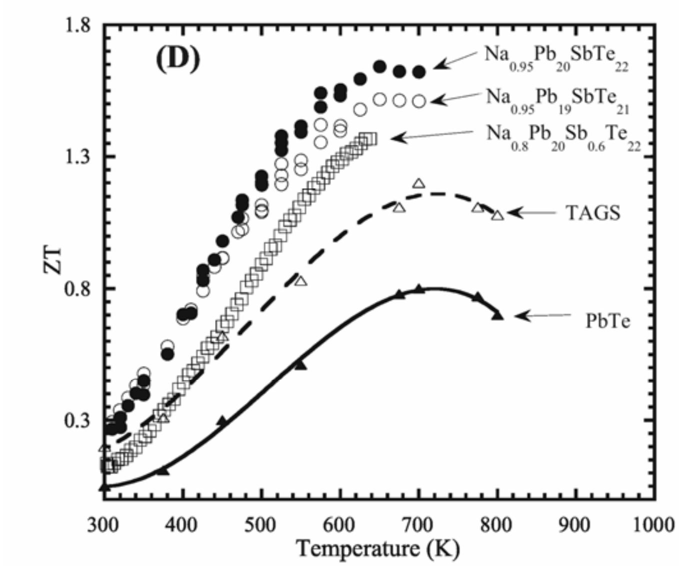


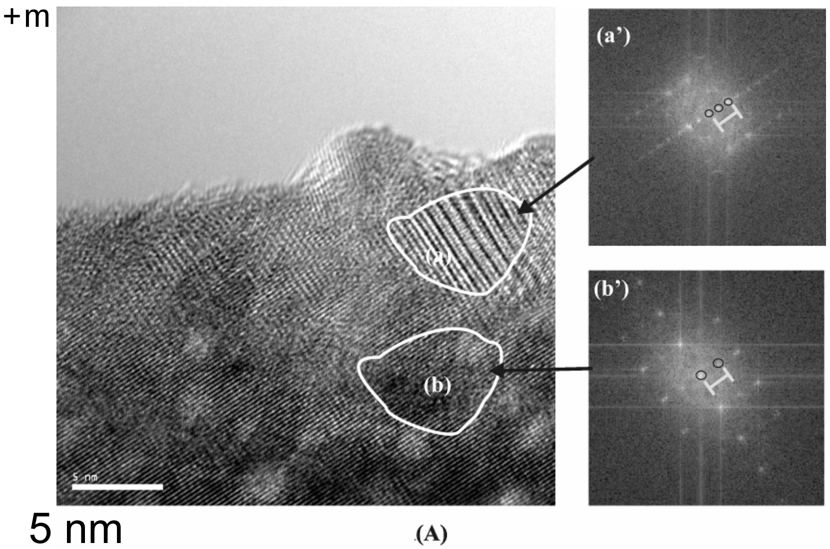
J. Androulakis, K. F. Hsu, R. Pcionek, H. Kong, C. Uher, J. J. D'Angelo, A. Downey, T. Hogan, M. G. Kanatzidis, *Advanced Materials* **2006**, 18, 1170

Na-based materials (SALT-m)

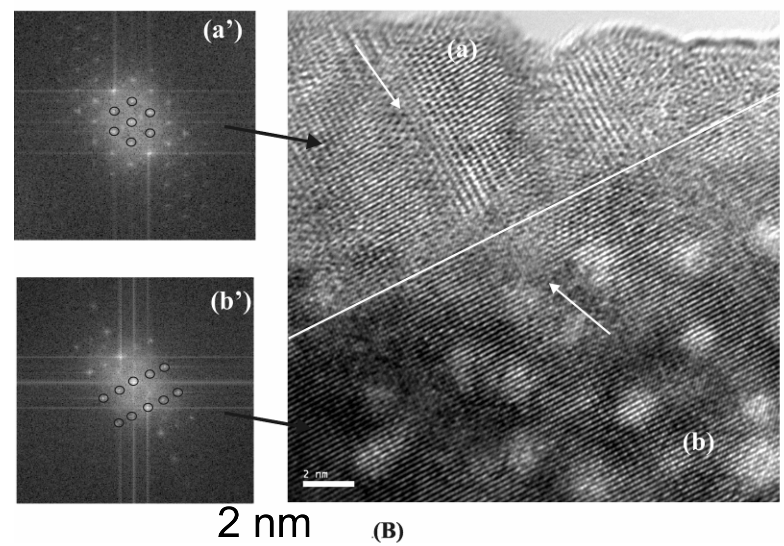
New high ZT p-type material $Na_{1-x}Pb_mSbTe_{2+m}$ *m*~19-21





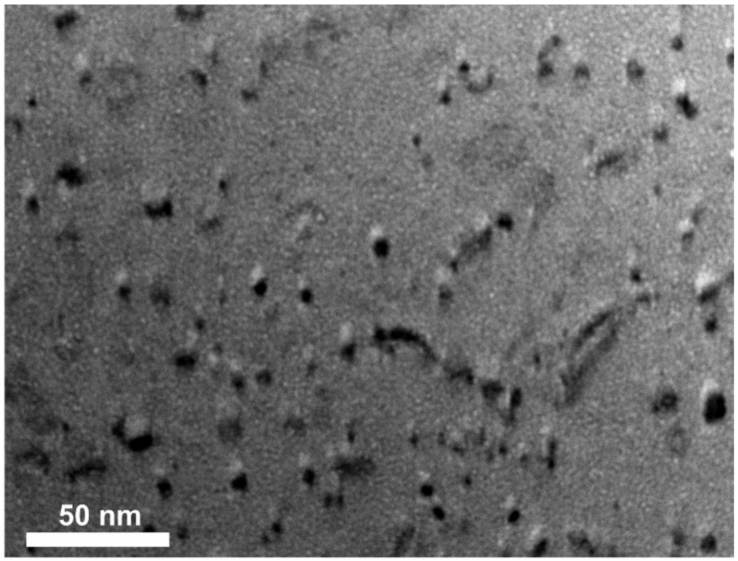


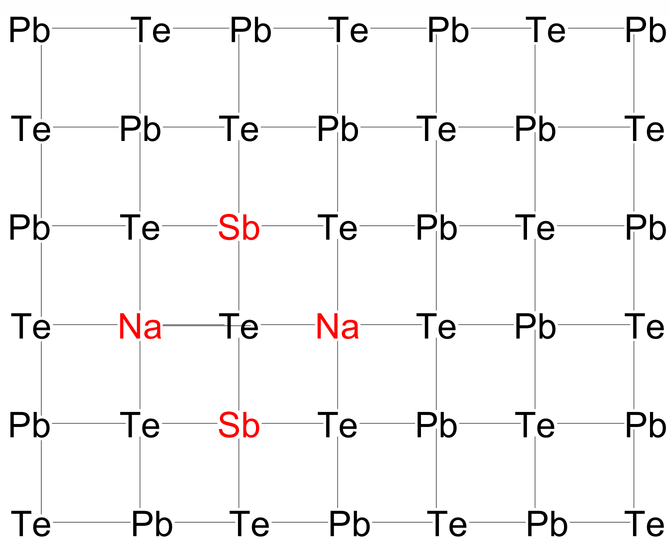
(A)

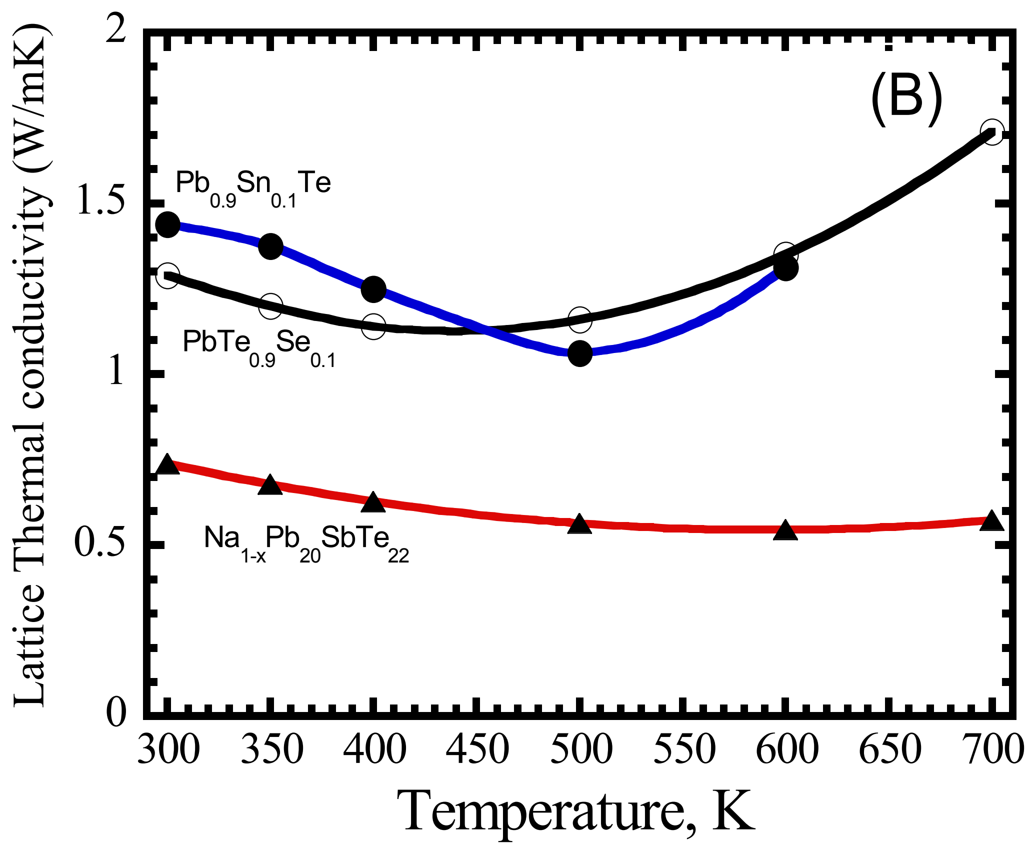


(B)

What is nanostructuring worth?

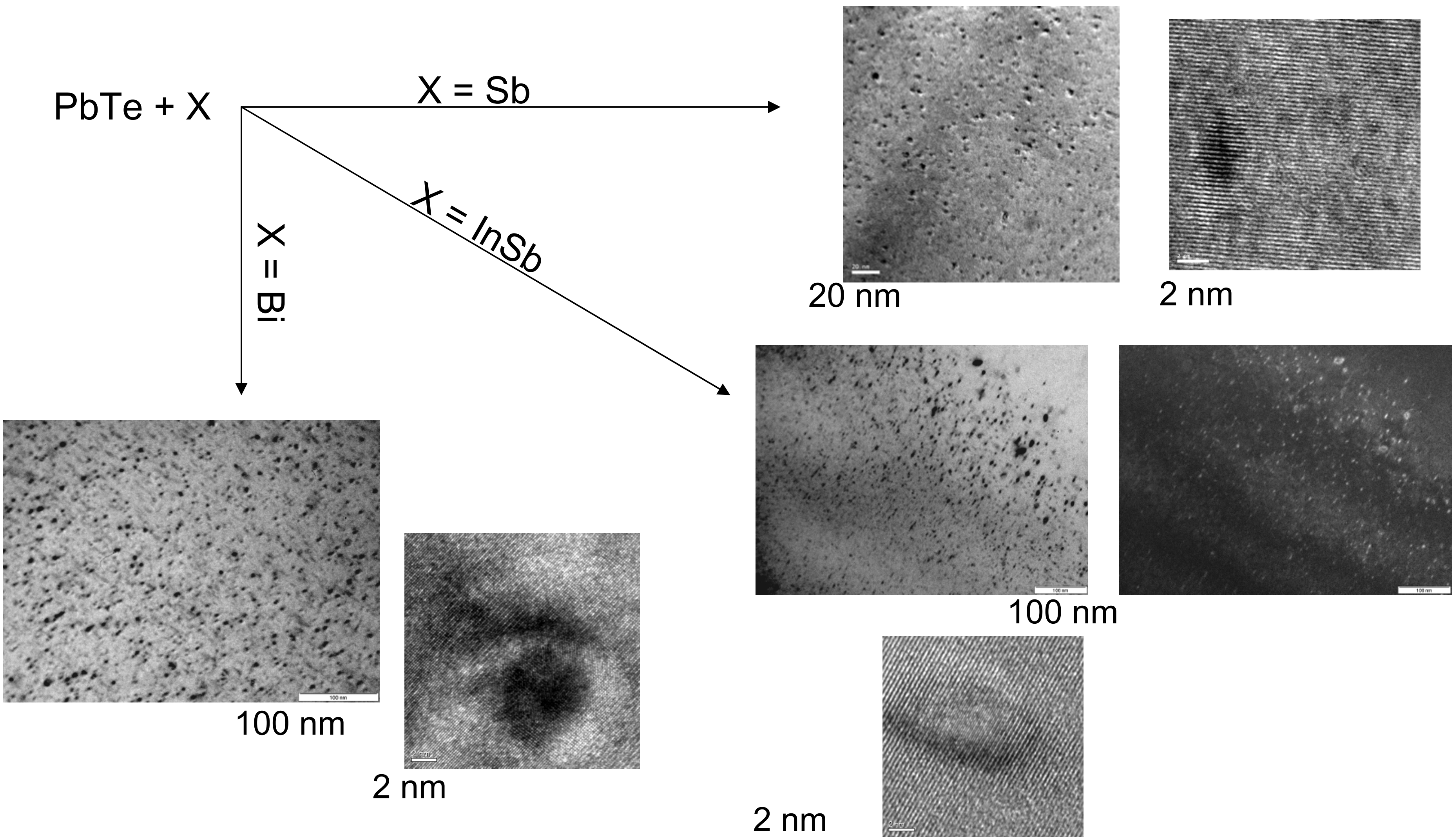




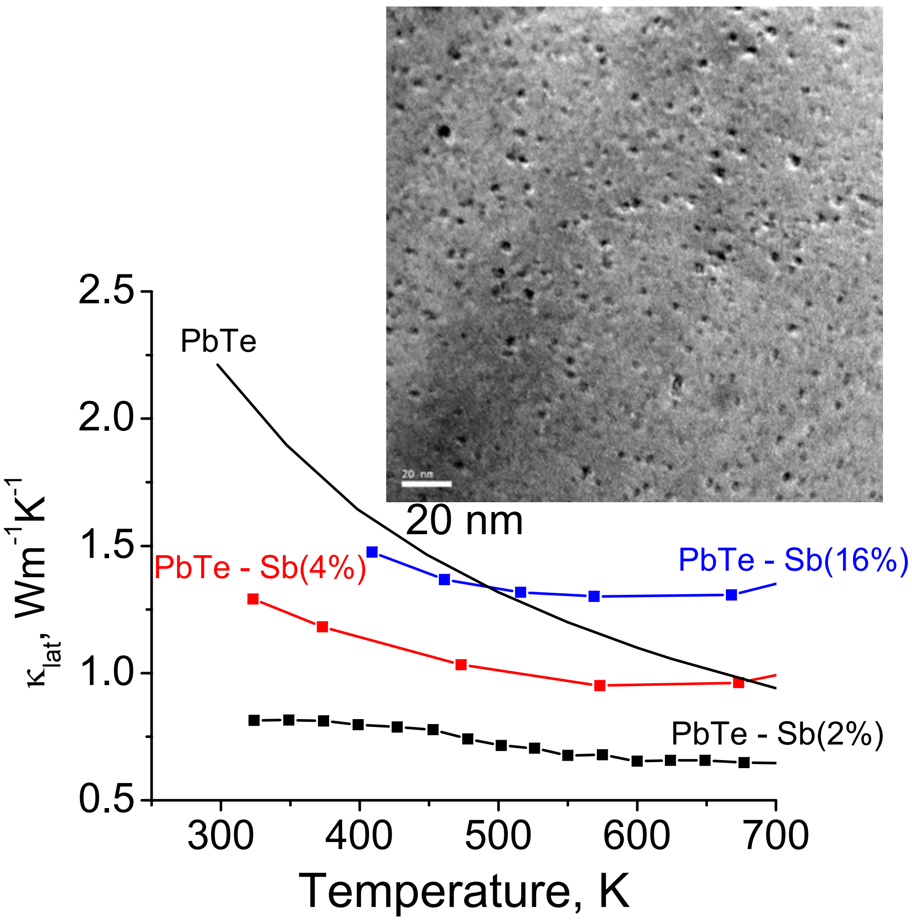


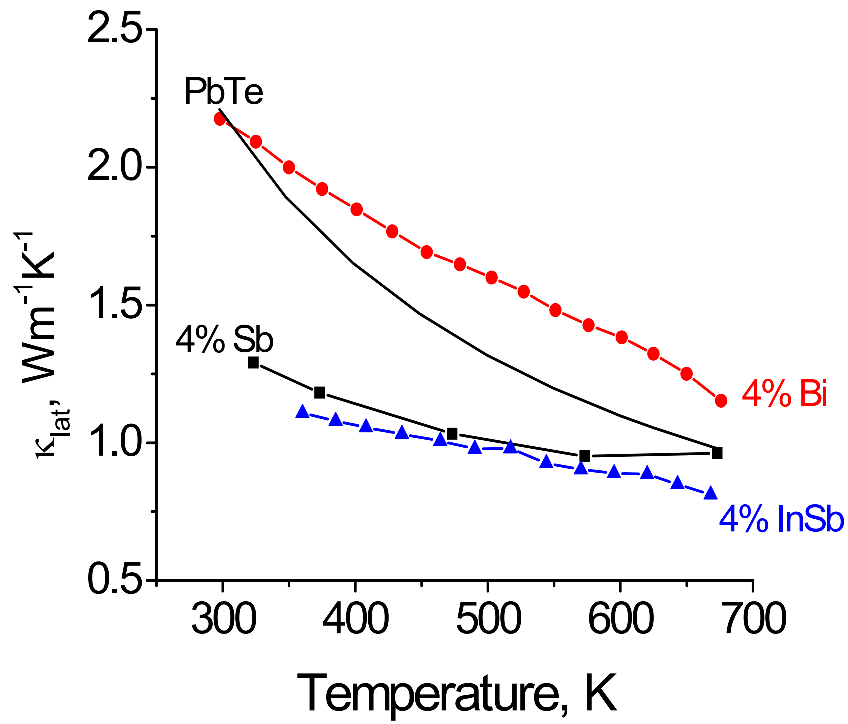
P. F. P. Poudeu, J. D'Angelo, A. D. Downey, J. L. Short,
T. P. Hogan, M. G. Kanatzidis, *Angew. Chem. Int. Ed.* **2006**, 45, 1

Matrix Encapsulation as a Route to Nanostructured PbTe



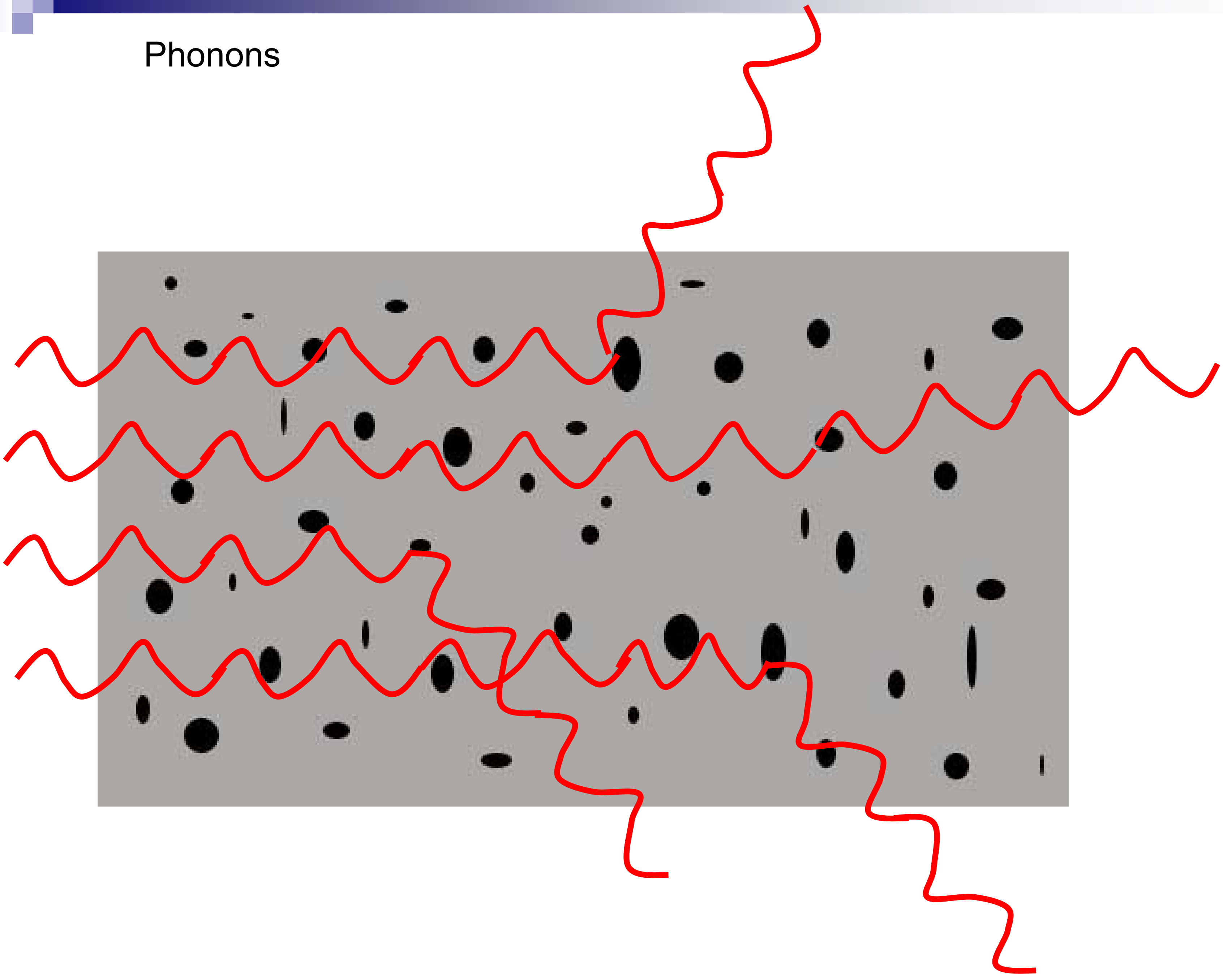
Nanocrystals of Sb in PbTe



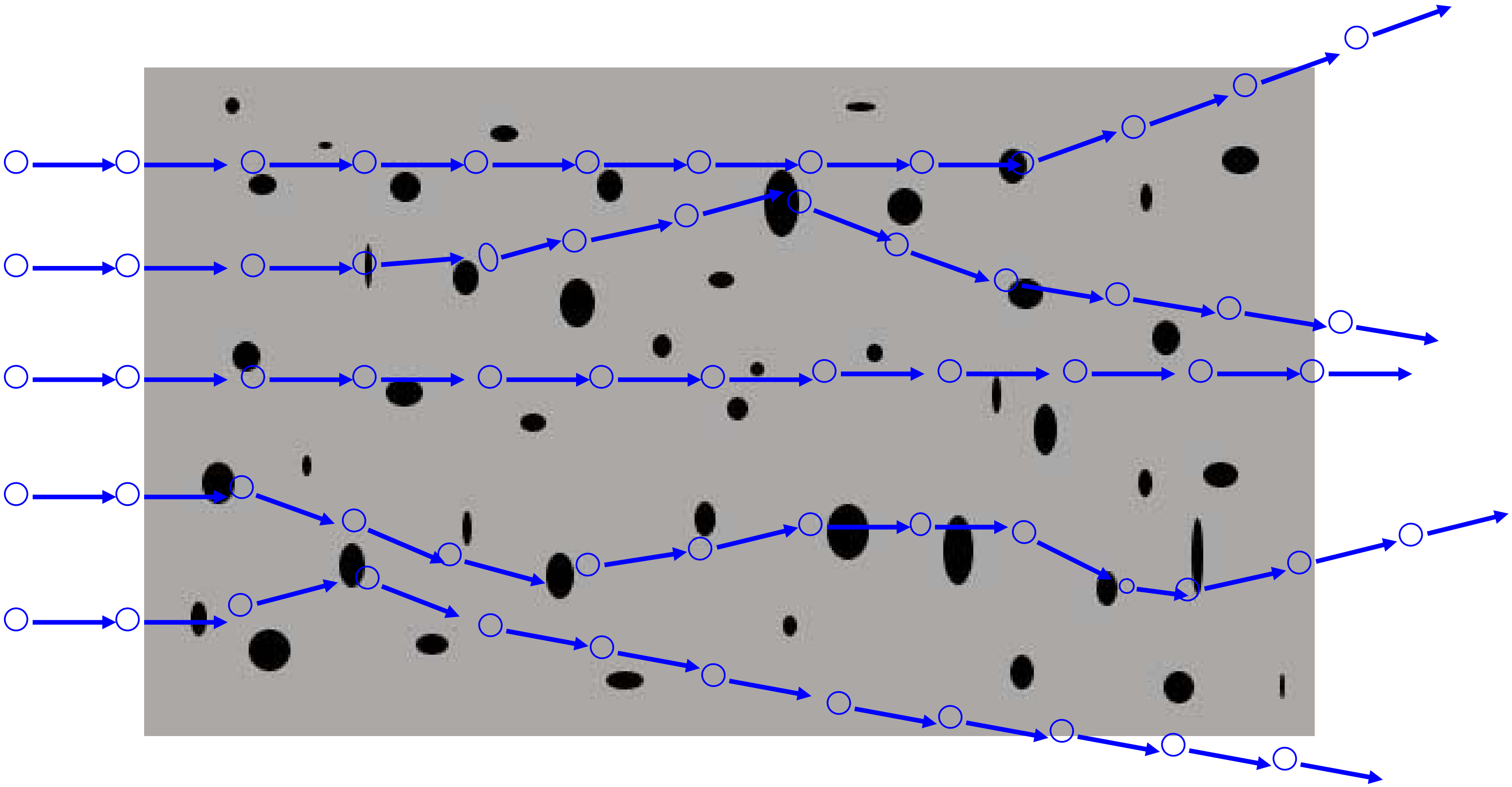


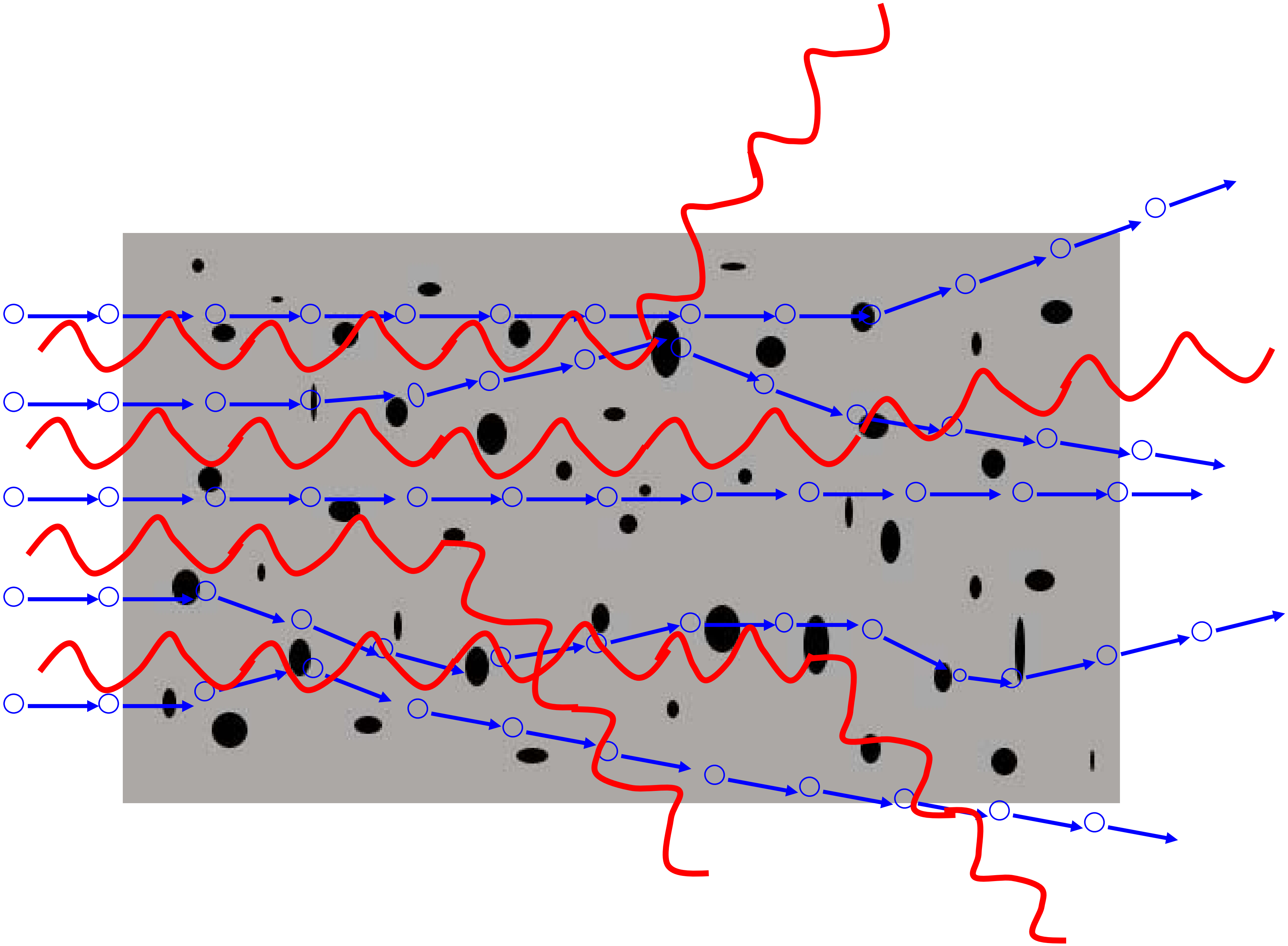
- An optimum concentration of nanoscale second phase is necessary
- Mass fluctuations play a role in thermal conductivity reduction
- Lattice thermal conductivity reduced, however ZT low due to small Seebeck

Phonons



Electrons

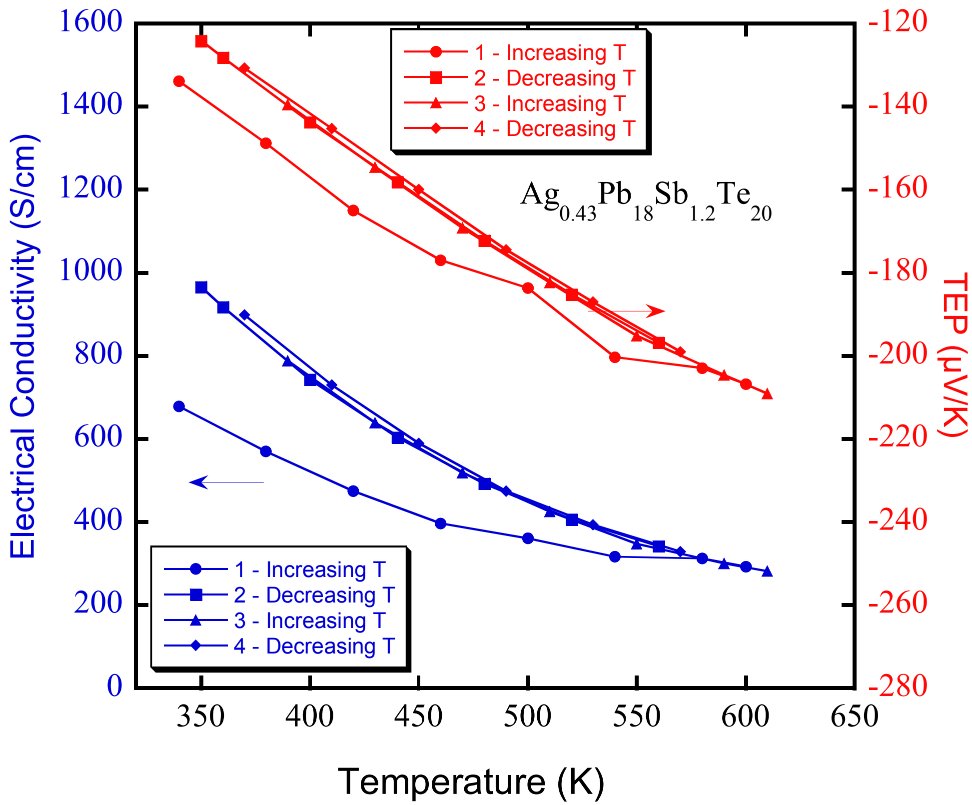




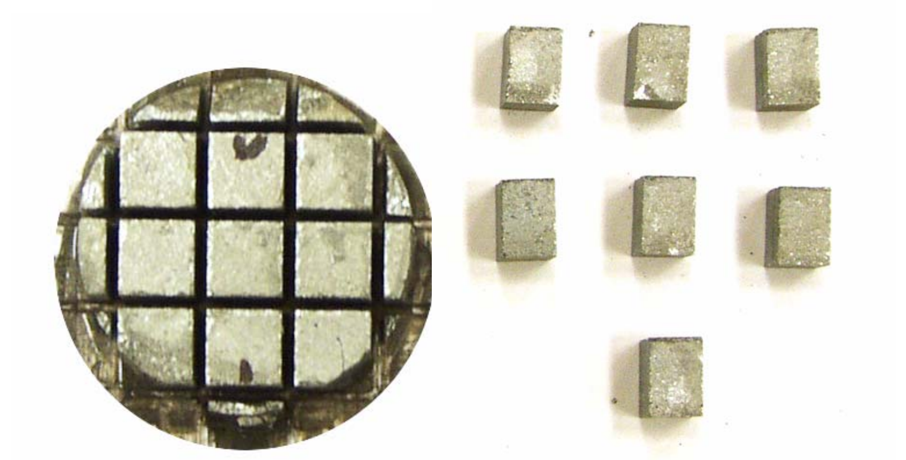
Completed and Processed Ingot

Schock

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



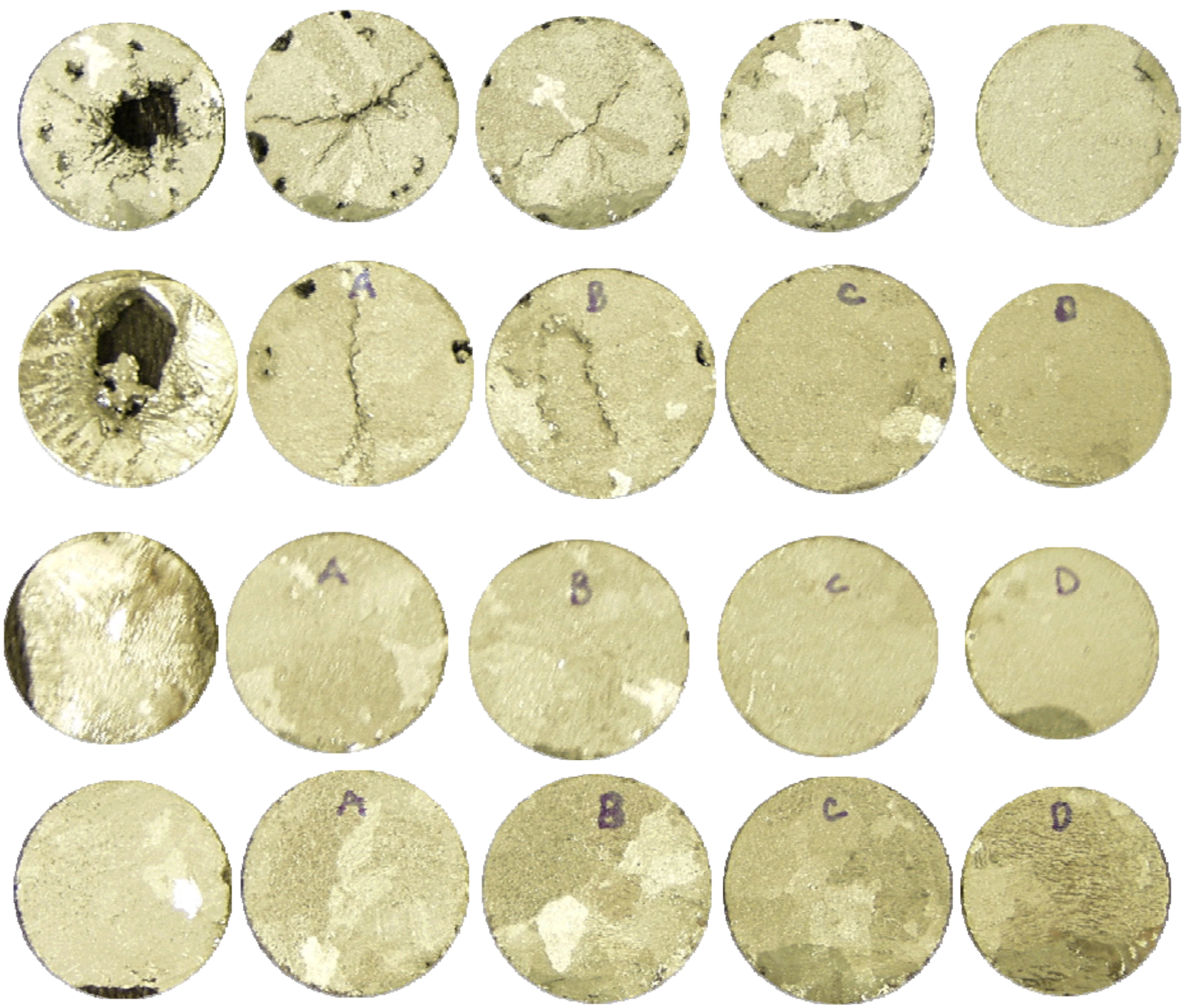
Temperature cyclability



Heating and Cooling Optimization of LAST

$Ag_{0.43}Pb_{18}Sb_{1.2}Te_{20}$

Cool from 1020ºC to 700, 800, 825, 850, 875, 900°C typically from one – two hours



ETN61

1020ºC to 700ºC @ 120ºC/hr

ETN64

1020ºC to 825ºC @ 97.5ºC/hr

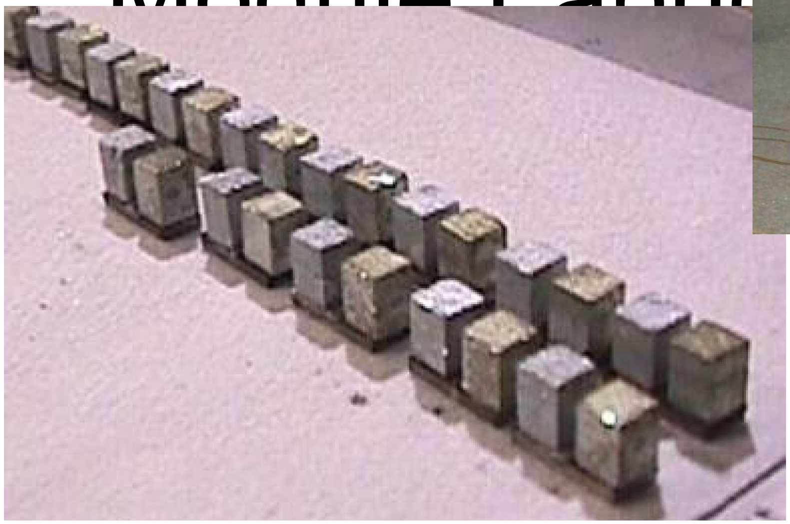
ETN65

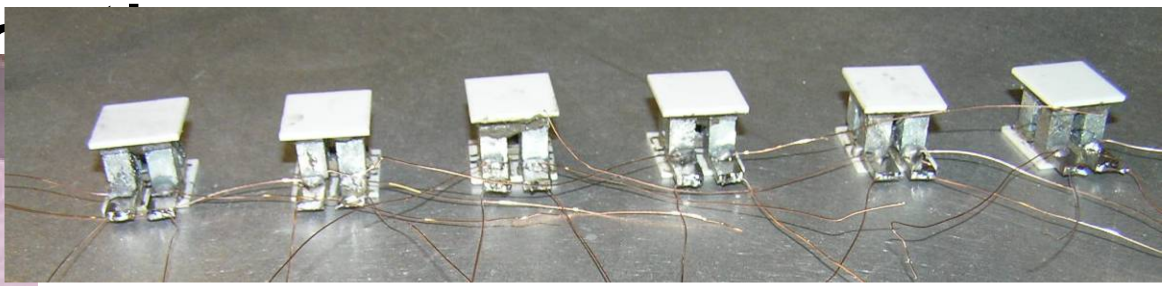
1020ºC to 875ºC @ 72.5ºC/hr

ETN68

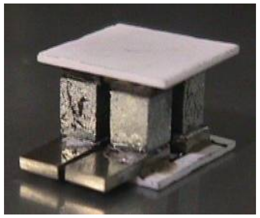
1020ºC to 900ºC @ 120ºC/hr

Module Fabric

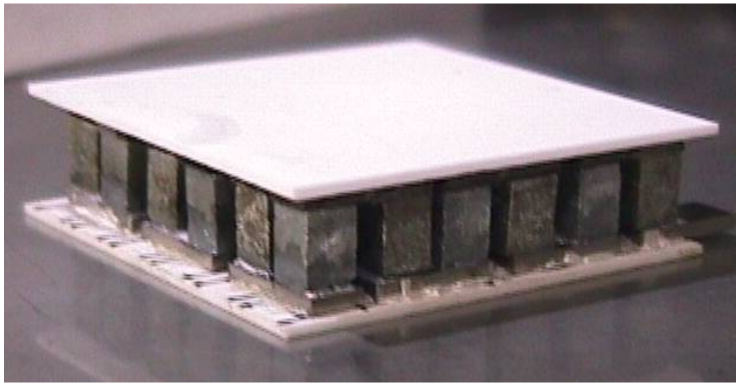


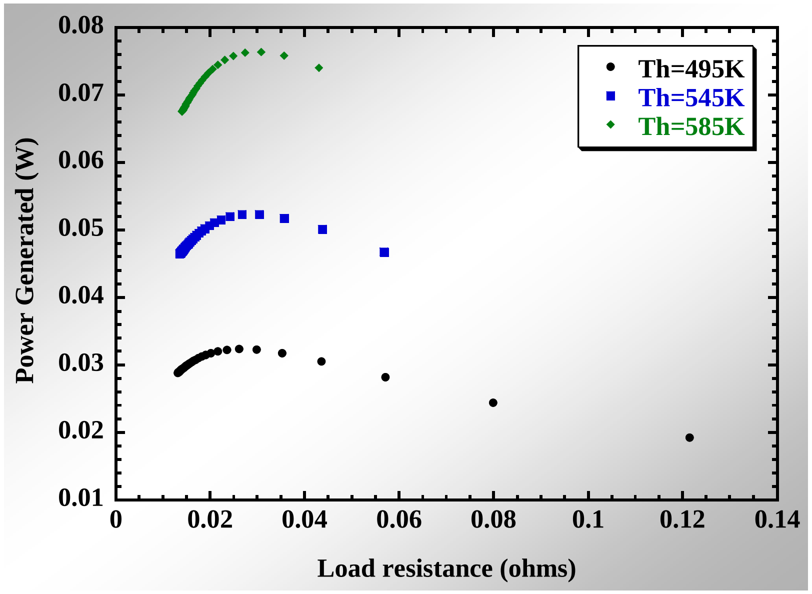


- Hot side diffusion contacts, and cold side solder contacts with <10 μW·cm2 have been achieved.



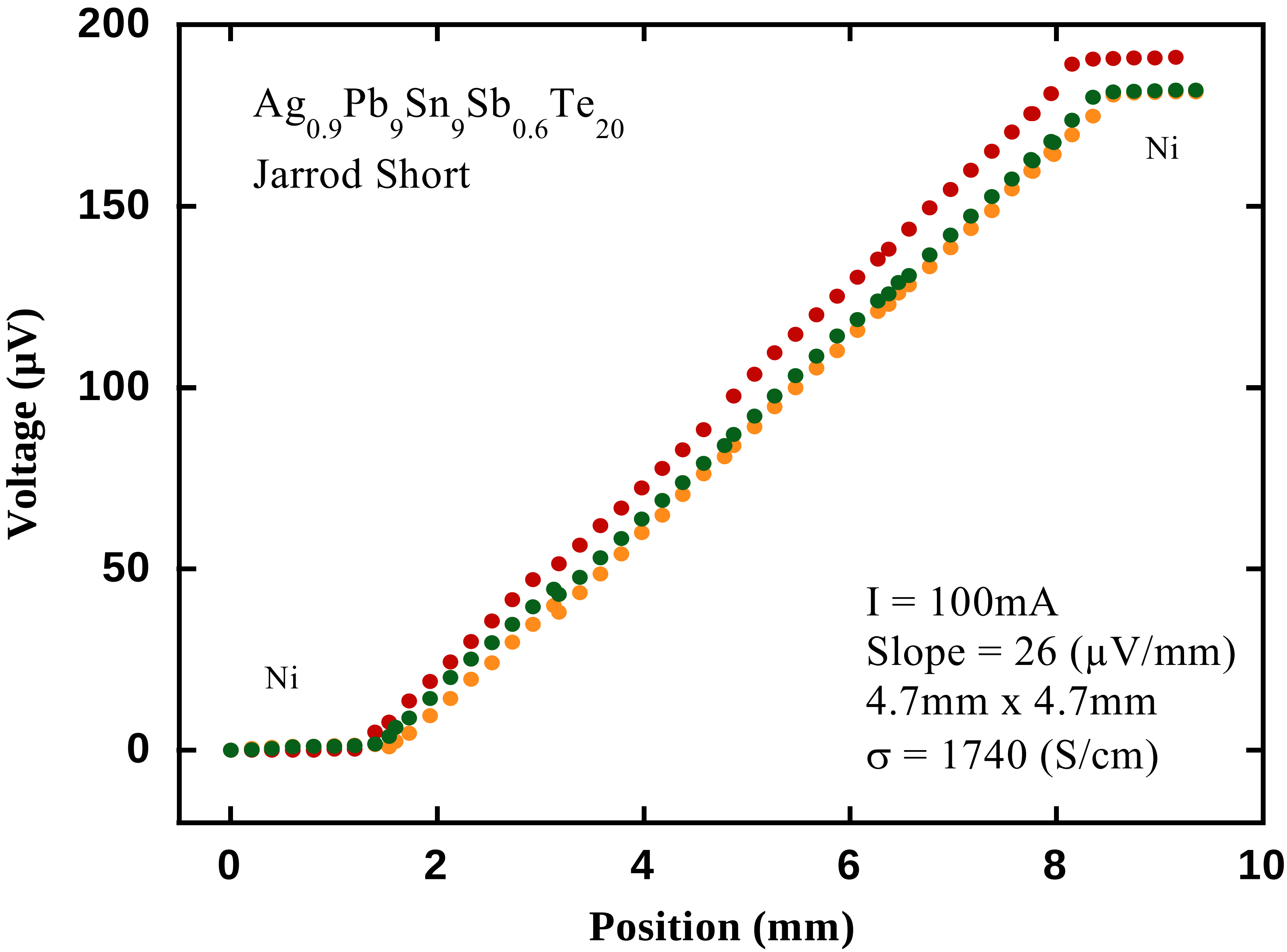
1.78mΩ total → 16.0μΩ·cm^2





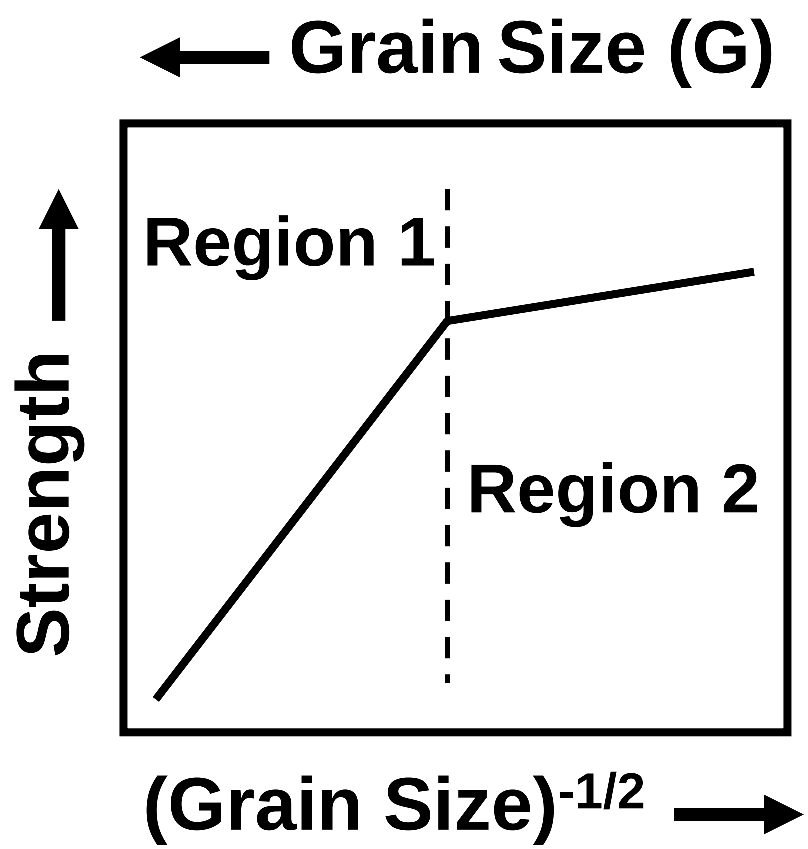
Scanning Probe Results

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.

- In region 1 (large grains), grain size dominates the fracture behavior
- In region 2 (smaller grains), grain size and surface defects contribute to fracture

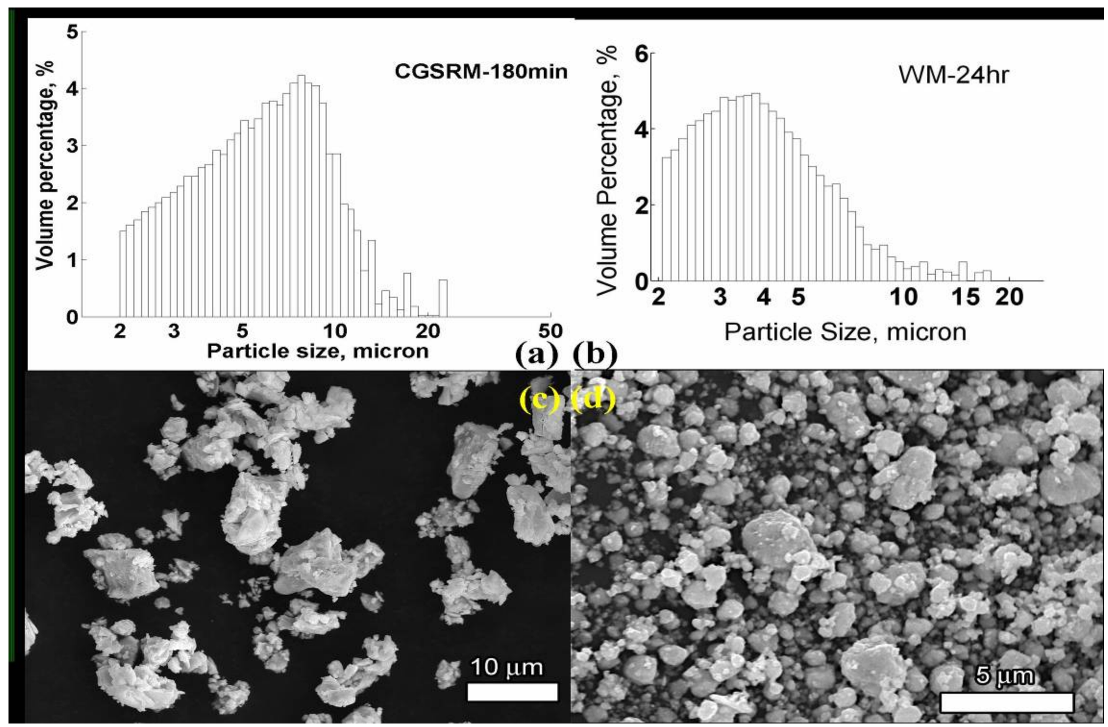
Hot pressing

Eldon Case

Powder Processing and Mechanical Characterization of LAST/T Materials

- To improve mechanical integrity, smaller grain size is needed.

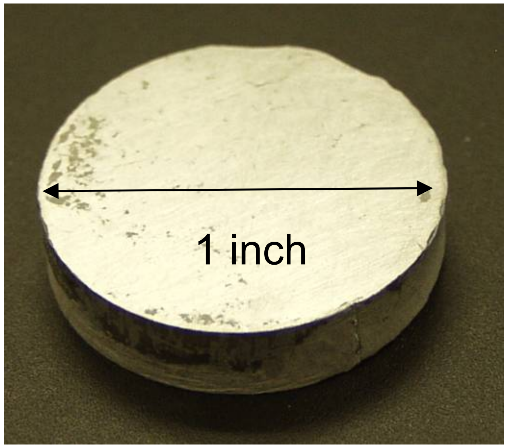
- Ingot LAST/T materials have a large mean grain size (~ 500 to 700 μm), resulting in poor mechanical properties.
- We utilize planetary ball milling to generate micron-scale powders from LAST/T ingots.
- To date, we have achieved equiaxed powders with a mean particle size of ~ 5 μm via dry milling.
- Wet milling studies demonstrate further size reduction with a mean grain sizes of ~ 2 to 3 μm.



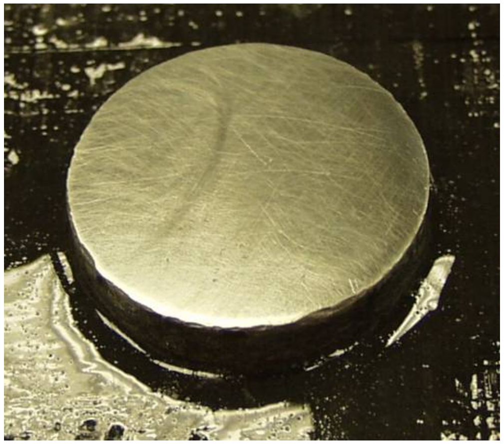
Hot Press Billets

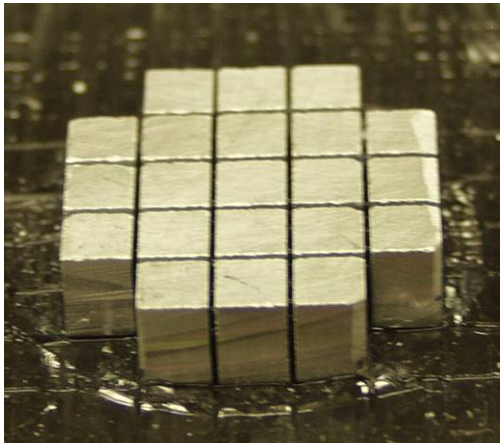
Schock, Case

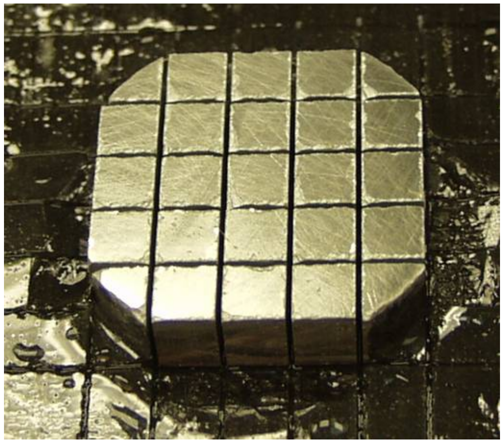
HPMSU-01



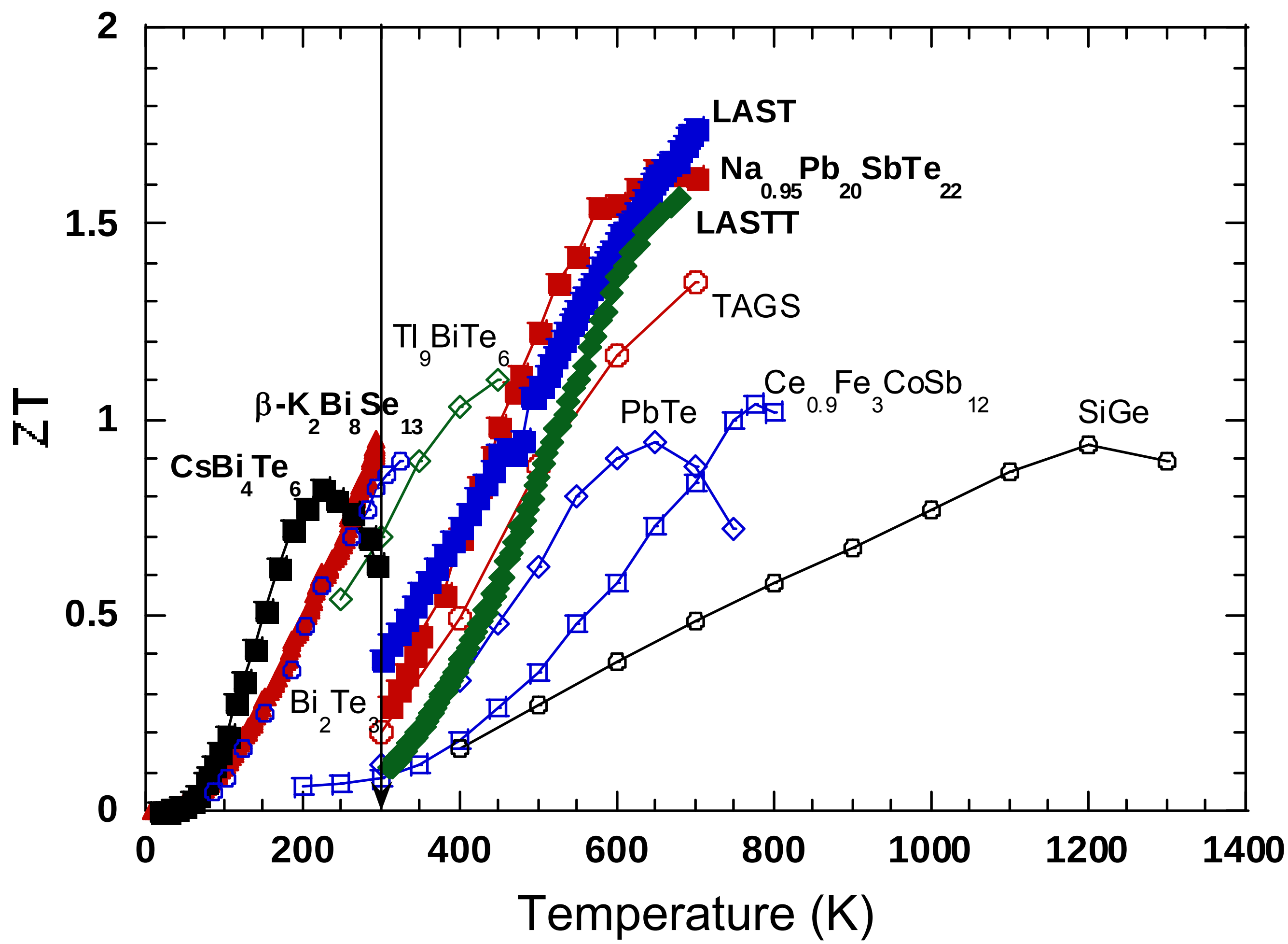
HPMSU-02







Best ZT Materials



Conclusions

- LAST, LASTT and SALT: promising thermoelectric materials for next generation power generation modules. (expected device efficiency ~14%)
- Nanostructures strongly reduce thermal conductivity.
- Nanostructures are closely linked to high ZT.
- Scaleup 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.

Students and postdocs

Graduate Students

- Joe Sootsman, Chemistry
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- Adam Downey, Electrical Engineering
- Jarrod Short, Electrical Engineering
- Jonathan D'Angelo, Electrical Engineering
- Fei Ren, Chem. Engineering and Materials Science
- 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
- Jim Salvador, Chemistry
- Chia-Her Lin, Chemistry
- Xun Shi, Physics U of Michigan

Undergraduates

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

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