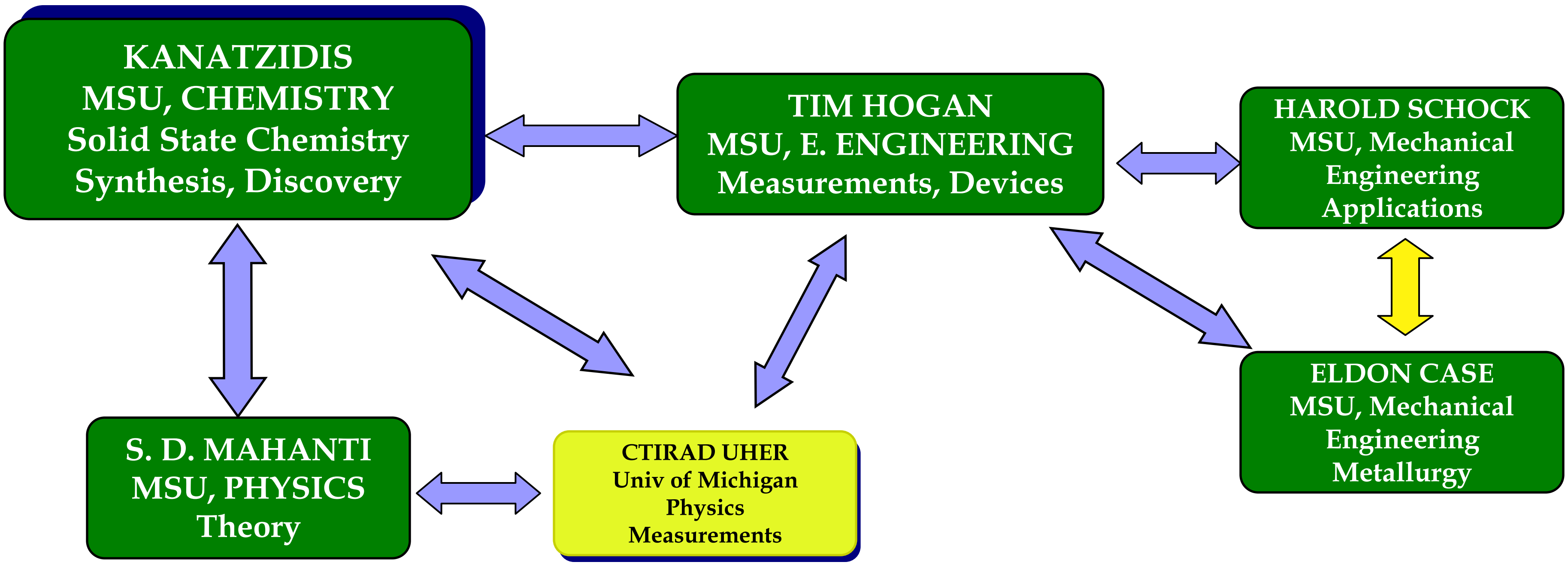
Direct Energy Conversion: Chemistry, Physics, Materials Science and Thermoelectrics

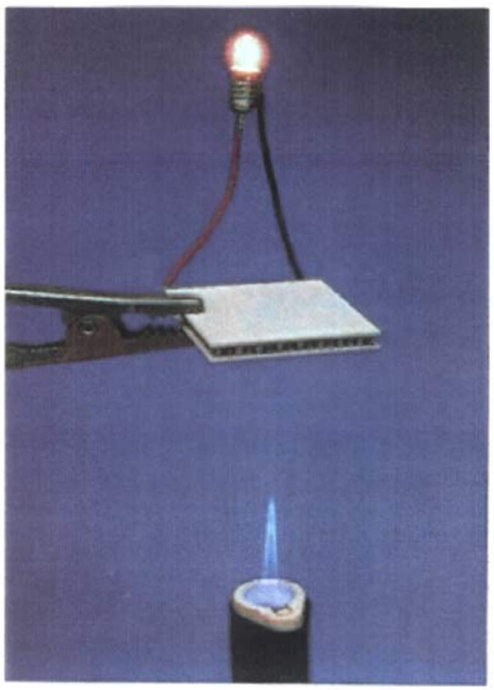
Office of Naval Research

MURI

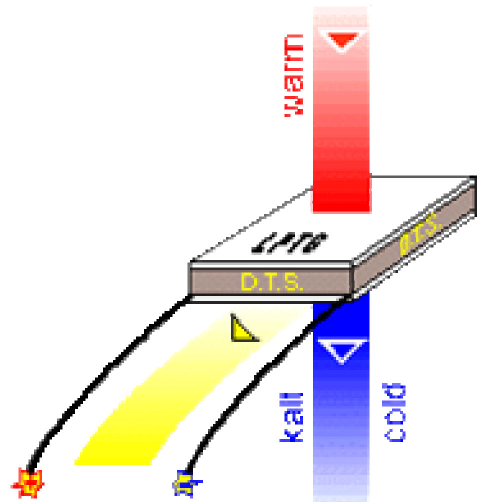


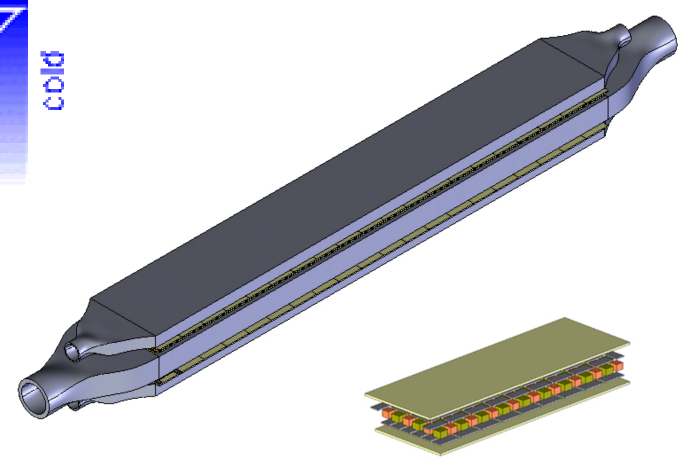
Heat to Electrical Energy Directly

Up to 20% conversion efficiency with right materials



Electrical
Power Generation





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

Schock group

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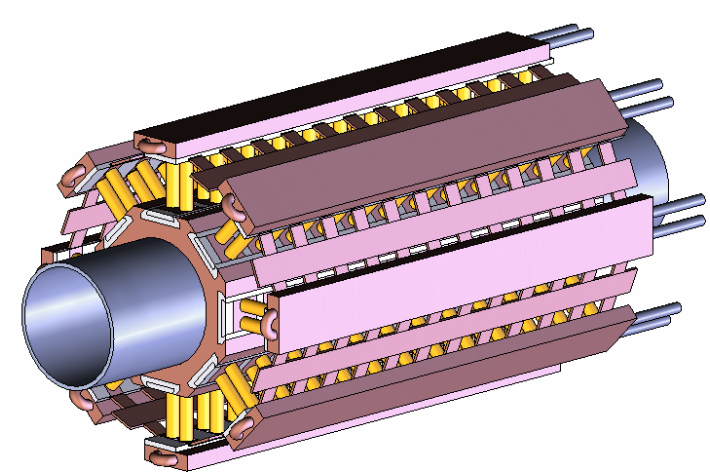
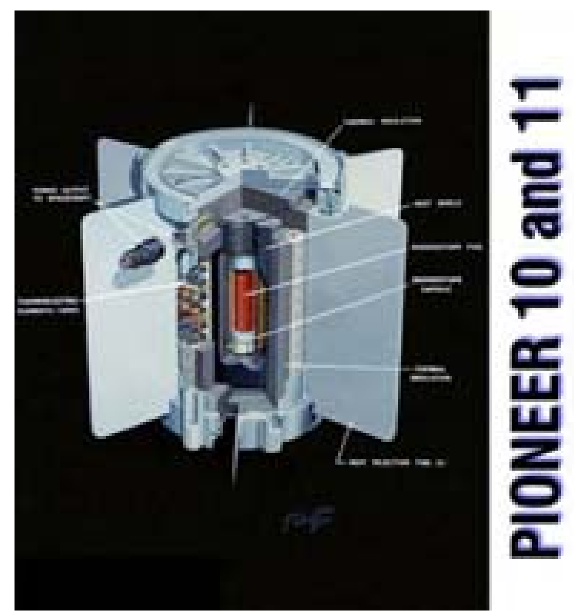
Thermoelectric applications

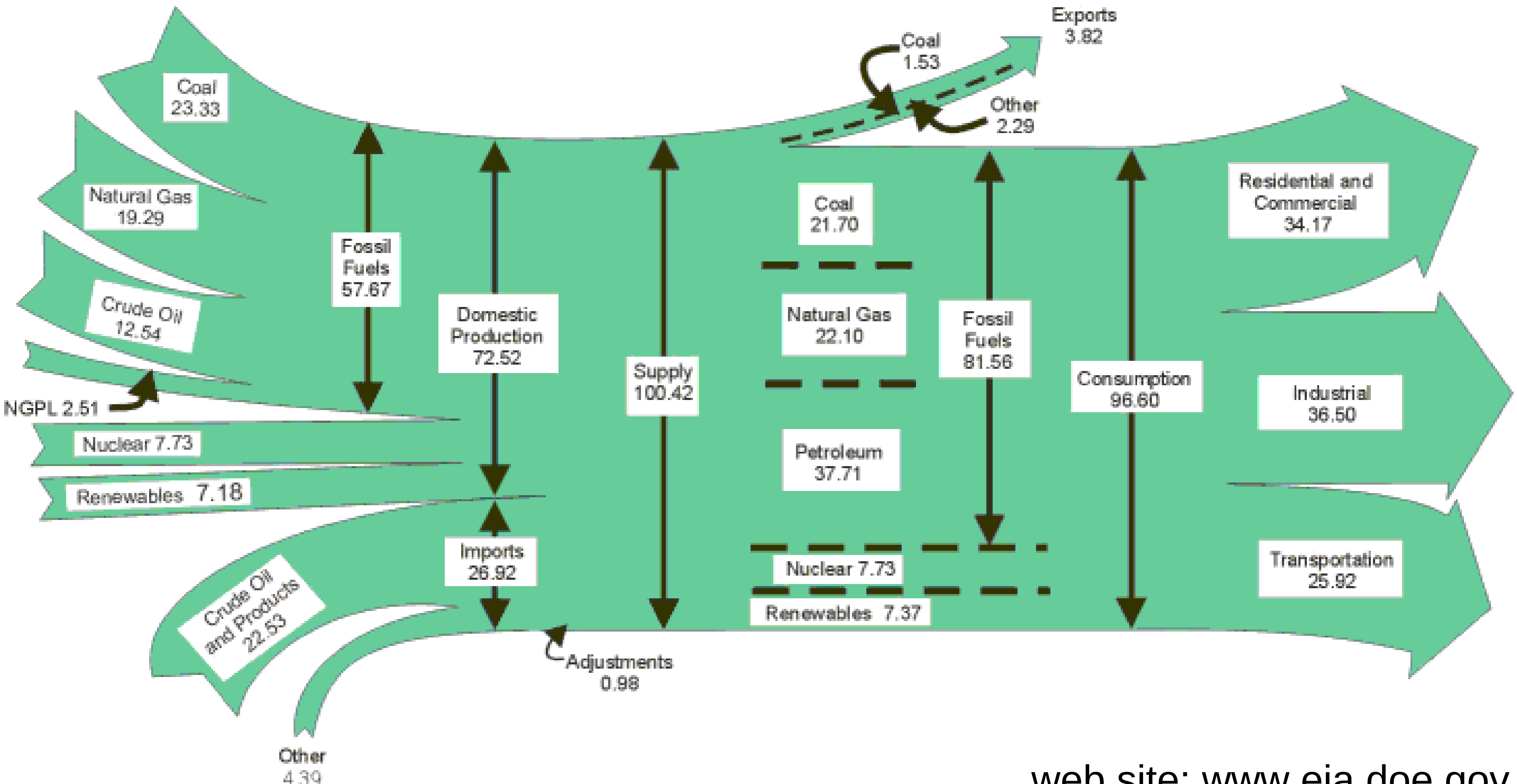
- Waste heat recovery
  - Automobiles
  - Over the road trucks
  - Utilities
  - Chemical plants





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

U.S. Energy Flow, 1999

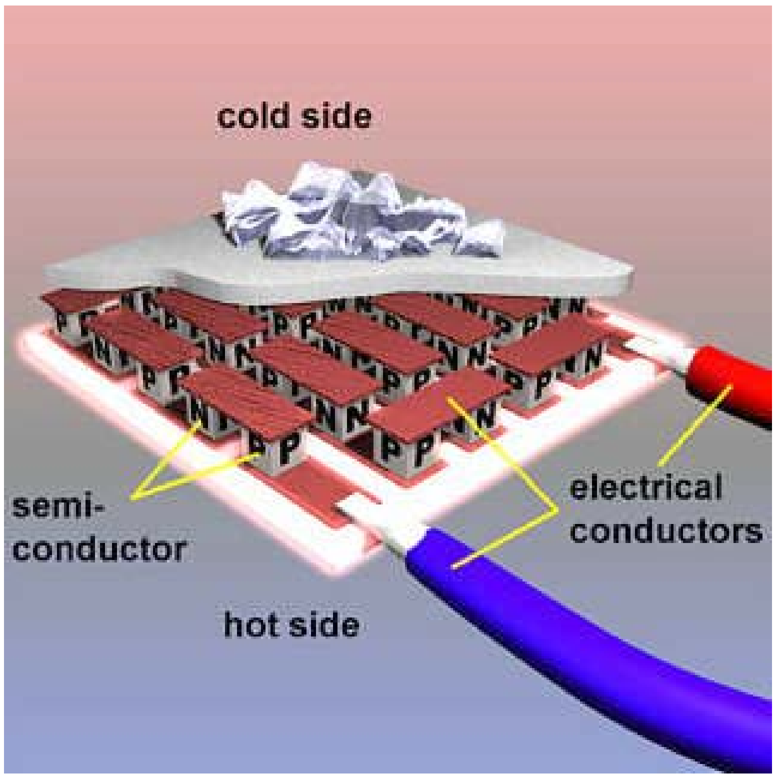


web site: www.eia.doe.gov

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

How does it work?

http://www.designinsite.dk



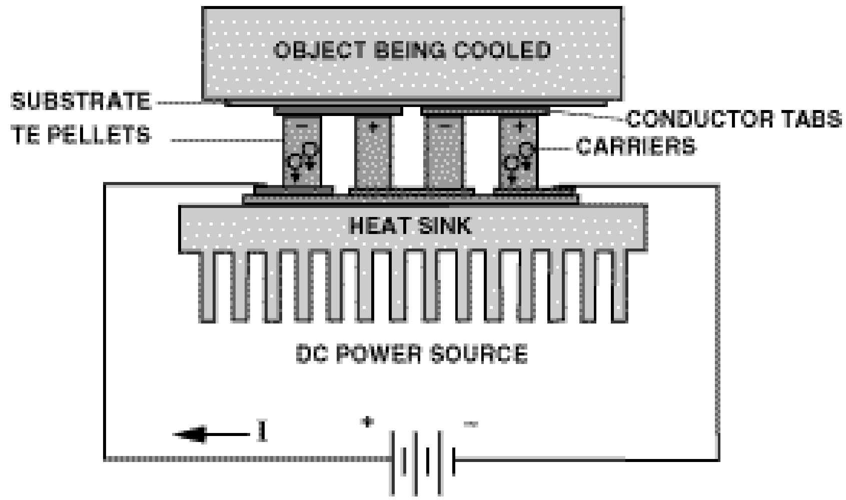
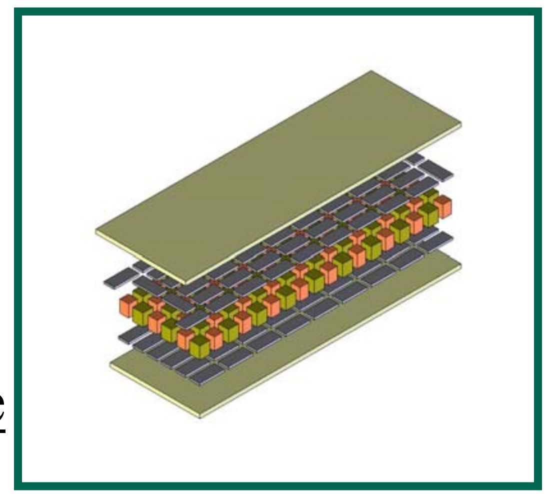


Figure 2

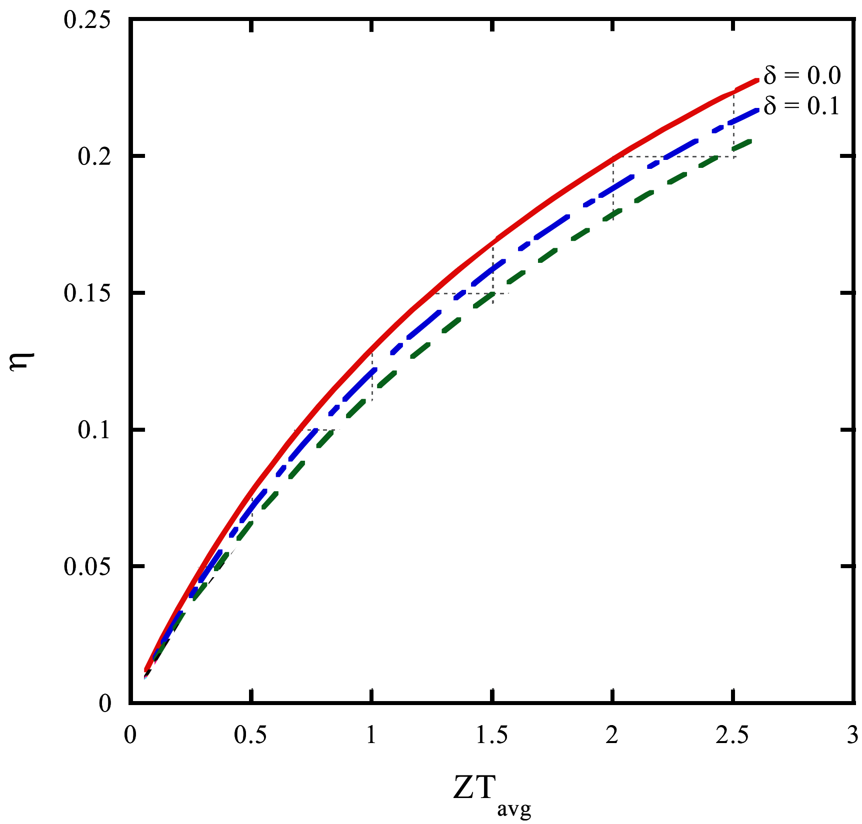


TE devices have <u>no moving parts, no noise, reliable</u>

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

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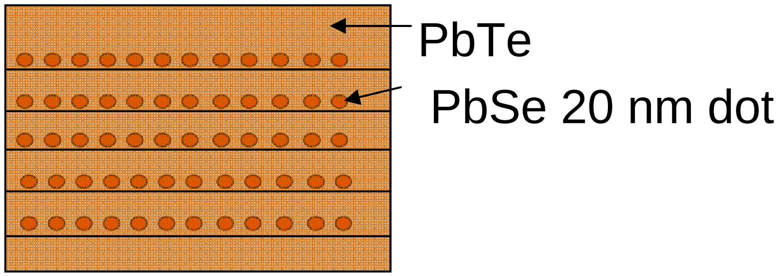
Today's situation

- The most efficient materials today for power generation: PbTe and TAGS (TeSbGeAg alloy)
- The most efficient material for cooling Bi_2Te_3
- 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 needed

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



Hicks LD, Dresselhaus MS *Phys. Rev*. B 47 1993 (24): 16631

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Some promising systems under investigation

- half-Heusler alloys (ZrNiSn)
- Zn_4Sb_3
- Clathrates
- Skutterudites ($CoSb_3$)
- Bulk nanocomposites based on PbTe
- Bulk nanocomposites based on Si-Ge
- $AgSbTe_2$/PbTe, $NaSbTe_2$/PbTe

See March 2006 issue of MRS Bulletin

ZT and Electronic Structure

Isotropic structure

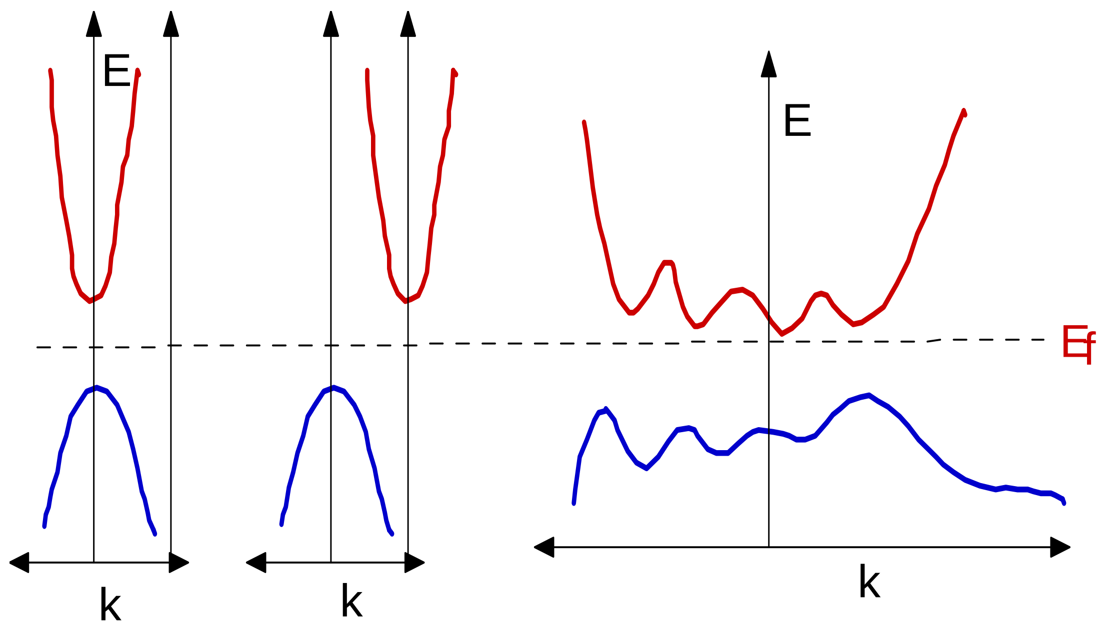
Anisotropic structure

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

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

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

Chemistry as a source of materials

Investigating the System:

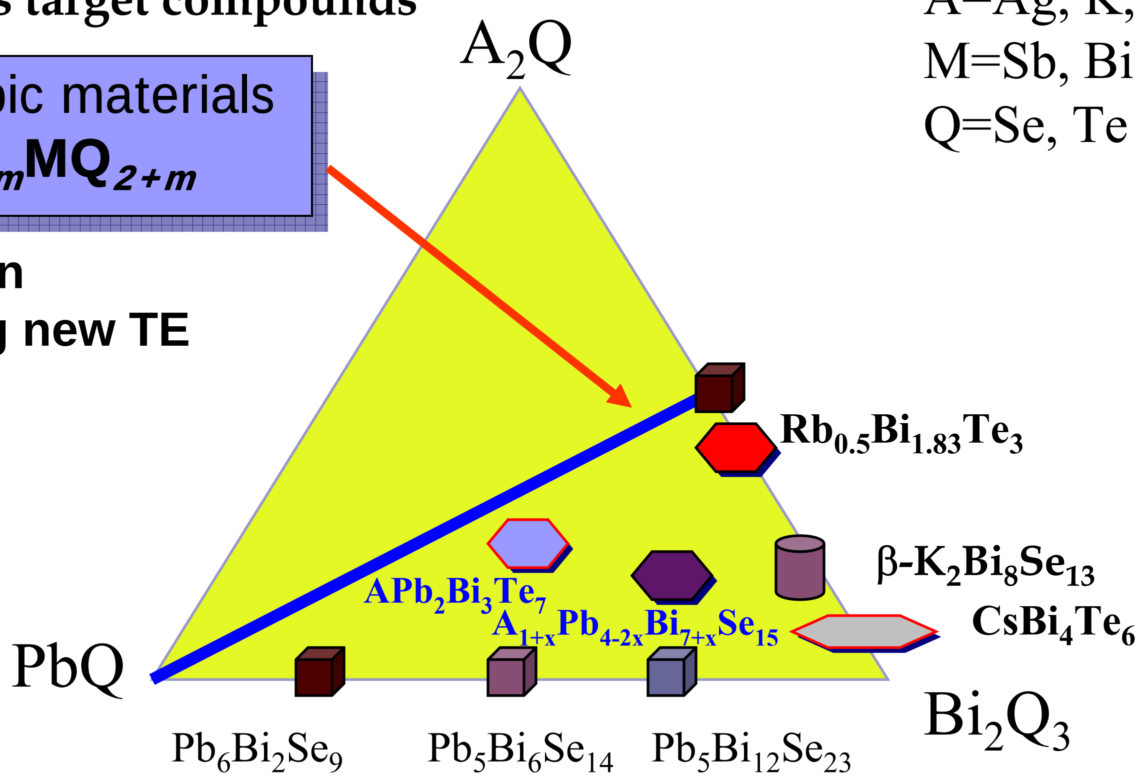
$A_2Q + PbQ + M_2Q_3$ ------> $(A_2Q)_n(PbQ)_m(M_2Q_3)_p$

Map generates target compounds

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

Cubic materials
AB_mMQ_{2+m}

Phases shown are promising new TE Materials



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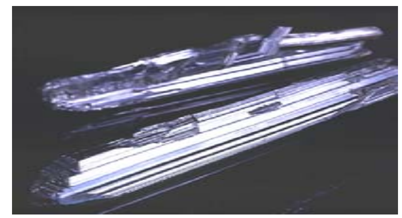
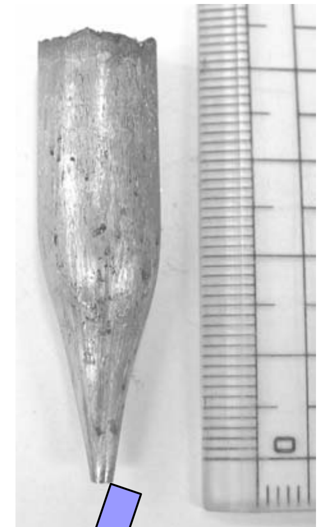
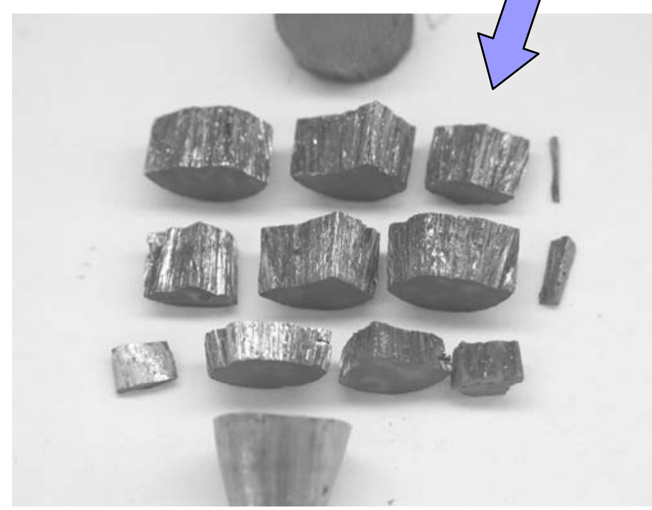
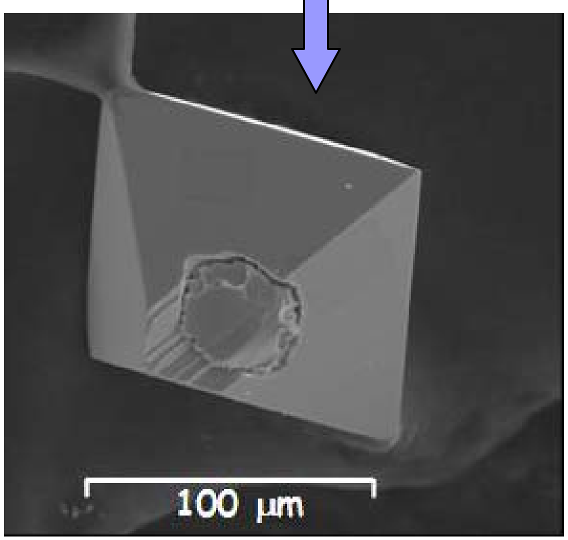
Our first contact with cubic $AgPb_mSbTe_{2+m}$

- $AgBi_3S_5$, $KPbBi_9Se_{13}$, $KPb_4Sb_7Se_{15}$
- $CsPbBi_3Te_6$, $CsPb_2Bi_3Te_7$, $CsPb_3Bi_3Te_8$,
- $RbPbBi_3Te_6$, $RbPb_2Bi_3Te_7$, $RbPb_3Bi_3Te_8$,
- $KPbBiSe_3$, $K_2PbBi_2Se_5$
- $K_2Pb_3Bi_2Te_7$, KPb_4SbTe_6

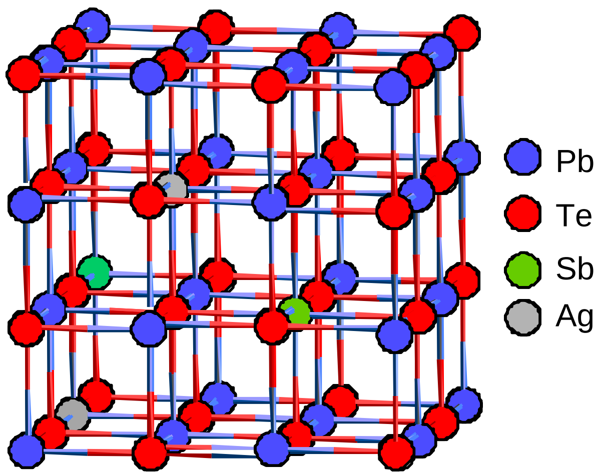


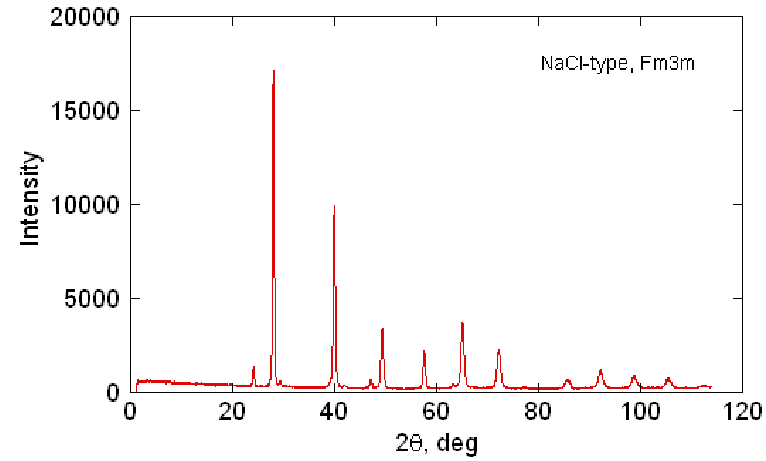


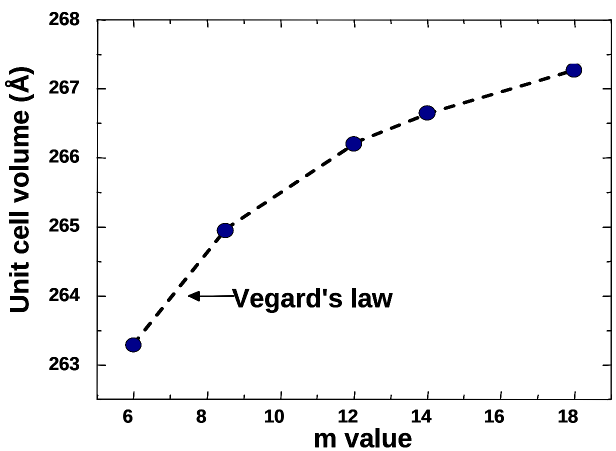


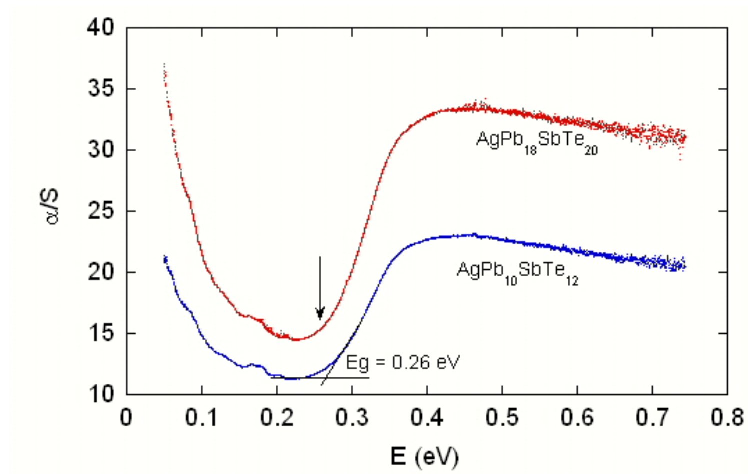


$AgPb_mSbTe_{2+m}$ (LAST-*m*)
$AgPb_m(Sb,Bi)Te_{2+m}$ (BLAST-*m*)



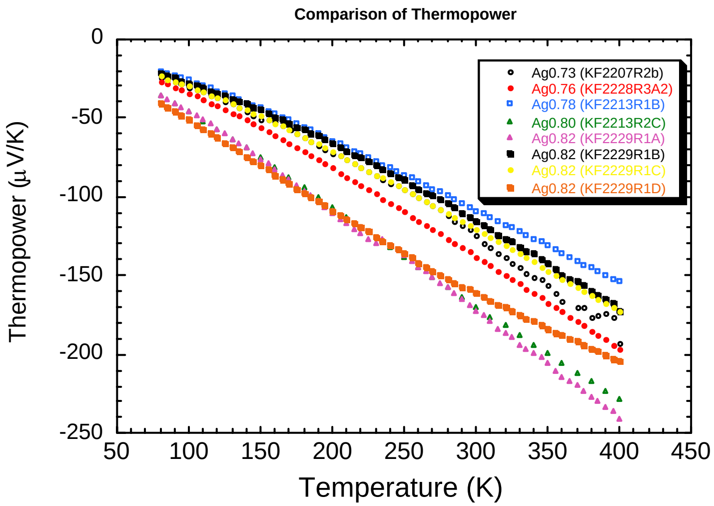


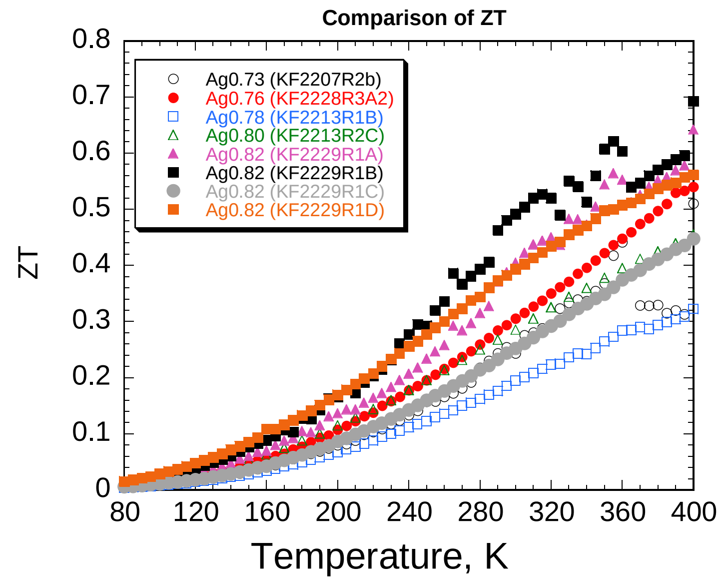


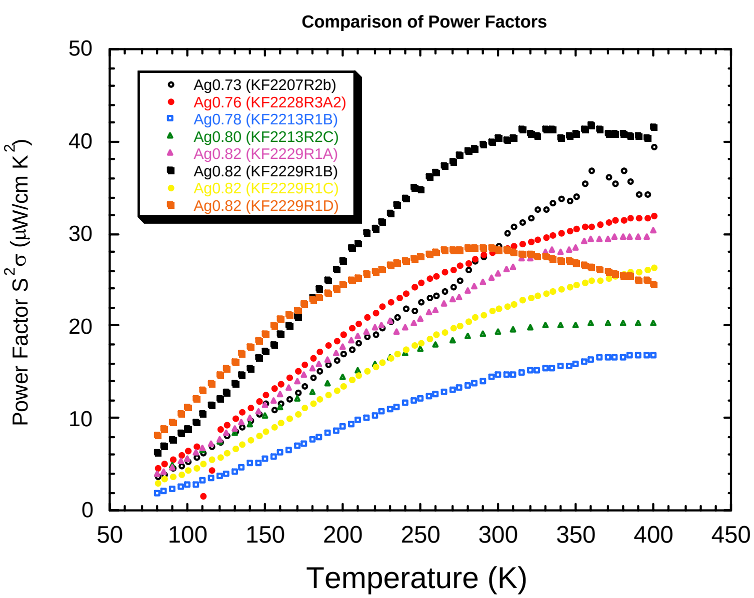


(1) (a) Rodot, H. *Compt. Rend.* **1959**, *249*, 1872-4.
(2) (a) Rosi, F. D.; Hockings, E. S.; Lindenblad, N. E. *Adv. Energy Convers.* **1961**, *1*, 151.

(LAST-18) $Ag_{1-x}Pb_{18}SbTe_{20}$: Tunable properties Changing x

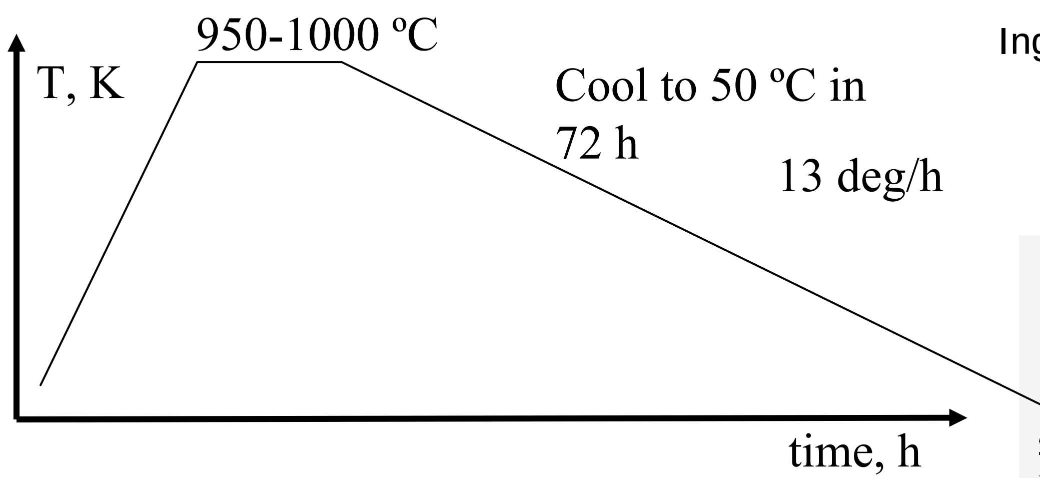






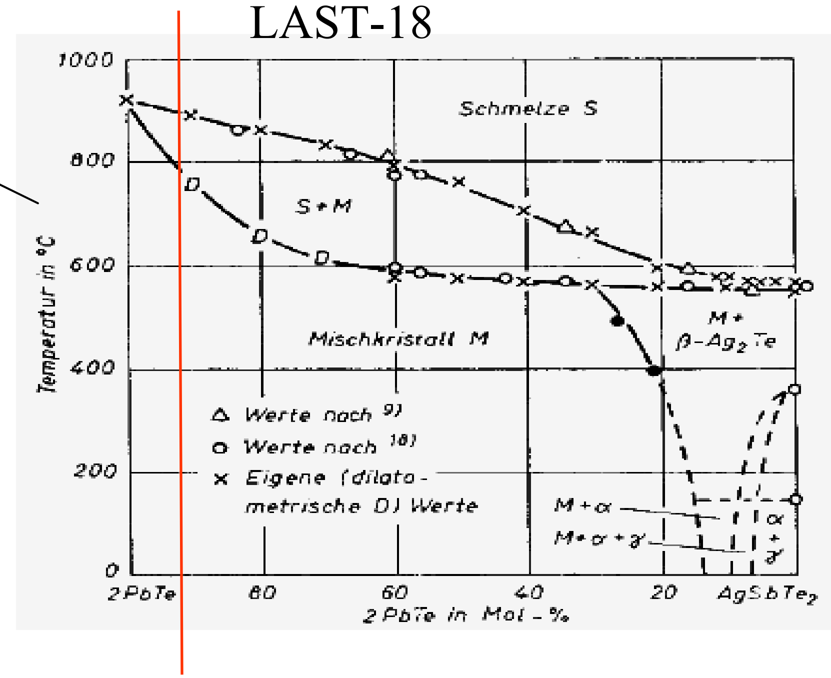
Synthesis: Heating cooling profiles

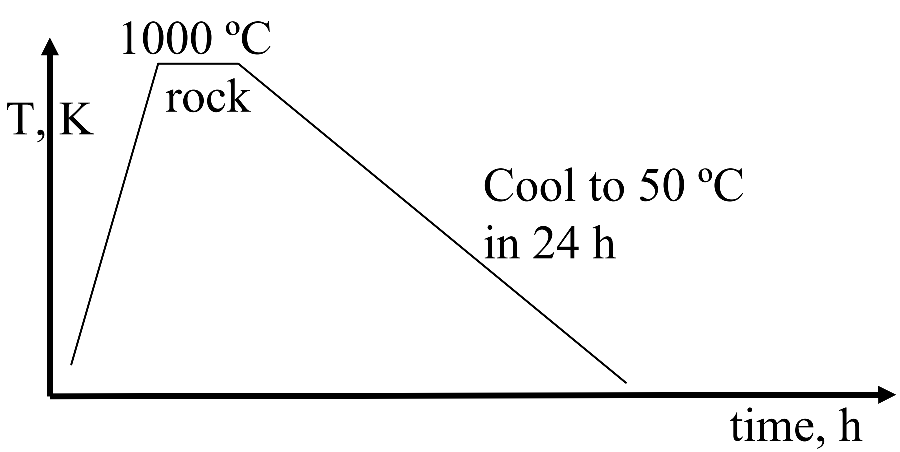
rock



Ingot properties very sensitive to cooling profile

Gravity induced inhomogeneity



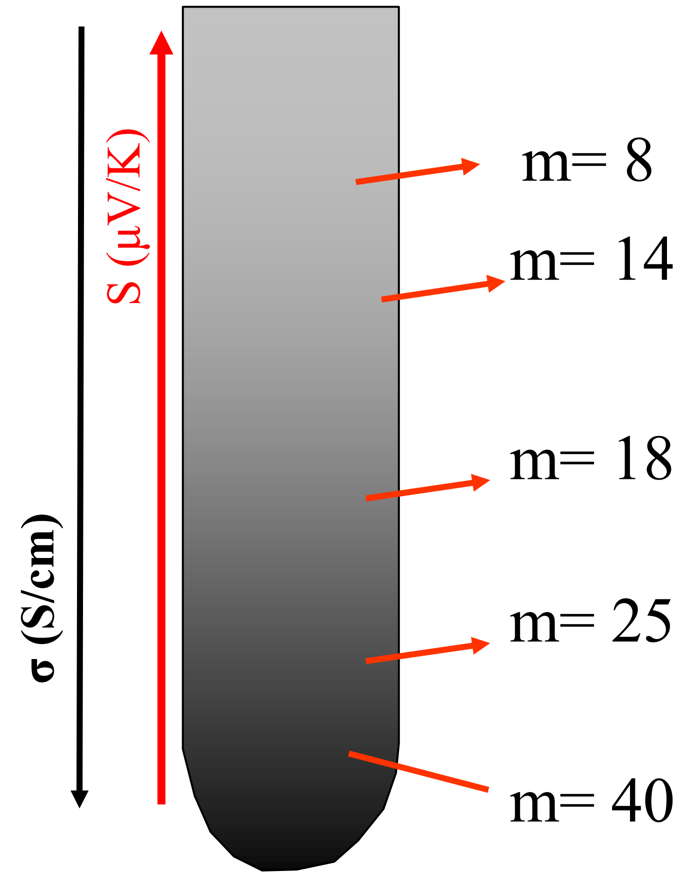


Wernick, J. H.. *Metallurg. Soc. Conf. Proc.* (1960), 5 69-87.

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

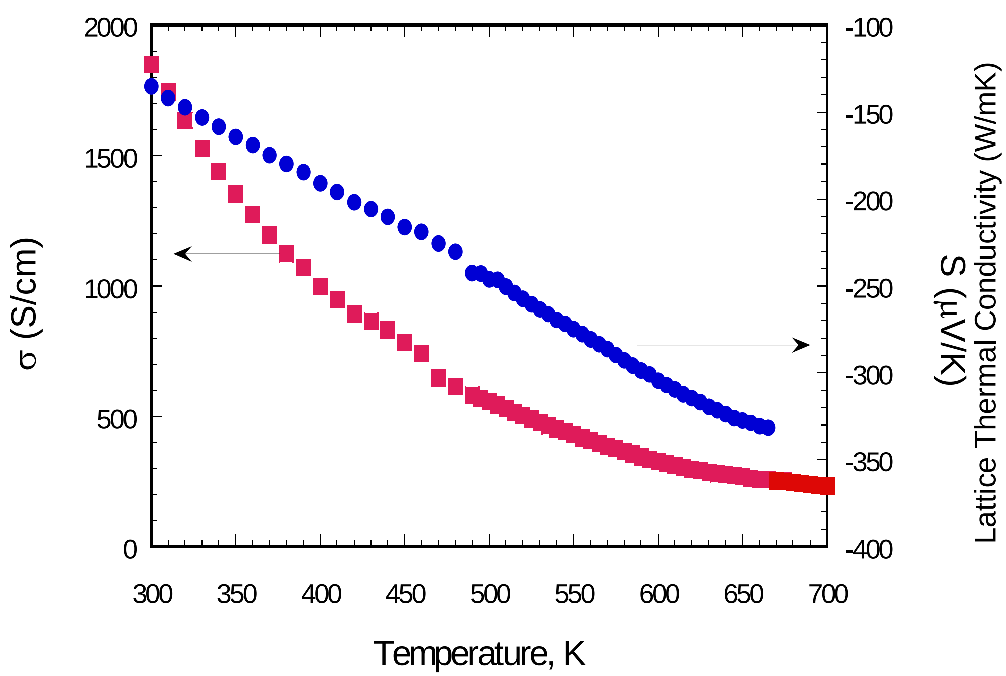
Samples cooled slowly from liquid to solid

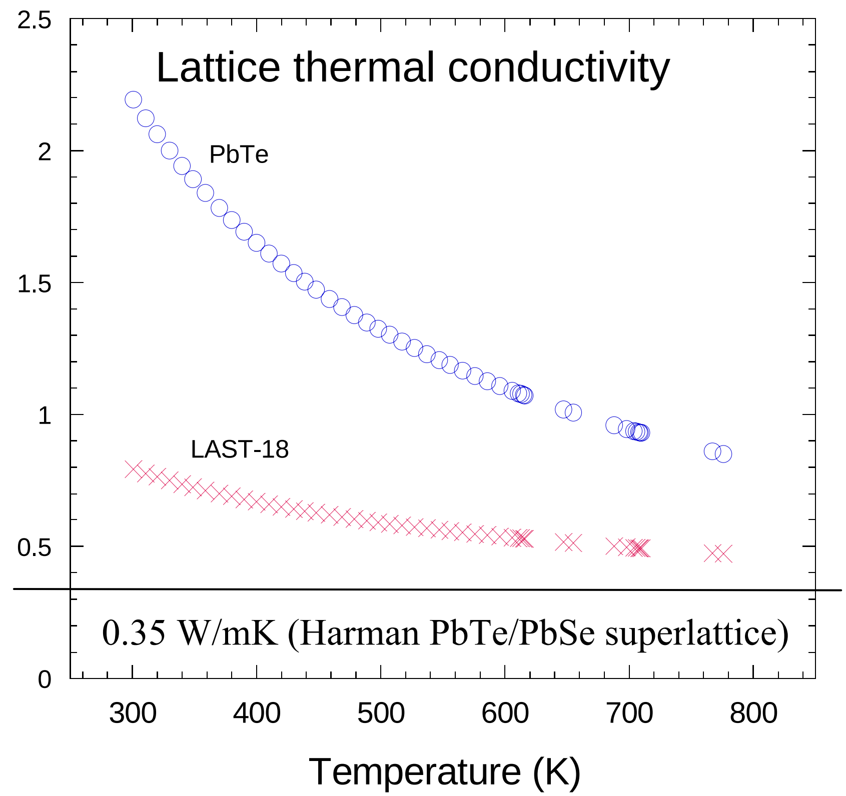
- Strongly varying composition from top to bottom.
- Strongly varying properties from top to bottom.
- “Sweet” spot exists with very high ZT.
- Mechanical properties weak.



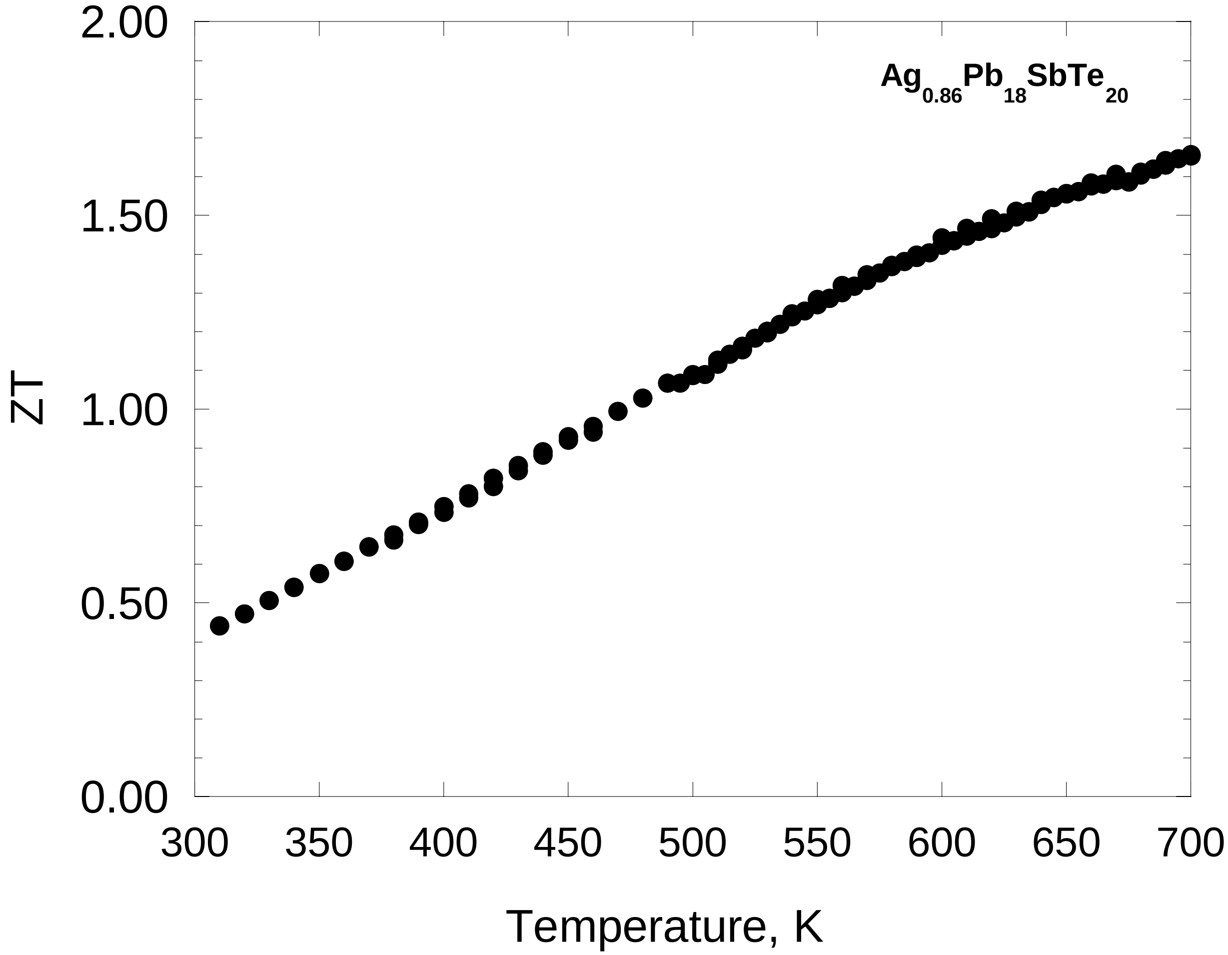
Strong composition grading along ingot

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





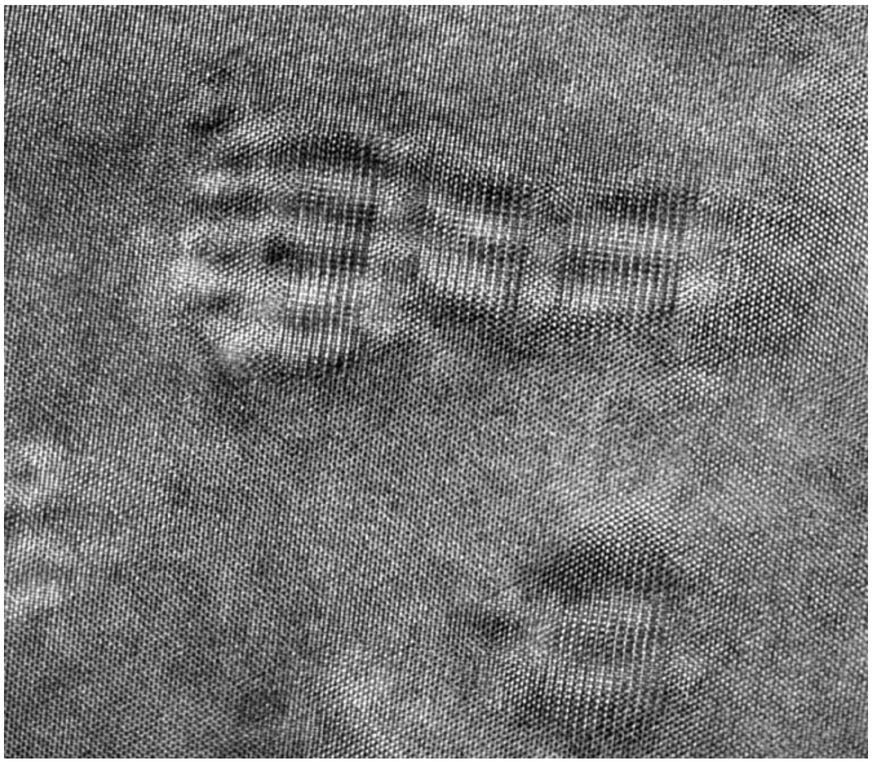
$Ag_{1-x}Pb_{18}SbTe_{20}$

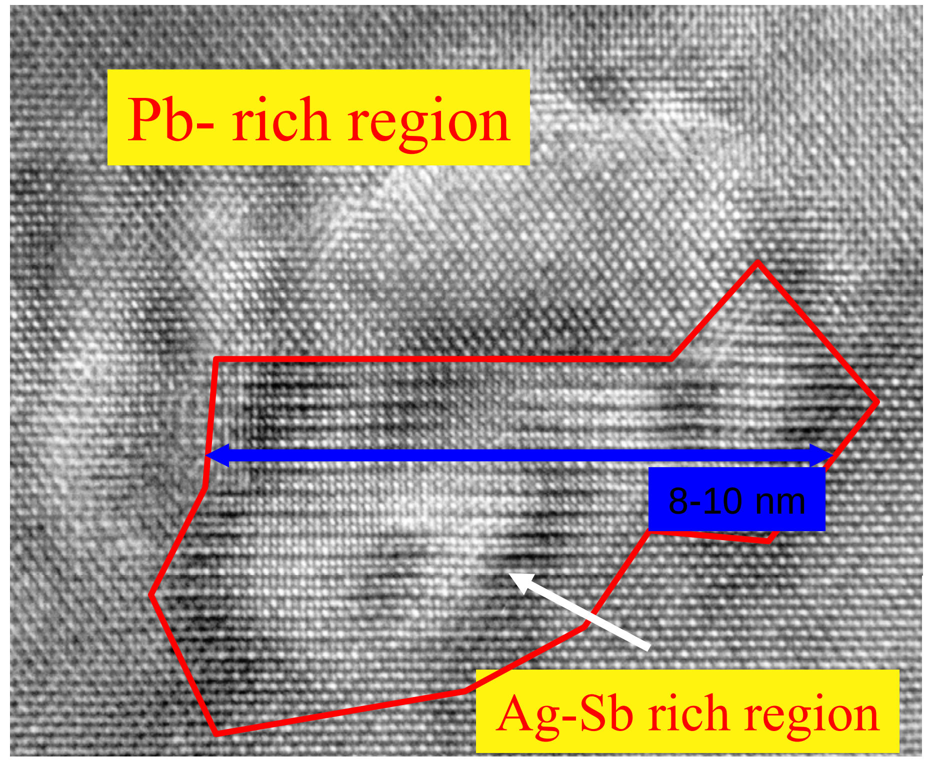


Hsu KF, Loo S, Guo F, Chen W, Dyck JS, Uher C, Hogan T, Polychroniadis EK, Kanatzidis MG *Science*, **2004**, 303, 818

What is the origin of the TE properties of $AgPb_mSbTe_{m+2}$ systems?

HRTEM
Coherently embedded nanocrystals

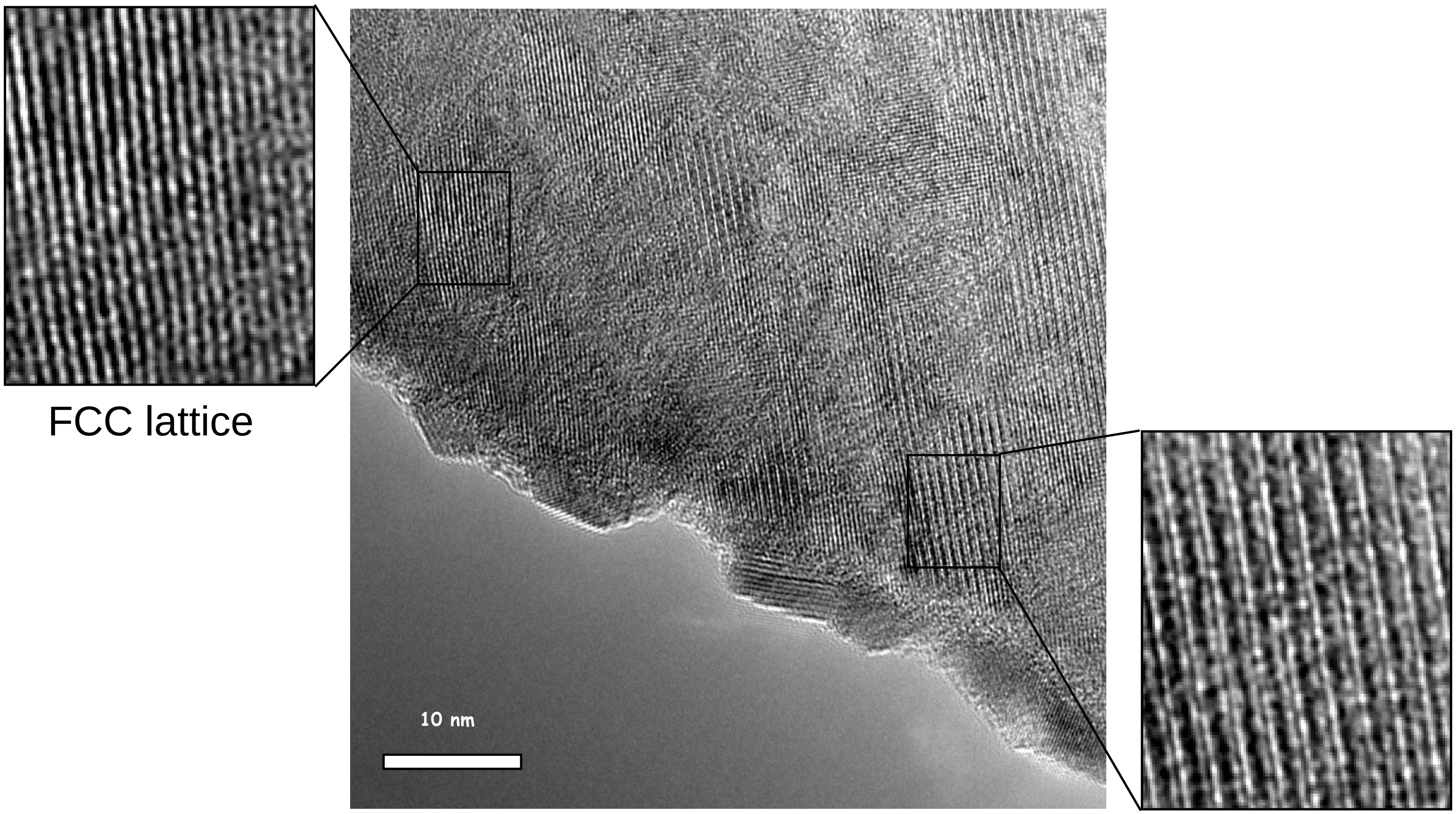




Polychroniadis, Frangis, 2004

LAST-18 κ_{latt}=1.2 W/m-K at 300 K
PbTe κ_{latt}=2.2 W/m-K at 300 K

Coherent compositional fluctuations in $AgPb_mSbTe_{m+2}$

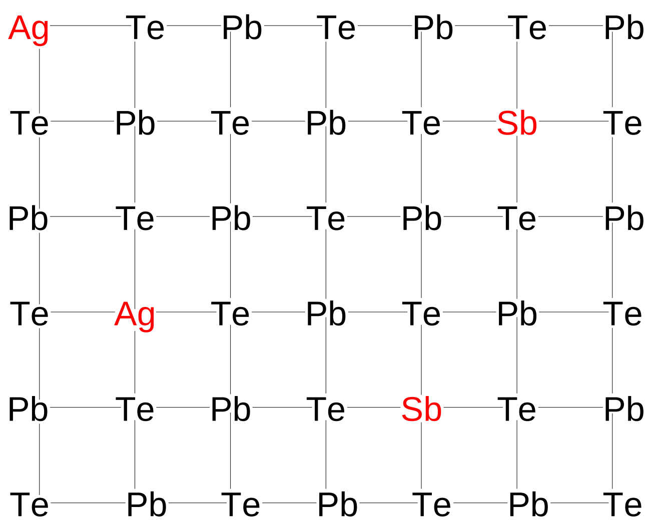


FCC lattice

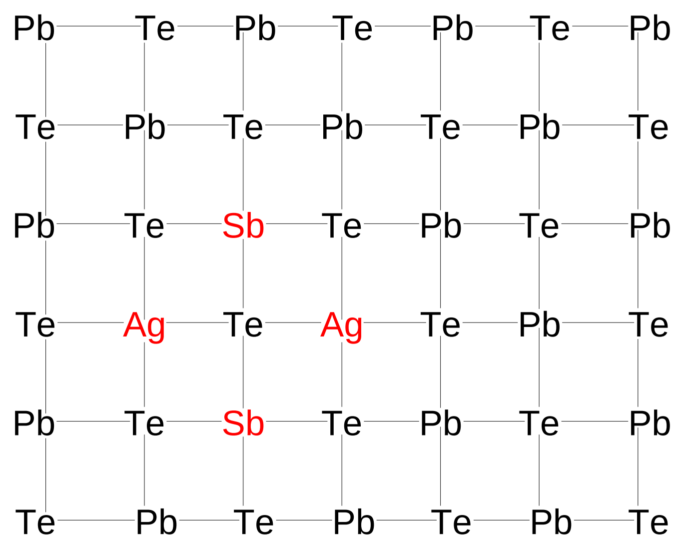
Ag, Sb, Pb ordering

Driving force for segregation

Ag^{+}/Sb^{3+} pair: stable



Dissociated state..unstable

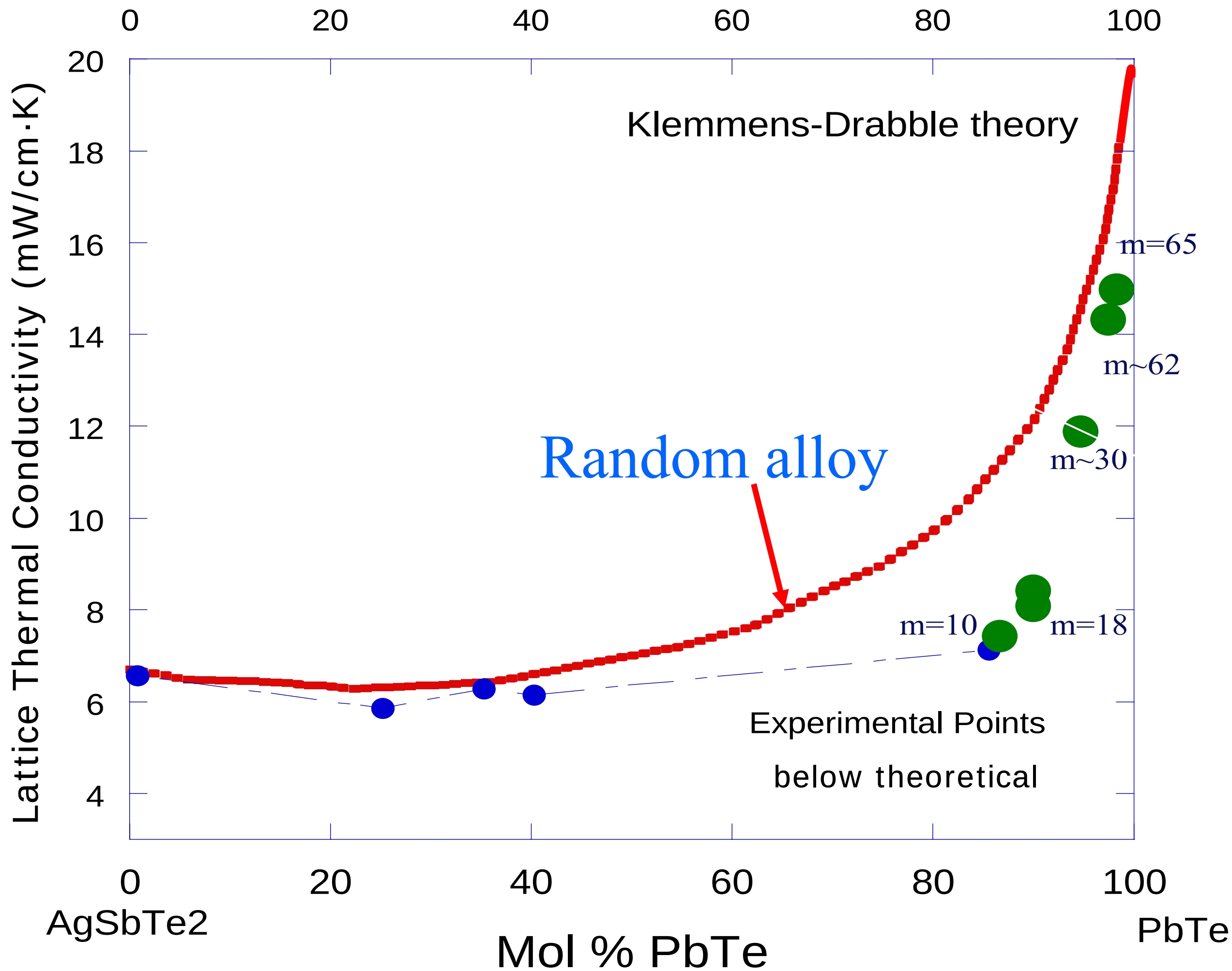


Associated state..stable

Any +1/+3 pair

LAST-m

Solid solutions in $(AgSbTe_2)_{1-x}(PbTe)_x$



T. Irie *Jap. J. Appl. Phys*. 1966, 5, 854

PRL 96, 045901 (2006) PHYSICAL REVIEW LETTERS week ending 3 FEBRUARY 2006

Thermal Conductivity Reduction and Thermoelectric Figure of Merit Increase by Embedding Nanoparticles in Crystalline Semiconductors

Woochul Kim,[1] Joshua Zide,[2] Arthur Gossard,[2] Dmitri Klenov,[2] Susanne Stemmer,[2]
Ali Shakouri,[3] and Arun Majumdar[1,4,*]

[1]*Department of Mechanical Engineering, University of California, Berkeley, California 94720, USA*
[2]*Department of Materials, University of California, Santa Barbara, California 93106, USA*
[3]*Department of Electrical Engineering, University of California, Santa Cruz, California 95064, USA*
[4]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

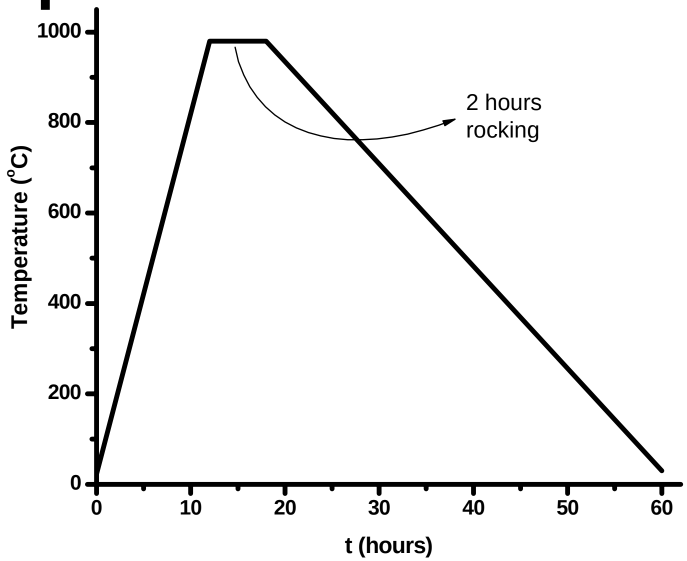
(Received 13 September 2005; published 2 February 2006)

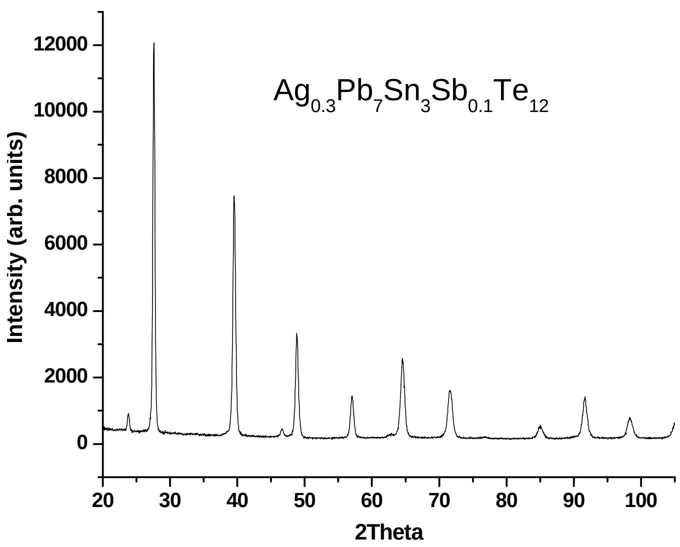
Atomic substitution in alloys can efficiently scatter phonons, thereby reducing the thermal conductivity in crystalline solids to the "alloy limit." Using $In_{0.53}Ga_{0.47}As$ containing ErAs nanoparticles, we demonstrate thermal conductivity reduction by almost a factor of 2 below the alloy limit and a corresponding increase in the thermoelectric figure of merit by a factor of 2. A theoretical model suggests that while point defects in alloys efficiently scatter short-wavelength phonons, the ErAs nanoparticles provide an additional scattering mechanism for the mid-to-long-wavelength phonons.

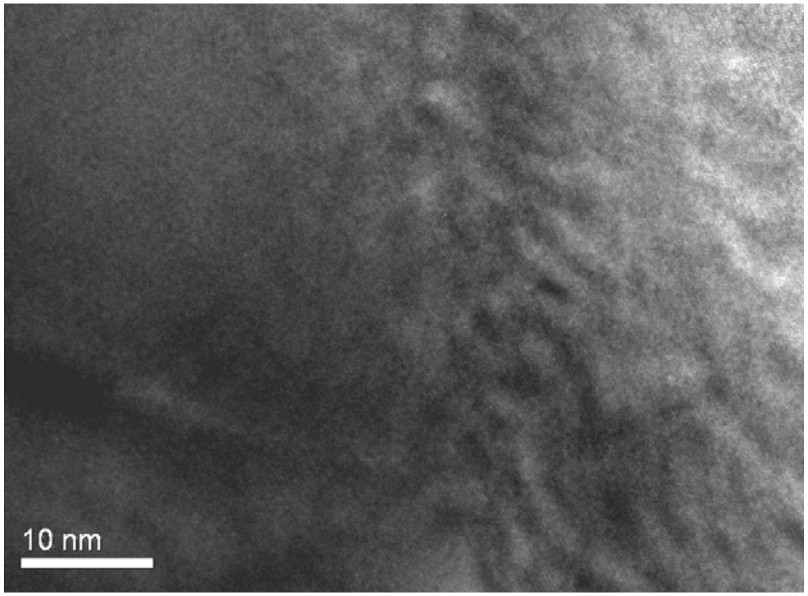
DOI: 10.1103/PhysRevLett.96.045901 PACS numbers: 65.40.−b, 63.22.+m, 65.80.+n, 66.60.+a

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 $AgPb_{10}Sn_8SbTe_{20}$, $Ag_xPb_7Sn_3Sb_yTe_{12}$,
  Very low lattice thermal conductivity
- Good homogeneity

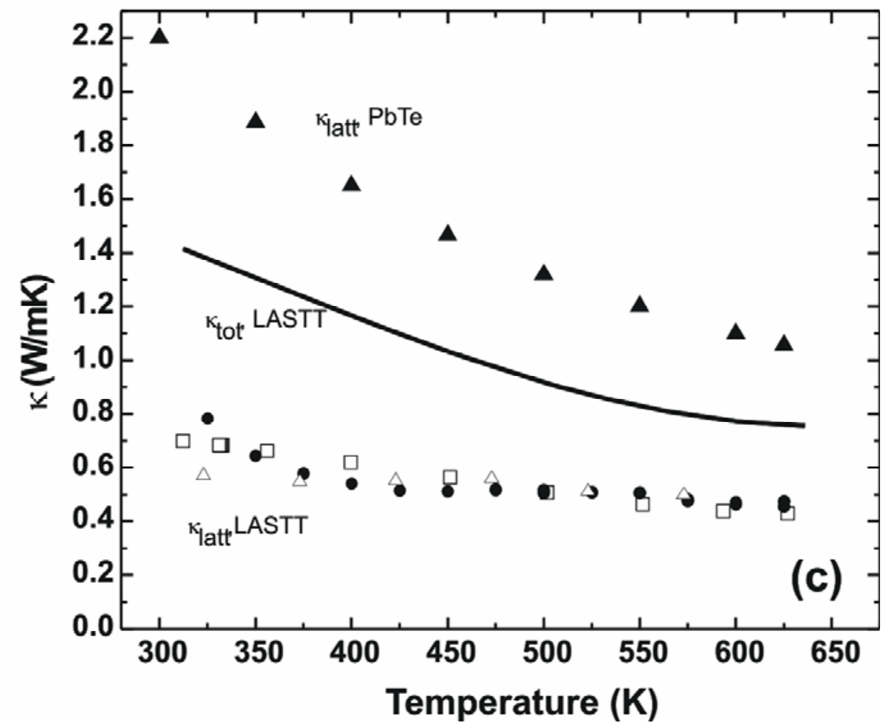


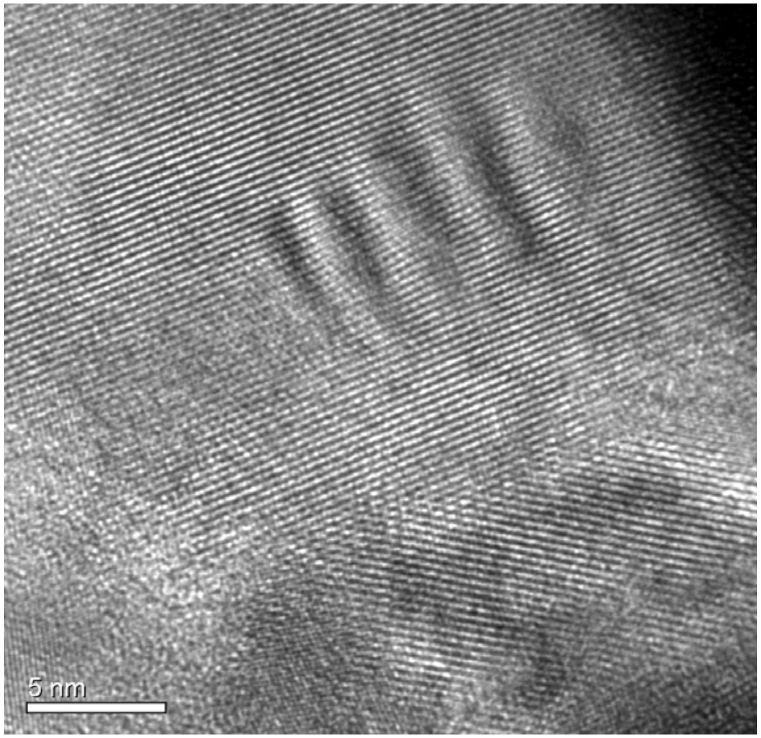




LASTT-16

Very low lattice thermal conductivity

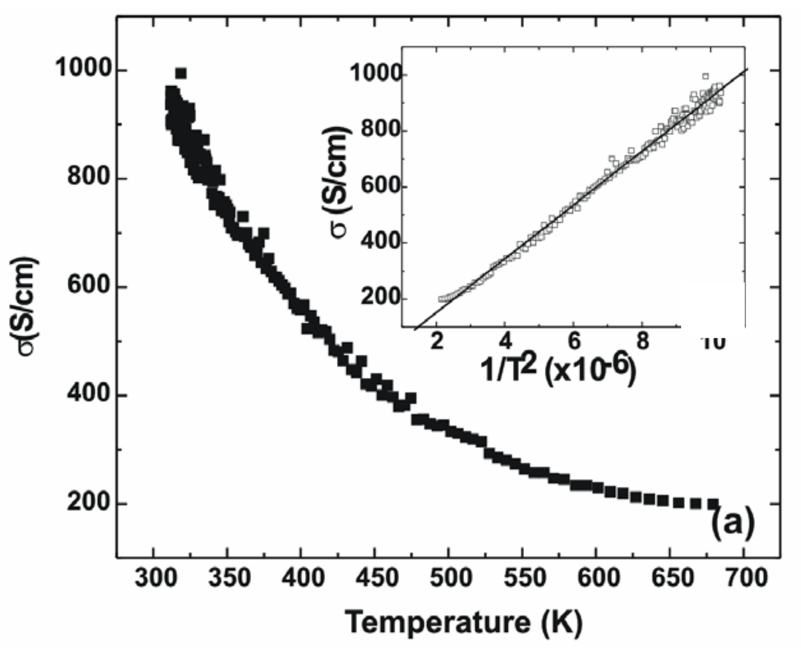


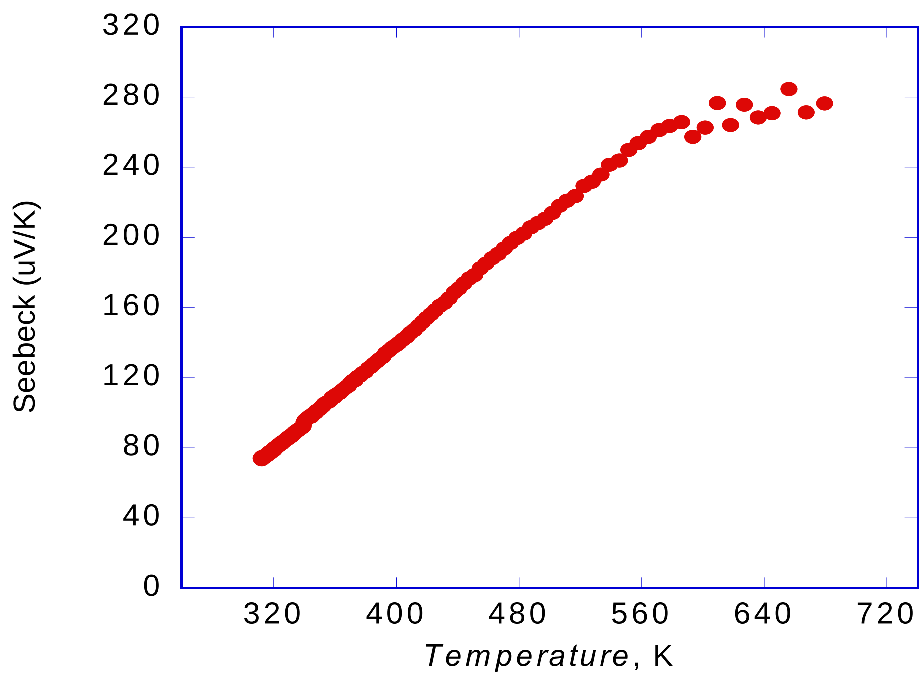


κ_{latt} =0.5 W/m·K at 650 K

Androulakis, Hsu, Hogan, Uher, Kanatzidis *Advanced Mater*. 2006, in press

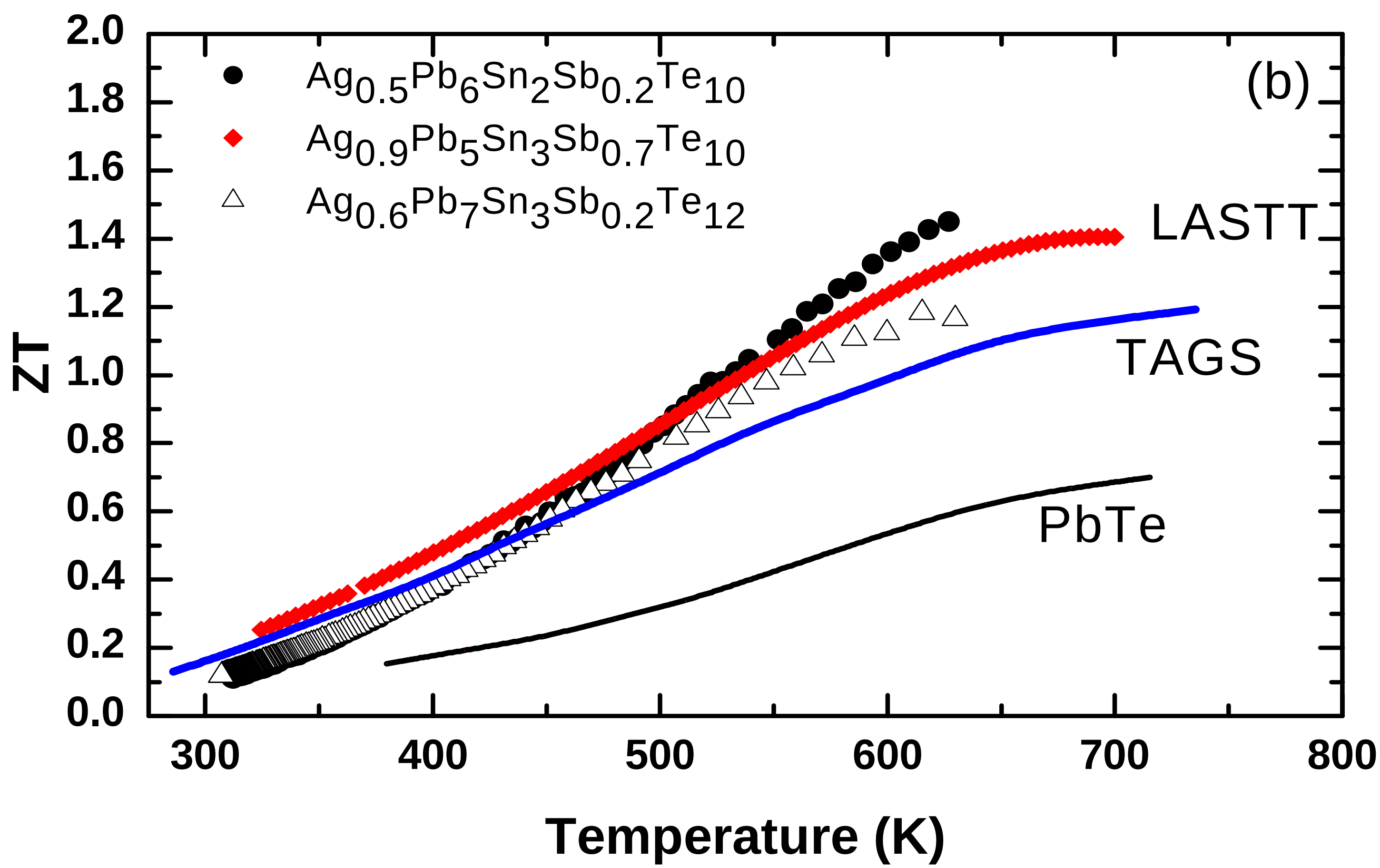
LASTT-16: $AgPb_{12}Sn_4Sb_{0.4}Te_{20}$





Androulakis, Hsu, Hogan, Uher, Kanatzidis *Advanced Mater*. 2006, in press

Figure of Merit LASTT (p-type)



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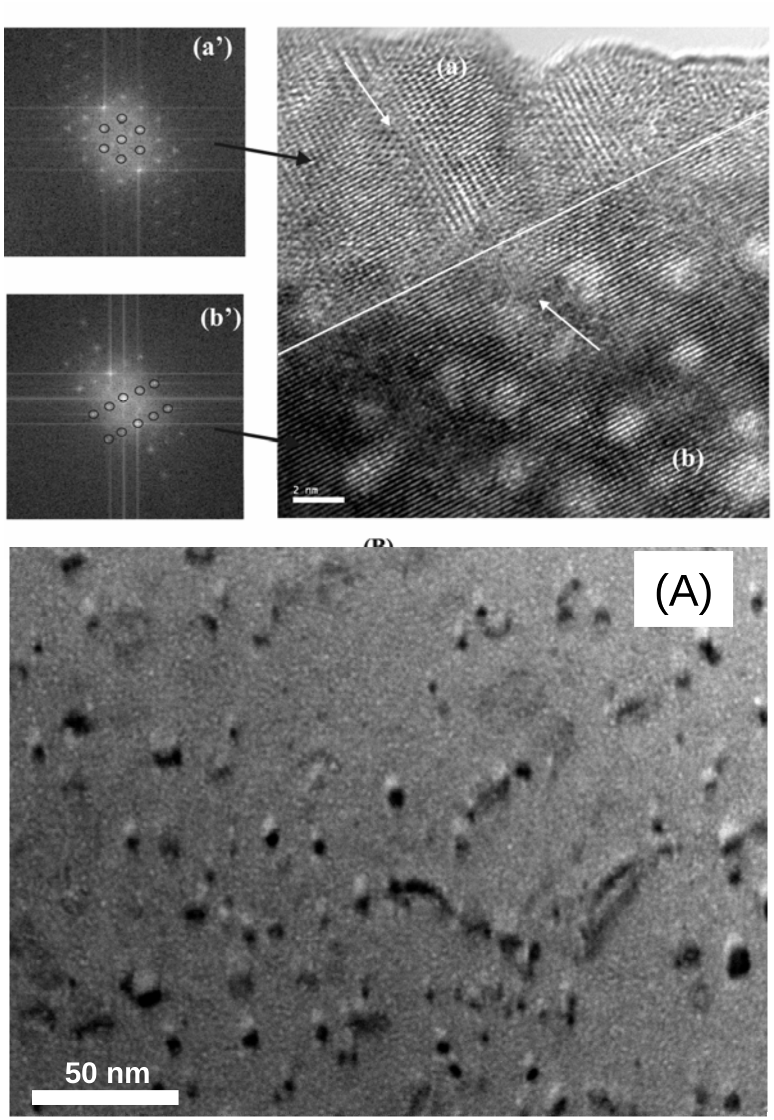
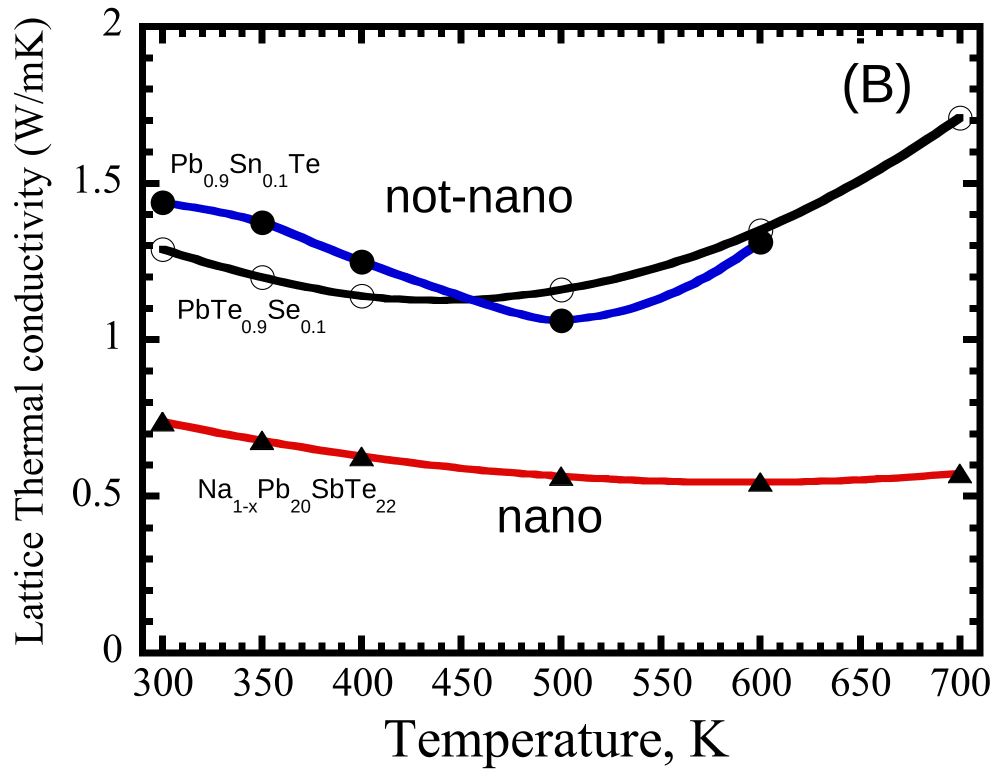
Androulakis, Hsu, Hogan, Uher, Kanatzidis *Advanced Mater*. 2006, in press

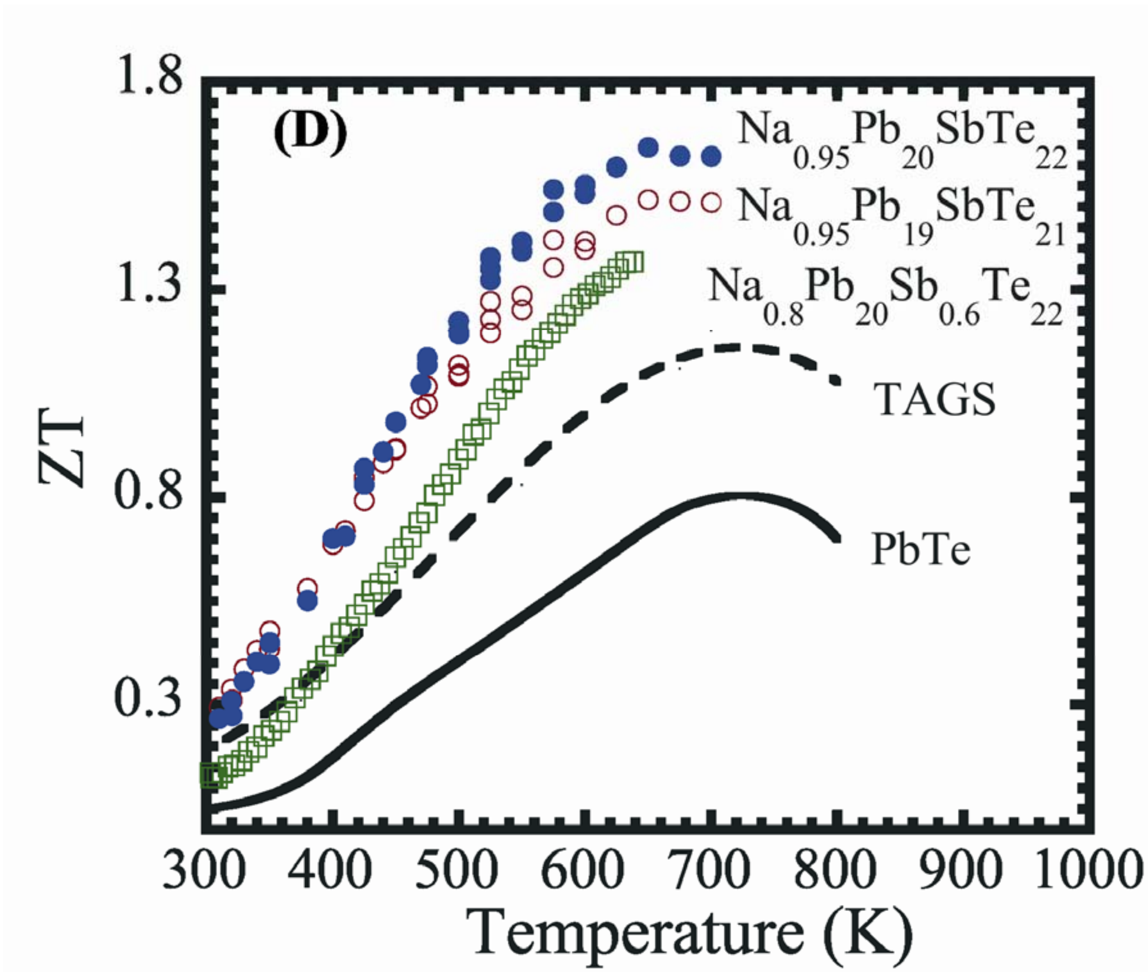
NaPb$_{20}$SbTe$_{22}$ (SALT-20)





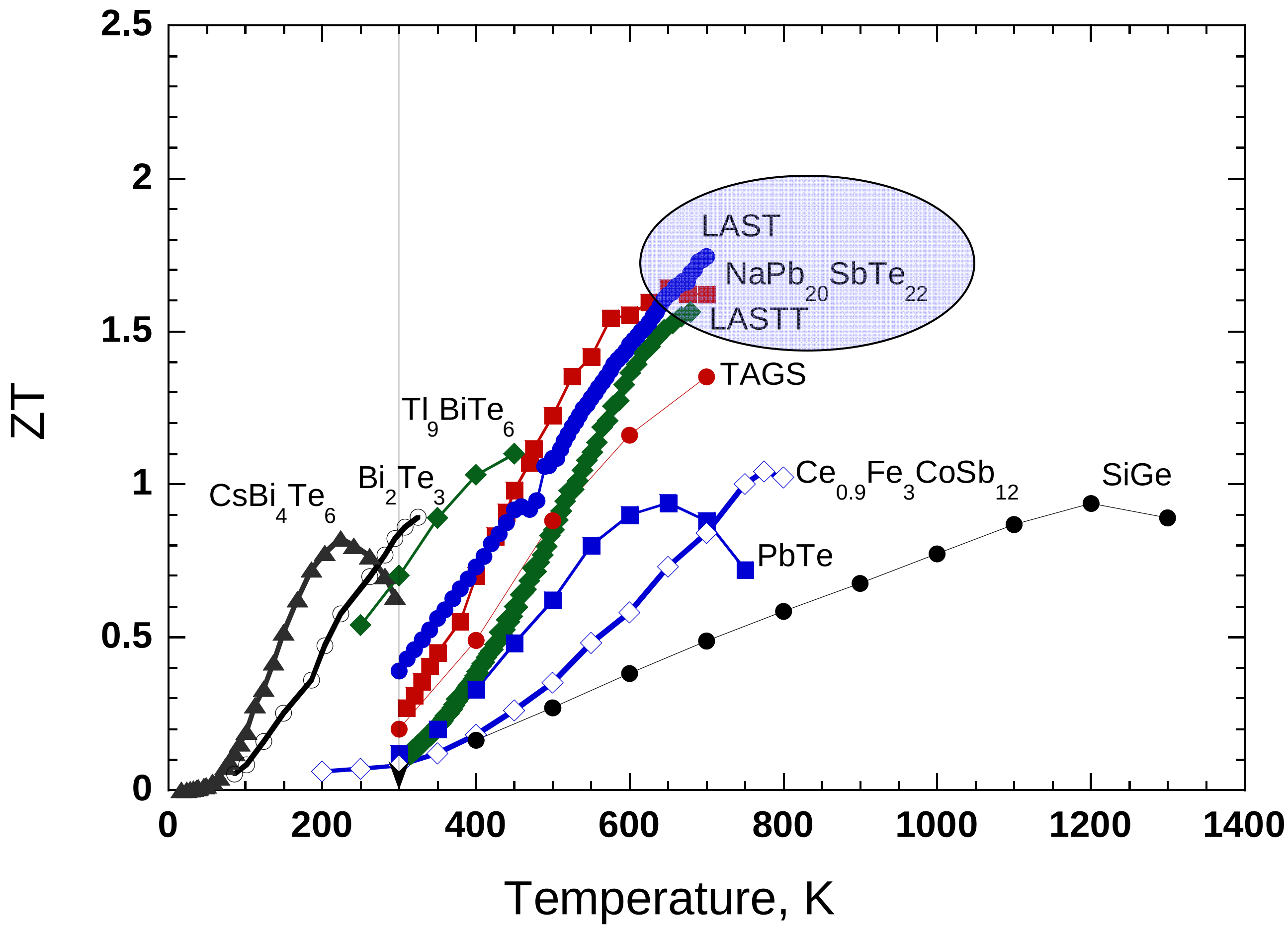
Poudeu, Hogan, Kanatzidis *Angew. Chemie*, 2006,

SALT-20



Poudeu, Hogan, Kanatzidis *Angew. Chemie*, 2006,

State of the art - bulk



Conclusions

- New approaches are succeeding in raising ZT
- The $(A_2Q)_n(PbQ)_m(Bi_2Q_3)_p$ (Q=Se, Te) system is a rich source of new materials
- Several new promising compounds identified
  - strongly anisotropic
  - cubic
  - nanostructured
- LAST, LASTT and SALT family of materials
  - nanostructured
  - superior ZT
- Strong thermal conductivity reduction achieved through nanostructuring
- Doping studies and processing conditions are important in ZT optimization

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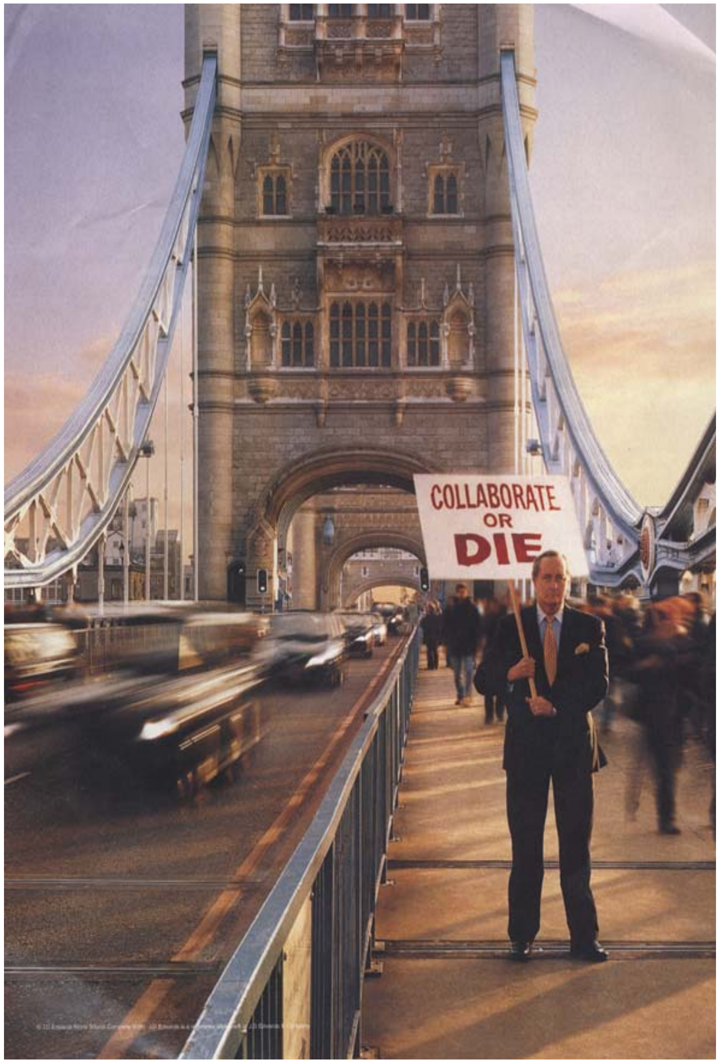
Outlook

- Further progress is expected on the TE figure of merit
- Fundamental challenge:
  - Translate current theoretical physical predictions on how to enhance Power Factor ($\sigma \cdot S^2$) into actual chemistry in the laboratory
  - Achieve minimum thermal conductivity (~0.3 W/mK) in a bulk (nano)crystalline TE material
- Research in new materials should focus on
  - Understanding and controlling carrier scattering
  - Controlling nanostructuring to manipulate phonon propagation
  - Discovering new compounds
- Long term: Waste heat recovery and conversion could be impacted on a massive scale with low cost materials if ZT>2-3.
- Thermoelectrics could help utilize existing depletable energy resources more effectively
- Thermoelectrics could also play role in renewable energy (e.g. solar, etc)

Collaborators

- Tim Hogan, Dept of Electrical Engineering, MSU
- S. D. (Bhanu) Mahanti, Dept. of Physics, MSU
- Ctirad Uher, Dept. of Physics, U of Michigan
- Simon Billinge, Physics, MSU
- Eldon Case, MSU
- Harold Schock, MSU
- Bruce Cook, Iowa State
- Terry Tritt, Clemson U
- Art Schultz, Argonne NL



TE Research group

- Dr Duck young Chung
- Joseph Sootsman
- Dr Kuei fang Hsu
- Dr Eric Quarez
- Aurelie Guegen
- Ferdinand Poudeu
- Jun-Ho Kim
- Dr John Androulakis