Thermal Properties

- How does a material respond to heat?
- How do we define and measure...
  - -- heat capacity
  - -- coefficient of thermal expansion
  - -- thermal conductivity
  - -- thermal shock resistance
- How do ceramics, metals, and polymers rank?

Heat Capacity

- General: The ability of a material to absorb heat.
- Quantitative: The energy required to increase the temperature of the material.

energy input (J/mol)

heat capacity (J/mol-K) → $$C = \frac{dQ}{dT}$$

temperature change (K)

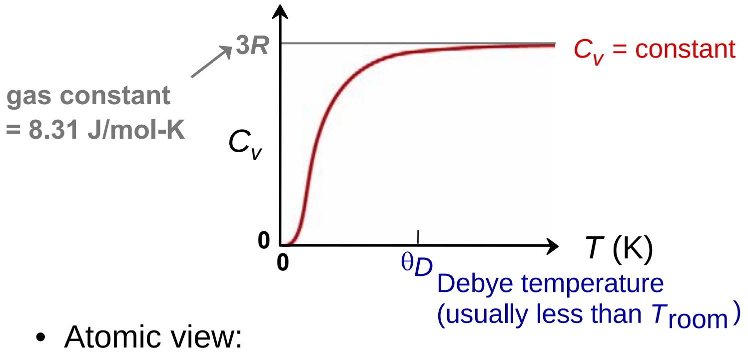
- Two ways to measure heat capacity:
  - C_p : Heat capacity at constant pressure.
  - C_v : Heat capacity at constant volume.

$$C_p > C_v$$

- Specific heat has typical units of $\frac{\text{J}}{\text{kg}\cdot\text{K}}$

Heat Capacity vs *T*

- Heat capacity...
  -- increases with temperature
  -- reaches a limiting value of 3*R*

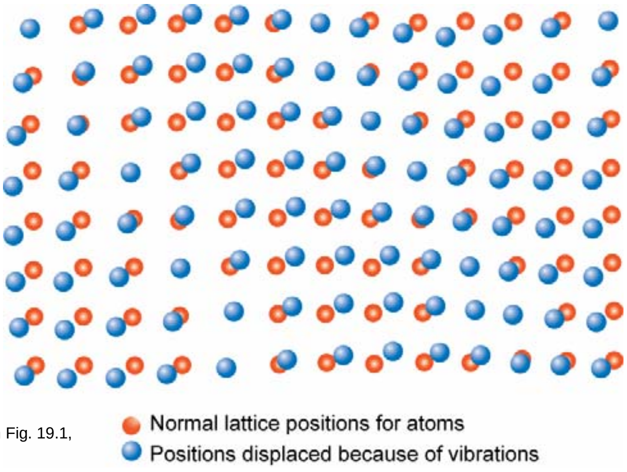


- Atomic view:
  -- Energy is stored as atomic vibrations, rotations, and electronic excitations.
  -- As *T* goes up, so does the avg. energy of atomic vibr. etc.

Energy Storage

How is the energy stored?

Phonons – thermal waves - vibrational modes



Adapted from Fig. 19.1,
Callister 7e.

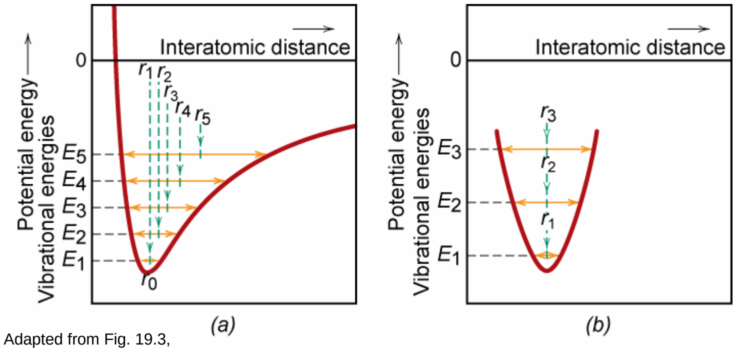
Energy Storage

- Other small contributions to energy storage

  Electron energy levels

    Dominate for ceramics & plastics

  Energy storage in vibrational modes



Adapted from Fig. 19.3, *Callister 7e*.

Heat Capacity: Comparison

increasing c_p

material	c_p (J/kg-K) at room T
• <u>Polymers</u>	
Polypropylene	1925
Polyethylene	1850
Polystyrene	1170
Teflon	1050
• <u>Ceramics</u>	
Magnesia (MgO)	940
Alumina (Al_2O_3)	775
Glass	840
• <u>Metals</u>	
Aluminum	900
Steel	486
Tungsten	138
Gold	128

c_p: (J/kg-K)

C_p: (J/mol-K)

- c_p significantly larger for polymers.

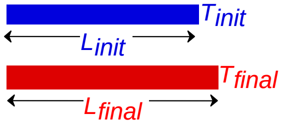
Selected values from Table 19.1, *Callister 7e*.

Thermal Expansion

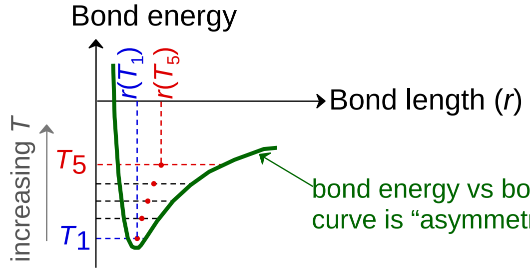
- **Materials change size when heating.**

$$\frac{L_{final} - L_{initial}}{L_{initial}} = \alpha(T_{final} - T_{initial})$$

coefficient of thermal expansion (1/K or 1/°C)



- **Atomic view: Mean bond length increases with *T*.**



bond energy vs bond length curve is "asymmetric"

Thermal Expansion: Comparison

Material	α_ℓ (10^{-6}/K) at room T
• Polymers	
Polypropylene	145-180
Polyethylene	106-198
Polystyrene	90-150
Teflon	126-216
• Metals	
Aluminum	23.6
Steel	12
Tungsten	4.5
Gold	14.2
• Ceramics	
Magnesia (MgO)	13.5
Alumina (Al_2O_3)	7.6
Soda-lime glass	9
Silica (cryst. SiO_2)	0.4

Polymers have smaller α_ℓ because of weak secondary bonds

- **α generally decrease with increasing bond energy.**

Selected values from Table 19.1, *Callister 7e*.

Thermal Conductivity

- General: The ability of a material to transfer heat.
- Quantitative:

$$q = -k\frac{dT}{dx}$$

heat flux **(J/m^2-s)**

temperature gradient

thermal conductivity (J/m-K-s)

Fourier's Law

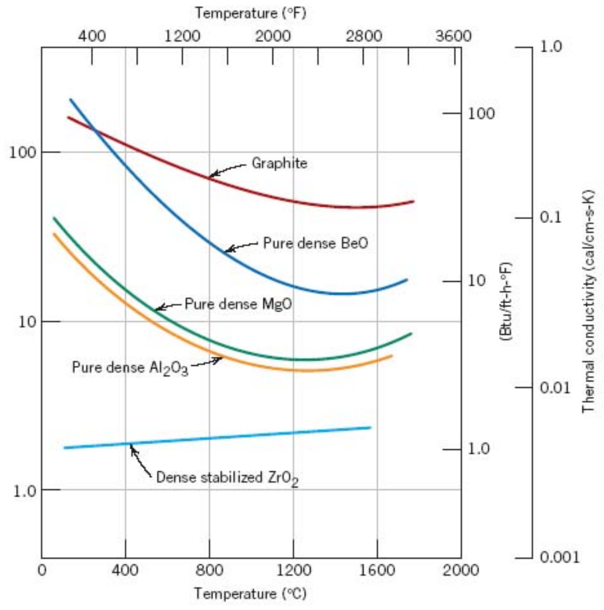
- Atomic view: Atomic vibrations in hotter region carry energy (vibrations) to cooler regions.

Thermal Conductivity: Comparison

Material	k (W/m-K)	Energy Transfer
• **Metals**		
Aluminum	**247**	**By vibration of atoms and motion of electrons**
Steel	**52**	
Tungsten	**178**	
Gold	**315**	
• **Ceramics**		
Magnesia (MgO)	**38**	**By vibration of atoms**
Alumina (Al_2O_3)	**39**	
Soda-lime glass	**1.7**	
Silica (cryst. SiO_2)	**1.4**	
• **Polymers**		
Polypropylene	**0.12**	**By vibration/ rotation of chain molecules**
Polyethylene	**0.46-0.50**	
Polystyrene	**0.13**	
Teflon	**0.25**	

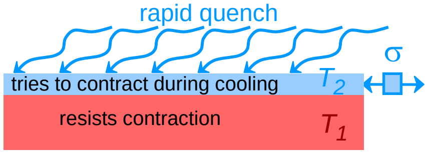
Selected values from Table 19.1, *Callister 7e*.

Thermal Conductivity: Comparison



Thermal Shock Resistance

- Occurs due to: uneven heating/cooling.
- Ex: Assume top thin layer is rapidly cooled from T_1 to T_2:



Tension develops at surface

$$\sigma = -E\alpha(T_1 - T_2)$$

Temperature difference that can be produced by cooling:

$$(T_1 - T_2) = \frac{\text{quench rate}}{k}$$

Critical temperature difference for fracture (set σ = σf)

$$(T_1 - T_2)_{\text{fracture}} = \frac{\sigma_f}{E\alpha}$$

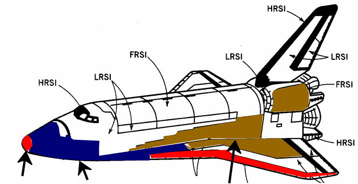
set equal

- Result: $(\text{quench rate})_{\text{for fracture}} \propto \dfrac{\sigma_f k}{E\alpha}$
- Large thermal shock resistance when $\dfrac{\sigma_f k}{E\alpha}$ is large.

Thermal Protection System

- Application:


Space Shuttle Orbiter



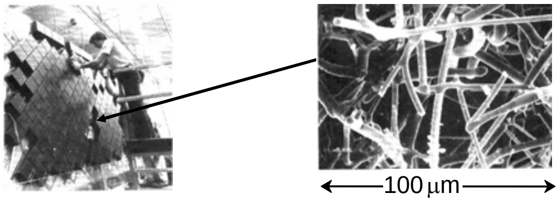
reinf C-C (1650°C)

silica tiles (400-1260°C)

nylon felt, silicon rubber coating (400°C)

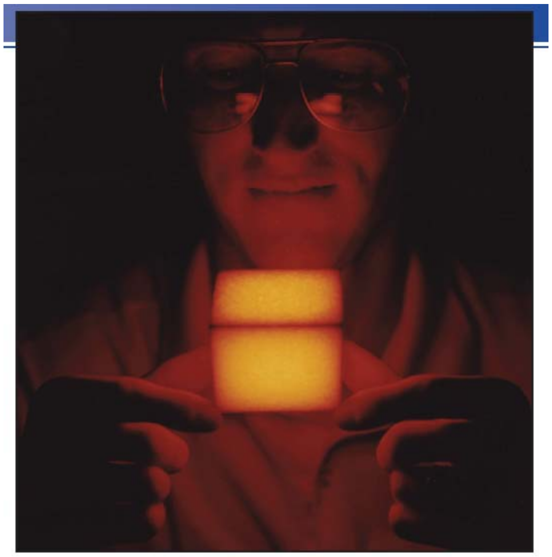
- Silica tiles (400-1260°C):
  --large scale application

--microstructure:



~90% porosity!
Si fibers bonded to one another during heat treatment.

Thermal Protection System



a white-hot cube of a silica fiber insulation material

seconds from furnace (~1250°C)

thermal conductivity very small

heat conduction from interior is extremely slow

Summary

- **A material responds to heat by:**
  - -- increased vibrational energy
  - -- redistribution of this energy to achieve thermal equil.
- **Heat capacity:**
  - -- energy required to increase a unit mass by a unit T.
  - -- polymers have the largest values.
- **Coefficient of thermal expansion:**
  - -- the stress-free strain induced by heating by a unit T.
  - -- polymers have the largest values.
- **Thermal conductivity:**
  - -- the ability of a material to transfer heat.
  - -- metals have the largest values.
- **Thermal shock resistance:**
  - -- the ability of a material to be rapidly cooled and not crack. Maximize $\sigma_f k/E\alpha$.

Why Thermoelectrics?

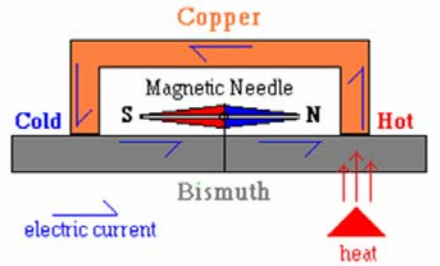
- **Direct conversion between heat & electricity**
- **Waste heat recovery**
  - **~ 65% of energy is lost as heat**
  - **~ $265 billion/yr in the US**
- **Solid-state refrigeration**
  - **no moving parts = durable & silent**
  - **compact, ideal for microelectronics**
  - **no greenhouse or ozone depleting gasses**
- **More efficient materials are needed**

Slides modified from Matt Thorum, UIUC.
Service, R. F. *Science* **2004,** *306,* 806.

Seebeck Effect – 1820's

- **Two metals soldered into a loop**
- **Heat or cool one junction**
- **Current flow deflects compass needle**
- **Magnitude depends on choice of metals**

Thomas Seebeck and his apparatus



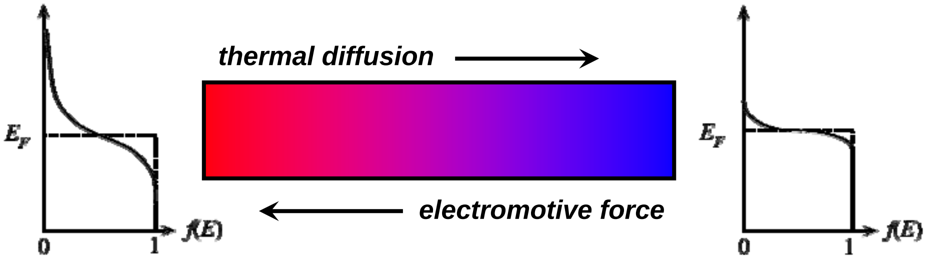
http://chem.ch.huji.ac.il/~eugeniik/history/seebeck.html

Physical Origins of the Seebeck Effect

- **Two fundamental principles:**

  thermal distribution of e^- energies around E_F

  e^- mobility (conductivity) varies with E (DOS)



thermal diffusion →

← *electromotive force*

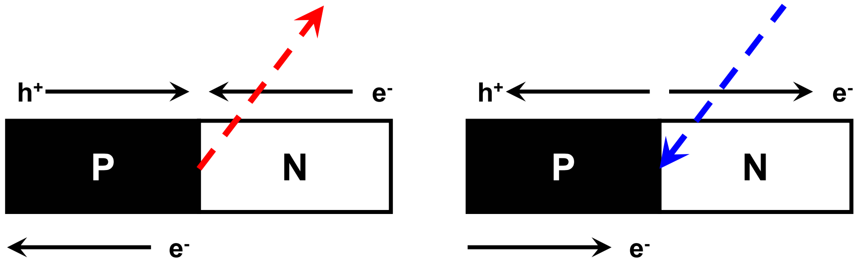
$$S = \frac{\Delta V}{\Delta T} \approx \frac{heat}{carrier \cdot T}$$

Peltier Effect

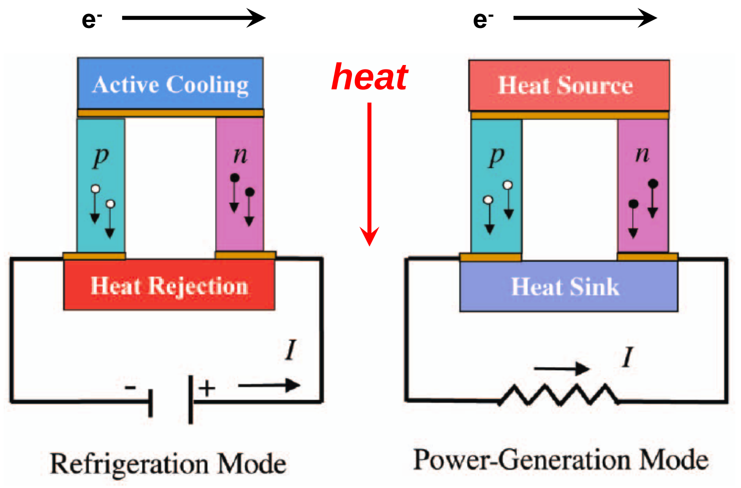
- 1834: Observed by Jean Peltier

  passed current through a Bi/Sb junction

  junction heated or cooled
- Closely related to the Seebeck Effect
- Charge carriers also carry heat



Thermoelectric Devices



Refrigeration Mode

Power-Generation Mode

Tritt, T. M. et al. *MRS Bulletin* **2006,** *31,* 188.

Minimizing Thermal Conductivity

- Electronic part is proportional to σ
- Lattice part can be minimized
- Want a “phonon glass/electron crystal”
  - grain boundaries
  - point defects
  - random-alloy disorder
  - “rattlers”
  - nanostructures

$$\kappa = \kappa_e + \kappa_l$$

Tritt, T. M. et al. *MRS Bulletin* **2006,** *31,* 188.

ZT – The Figure of Merit

Power Factor
S: Seebeck coefficient
σ: electrical conductivity

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

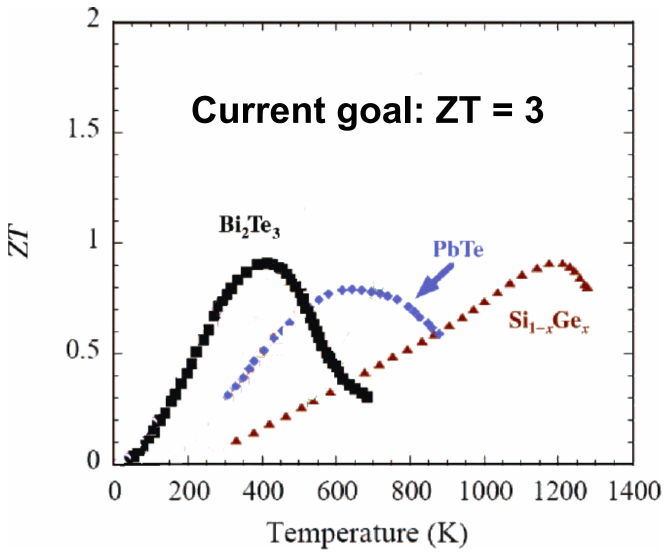
thermal conductivity

Efficiency (η)

$$\eta = \frac{T_H - T_C}{T_H}\left[\frac{\sqrt{1+ZT_M}-1}{\sqrt{1+ZT_M}+(T_C/T_H)}\right]$$

- **Reduces to the Carnot efficiency at high ZT**
- **No thermodynamic limit to ZT**
- **Want a large ZT over a large ΔT**

State-of-the-Art Materials



Current goal: ZT = 3

Tritt, T. M. et al. *MRS Bulletin* **2006,** *31,* 188.

Maximizing the Power Factor ($S^2\sigma$)

- **Maximize change in DOS at E_F**
- **Semiconductors:**

  narrow band-gap with high mobility carriers

  highly doped

  small number of minority carriers (E_g ~ 10kT)

  complicated band structures

  quantum effects in nanomaterials
- **S > 225 μV / K for ZT = 2**

Tritt, T. M. et al. *MRS Bulletin* **2006,** *31,* 188.

Advanced Materials

- **Thin-films:**

  Bi_2Te_3 / Sb_2Te_3
  superlattices (SL)

  PbSe / PbTe
  quantum dot superlattices (QDSL)
- **Bulk materials with nanoscale features:**

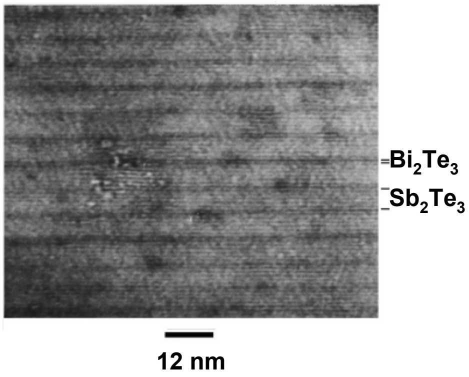
  $CsBiTe_6$
  nanoscale ribbons

  $AgPb_{18}SbTe_{20}$ (LAST) & $NaPb_{20}SbTe_{22}$ (SALT)
  coherent endotaxial nanodots

Bi_2Te_3/Sb_2Te_3 Superlattices

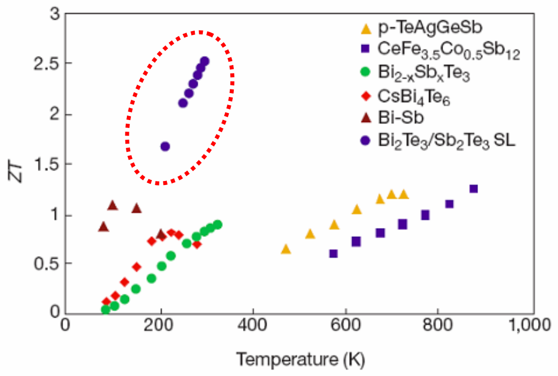
- **Alternating thin films deposited by MOCVD**
- **10Å Bi_2Te_3 / 50Å Sb_2Te_3**
- **Epitaxial growth on 225°C [100] GaAs**
- **Phonons scatter off interfaces**
- **Carriers retain high mobility**

TEM of cross-section



Venkatasubramanian, R. et al. *App. Phys. Lett.* **1999,** *75,*1104.

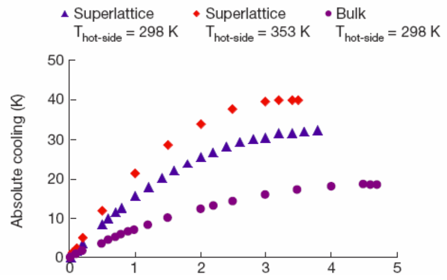
Breaking the ZT ~ 1 Barrier

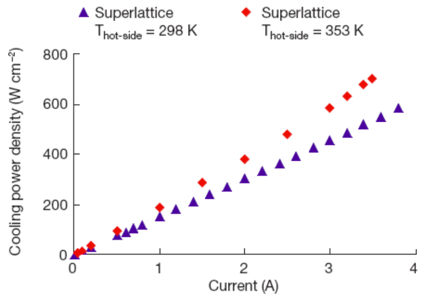


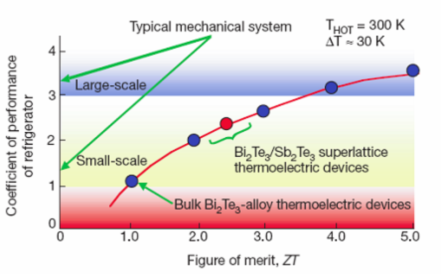
- **Seebeck coefficient:**
  $S \sim 243\ \mu V\ K^{-1}$
  (same as bulk)
- **Thermal conductivity:**
  $\kappa_l \sim 0.22\ W\ m^{-1}\ K^{-1}$
  (vs. ~ 0.49 in bulk)

Venkatasubramanian, R. et al. *Nature* **2001,** *413,*597.

Thin-film Cooling Devices







- **Heat flux: ~ 700 W cm^2 (vs. ~ 2 W cm^2 in bulk)**
- **p-type elements only (n-type still lacking)**

Venkatasubramanian, R. et al. *Nature* **2001,** *413,*597.

PbSe/PbTe Quantum Dot Superlattices

- **QDSL growth via Molecular beam epitaxy**

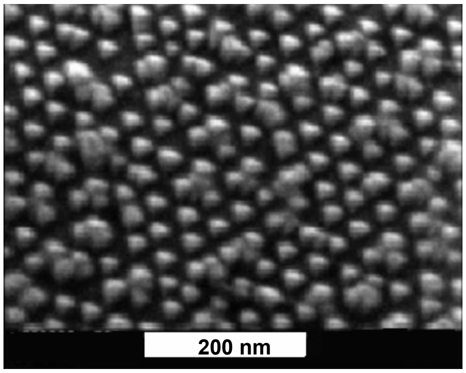
  ~ 5 % Lattice Mismatch in Pb-chalcogenides

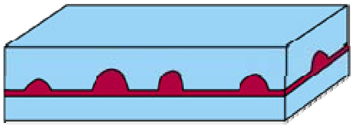
  Stranski-Krastanov (Island) growth mode

  ~ 8000 13-nm thick layers (~0.1 mm film)

  T must be 593-603 K

PbSe QDSL on PbTe



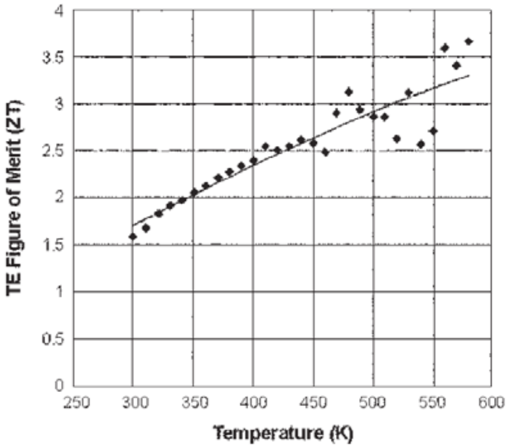


Enormous # of interfaces to scatter phonons!

Harman, T. C. et al. *Science* **2002,** *297,* 2229.
Herz, L. M. et al. *Nature Materials* **2002,** *1,* 212.
Harman, T. C. et al. *J. Electron. Mater.* **1996,** *25,* 1121.

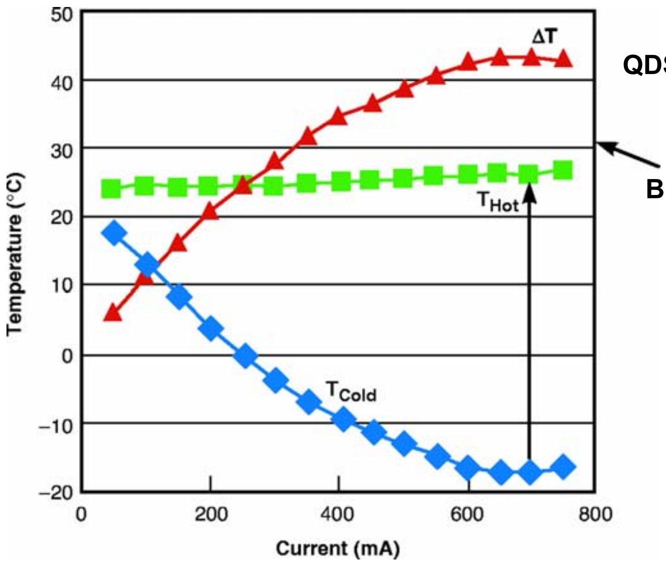
Highest ZT Claimed to Date

- **Seebeck coefficient:**
  $S \sim 220\ \mu V\ K^{-1}$
  (same as bulk)
- **Thermal conductivity:**
  $\kappa \sim 0.62\ W\ m^{-1}\ K^{-1}$
  (vs. ~ 1.6 in bulk)
- **Measured || to planes**



Harman, T. C. et al. *Science* **2002,** *297,* 2229.
Harman, T. C. et al. *J. Electron. Mater.* **2005,** *34,* L19.

Cooling with QDSL Devices: Results



QDSL ΔT = 43.7 K

Bulk ΔT = 30.8 K

Harman, T. C. et al. *Science* **2002,** *297,* 2229.

Thin-films vs. Bulk Materials

- **Thin films:**

  best performance

  “micro” applications

- **Bulk materials:**

  large quantities

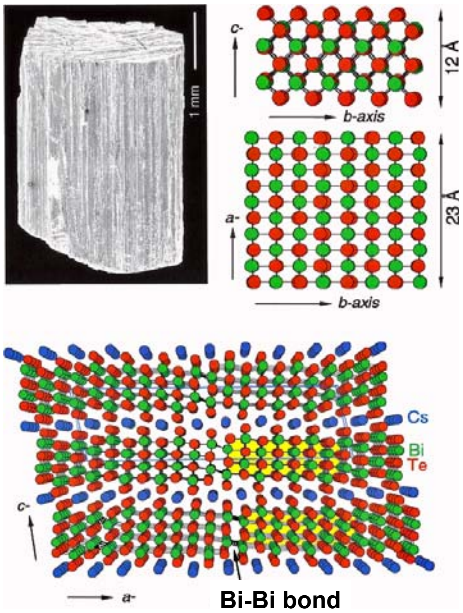
  easy fabrication

  may be isotropic

  stable at higher T’s (in general)

➔ Bulk material with thin-film performance is ***highly*** desired!

$CsBi_4Te_6$



- **Synthesized from the elements at 600°C**
- **Anisotropic Structure**

  Needle-like crystals

  $[Bi_4Te_6]^-$ ribbons

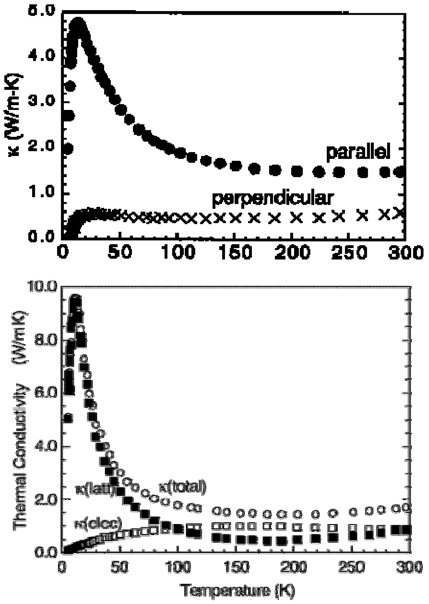
  Cs^+ layers

  Bi-Bi bond unexpected

- **Amenable to doping**

Chung, D. et al. *Science* **2000,** *287, 1024.*

Thermal Properties



- **Strongly anisotropic**
- **Slightly reduced**

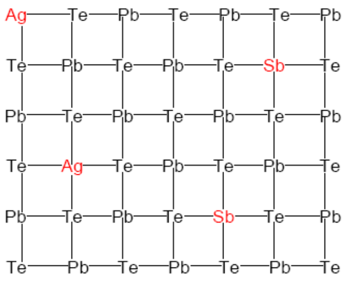
κ_{total} ~ 0.87 W m^{-1} K^{-1} (vs. ~ 1.1 in Bi_2Te_3)

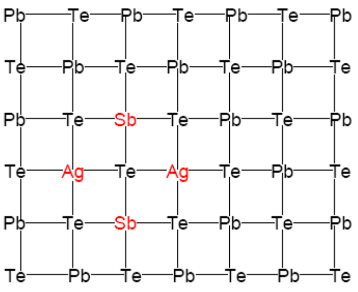
κ_{lat} ~ 1.2 – 1.8 W m^{-1} K^{-1} (vs. ~ 1.6 in Bi_2Te_3)

Chung, D. et al. *Science* **2000,** *287, 1024.*
Chung, D. et al. *J. Am. Chem. Soc.* **2004,** *126,* 6414.

Bulk Materials w/ Endotaxial Nanodots

- **Based on PbTe**
- **Two Pb^{2+} sites substituted w/ any M^+ / M^{3+} pair**



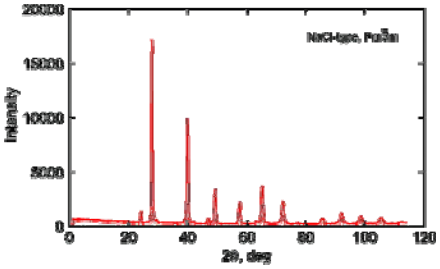


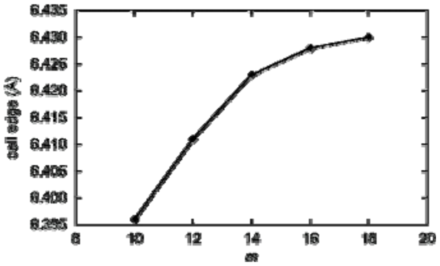
Dissociated State – unstable

Associated State – stable

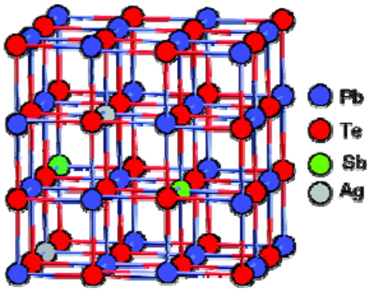
Kanatzidis, M. G. *American Physical Society Meeting,* Baltimore, March 2006

LAST-*m*: Bulk Structure



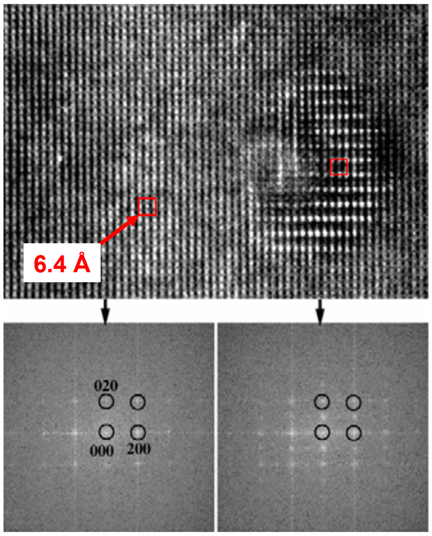


- $AgPb_mSbTe_{2+m}$ (*m* = 10 – 20)
- Synthesized from elements at 850° C
- Bulk cubic compound (NaCl type)
- Isotropic morphology
- High crystal symmetry



Hsu, K. F. et al. *Science* **2004,** *303,* 818.

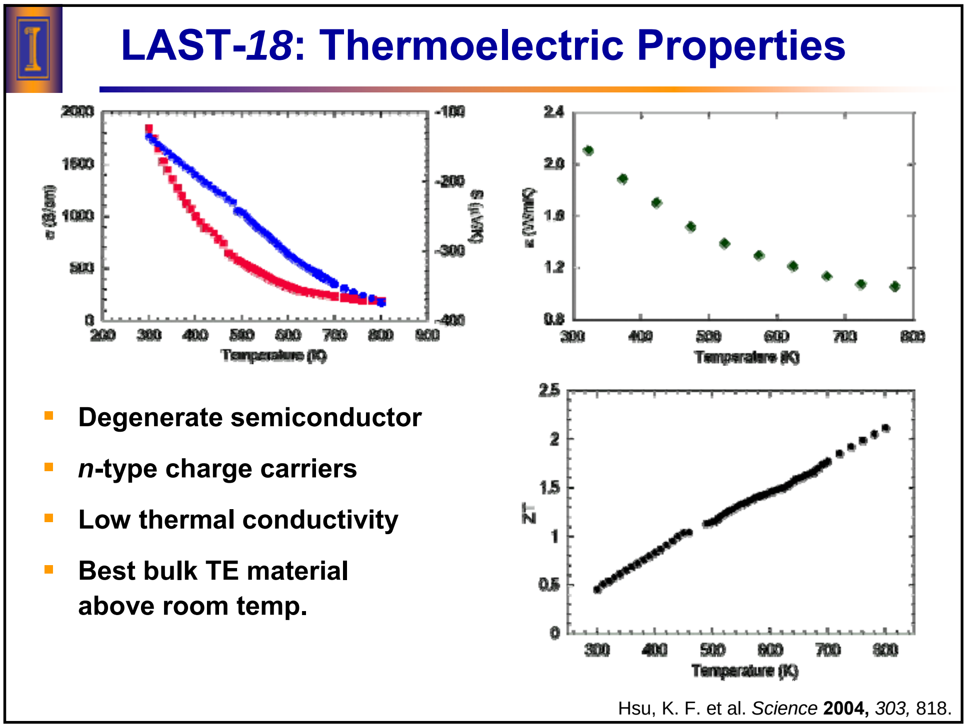
HRTEM of LAST-18



FFT's of indicated areas

- Not solid solutions
- Coherent endotaxial nanocrystals (2-4 nm)
- Ag/Sb rich dots
- Carriers pass through unimpeded
- Phonons scatter

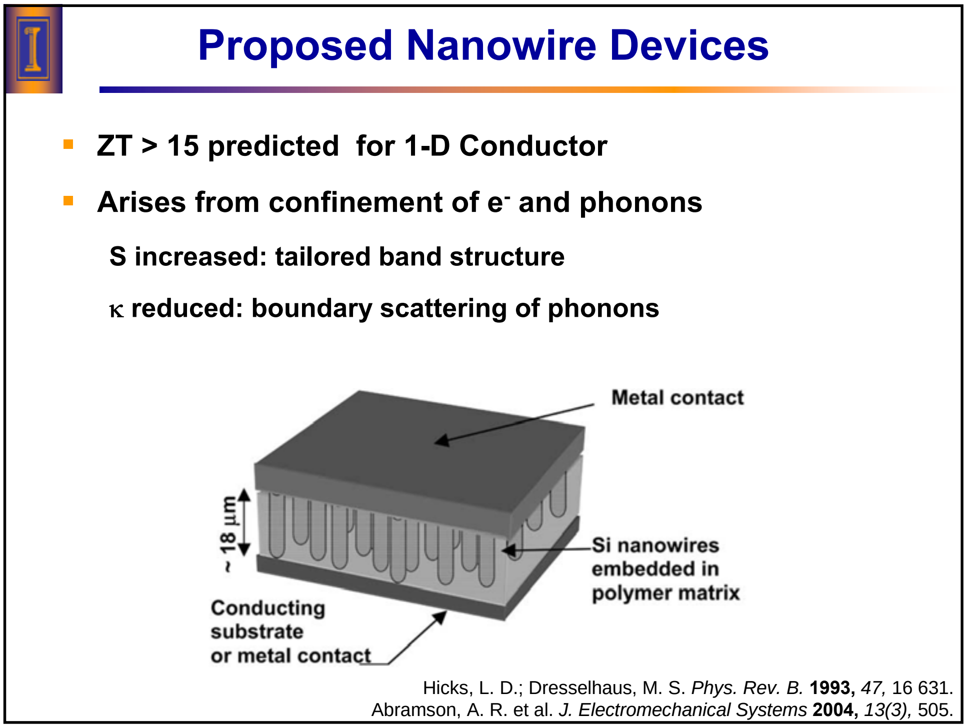
Quarez, E. et al. *J. Am. Chem. Soc.* **2005,** *127,* 9177.



LAST-*18*: Thermoelectric Properties

- **Degenerate semiconductor**
- ***n*-type charge carriers**
- **Low thermal conductivity**
- **Best bulk TE material above room temp.**

Hsu, K. F. et al. *Science* **2004,** *303,* 818.



Proposed Nanowire Devices

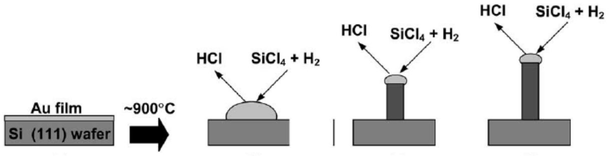
- **ZT > 15 predicted for 1-D Conductor**
- **Arises from confinement of e^- and phonons**

  S increased: tailored band structure

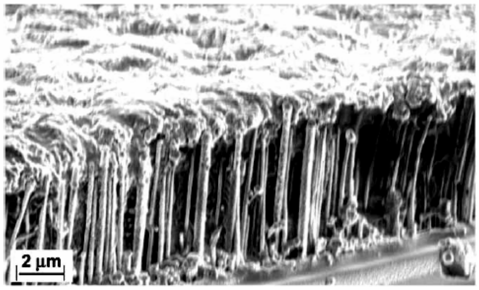
  κ reduced: boundary scattering of phonons

Hicks, L. D.; Dresselhaus, M. S. *Phys. Rev. B.* **1993,** *47,* 16 631.
Abramson, A. R. et al. *J. Electromechanical Systems* **2004,** *13(3),* 505.

Si / Parylene Nanowire Composite



VLS Growth



ZT ~ 3.6 x 10^{-4}

Problem: low σ
~ 2.9 S / cm

Abramson, A. R. et al. *J. Electromechanical Systems* **2004,** *13(3),* 505.

Conclusions

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

- **Technology of choice when size and durability matter more than efficiency**
- **Advances in TE materials in the 6 yrs. have been remarkable:**
  - **ZT has tripled in nanoscale materials**
  - **ZT has doubled in bulk materials**
  - **Due to nanoscale features**
- **Further enhancements in ZT are still needed**

Future Directions

- Further optimization of quaternary semiconductors & superlattices
- Oxide materials
  - Stable in air at high temperatures
  - $Na_xCo_2O_4$ has high S (~ 300 μV / K), but ZT still low
- Organic Conductors
  - Very low κ (~ 0.1 W m^{-1} K^{-1})
  - Many synthetic opportunities
- Nanowire / QD Devices

Lee, M. et al. *Nature Matterials* **2006,** *5,* 537.
Yan, H. et al. *J. Therm. Anal. & Cal.* **2002,** *69,* 887.