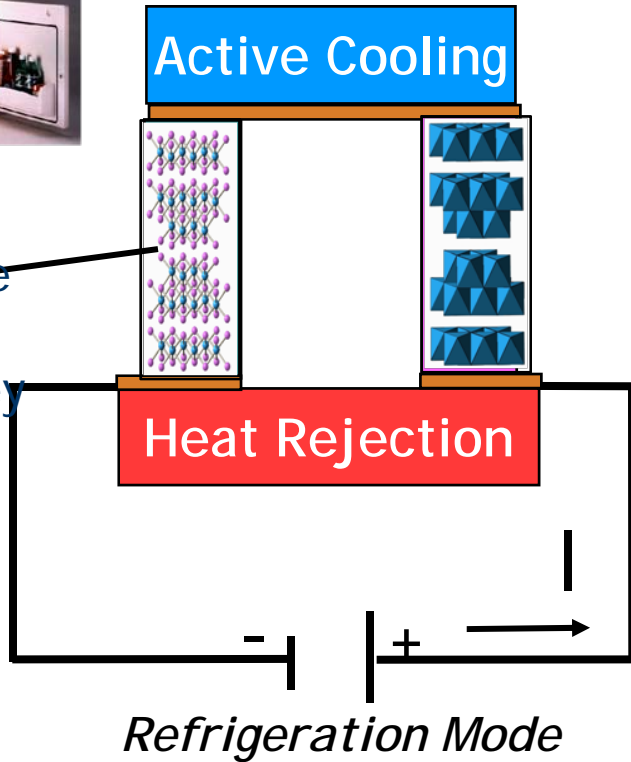


## Peltier Effect

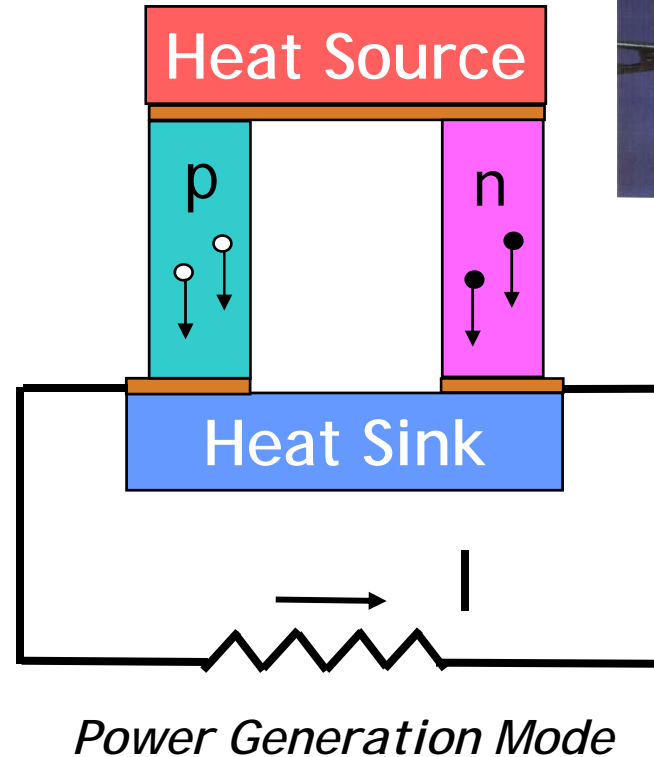


Solid State materials are the key



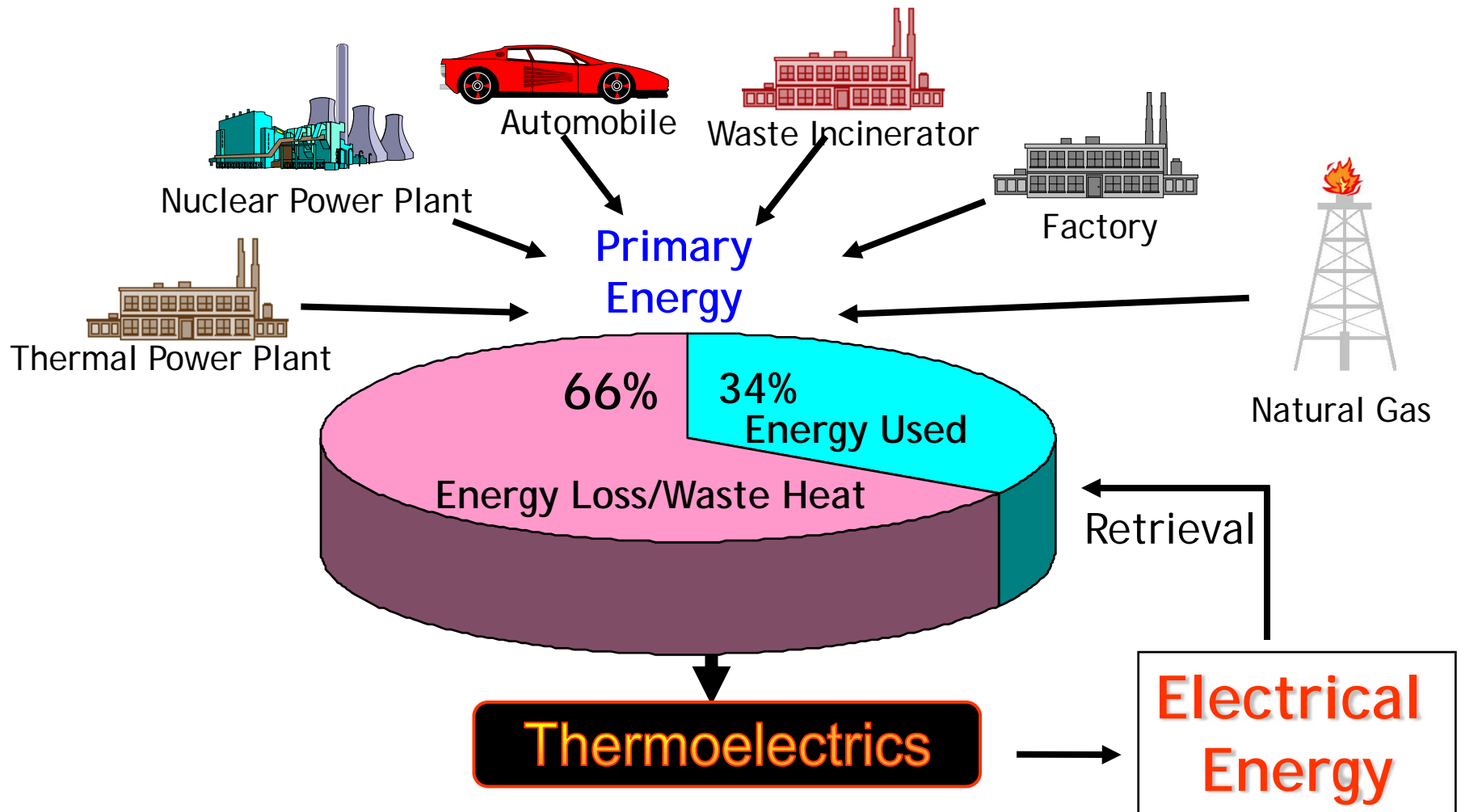
“Refrigeration without moving parts and chemical refrigerant”

## Seebeck Effect

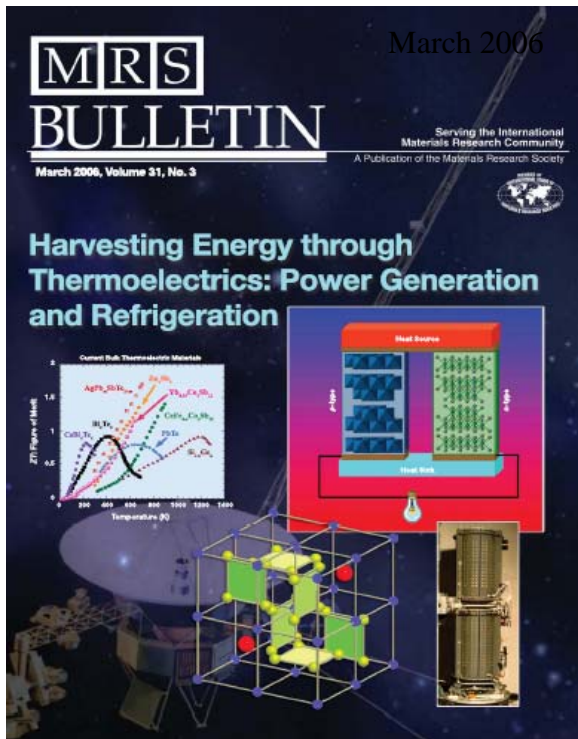


“Electricity from waste-heat”

# Class 12: Thermoelectrics



March 2006



*Guest Editors:*  
*Tritt and Subramanian*

Thermoelectric Materials, Phenomena, and Applications:  
A Bird's Eye View: **T. M. Tritt, M. A. Subramanian**

Recent Developments in Bulk Thermoelectric Materials:  
**G. S. Nolas, M. Kanatzidis**

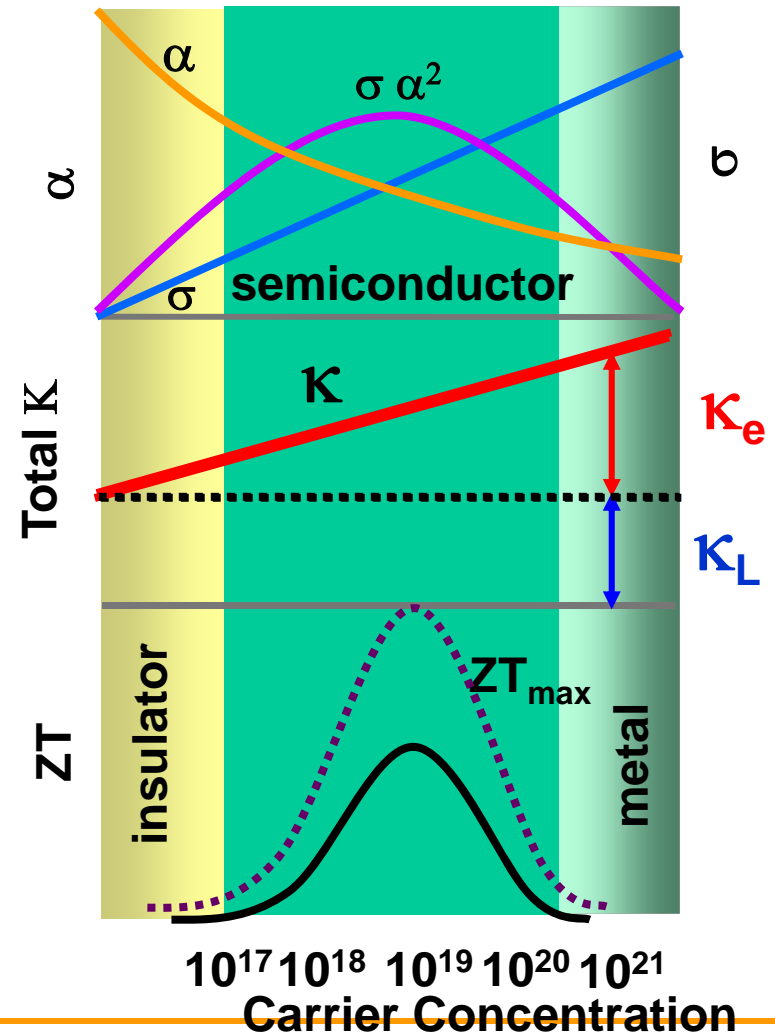
Properties of Nanostructured One-Dimensional and  
Composite: Thermoelectric Materials : A. M. Rao, X. Ji,  
and **T. M. Tritt**

$$ZT = \frac{\sigma \alpha^2}{(\kappa_e + \kappa_L)} \cdot T$$

*Electrical conductivity*  $\sigma$       *Seebeck coefficient or thermopower*  $(\Delta V/\Delta T)$   $\alpha$   
*Total thermal conductivity*  $(\kappa_e + \kappa_L)$

No upper limit for ZT

### Contra-indicated Properties



## Class 12: Thermoelectrics

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Glass (amorphous)  
*Very low*  
*thermal conductivity*

+



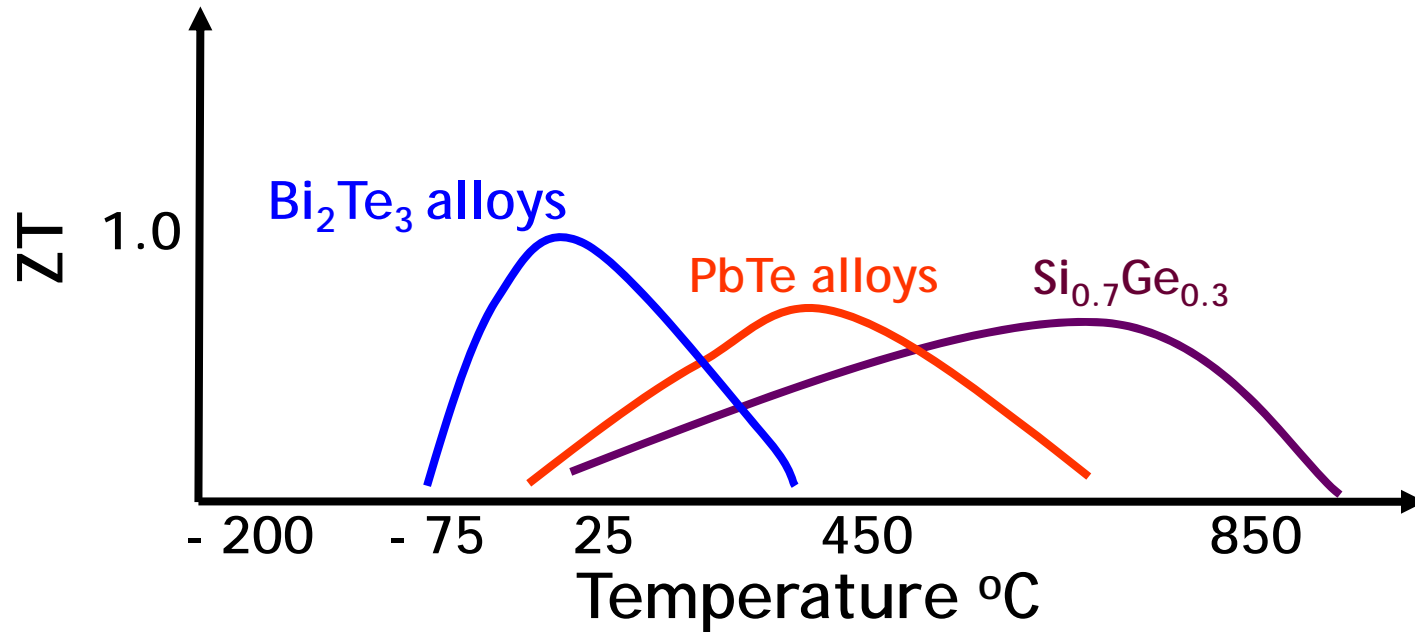
Metal  
*High*  
*electrical conductivity*

+



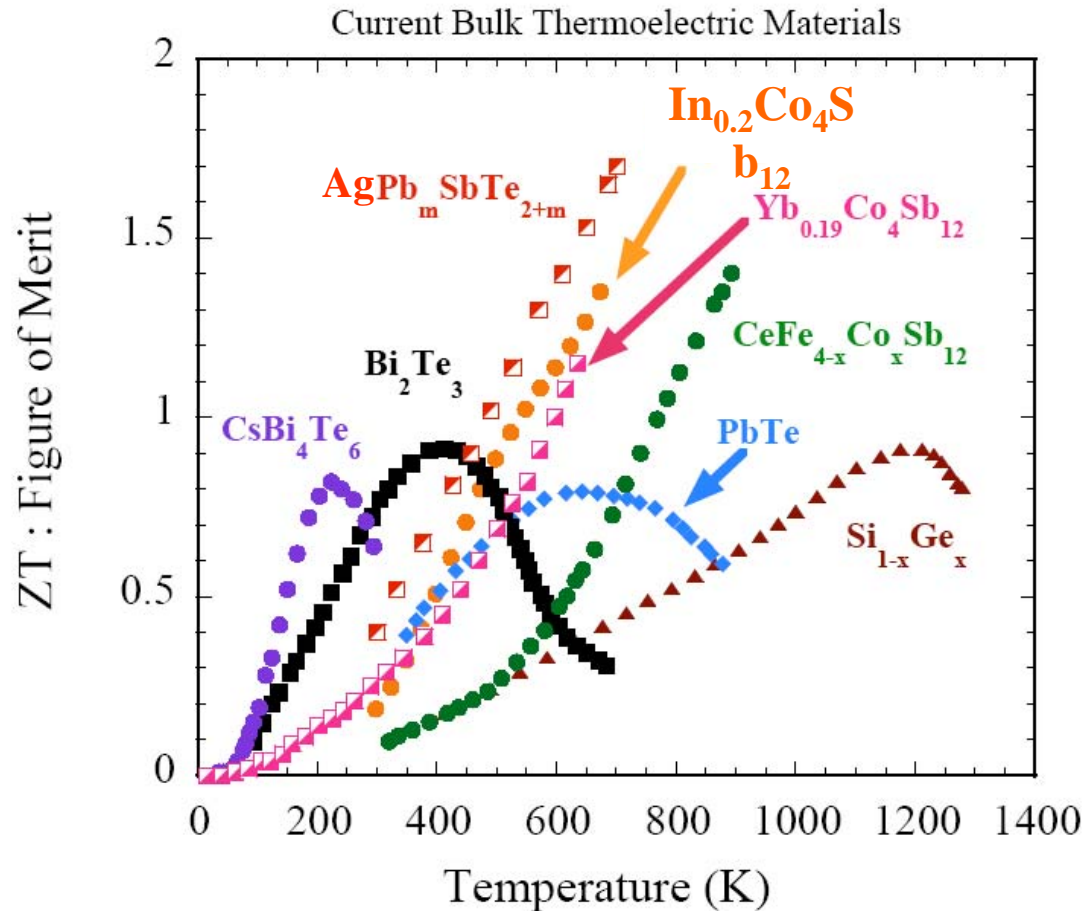
Semiconductor  
*High*  
*Thermopower*

$$ZT = \frac{\sigma \alpha^2}{(\kappa_e + \kappa_l)} \cdot T$$



- ➔ Narrow band gap semiconductors (increasing numerator)
- ➔ Elements of high atomic weight - e.g. Bi, Pb, Hg, Te (decreasing the denominator)

## Class 12: Thermoelectrics



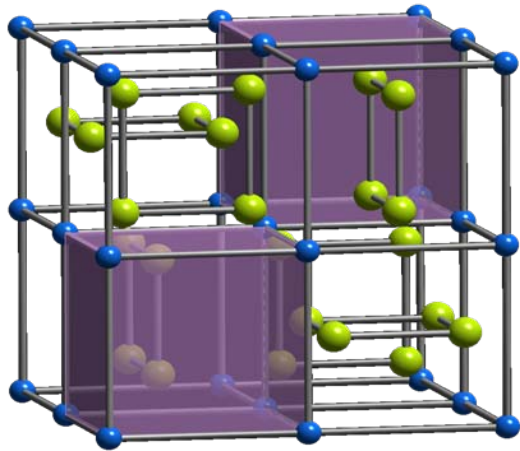
$\text{CsBi}_4\text{Te}_6$ :  
Kanatzidis et al., *Science*, 287,  
1024(2000)

$\text{AgPb}_m\text{SbTe}_{2+m}$ :  
Kanatzidis et al., *Science*, 303, 818  
(2004)

$\text{In}_{0.2}\text{Co}_4\text{Sb}_{12}$ :  
Subramanian et al., *Chemistry of  
Materials*, 18, 759 (2006)

$\text{Yb}_{0.19}\text{Co}_4\text{Sb}_{12}$ :  
Nolas, Tritt et al., *J. Appl. Phys.* 97,  
113715 (2005).

$$ZT = \frac{\sigma \alpha^2}{(\kappa_e + \kappa_L)} \cdot T$$

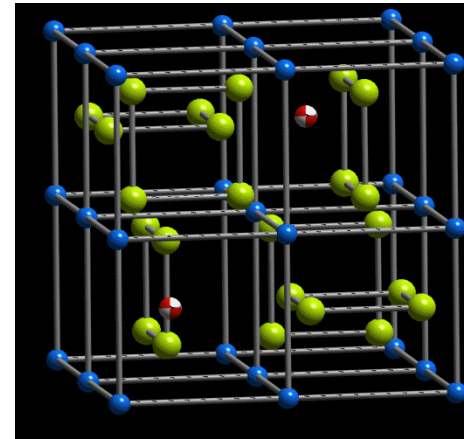


Co<sub>4</sub>Sb<sub>12</sub>

Large numerator

Large Denominator

ZT ~ 0.4 at 600K



R<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> (R = Rare-earth, In)

Large numerator

Small denominator

ZT~ 1.3 at 600K

Subramanian et al., *Chemistry of Materials*, 18, 759 (2006)

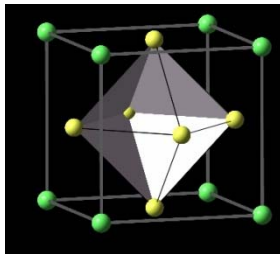
Nolas, Tritt et al., *J. Appl. Phys.* 97, 113715 (2005)

Singh et al., *Phys. Rev. B* 53, 6273 (2003)

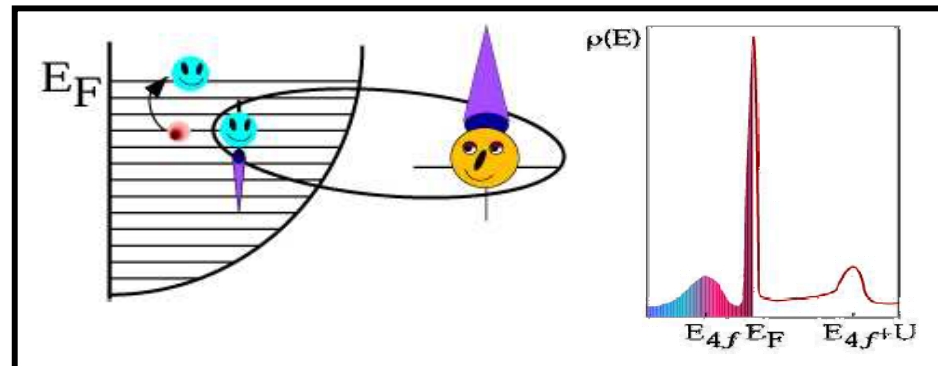


$$ZT = \frac{\sigma \alpha^2}{(\kappa_e + \kappa_l)} \cdot T$$

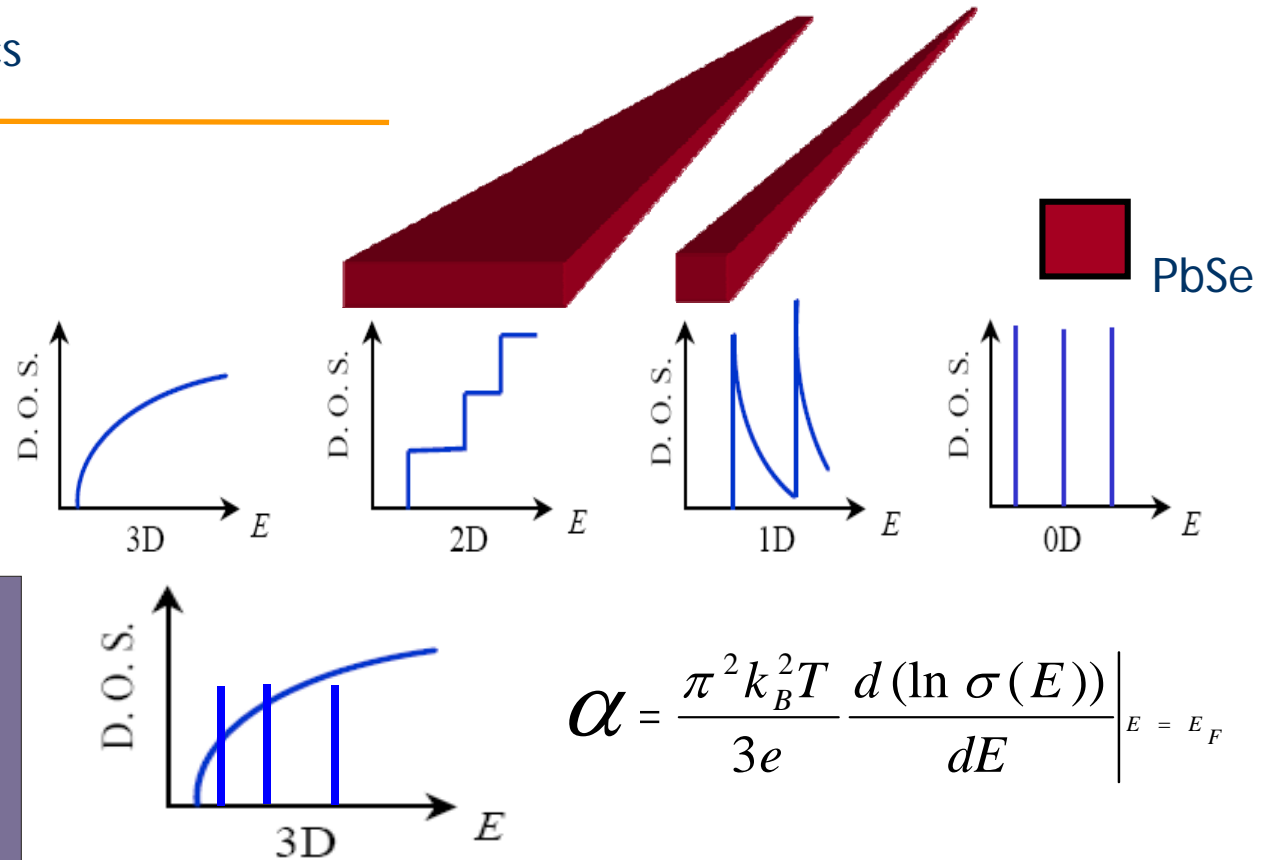
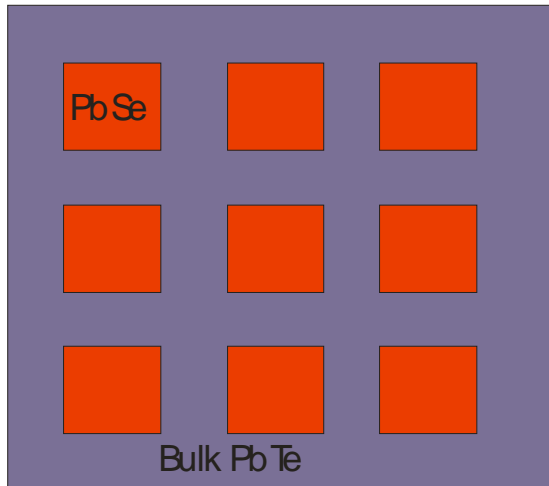
- Intermetallics with rare earths in intermediate valence states
  - Yb <sup>2+,3+</sup> (4f<sup>13</sup>-4f<sup>14</sup>) ; Ce <sup>3+,4+</sup> (4f<sup>1</sup>-4f<sup>0</sup>)
  - Large Density of States at the Fermi Level
    - interaction between conduction electrons and partially localized 4f electrons leads to large  $\alpha$
    - very large numerator (power factor)
    - large denominator (thermal conductivity) - low ZT



*YbAl<sub>3</sub> and CePd<sub>3</sub>*

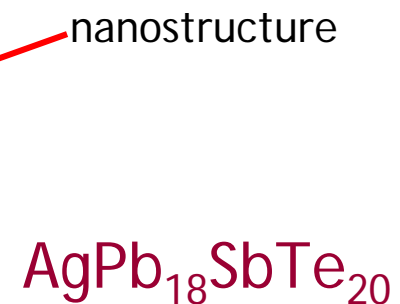
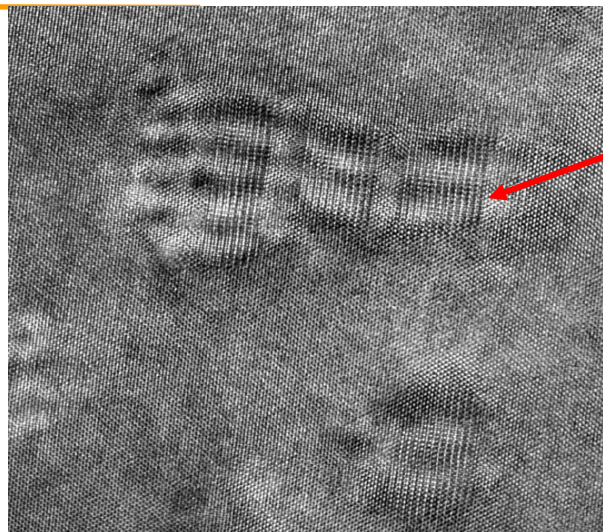
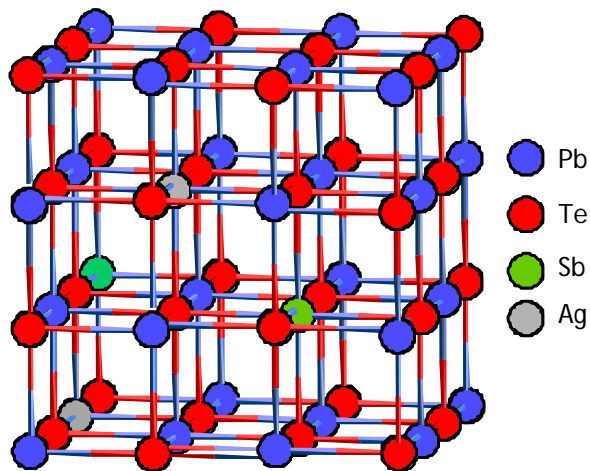


# Class 12: Thermoelectrics

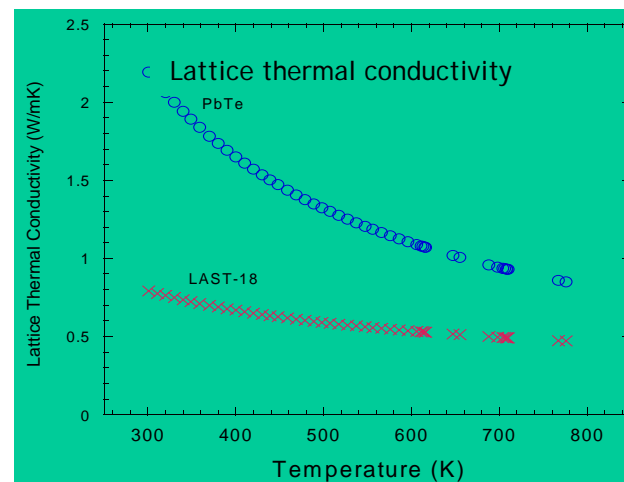
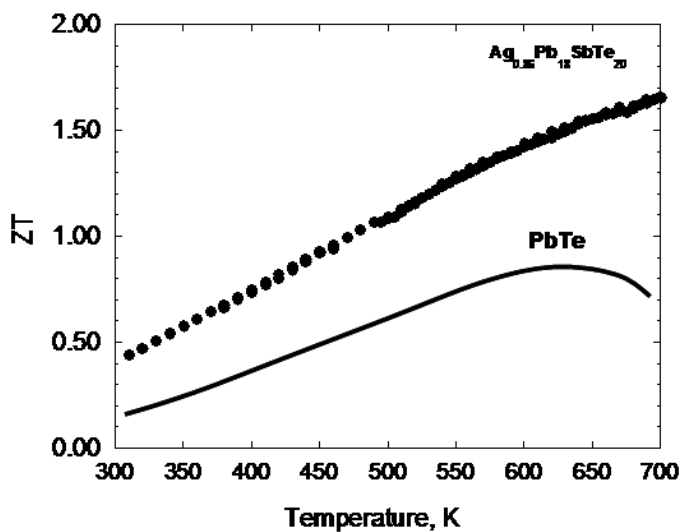


- Electronic properties may be dramatically modified due to carrier confinement in nanostructures
- Thermoelectric power enhancement (rippling effect on DOS)

# Class 12: Thermoelectrics



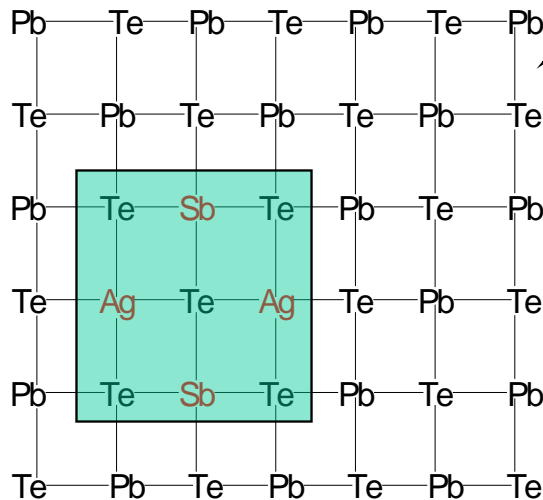
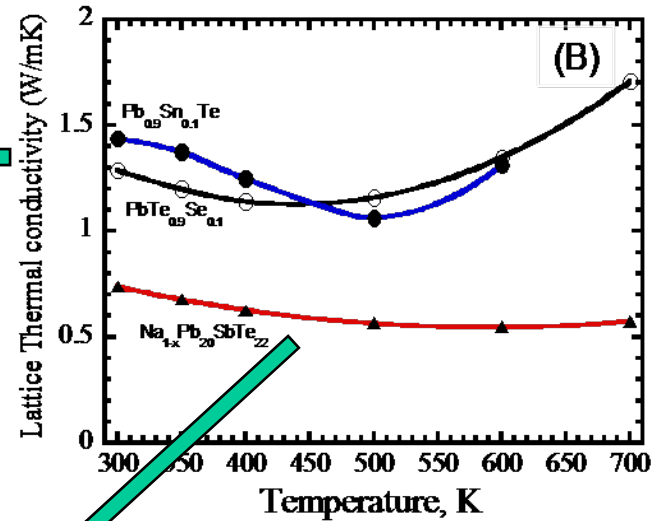
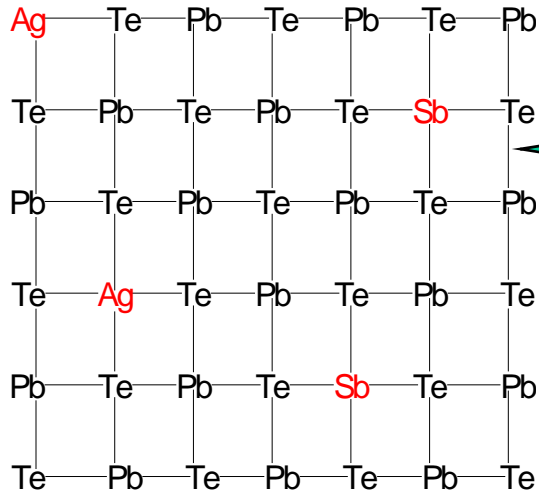
Power factor still high



Kanatzidis et al *Science*, 2004, 303, 818

# Class 12: Thermoelectrics

Dissociated state..unstable



Associated state..stable