Thermoelectric power generation-materials

what makes a good thermoelectric:

$$ZT = \frac{\alpha^2}{\rho\lambda} T$$

conflicting requirements

α – **Seebeck coefficient** - large
ρ – **resistivity** - small
λ – **thermal conductivity** - small

- **development of novel materials**
- **material tailoring – crystal chemistry**
- **composites–microstructure,nanostructure**

up-to-date best bulk thermoelectrics: - Bi_2Te_3/Sb_2Te_3, PbTe, Si-Ge

NEW BULK MATERIALS:
Skutterudites, Heussler alloys, complex chalcogenides, oxides

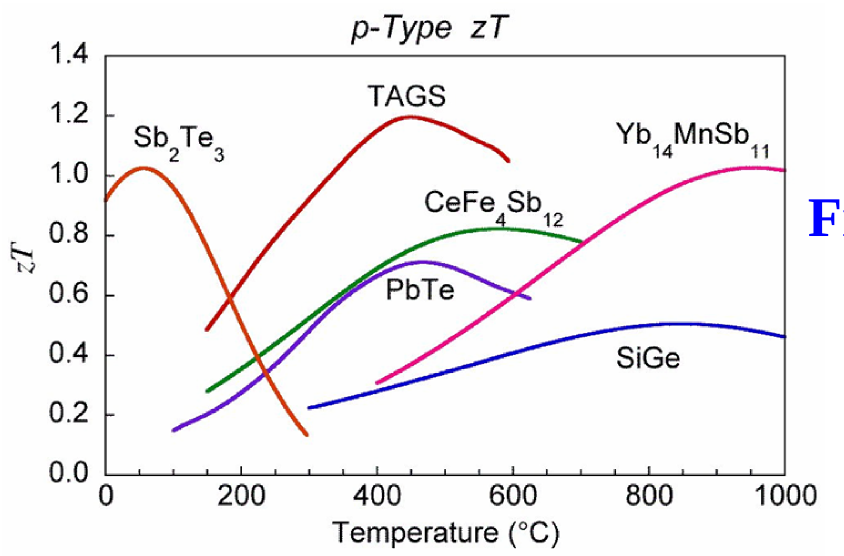
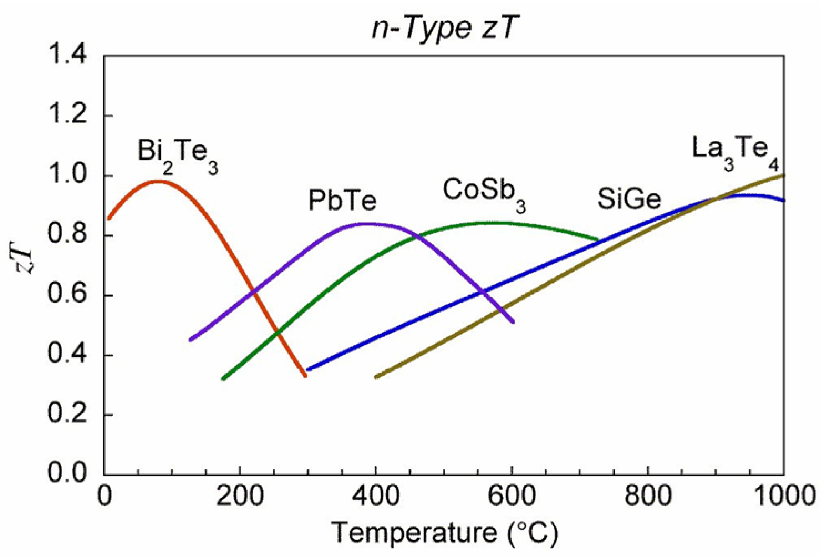


Figure of Merit

ZT



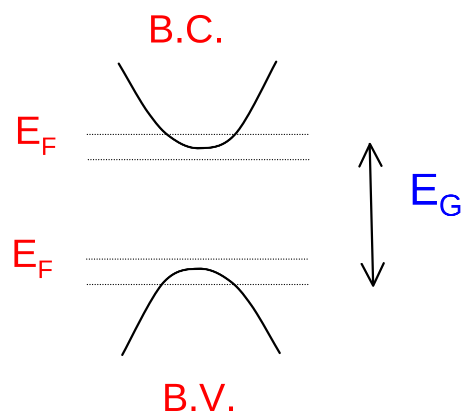
Classical guidelines for thermoelectric materials :
- semiconductors, but which???

α, ρ, λ ⟷ Electronic structure, scattering mechanism, phonon spectrum,…

Two approaches:
- ✓ Boltzman Equation of transport
- ✓ Kubo formalism…

Increase of ZT

$$ZT = \frac{\alpha^2}{\rho(\lambda_{electron} + \lambda_{lattice})} T$$



➡ To ajust Fermi level E_F (optimal doping,…)

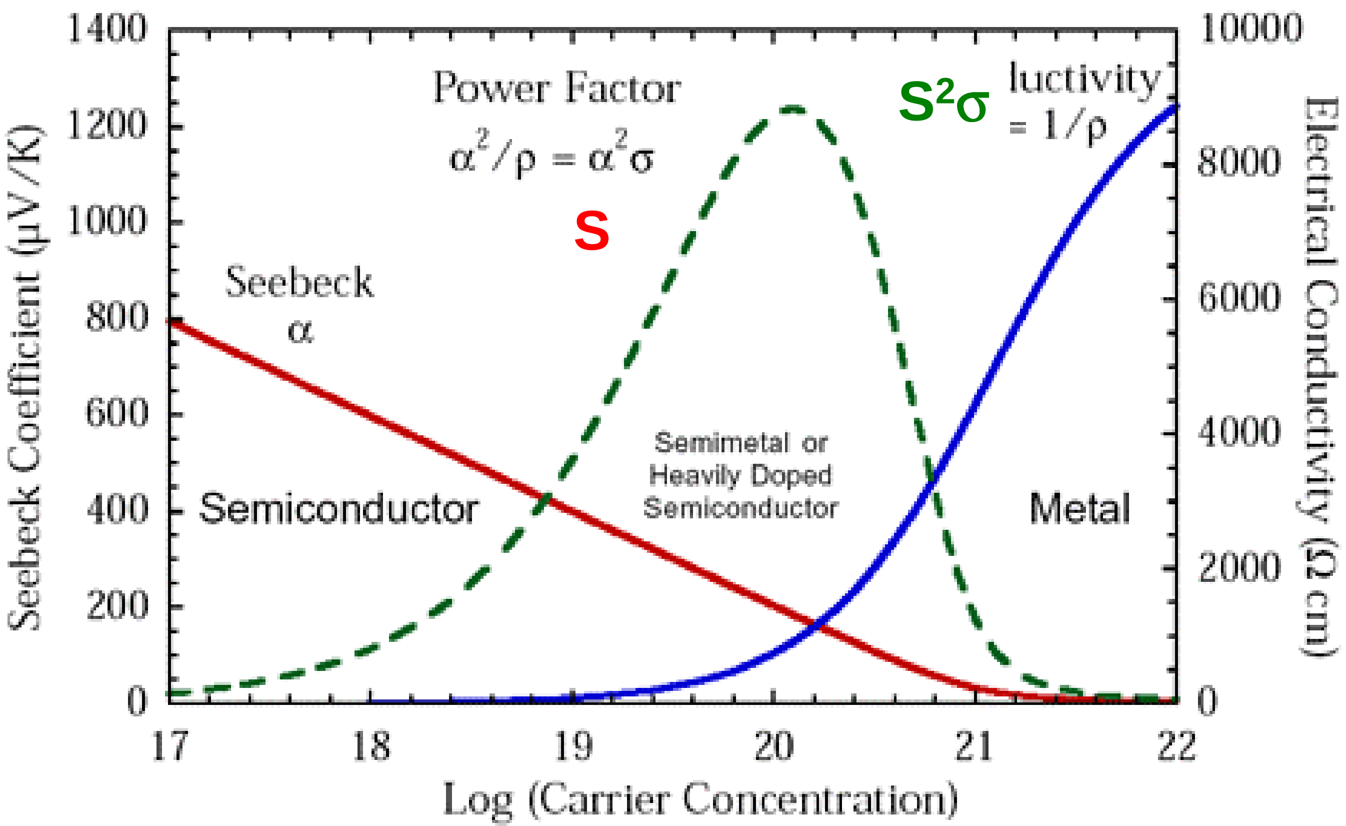
E_F should be at the edge of the band, sharp variation of DOS, ⇔ $\alpha \sim \pm 200\ \mu V/K$

➡ $\frac{\mu}{\lambda_{lattice}} (m^*)^{3/2}$ highest as possible

Semiconductors with a high mobility (μ), high effective mass (m^*) and low thermal conductivity of the lattice ($\lambda_{lattice}$)

Which materials are interesting???
– semiconductors –

Optimizing power factor ➡ highly doped semiconductors



For almost all typical thermoelectric materials, namely **<u>low gap semiconductors</u>**, if doping is increased, the electrical conductivity increases but the Seebeck coefficient is reduced.

$$P_f = \frac{\alpha^2}{\rho}$$

The Thermoelectric Figure of Merit (ZT)

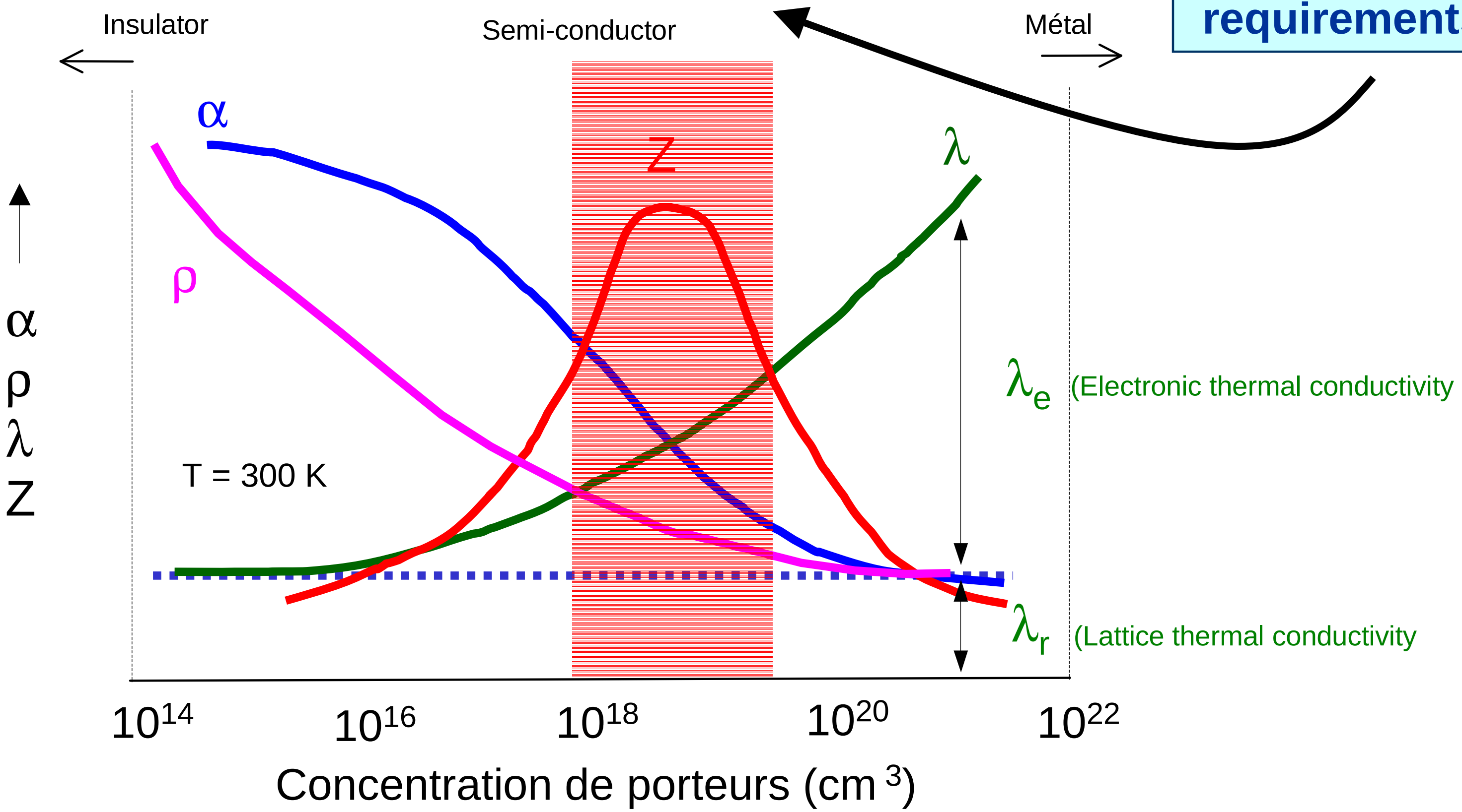
Optimizing Figure of merit ZT

minimize the thermal conductivity

$$ZT = \frac{\alpha^2}{\rho\lambda}T \qquad Z = \frac{\alpha^2}{\rho\lambda}$$

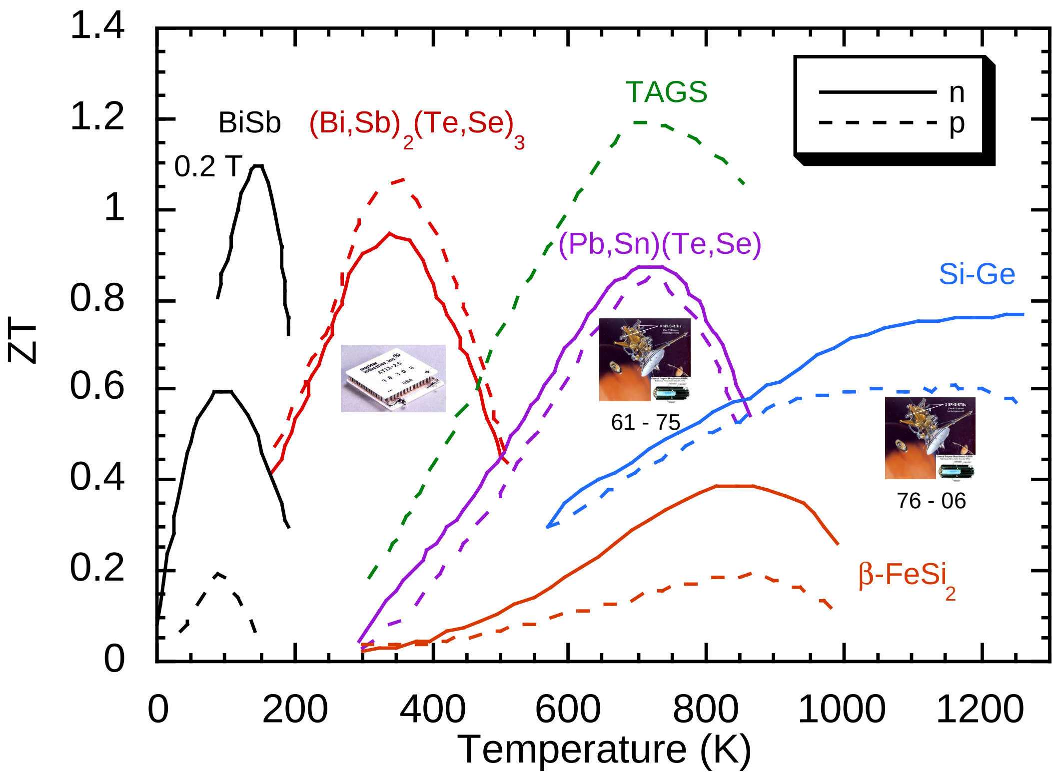
Ideal material : α ↑, ρ ↓, λ↓ but α ↑ ⇔ρ ↑ et ρ ↓ ⇔λ↑

conflicting requirements

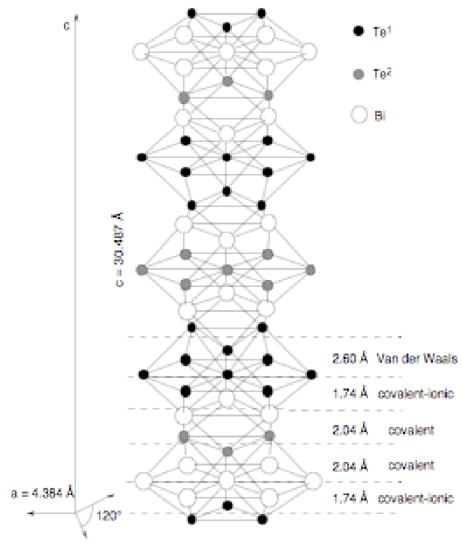


Best compromise ➡ still highly doped semiconductors ($\lambda = \lambda_e + \lambda_r$)

1930 - 1995 : Classical materials…
Limits in ZT (~ 1) …Limits in temperature (T< 250 ºC)



TAGS : $(AgSbTe_2)_{1-x}(GeTe)_x$



- SC low gap + heavy elements
- ZT optimized only for narrow temperature window
- At T ~ 300 K used solutions based on Te, namely (Bi_2Te_3)
- ZT ~ 1 standard

Since 1995 - … : New orientations

Environmental problems (Kyoto…), energy, waste heat, etc → New interest in thermoelectricity (USA, Japon, Europe is still on the tail….)
Proposal of new concepts to target new matrials, need systems with ZT>1

Thermoelectrics based on lowered dimensionality,nanostructuring, …

Identification of new bulk materials….

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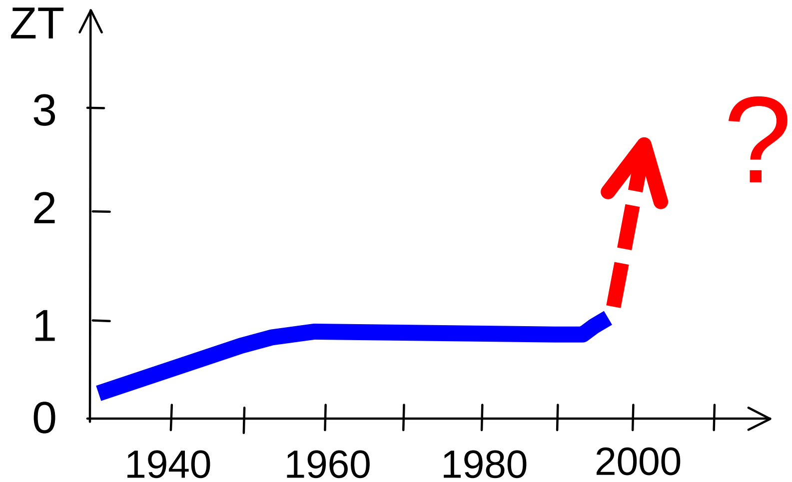

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Motivation for Nanotechnology in Thermoelectricity

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(2D quantum wells, 1D nanowires, 0D quantum dots)

Seebeck Coefficient — Conductivity — Temperature

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

Thermal Conductivity

ZT ~ 3 for desired goal

Difficulties in increasing *ZT* in bulk materials:

$S \uparrow \Longleftrightarrow \sigma \downarrow$

$\sigma \uparrow \Longleftrightarrow S \downarrow$ and $\kappa \uparrow$

$\Rightarrow$ A limit to *Z* is rapidly obtained in conventional materials

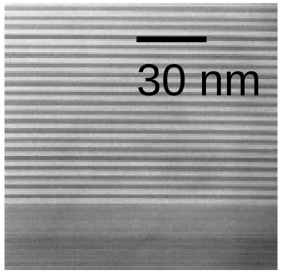
$\Rightarrow$ So far, best bulk material ($Bi_{0.5}Sb_{1.5}Te_3$) has *ZT* ~ 1 at 300 K

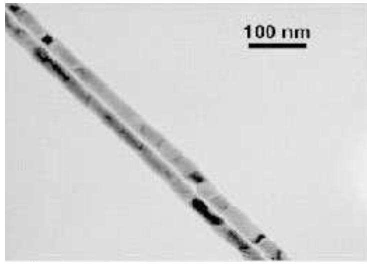
Low dimensional physics gives additional control:

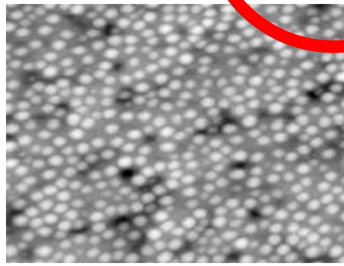
- Enhanced density of states due to quantum confinement effects
  - $\Rightarrow$ Increase *S* without reducing σ
- Boundary scattering at interfaces can reduce κ more than σ
- Possibility of materials engineering to further improve *ZT*

Low dimensionality- impact on thermopower, thermal conductivity

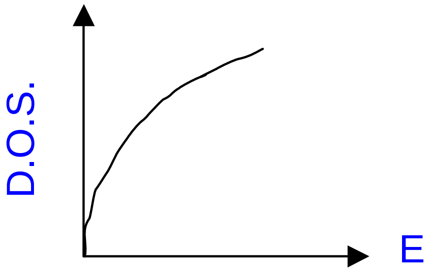
1

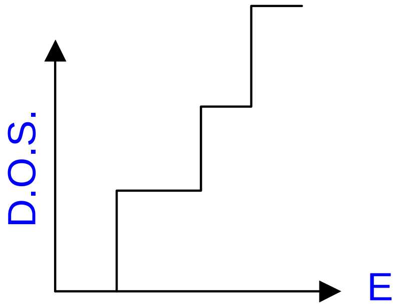


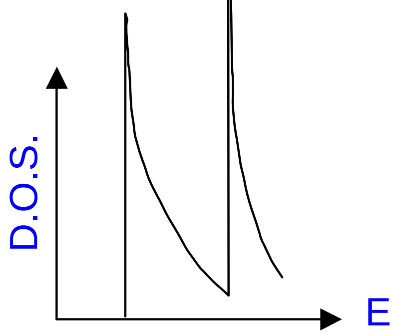


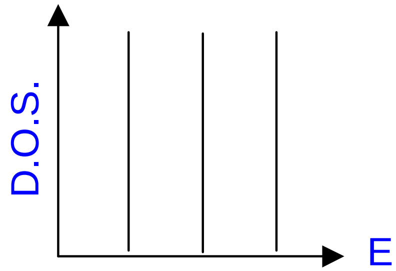


3 D | 2 D | 1 D | 0 D









- (D.O.S.) more favourable (stronger dependence of DOS on E)

➔ increase of α without increasing ρ

- additional degree of freedom (size) for tailoring of the transport
- possibility to explore the anisotropy of transport properties
- chance to decrese $\lambda_{lattice}$ due to phonon scattering on interfaces
- $ZT_{0D} > ZT_{1D} > ZT_{2D} > ZT_{3D}$

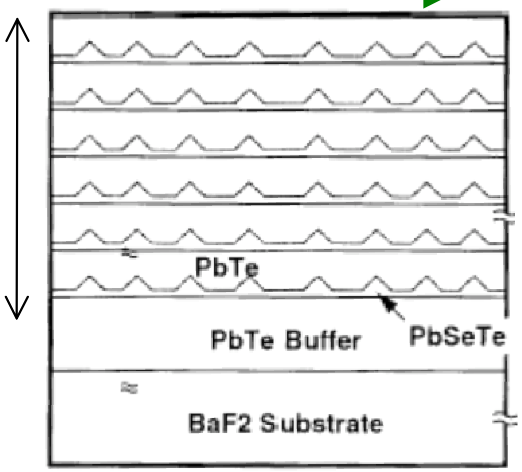
Theoretical predictions – decrease of the dimensionality

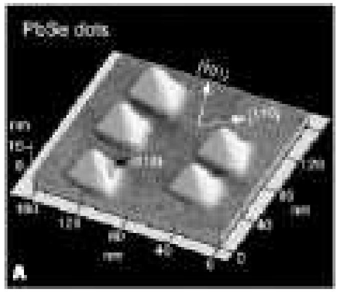
1

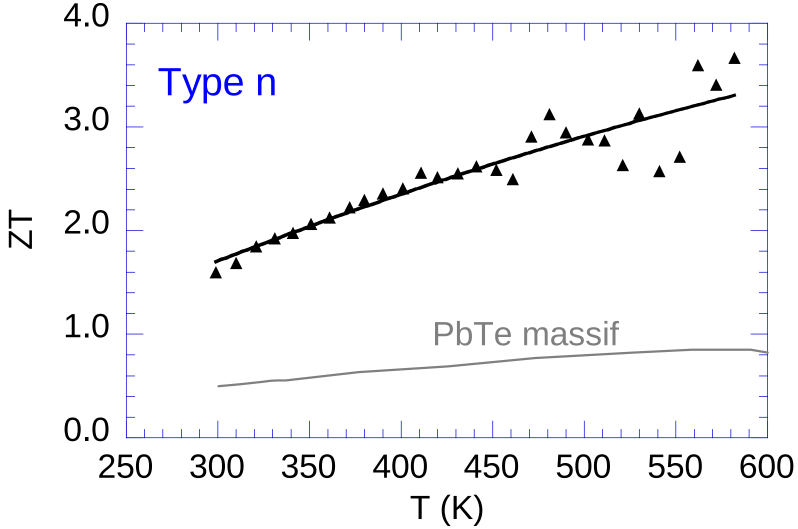
Heterostructures PbSeTe/PbTe (MBE)

Transport in the ab-plane

~ 100 µm







Plots de PbSeTe dans des couches de PbTe

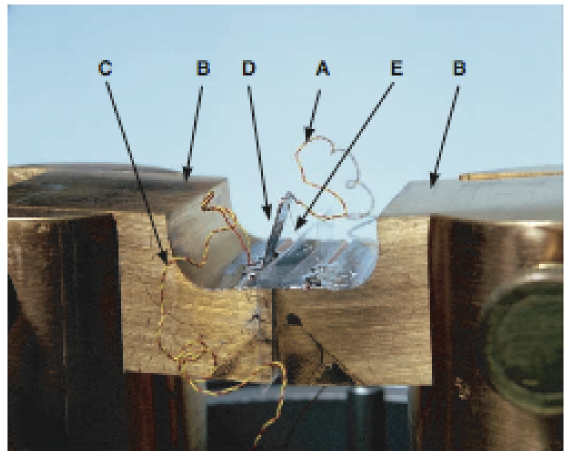
(Harman et al., J. Electron. Mater., **29**, L1, 2005)

- Type n : ZT ~ 1,5 à 300 K (compared to 0,45 pour PbTe bulk),
- ZT ~ 3,5 à 570 K
- Type p : ZT ~ 1,1 à 300 K.

DUE TO:

- Confinement of charge carriers in 2D
- Decrease of lattice thermal conductivity due to scattering

-EXAMPLE (laboratory):



(Harman et al., Science., **297**, 2002)

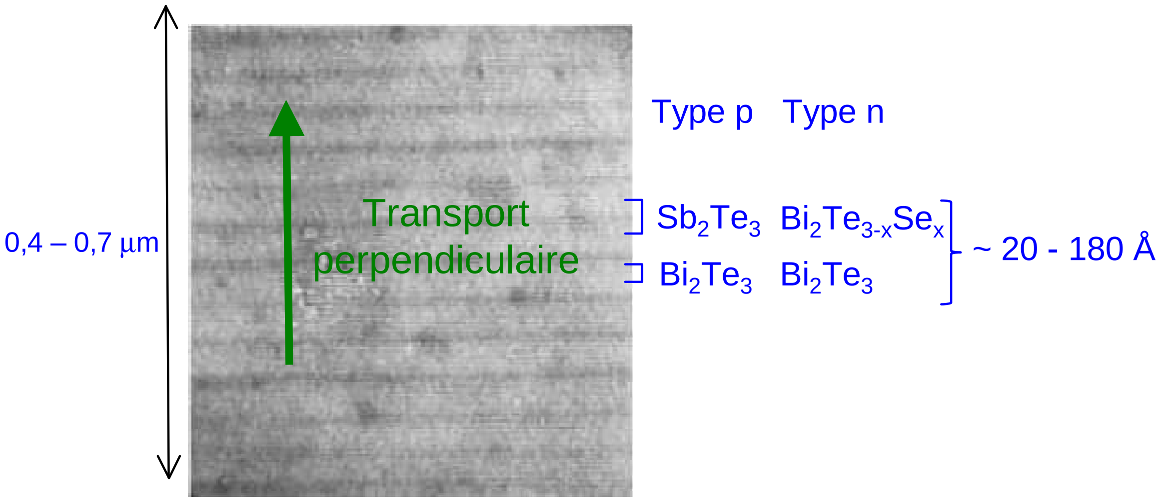
- Cooling: junction cooled 44 K below RT (31 K pour Bi_2Te_3)
- Power generation : 2,2 W/cm^2 for ΔT = 220 K

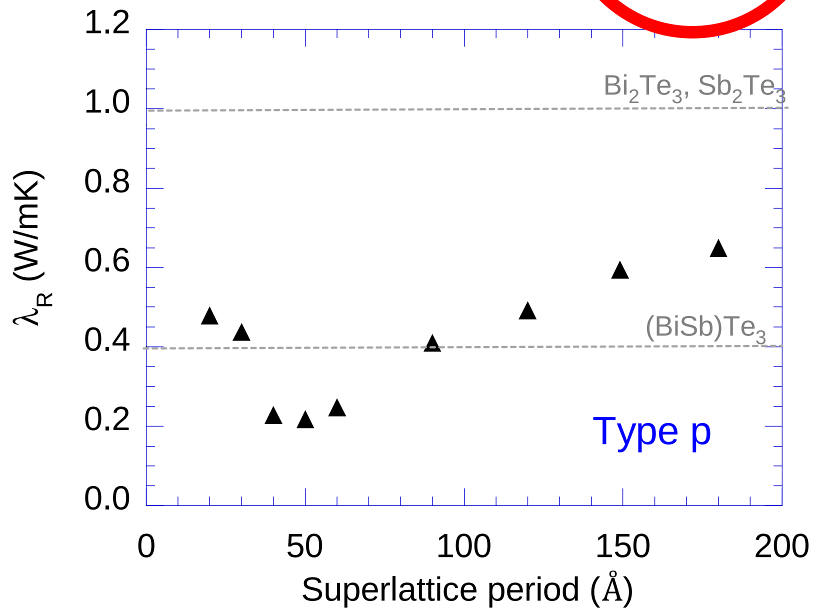
(Harman et al., APL., **88**, 243504, 2006)

Superstructures based on (Bi,Sb,Te,Se) - MOCVD

1

(Venkatasubramanian et al., PRB, **60**, 3091, 2000, Nature, **413**, 2001)





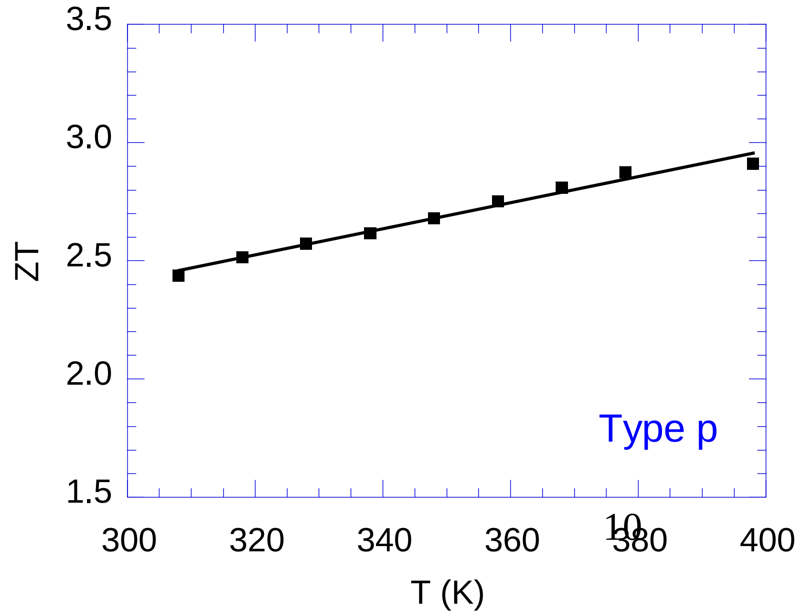
Negligible confinement of charge carriers **BUT**

Interfaces block short wavelength phonons!

Thermoelectric performance

Type p : ZT ~ 1,7 - 2,4 à 300 K

Type n : ZT ~ 1,4 à 300 K



SPIN off technology Nextreme THERMAL SOLUTIONS

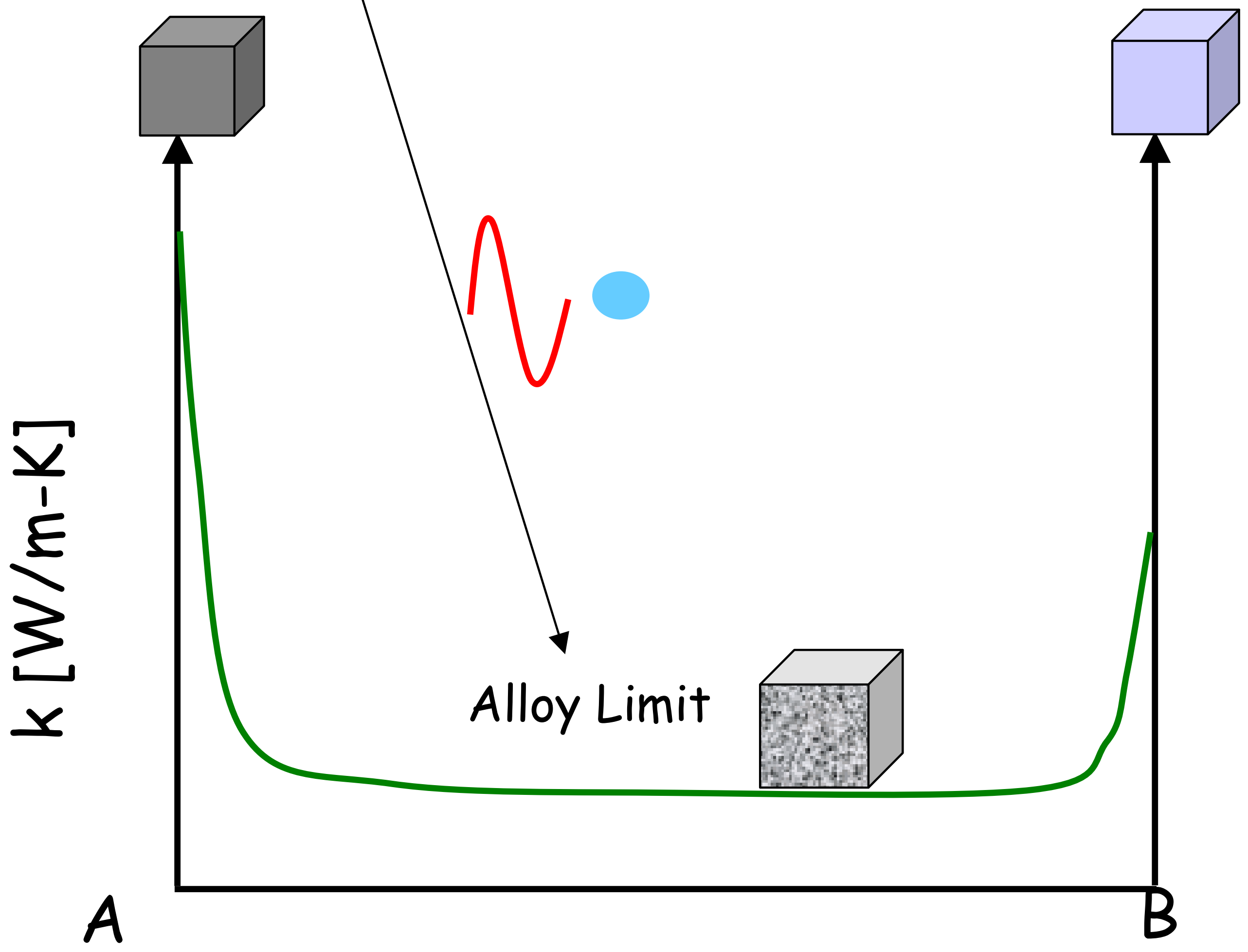
(www.nextremethermal.com)

Bulk Materials tailoring – decrease of thermal conductivity

1

Alloy Limit of Thermal Conductivity

$$ZT = \frac{\alpha^2}{\rho\lambda} T$$

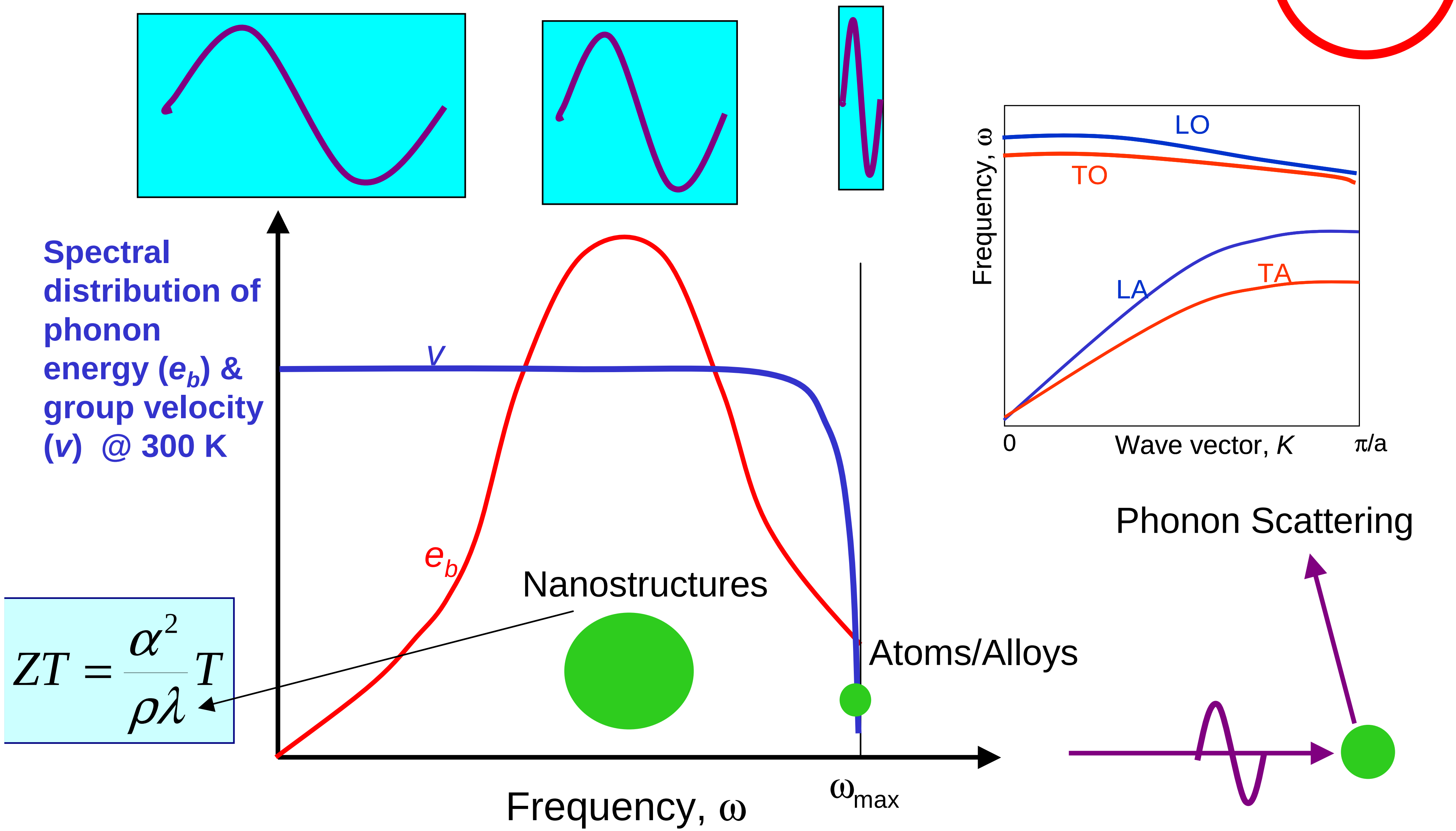


Impurity and alloy atoms scatter only short - λ phonons

that are absent at low T!

NANOSTRUCTURING- decrease of thermal conductivity: Phonon Scattering with Imbedded Nanostructures

1



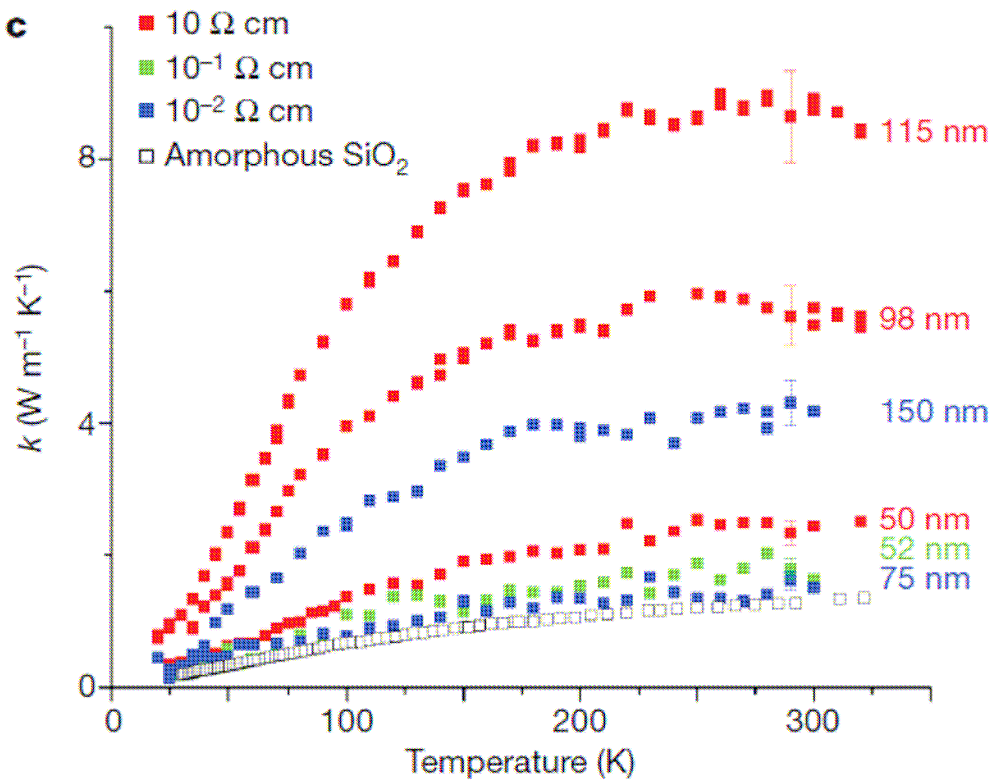
Long-wavelength or low-frequency phonons
are scattered by imbedded nanostructures!

NANOSTRUCTURING- decrease of thermal conductivity: Phonon Scattering on nanostructure interface

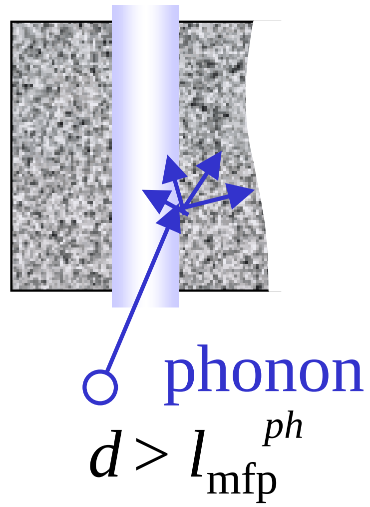
1

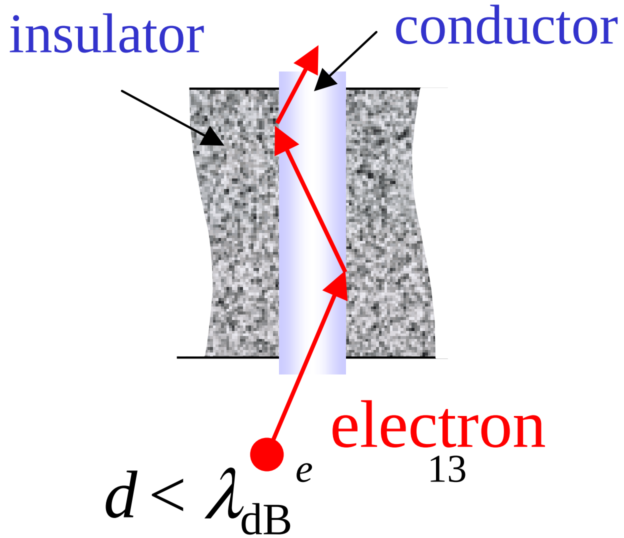
"Phonon engineering" thermoelectrics

Artificial nanostructuring: Si nanowires



(Hochbaum et al., Nature 451 (2008), 163)

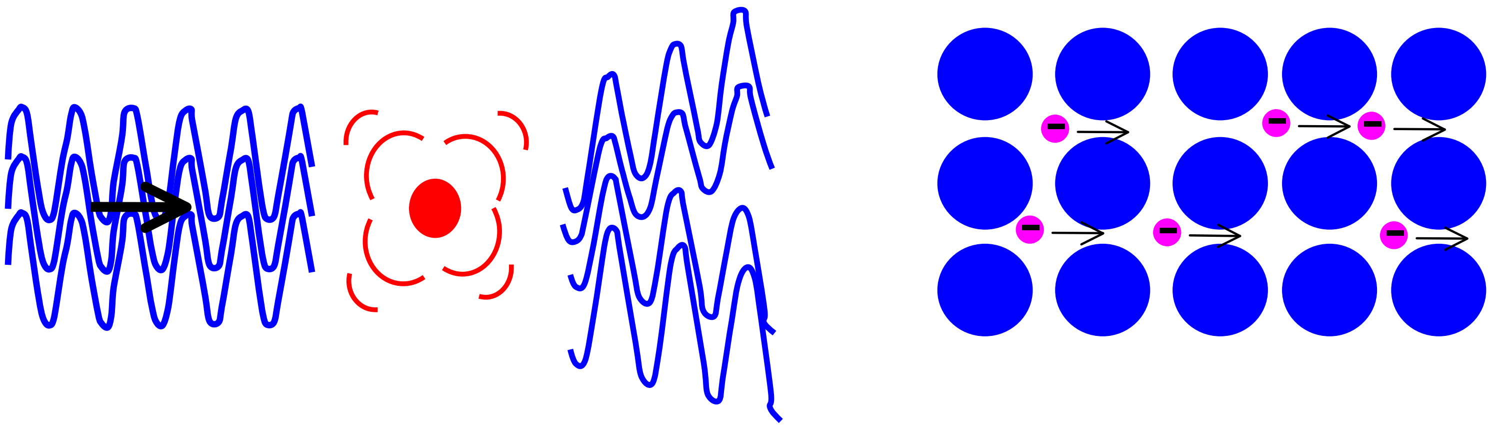




2

Complex material science and advanced synthesis technology:-

Open structures and very complex crystal structures with many atoms with different mass in unit cell can ⇔ identify materials with a weak link between thermal and electric properties⇔ **concept of «Phonon Glass Electron Crystal (called PGEC)», G. Slack, 1994.**



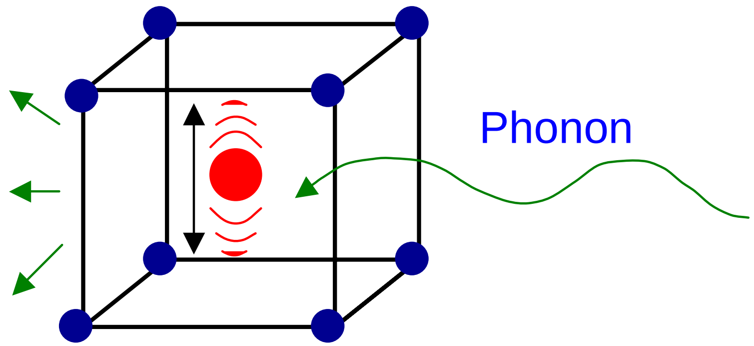
« Phonon Glass » ➔ l_{phonon} very low
λ_r very low

& « Electron crystal » ➔ $l_{electron}$ high
μ also high

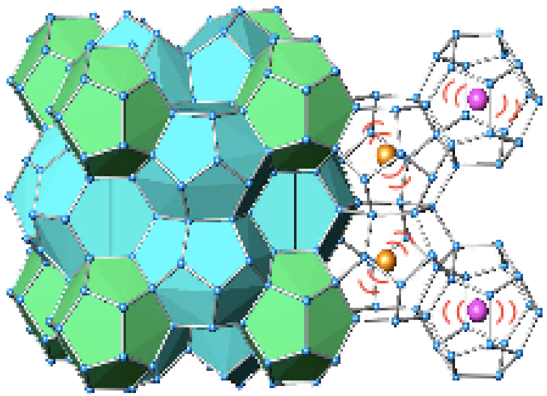
Open crystal structures : materials with «cages »

2

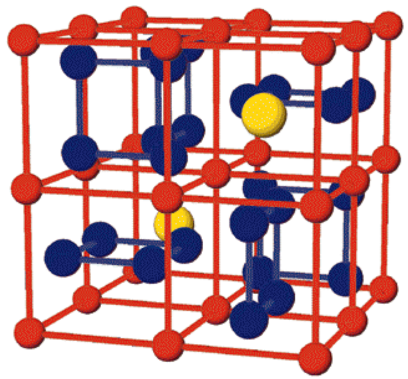
Materials with open crystallographic positions which can serve as efficient "host" for inserted atoms , only weakly bonded with basic structural frame ➔ can vibrate around central position (« rattlers ») ➔ heat carrying phonons experience thus important damping from these local Einstein modes….



Interesting materials…



Clathrates
($Ba_8Ga_{16}Ge_{30}$)



Skutterudites
(Co_4Sb_{12})

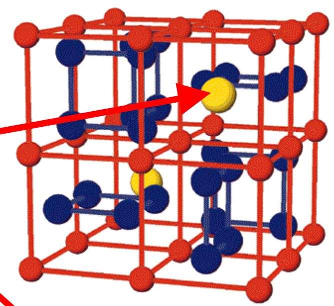
Decrease of thermal conductivity via phonon –phonon scattering

2

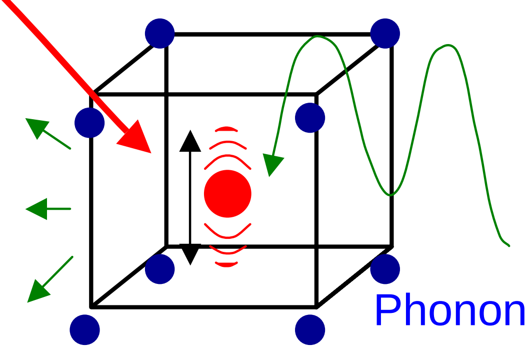
$$ZT = \frac{\alpha^2}{\rho\lambda} T$$

RATTLING ATOMS

Skutterudites (Co_4Sb_{12})

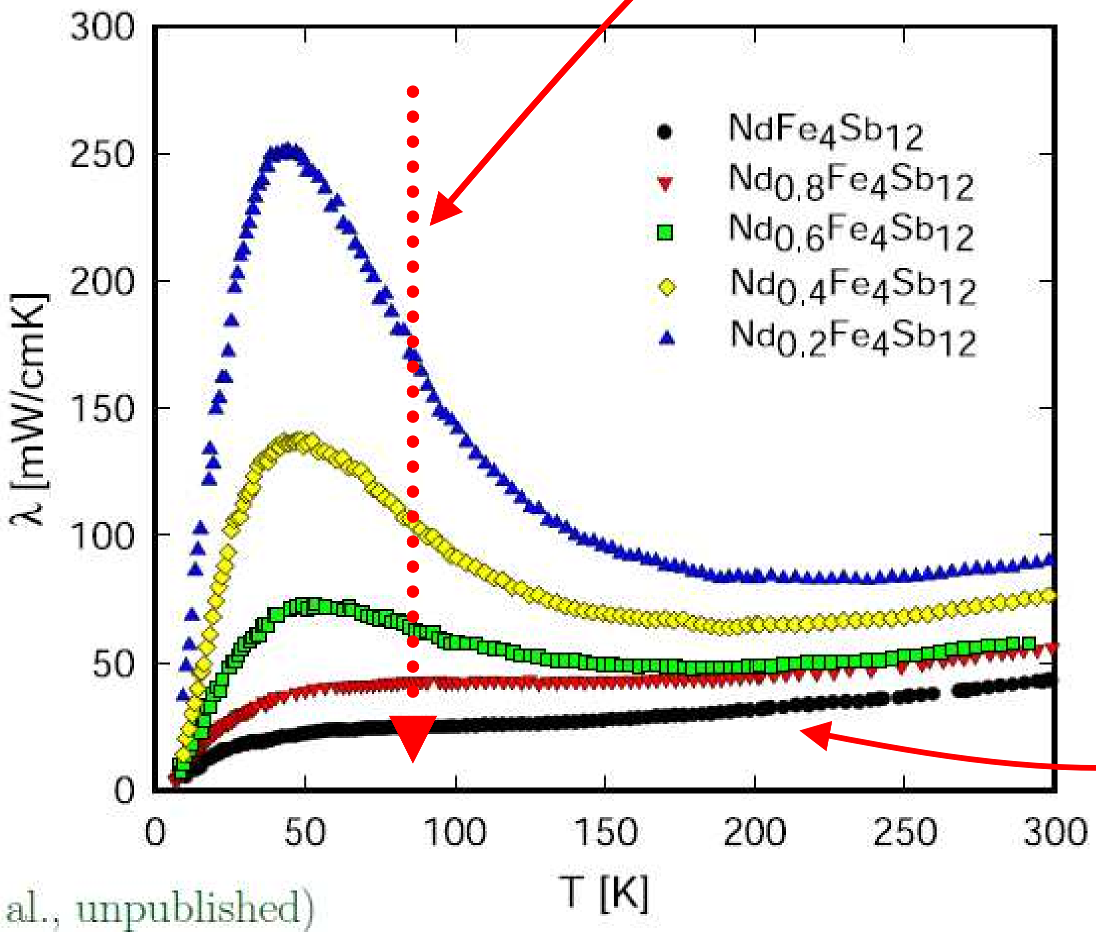


Scattering

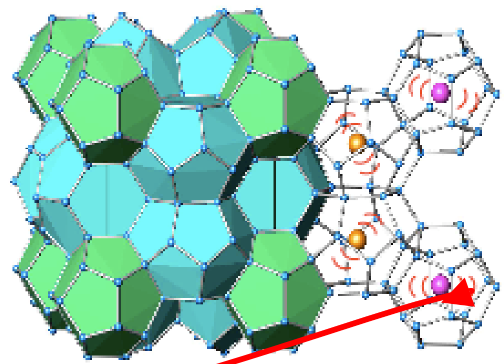


"Phonon engineering" thermoelectrics

Internal nanostructuring: The skutterudite $Nd_yFe_4Sb_{12}$



(Bauer et al., unpublished)



Clathrates ($Ba_8Ga_{16}Ge_{30}$)

Partially filled skutterudites based on Co_4Sb_{12}

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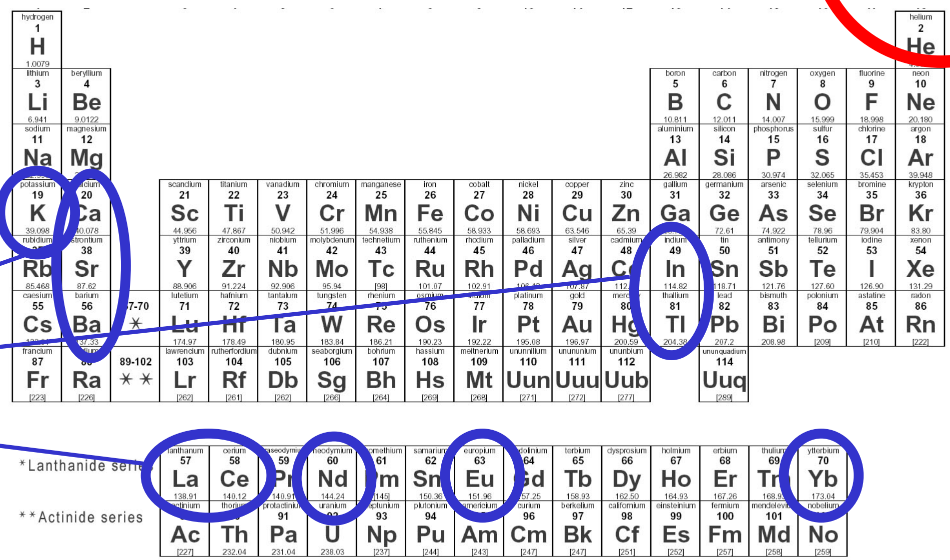
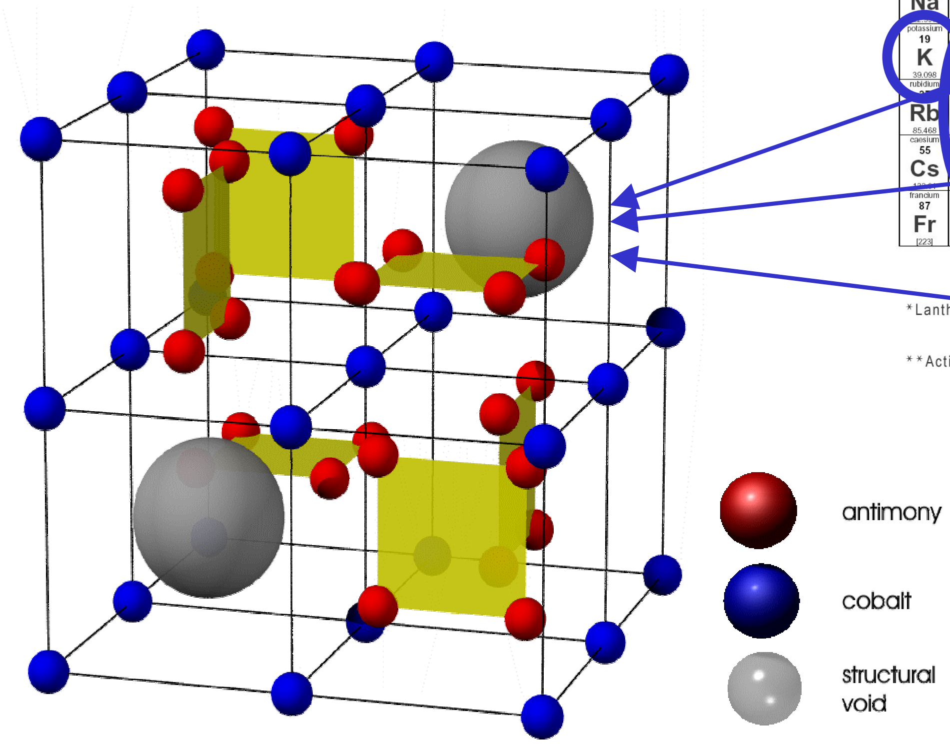
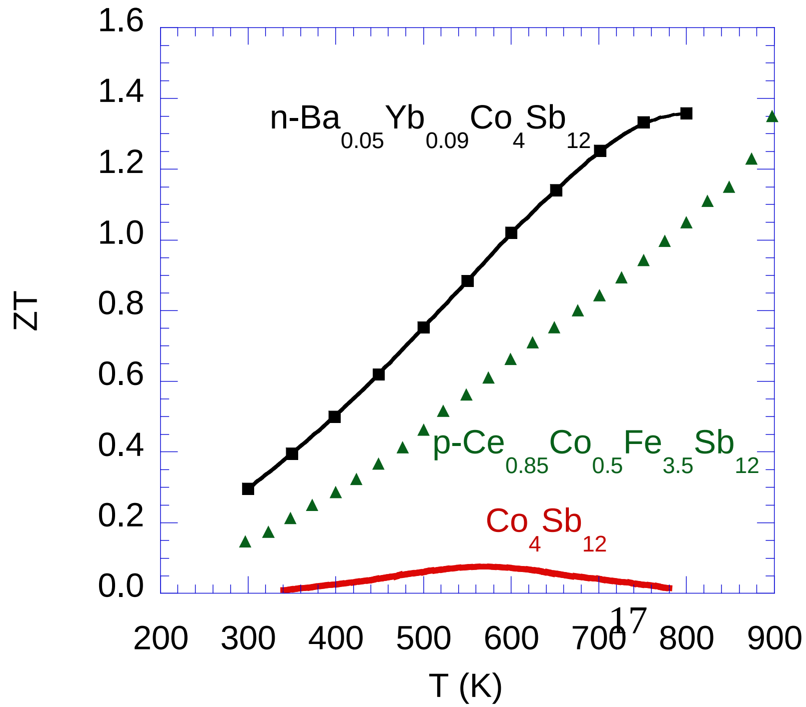






Rich class of compounds, voids, rattling, filling, doping,…

Materials n et p with ZT > 1 can be obtained…

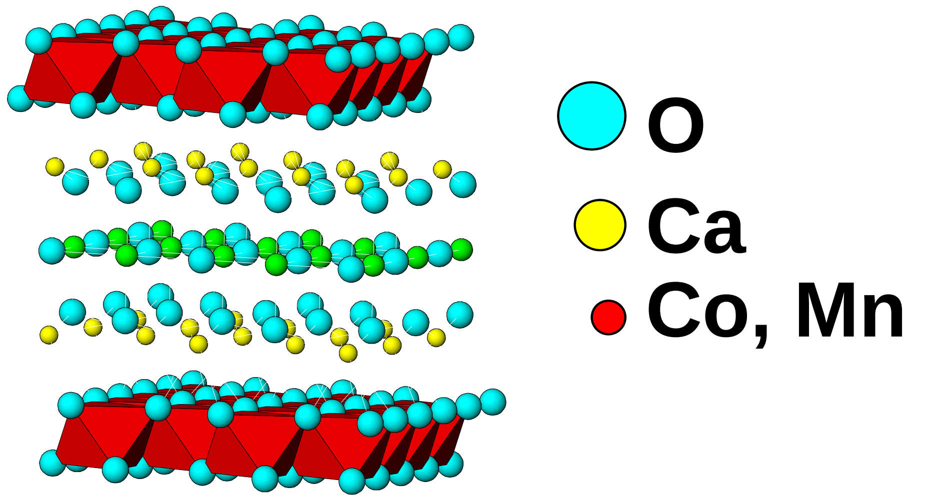
High Temperature Oxide Thermoelectrics

2

New class of compound, metallic oxides, stable chemically at high temperatures, studied are cobaltites and manganites, then chromites,..

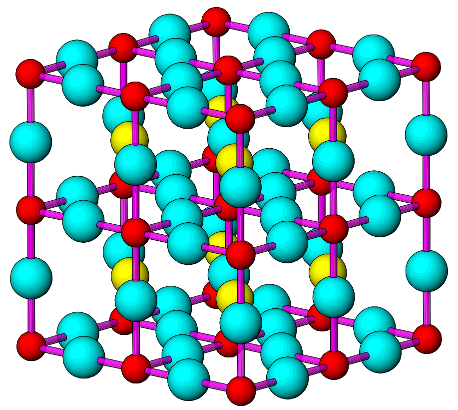
- **Layered cobaltites**
  - **$Ca_3Co_4O_9$**
  - **$(Bi,Pb)_2Sr_2Co_{1.82}O_y$**
  - **Na_xCoO_2**
- **3D - cobaltites**
- **2D - cuprates**

$\alpha > 0$



- **3D - Manganites**
  - **$Ca_{0.95}La_{0.05}MnO_3$**
- **3D - Titanates**
  - **$Sr_{0.95}La_{0.05}TiO_3$**
- **Spinels**

$\alpha < 0$



Gradual increase of ZT during last 60 years…