# Thermoelectricity I

# (tutorial & inorganic TE materials)

Javier Rodríguez-Viejo
Physics Department
Universitat Autònoma de Barcelona

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# OVERVIEW

**Basics and General Introduction.**

Concepts. Figure of Merit.

**Strategies to reduce thermal conductivity**

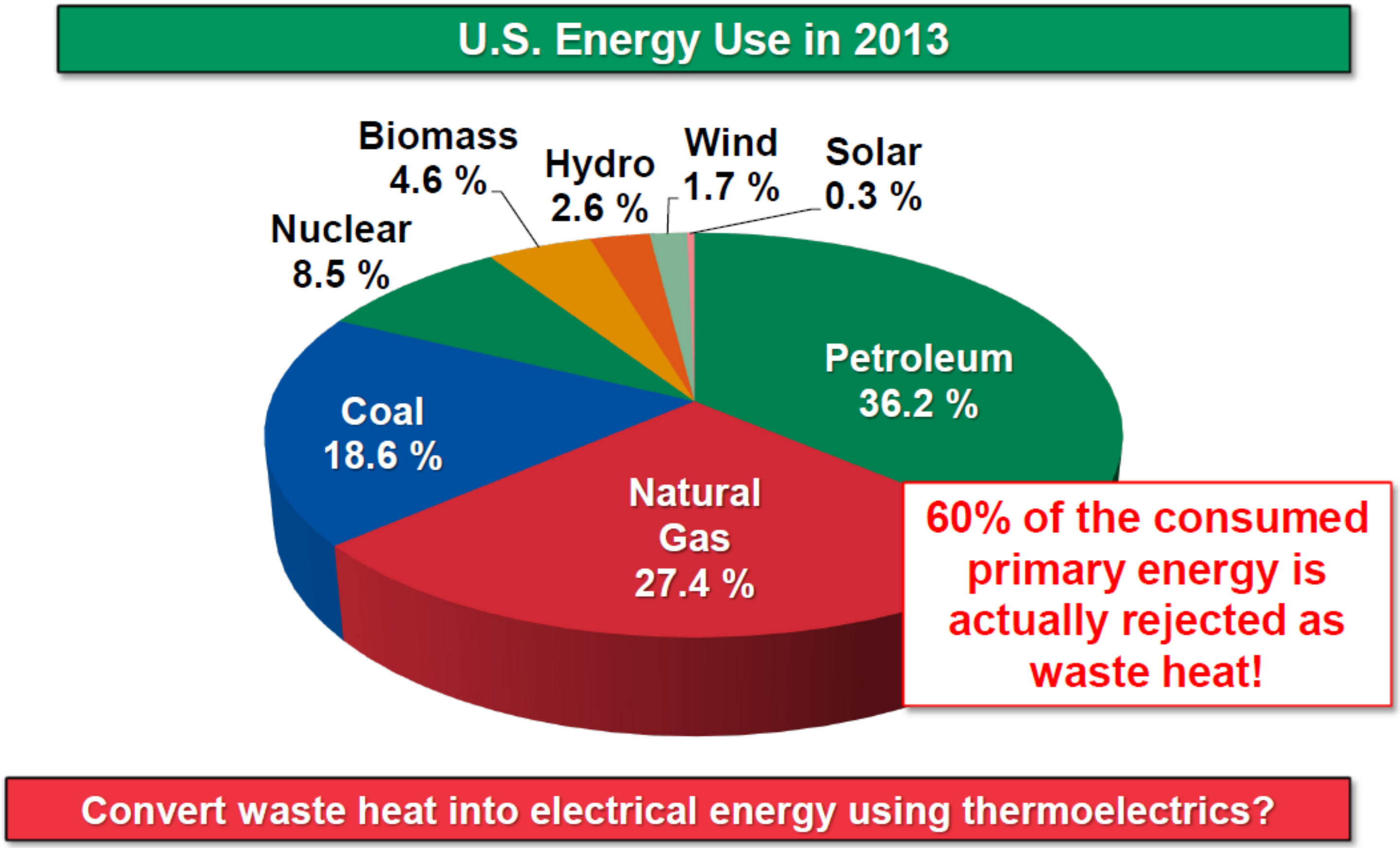
**Strategies to increase power factor**

**A short view on inorganic materials**

**Thermoelectric Devices & Applications**

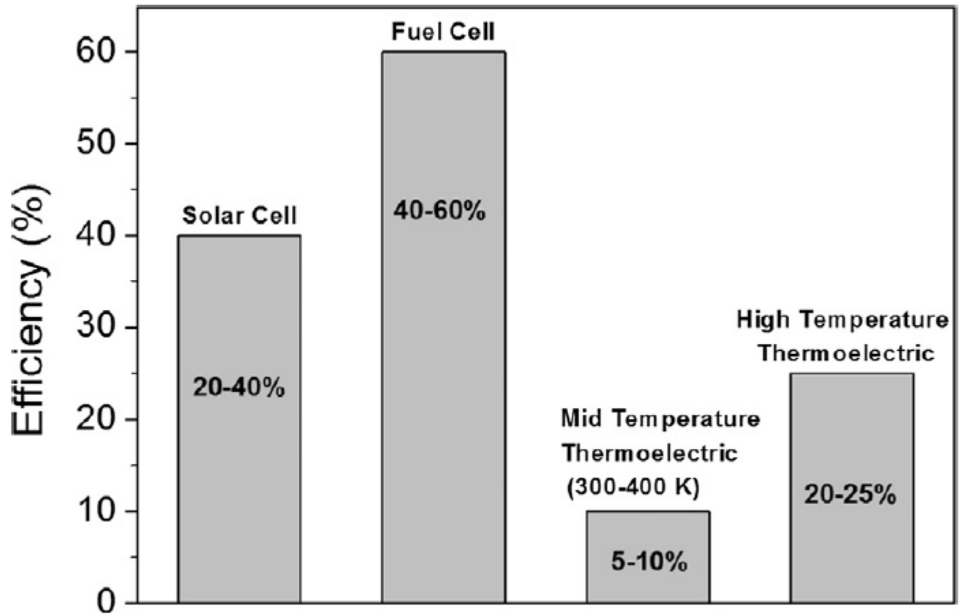
# ENERGY SOURCES

## There is plenty of waste heat around




Source: Kartounen

# Clean energy sources




Thermoelectric generation is still behind solar cell and fuel cell technologies

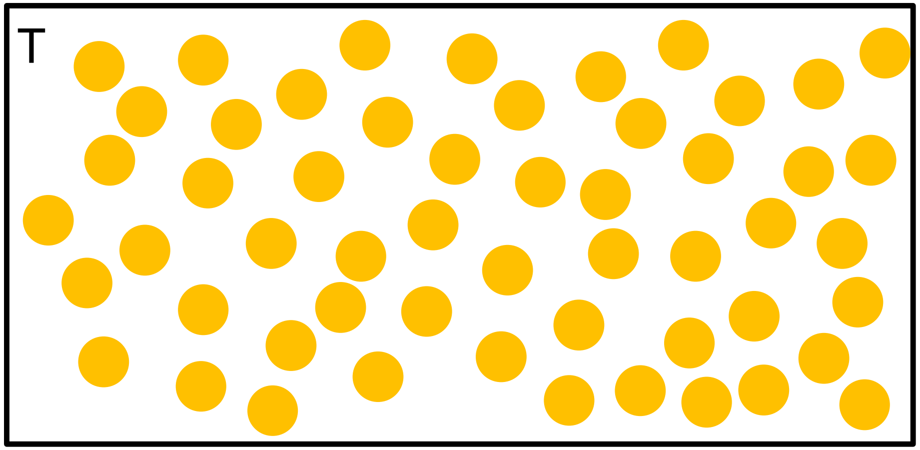
but

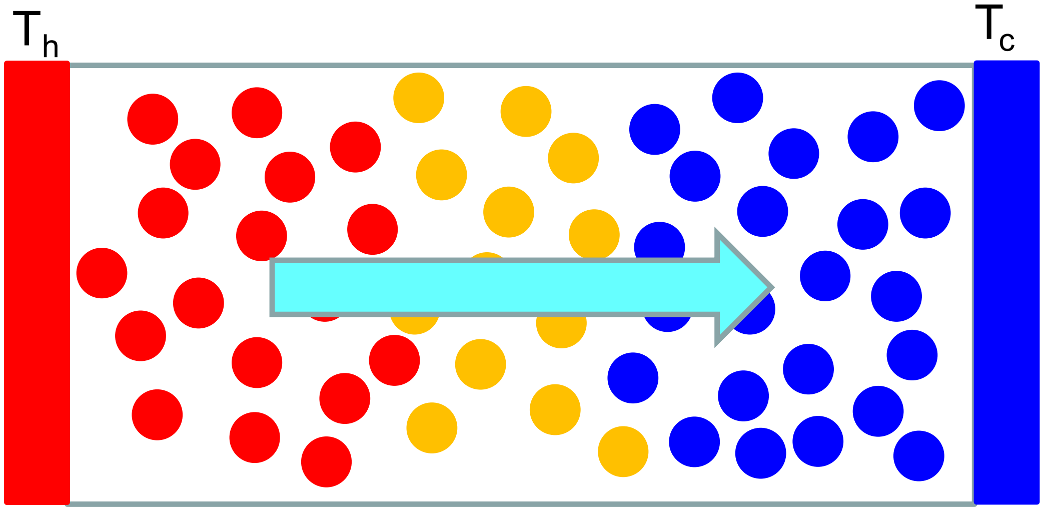
still useful to partially recover waste heat generated by combustion engines

# Principle

KINETIC THEORY

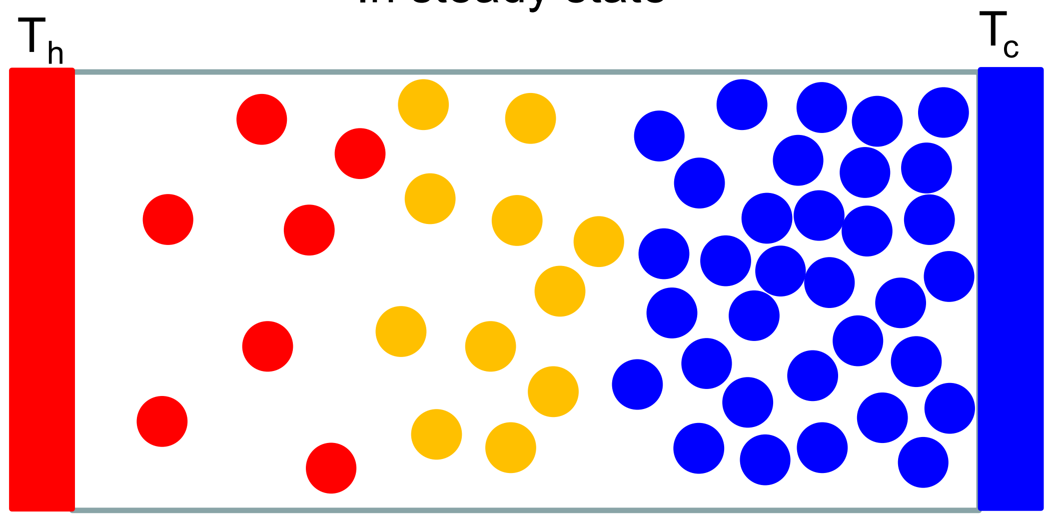
Gas particles
in equilibrium




$$J_T \propto \nabla T$$

In steady state



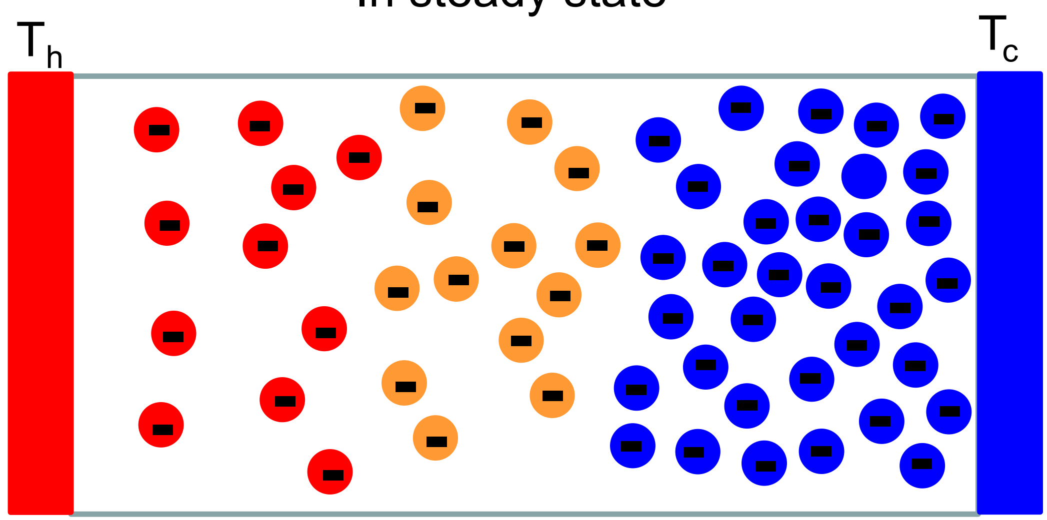

$J_T \propto \nabla T$

$J_C \propto \nabla c$

$J_T = J_C$

If particles are charged

In steady state

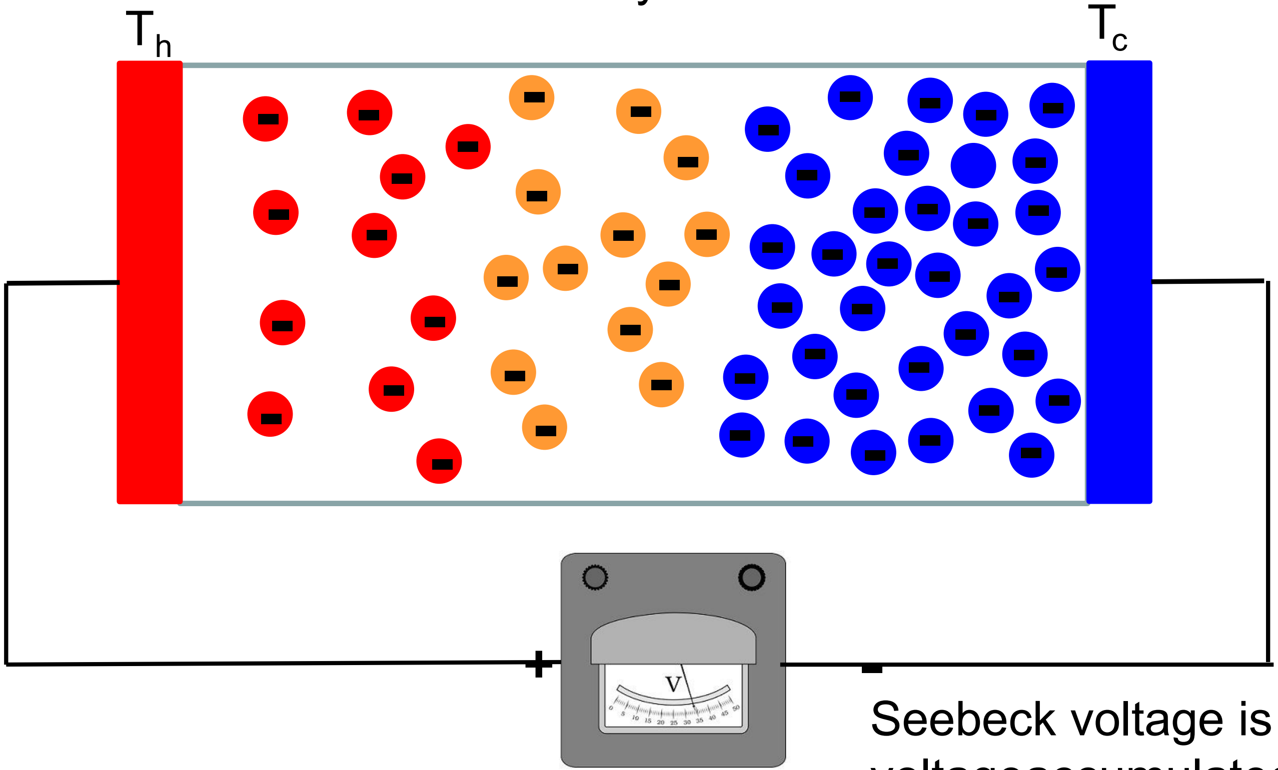



$J_T \propto \nabla T$

$J_E \propto \nabla \vec{E}$

$\boxed{J_T = J_E}$

In steady state




$\Delta V > 0$

Seebeck voltage is the steady-state voltageaccumulated under the open circuit conditions

$$S = -\frac{V_h - V_c}{T_h - T_c} = -\frac{\Delta V}{T_h - T_c}$$

**Seebeck voltage (1821)**

When a $\nabla T$ exists in bar a voltage develops between the two ends.

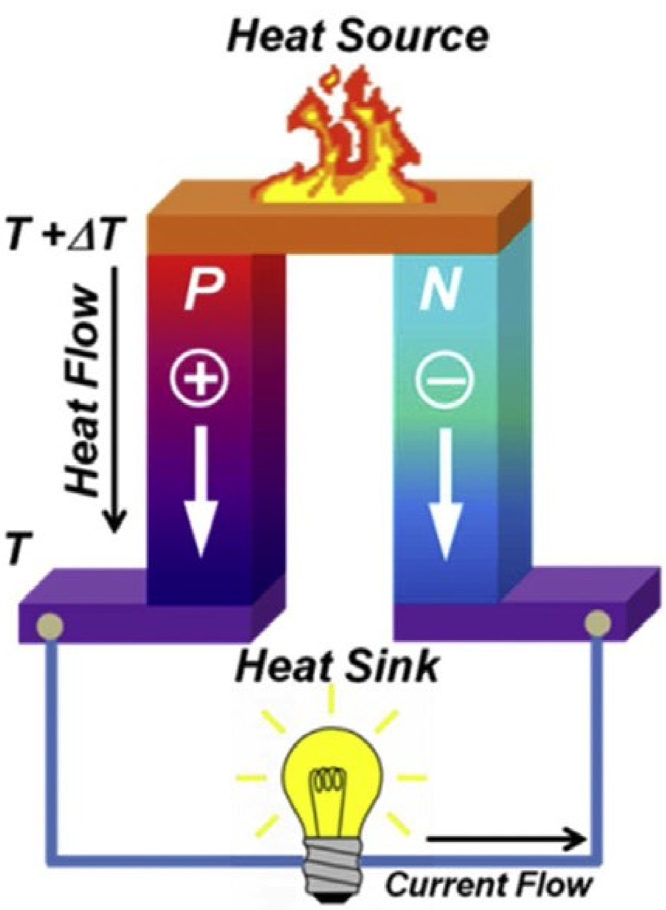
$S > 0$ p-type

$S < 0$ n-type

Except in very specific cases when slope is negative

$$\left\{\frac{\partial \log \sigma(\varepsilon)}{\partial E}\right\} < 0$$

# Thermoelectric Generation




Power output

S thermopower

σ electrical conductivity

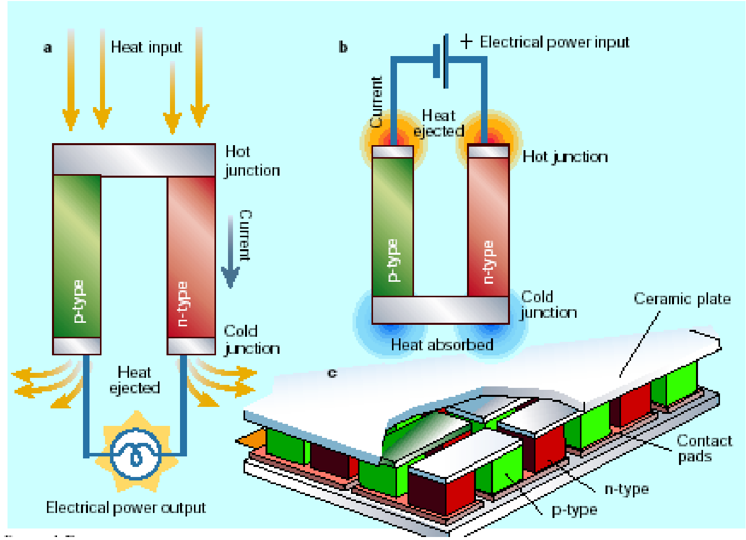
κ thermal conductivity

The idoneity of a TE material can be evaluated by

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

**FIGURE OF MERIT**

# FIGURE of MERIT & EFFICIENCY

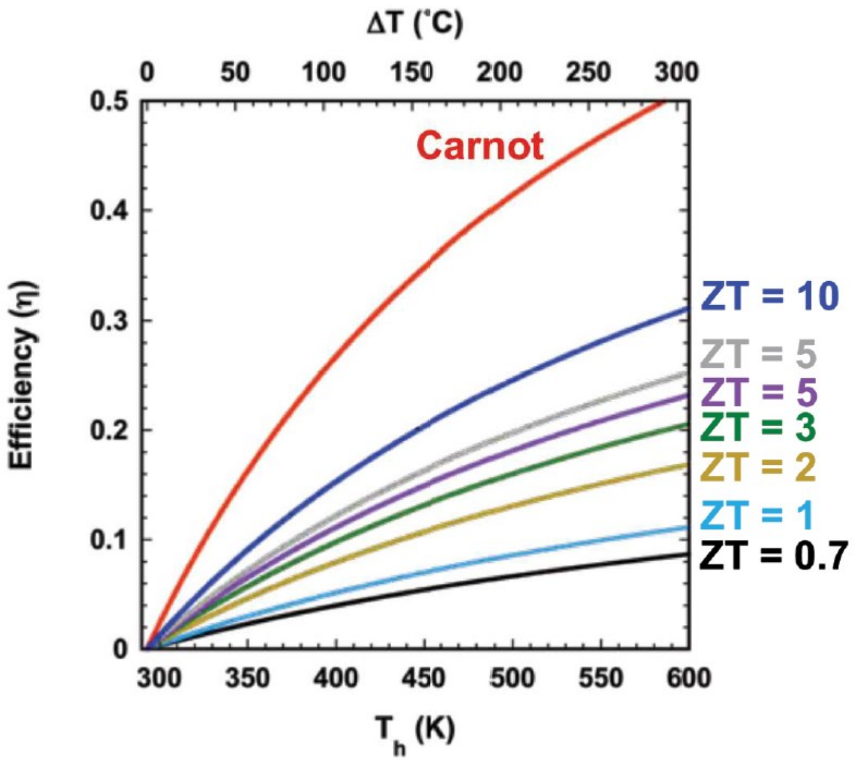



## Carnot efficiency

$$\eta_C = \frac{T_h - T_c}{T_c}$$

## Thermoelectric efficiency

$$\eta_{TE} = \eta_C \cdot \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_c}{T_h}}$$




$ZT < 1$ → very specialized applications

$ZT > 1$ → small-scale applications

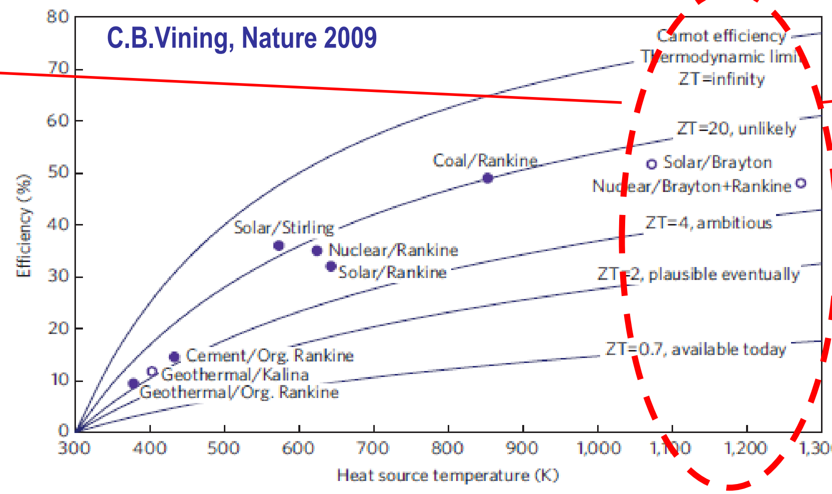
$ZT > 3$ → large-scale applications (currently, $ZT < 2$)

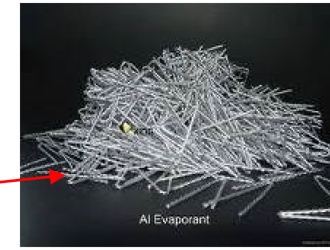
Gayner, Kar, PMS (2016)

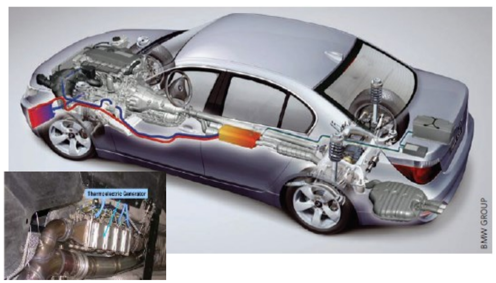
# Impact of ZT on power applications

High-T

## Large scale



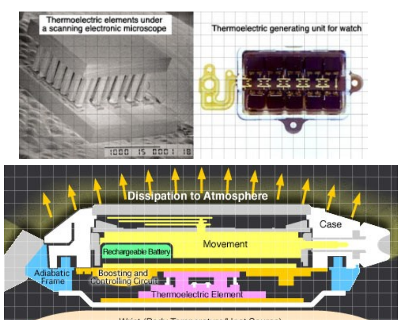



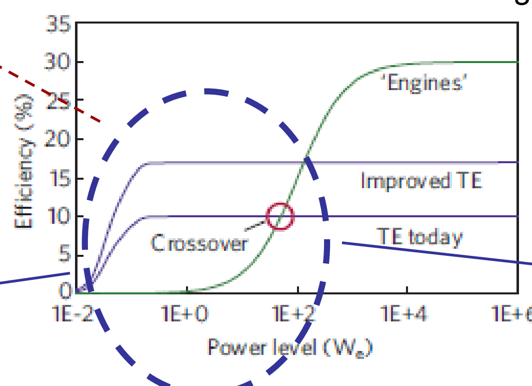



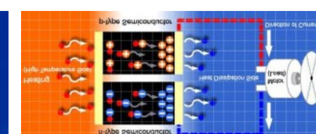
## Medium

Vining, Nature 2009

Low-T



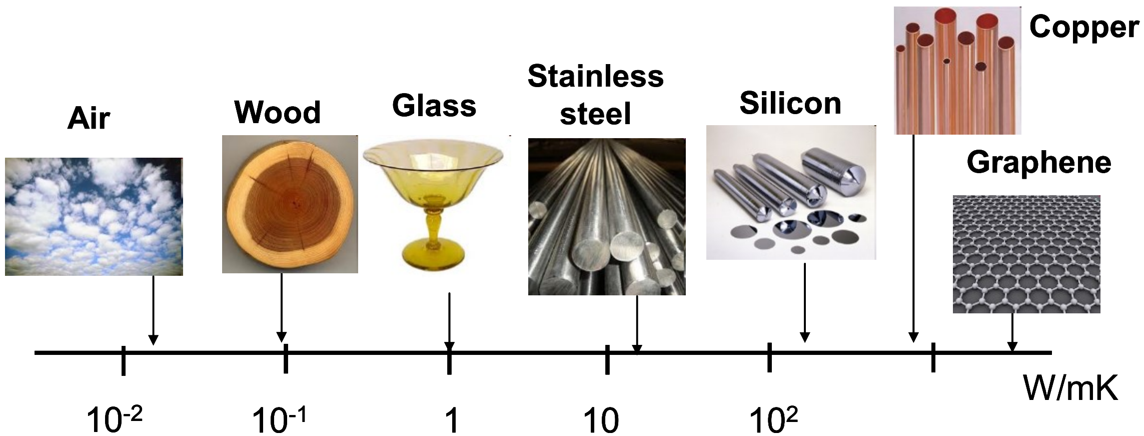
## Small scale

**Advantages**: No moving parts, little maintenance, no greenhouse gas emission

High efficiency requires maximizing ZT → Increase in $S^2\sigma$, Decrease in $\kappa$ → PHONON GLASS ELECTRON CONDUCTOR (Slack, 1994)

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

**No such material exists in Nature !!!**




**Good heat conductors are good electrical conductors**

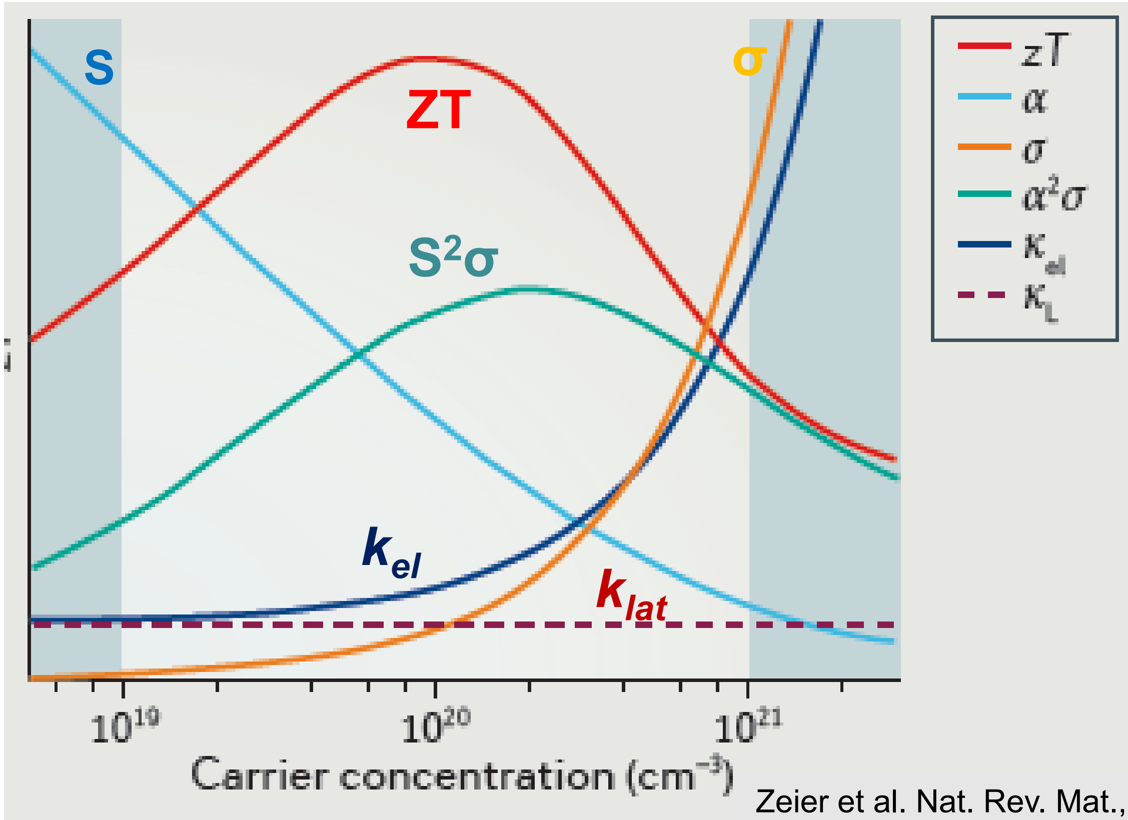
$k=k_l+k_e$:

metals have lots of free electrons ($k_e$ is large), while ceramics have few (only $k_l$ is active)

increasing k ↑

| 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 | |

# Tuning Seebeck, thermal & electrical conductivity




Zeier et al. Nat. Rev. Mat., 2016

Large values of ZT require high S, high σ and low κ ⟶ Difficult to accomplish

S ↑ ⇒ σ ↑

σ ↑ ⇒ κ ↑ ⟶ Wiedemann-Franz law

# Strategies to reduce thermal conductivity

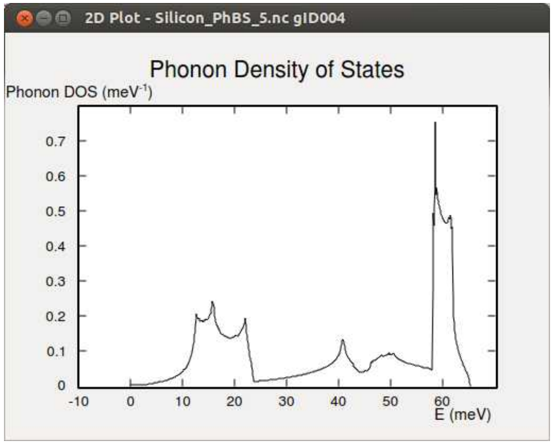
**Phonons (heat carriers)**

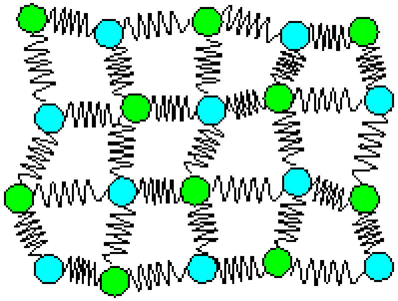
Quantized energy of lattice vibration

$$E = \hbar\omega = h\frac{c}{\lambda}$$

Based on spring and mass system

Phonons scattered whenever there is a difference in mass and/or spring constant.



# Heavy mass-concept

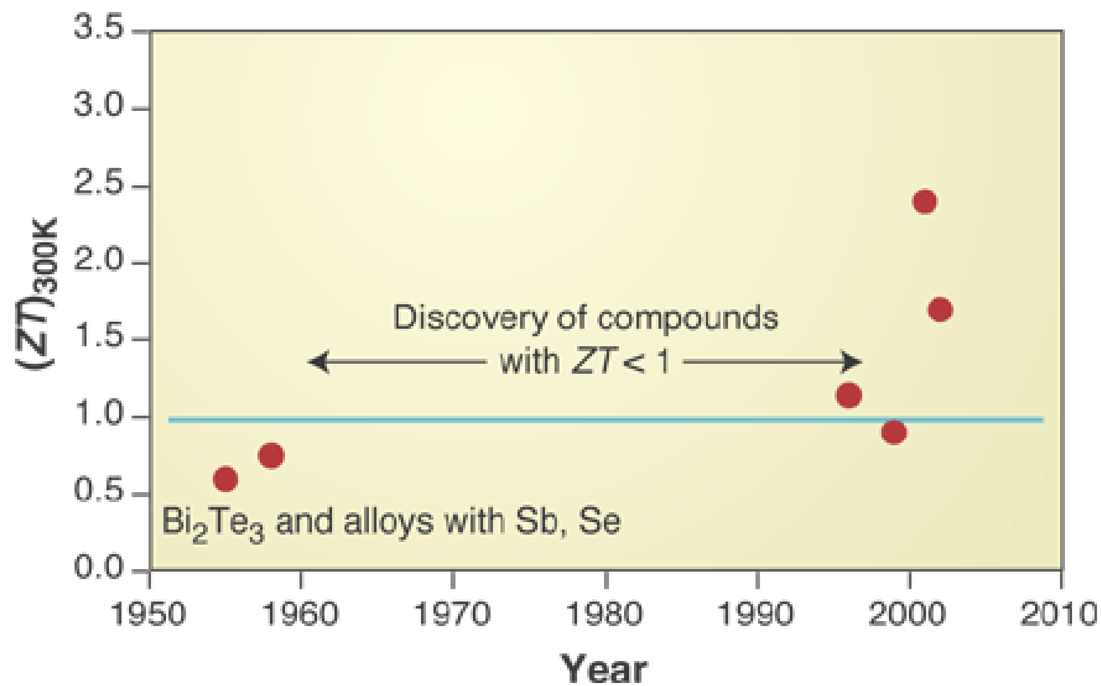
1950–1959: Ioffe stated that the thermal conductivity of semiconductors is a function of atomic weight. Generally, elements with large atomic weights have low thermal conductivity.

$$k = \frac{1}{3} C \cdot v \cdot l$$

Reducing $\kappa$ without affecting S and $\sigma$ is realized in semiconductors of high atomic weigth which reduces the speed of sound in the material and therefore $\kappa$.

STRATEGY USED 1950-1990

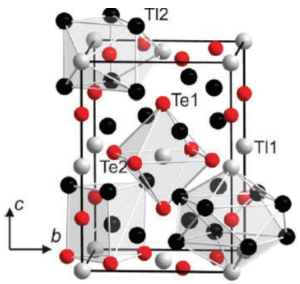
BiTe
PbTe
SbTe
and alloys



# Engineering phonon thermal transport

Reducing *k* without as much reduction of $\sigma$ and S

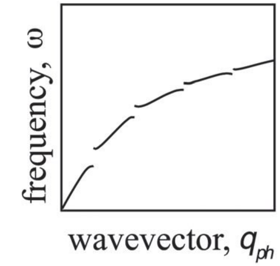
# Engineering phonon thermal transport




Large unit cell

$$\lim_{q_{ph}\to 0} v = c_s \sim \sqrt{\frac{E}{m}}$$

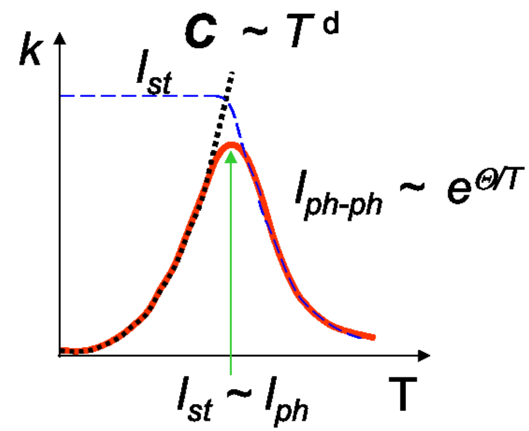
Heavy mass, $m$ & low elastic modulus, $E$

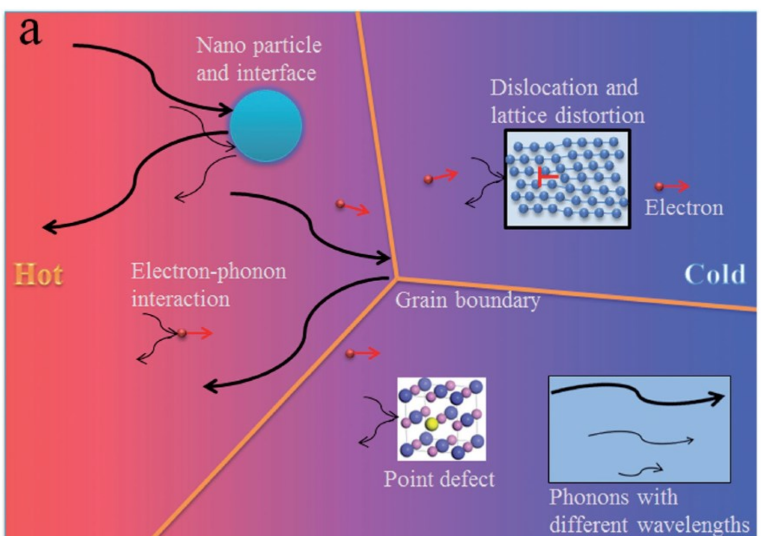



Phonon bandgaps

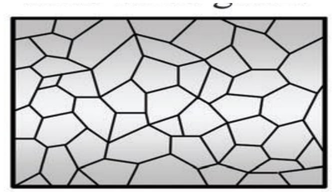
$$\kappa_{lat} = \frac{1}{3}\cdot\int C(\omega)\cdot l(\omega)\cdot v(\omega)\cdot d\omega$$

scattering

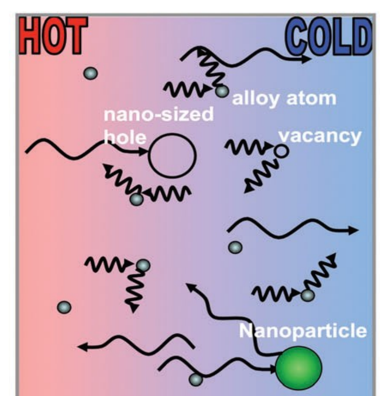



Grain-boundary scattering



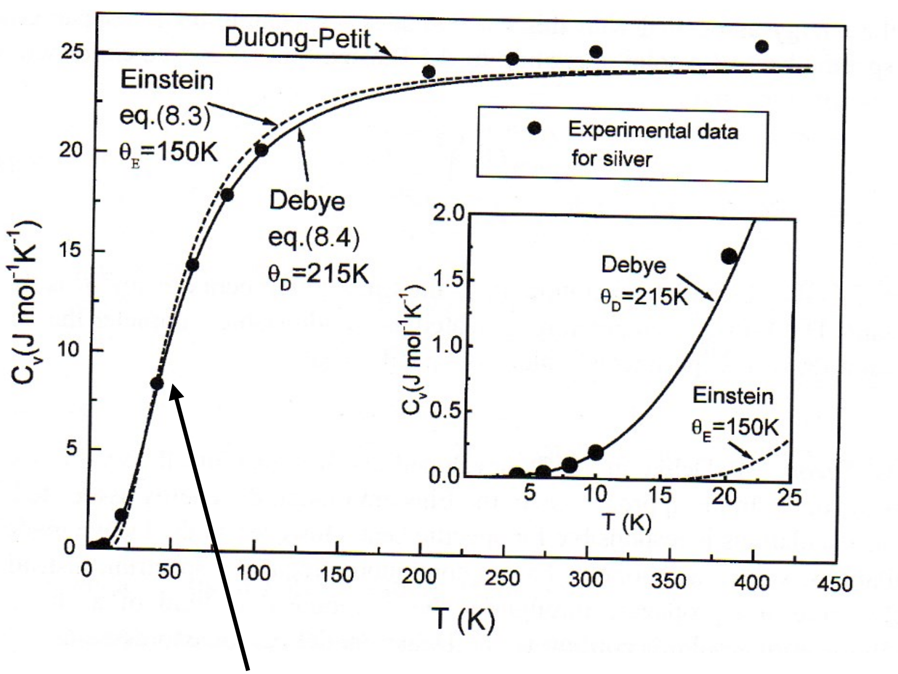
Impurity scattering



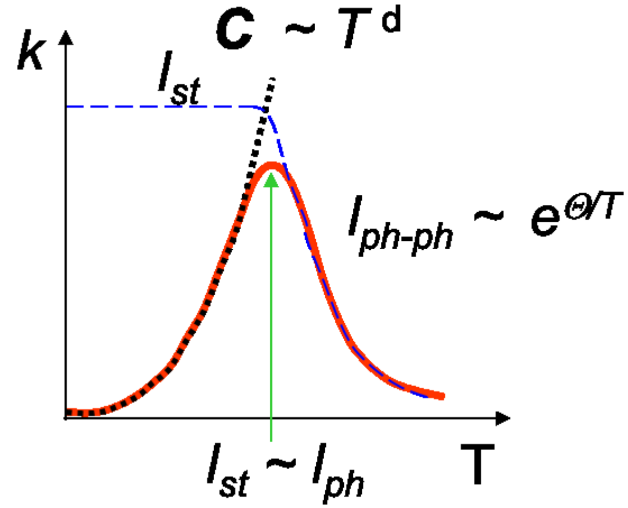

Yang et al. Adv. Energy Mat. 2017

**Specific heat** → $C_V = \left(\frac{\partial E_{ph}}{\partial T}\right)_V$

If $T > \Theta$, $\boldsymbol{C} \sim constant$




Debye-like regime $T^3$



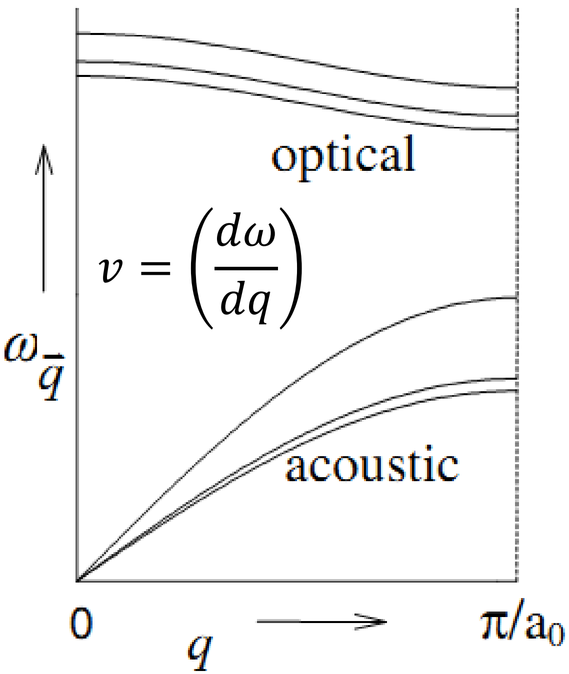

If $T \ll \Theta$, $\boldsymbol{C} \sim T^d$ (d: dimension)

**Size-effects: useful at very low-T's**

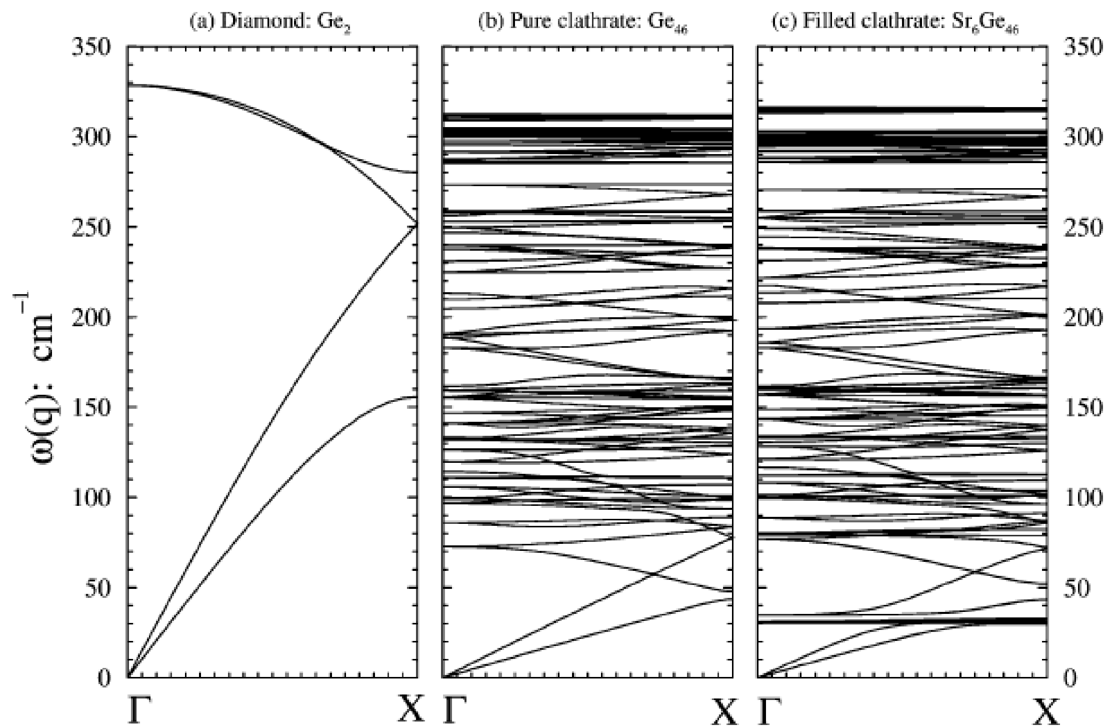
Size of the crystal is of atomic scale so lattice vibrations are confined and dispersion relation is modified

# Phonon group velocity

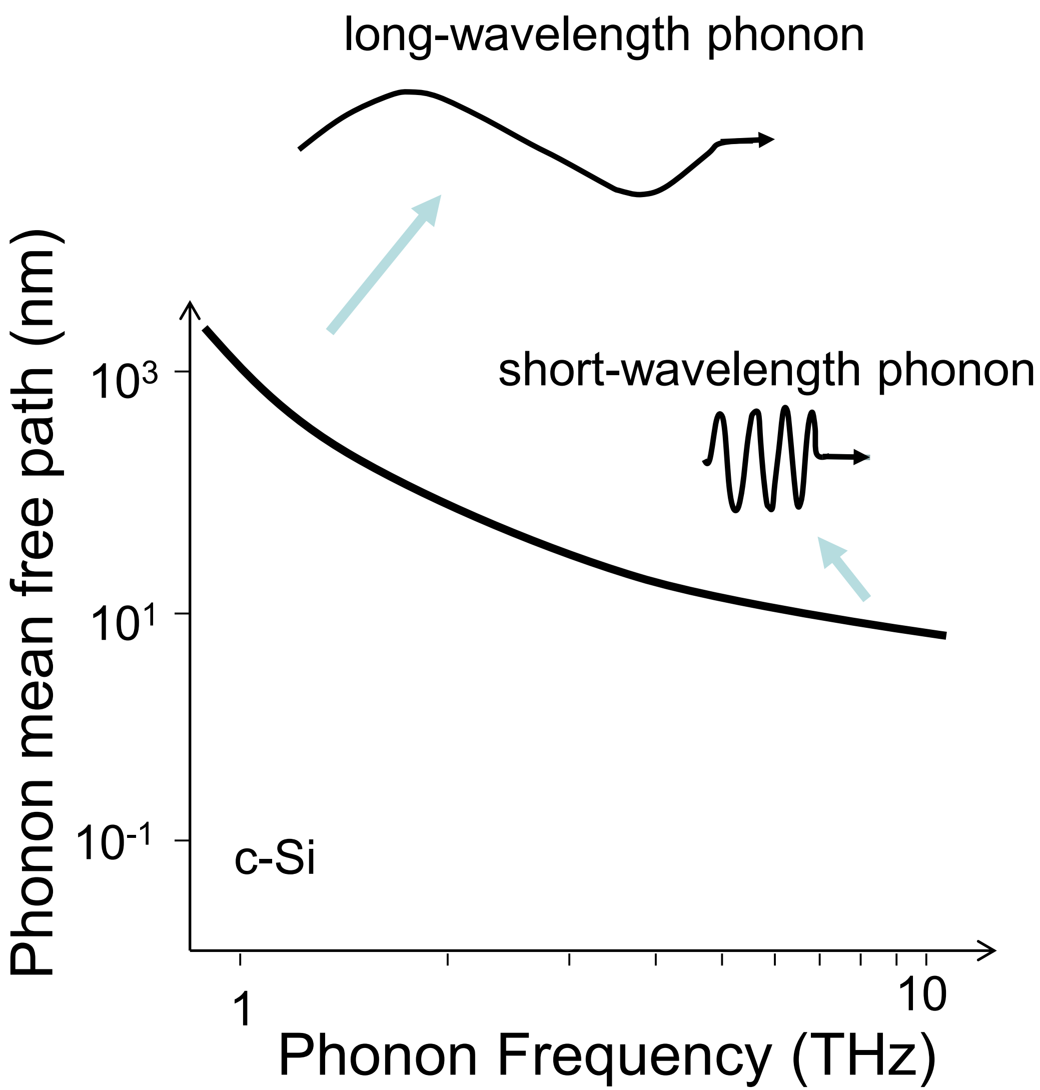
Optical branches:
Small sound velocity




i) **Increasing the number of atoms** in the unit cell



**Phonon mean free path** (average distance between collisions)




At room T

PHONONS

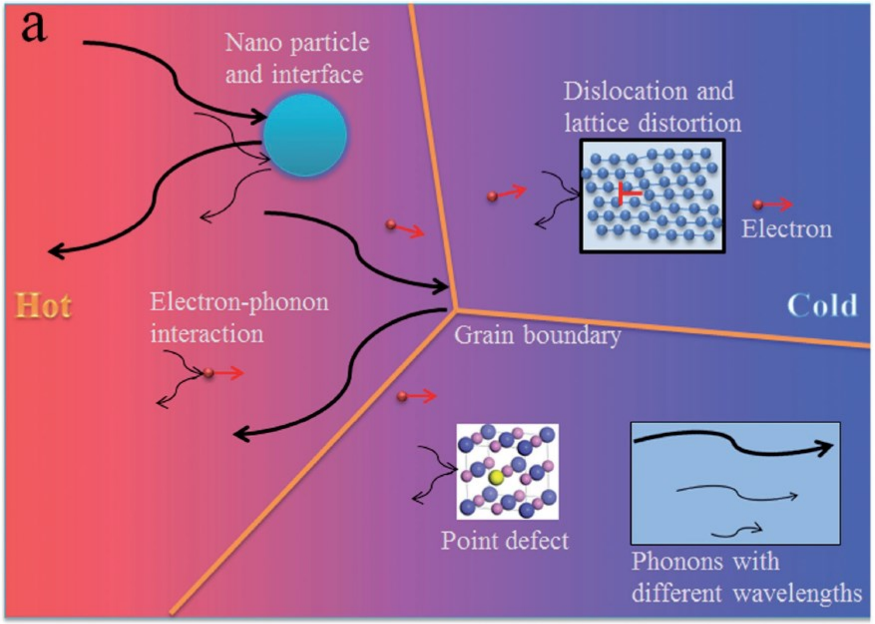
| Wavelength | Mean freepath |
| --- | --- |
| Dominant heat-carrying 5-10 nm but broadband | 10-100's nm |

ELECTRONS

| Wavelength | Mean freepath |
| --- | --- |
| 1-3 nm | 1-5 nm |

$$\frac{1}{l_{eff}} = \frac{1}{l_b} + \frac{1}{l_i} + \frac{1}{l_{ph}}$$

$l_b$ boundary scattering
$l_i$ impurity scattering
$l_{ph}$ phonon-phonon scattering




**Wien's law holds for phonons**

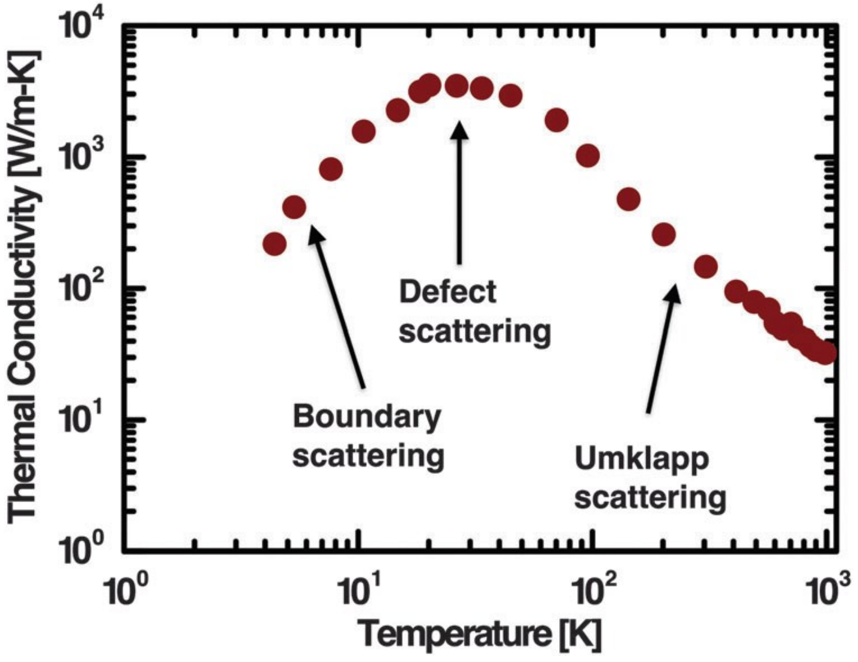
$$\lambda_{max} \cdot T \approx cte$$

Long $\lambda$ phonons carry most heat at low T

Boundary scatt. at low-T

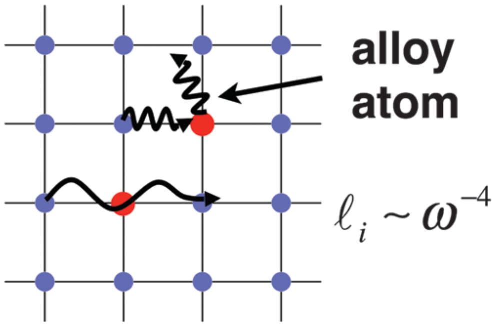
As T increases $\lambda_{ph}$ dominant phonons decreases

At high T ph-ph scattering



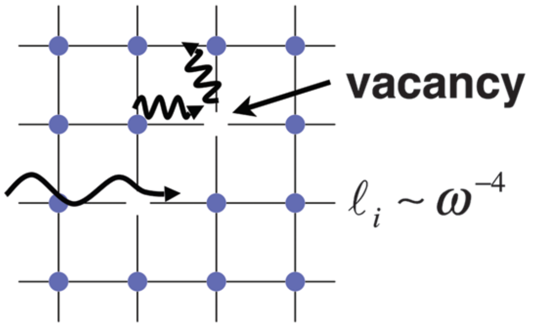
# DECREASING THE MEAN FREE PATH OF PHONONS:
## TOWARDS LOW THERMAL CONDUCTIVITY

### ALLOY LIMIT




Alloys: Lowest thermal conductivity in crystalline solids

Atomic substitutions heavily scatter phonons



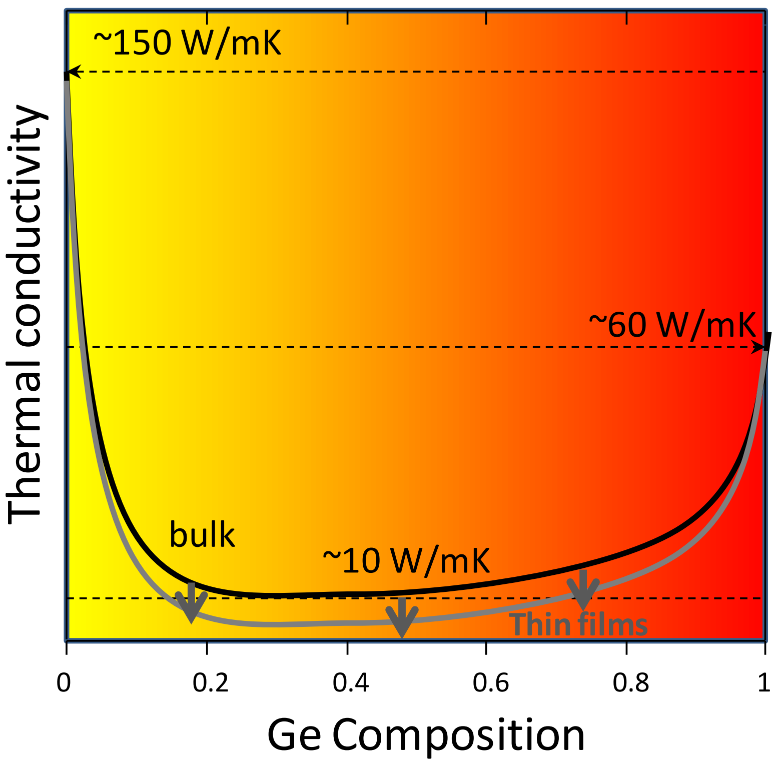

Rayleig scattering regime: scattering cross section

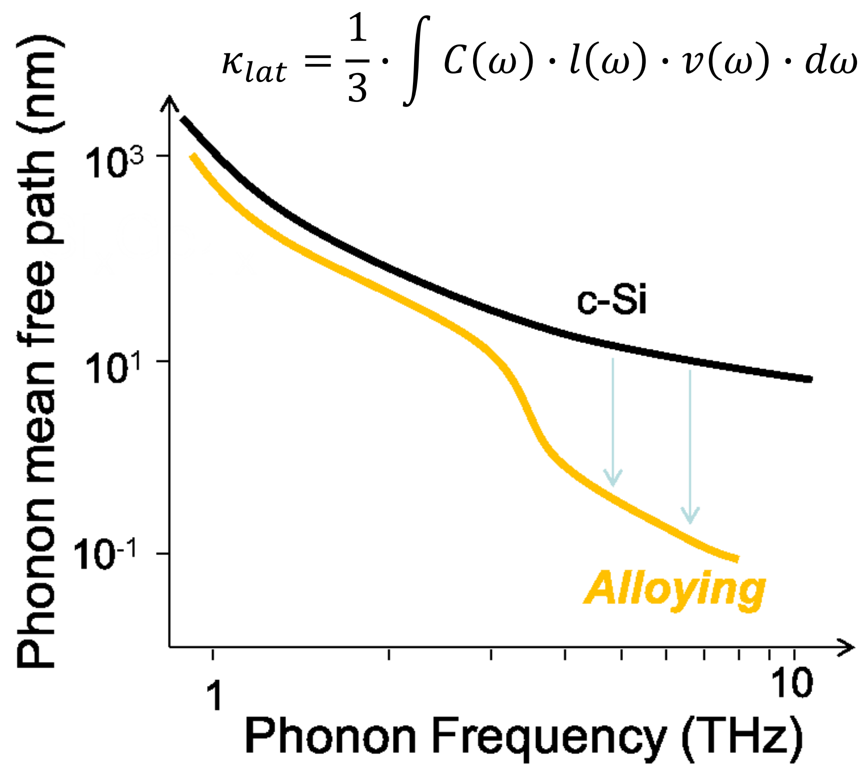
$$\sigma \sim b^6/\lambda^4$$

If atoms have b ~ 1Å ⇨ Alloys scatter short-wave phonons more effectively than mid-long-wave phonons

# ALLOYING

Mainly affects short-wavelength (high frequency)phonons



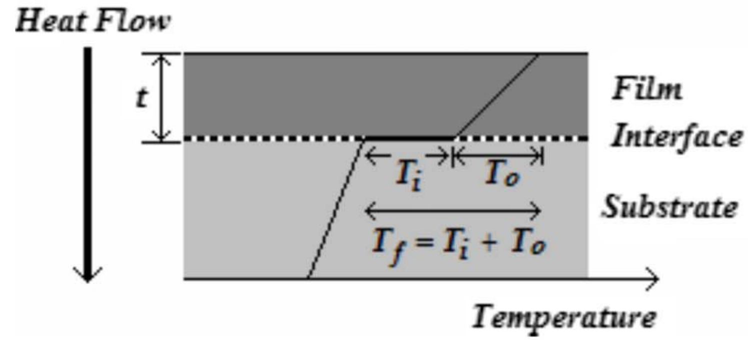




Mass disorder induces strong reduction of thermal conductivity

Maximum variation below 10 at % Ge
*k* constant between 20-70 at % Ge

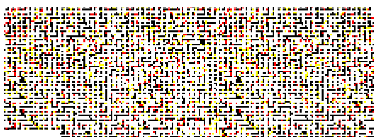
If mid- to long-phonons could be scatterered, then alloy limit can be beaten !!!!!!

# THIN FILMS & SUPERLATTICES

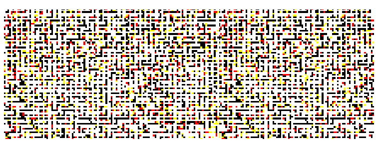



Phonon-blocking/electron transmitting interfaces in Si/Ge and other SLs

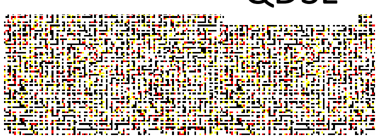
Use of the acoustic mismatch between the SL components to reduce $\kappa_{ph}$.



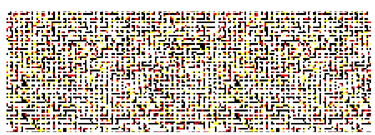
SL



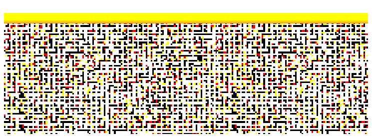
QDSL



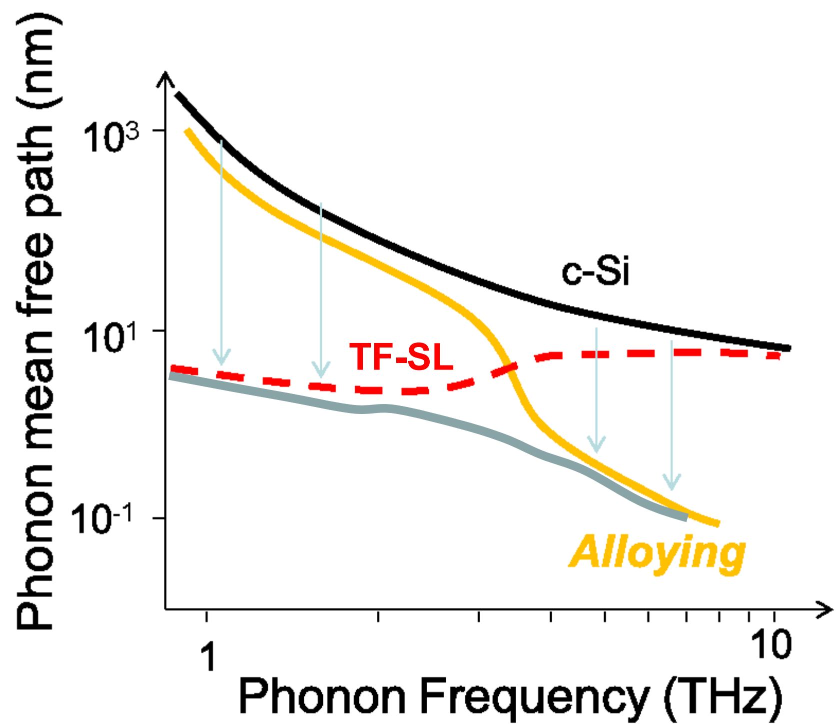
Reduce period



Maximize dot coverage

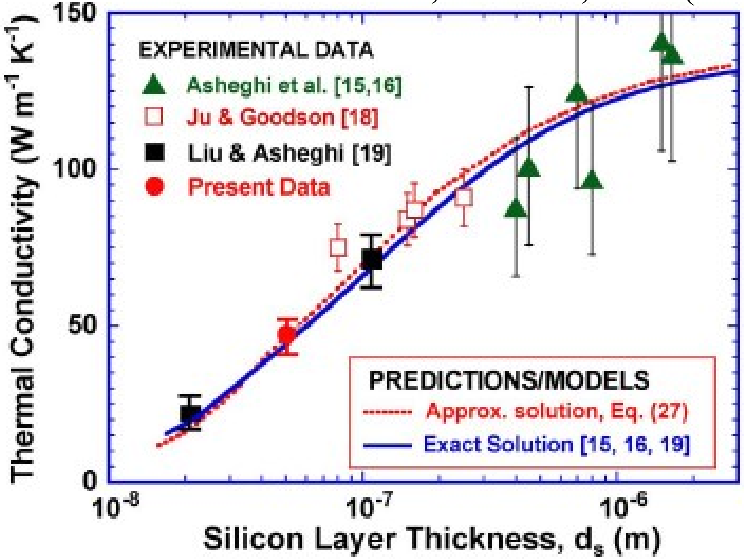


Surface seggregation SL

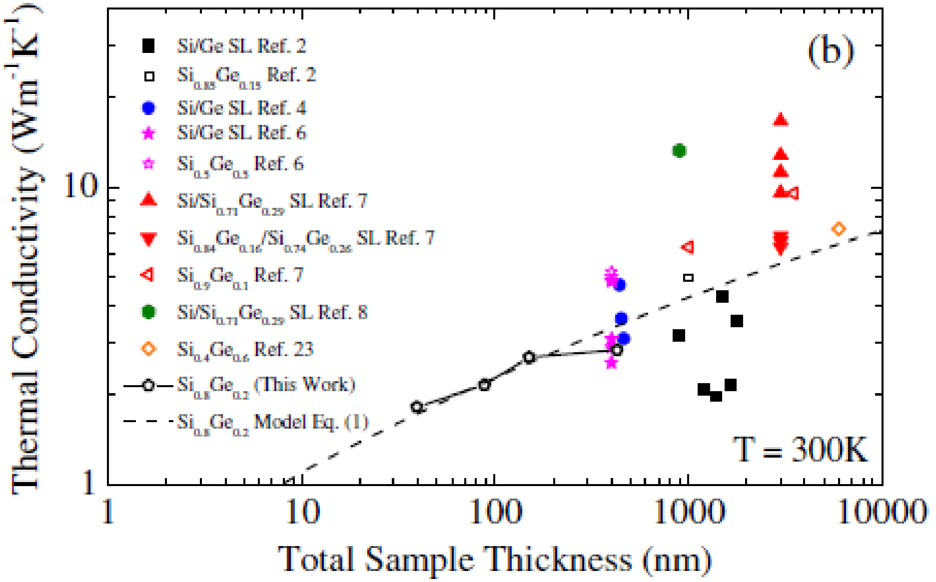


# Thin films of Si

Goodson et al., *APL.* 74, 3005 (1999)

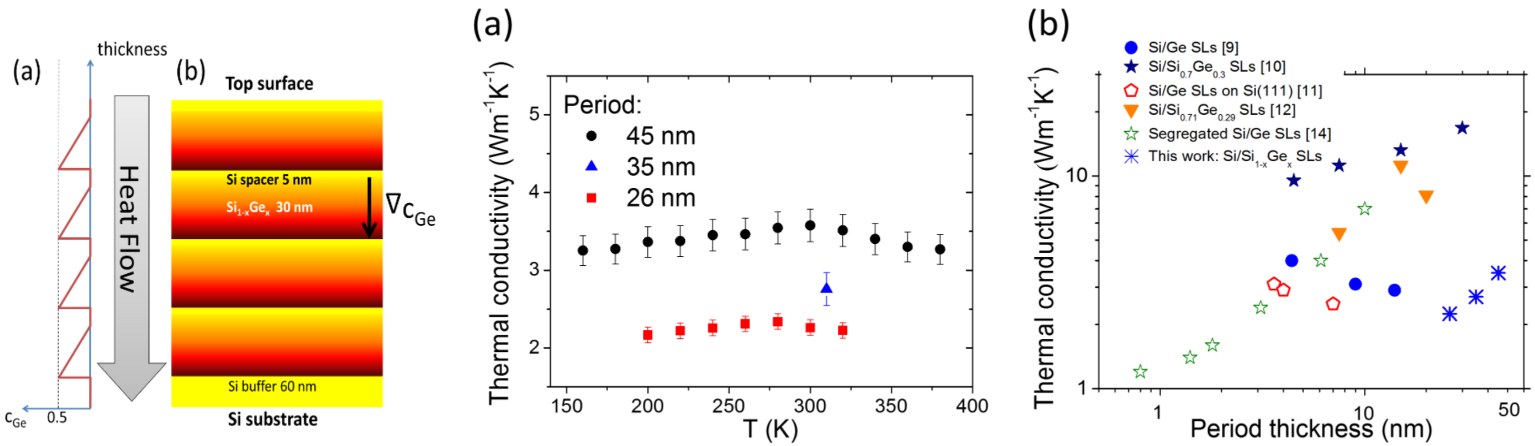



# Thin films of SiGe alloys



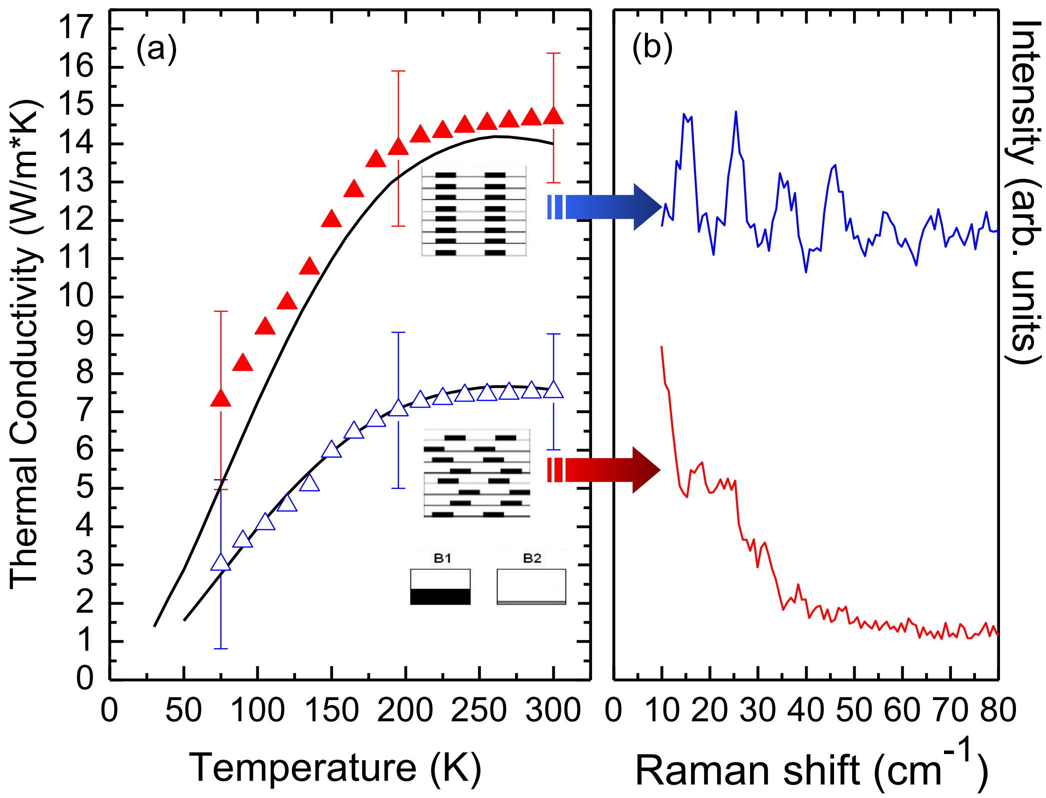

Cheaito et al. PRL 2012

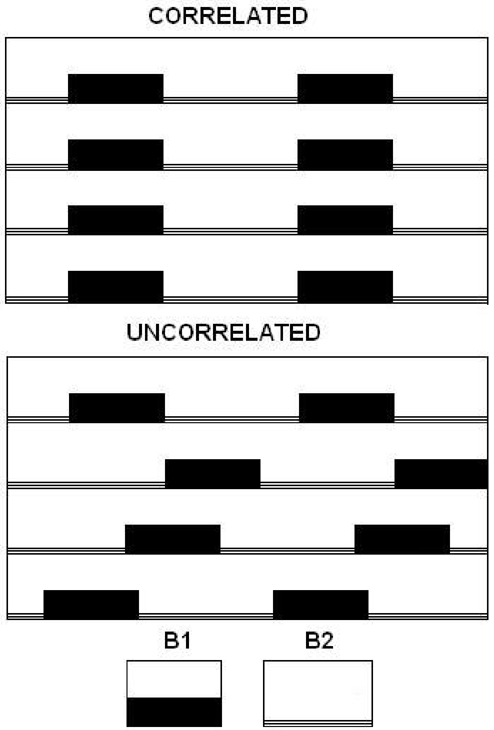
# SiGe Superlattices




UAB & ICMAB collaboration Nano Research 2017

# Thermal conductivity of Ge Quantum Dot Superlattices



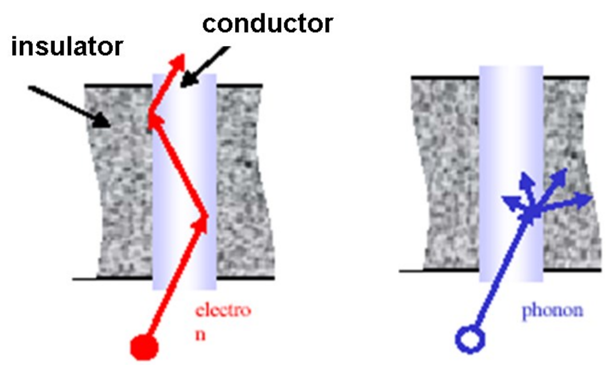

UAB-ICMAB collaboration, APL 2008

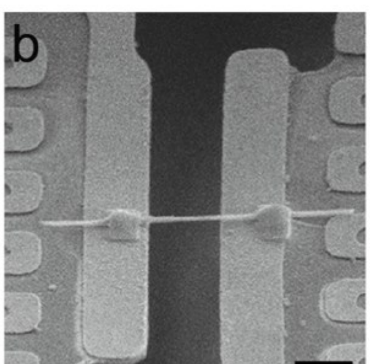
# Lower-D MATERIALS (nanowires)

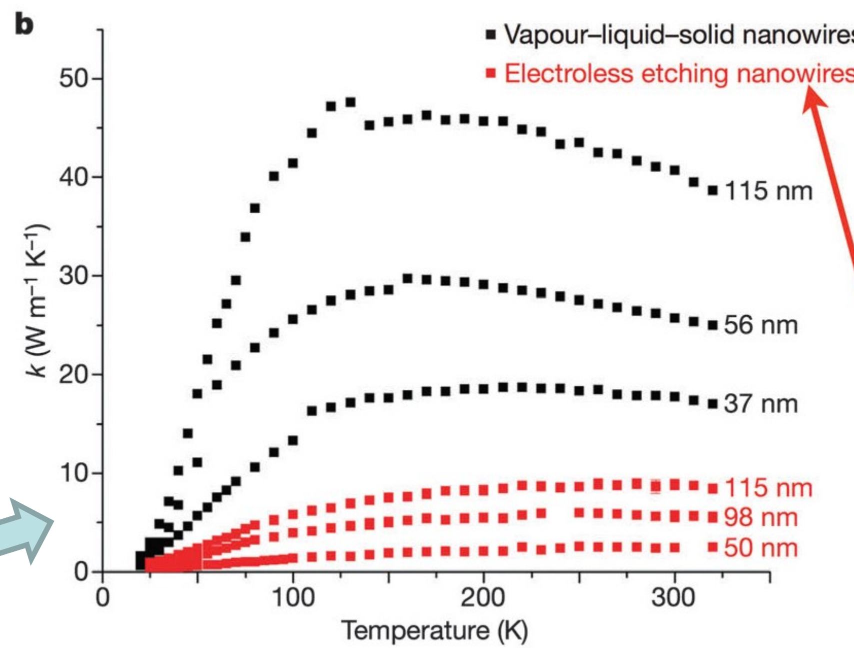
Increase boundary scattering of phonons at the barrier-well interfaces, without as large increase in electron scattering at the interface

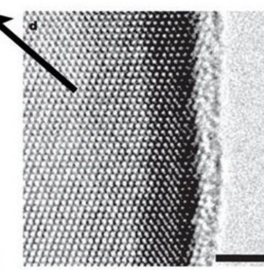
$\kappa \downarrow$ while keeping $\sigma \uparrow$

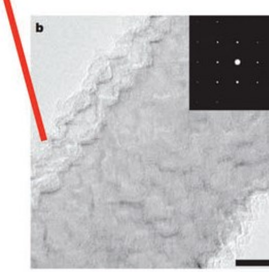
If the width of the semiconductor is smaller than the mean free path of phonons and larger than that of electrons or holes



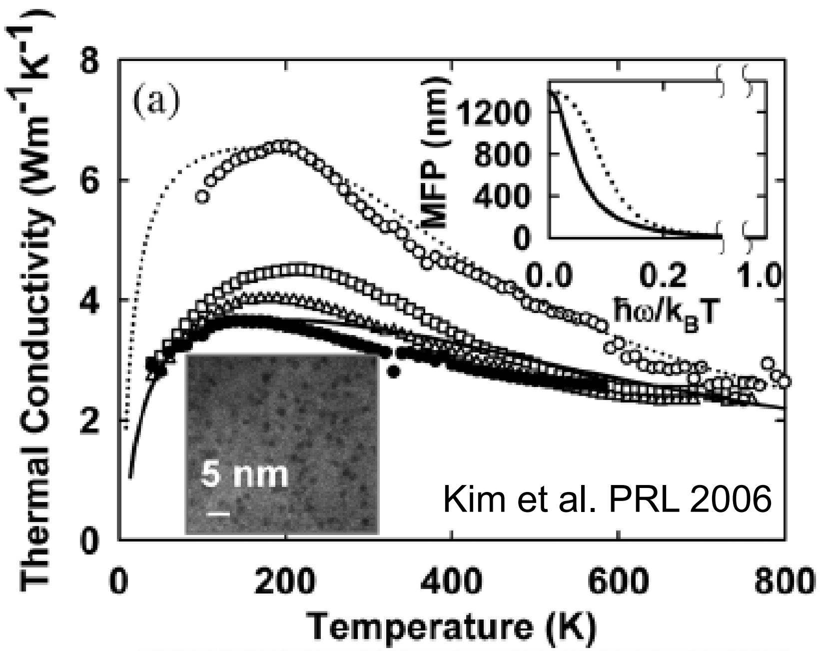



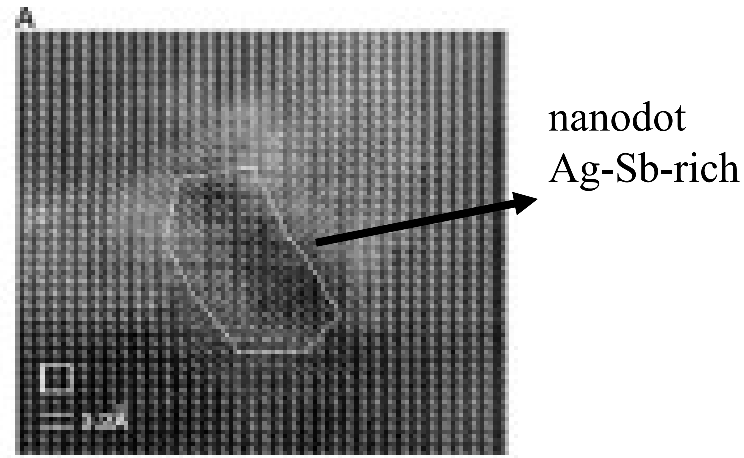


# Embedded nanostructures in semiconductor alloys

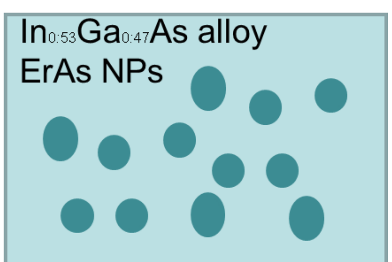
scatter the mid-to-long wavelength phonons more efficiently because the similarity in sizes, reducing $k$ below the alloy limit.




$AgPb_{18}SbTe_{20}$ Hsu et al. Science 303 (2004)




Reduction by 2 below alloy limit



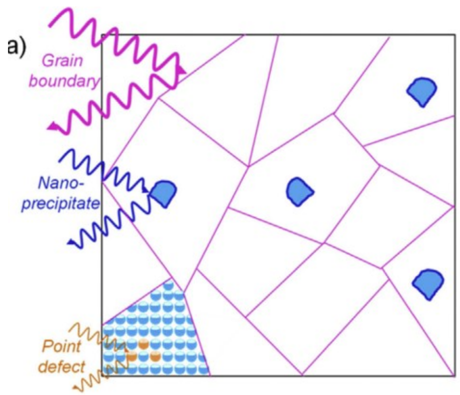

$k_{lat}$ = 1.30 W/mK at 300 K < bulk PbTe

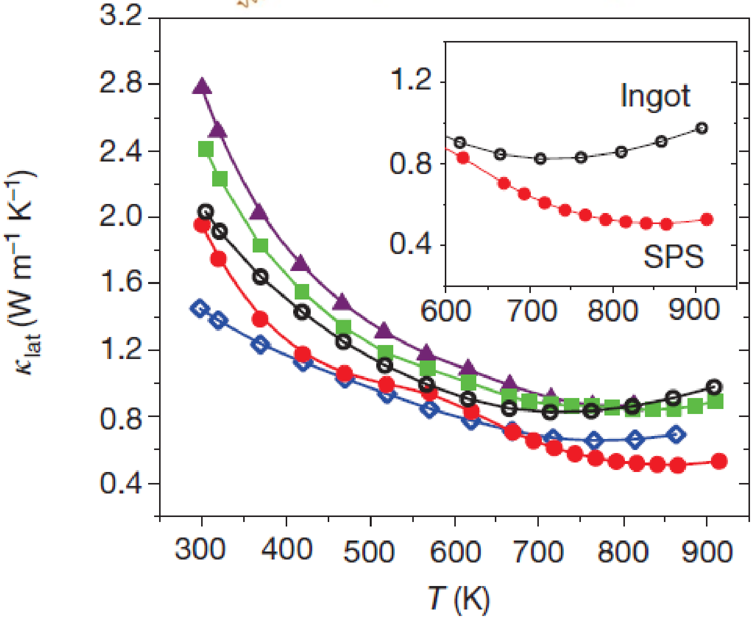
# ALL-SCALE HIERACHICAL ARCHITECTURES

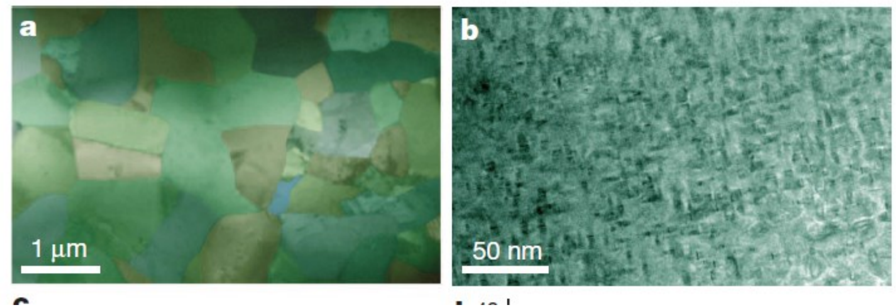
Na-doped PbTe:SrTe at 900 K

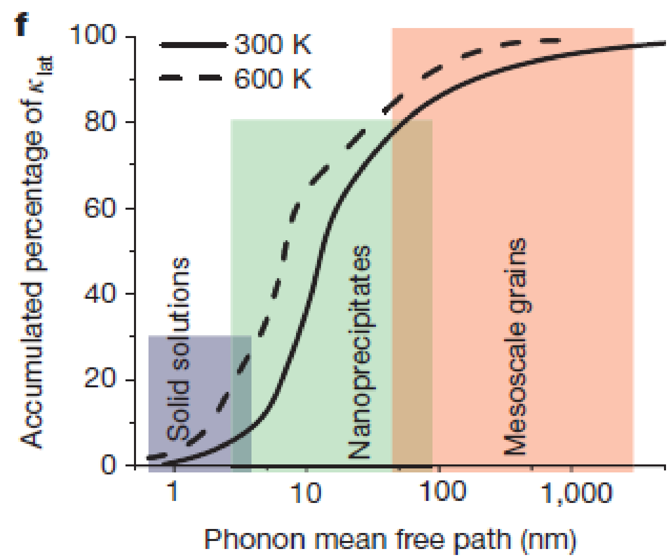
(solid-solution point defects, nm precipitates and gb's) broad spectrum of heat-carrying phonons,

p-type PbTe (doping with Na) nanostructured with SrTe at a concentration of 4 mole % and mesostructured with powder processing and spark plasma sintering



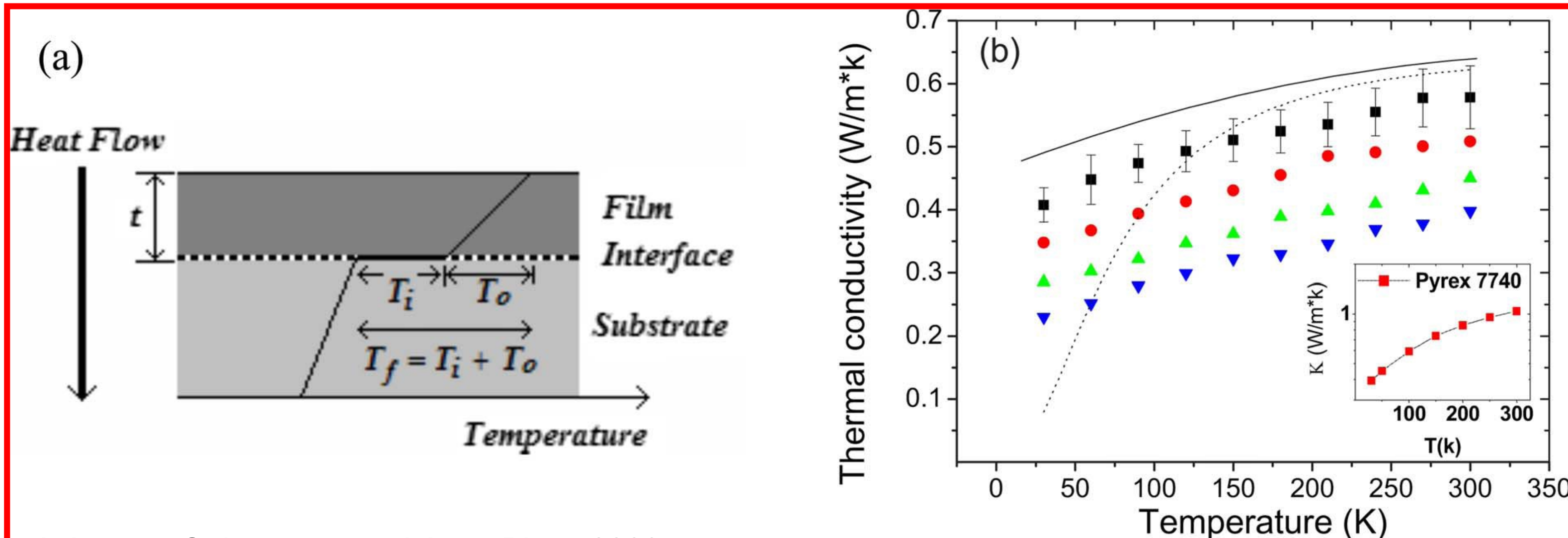




Kanatzidis et al. Nature (2014)

# Below the amorphous limit: Taking benefit of interfaces

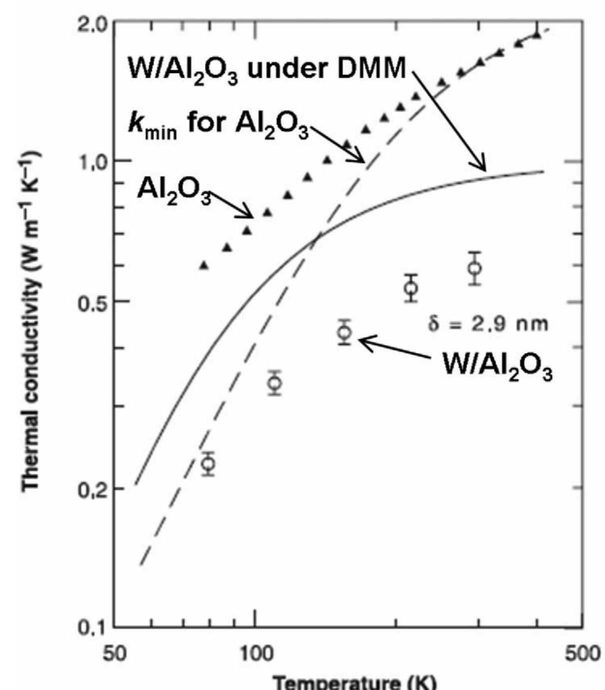



Increasing effect of interfaces

J. Alvarez-Quintana et al. J.Appl. Phys. 2009

$$k_{eff} = \frac{k_{layers}}{1 + k_{layers} \cdot \frac{R_{th}}{t}}$$

W/$Al_2O_3$ nanolaminate with layers few nm thick
and
high density of interfaces has
κ < amorphous limit

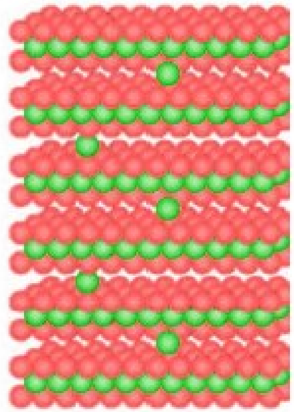



Costescu and Cahill et al. Science 2005

# Ultralow *k* in VdW stacks

Sequential bilayers of W and Se by MBE + 1h annealing for layered $WSe_2$ structure

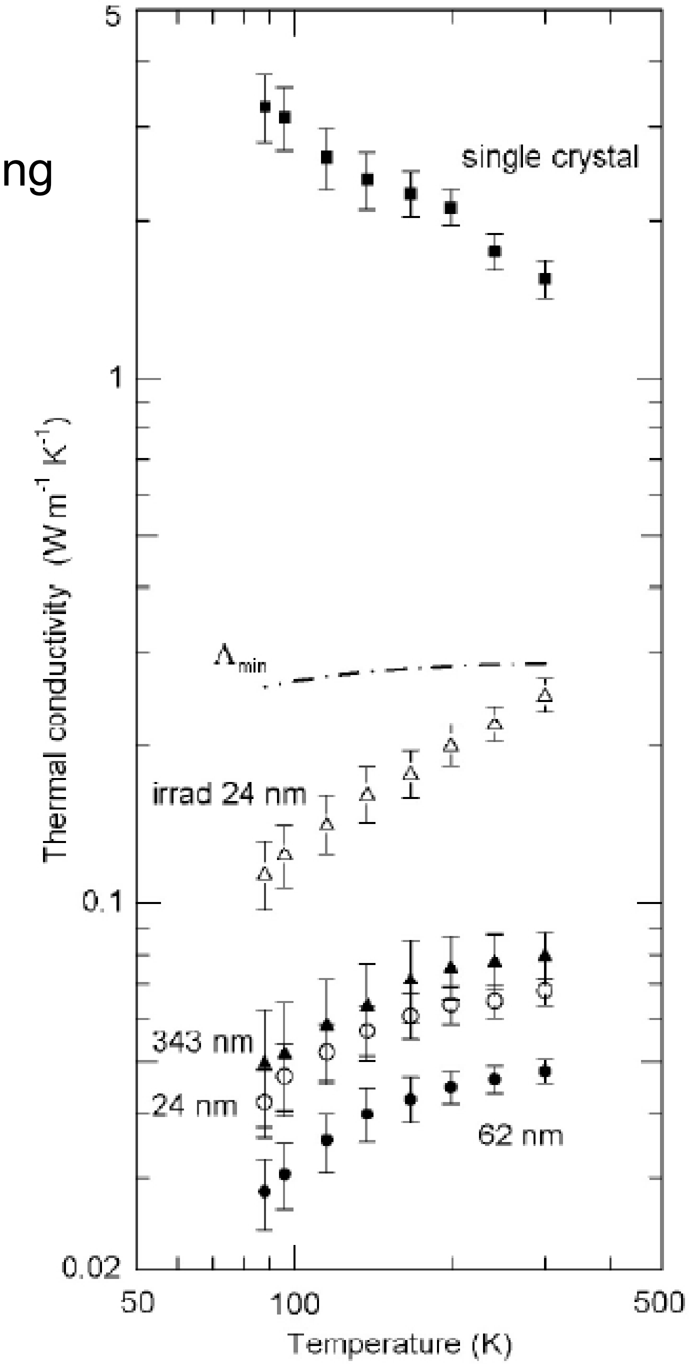
$WSe_2$



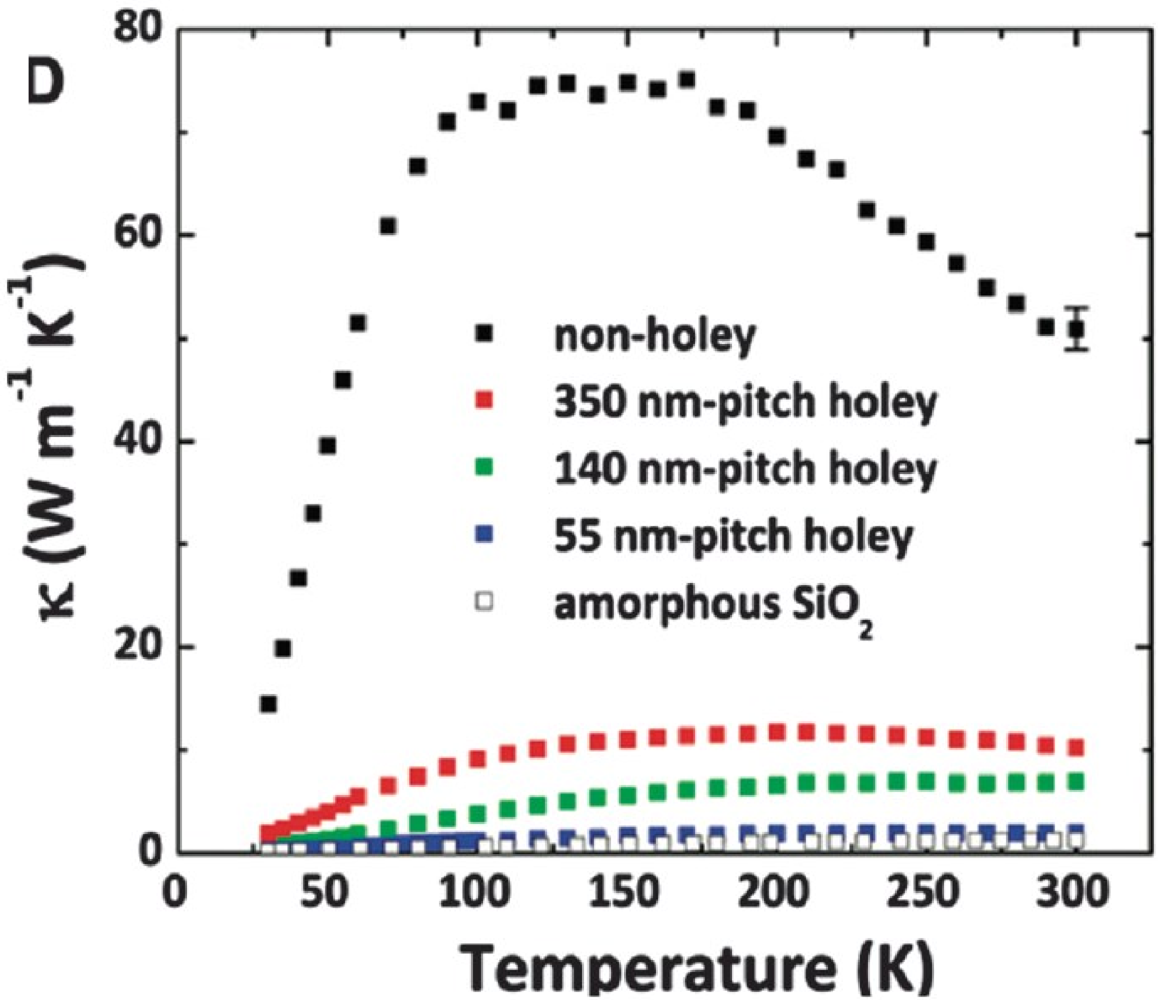
$k$(300K)=0.048 W/mK
6 times smalles than amorphous limit

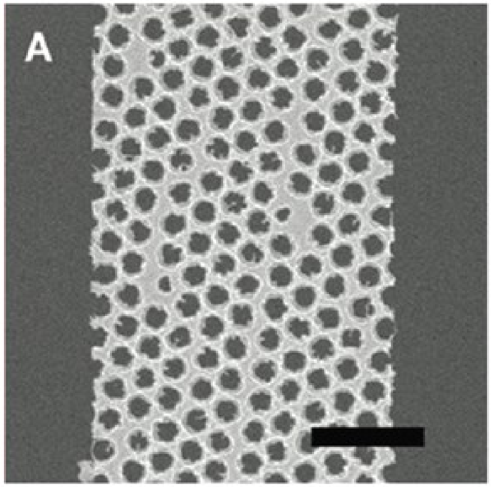
VdW interaction between $WSe_2$ adjacent layers +
+ disorder in c-axis induces phonon localization

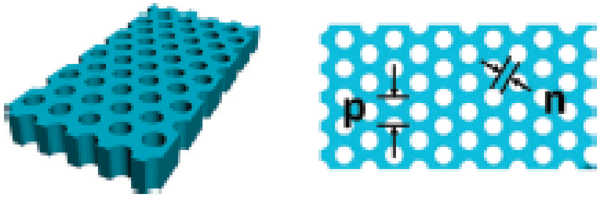
Cahill et al. Science 2007



# Nanostructured material: HOLEY SILICON



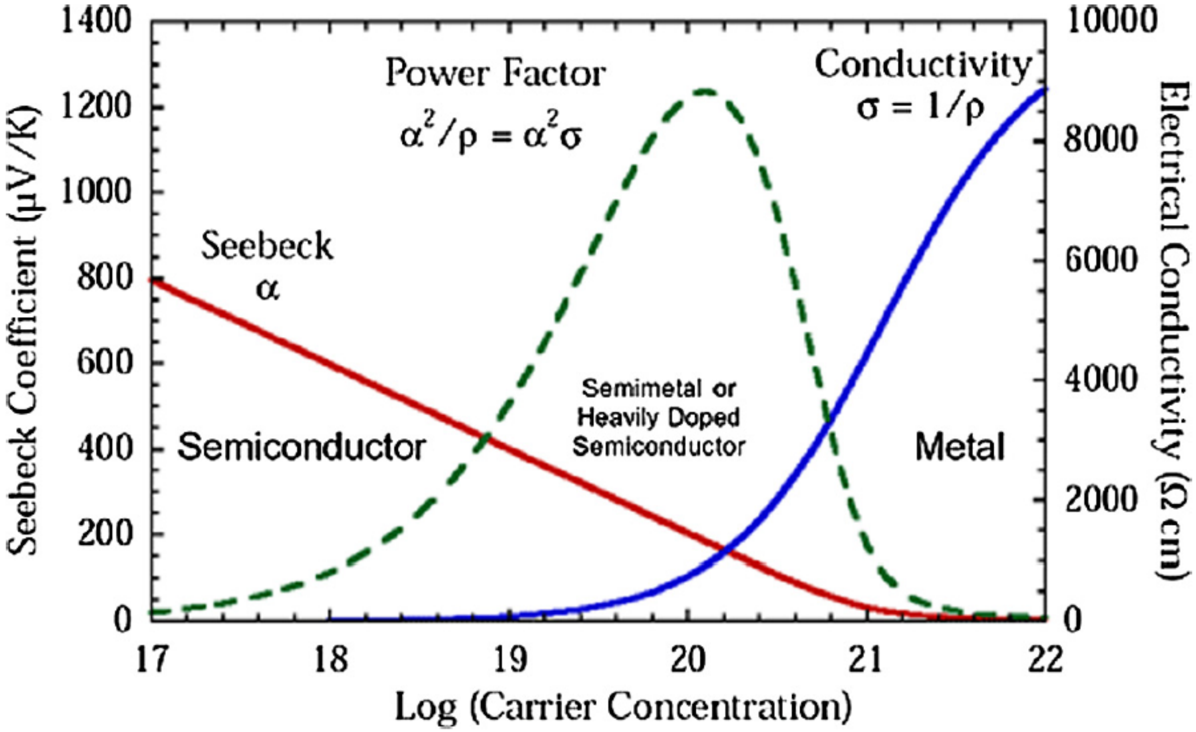




Tang et al. Nano Letters 2010

# Strategies to increase power factor

$$S^2 \sigma$$



# Mott relation

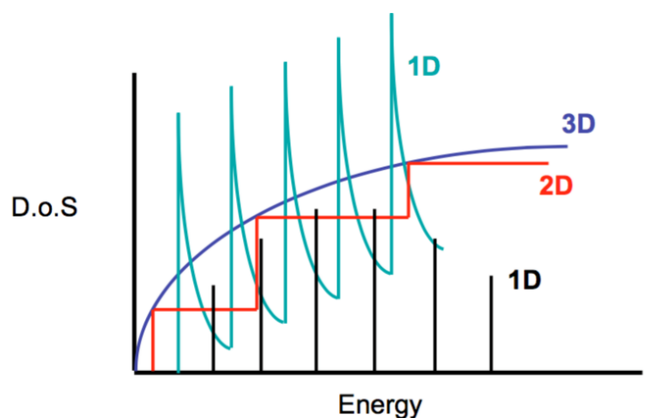
$$S = \frac{\pi^2}{3} \cdot \frac{k_B^2 T}{e} \cdot \left\{\frac{\partial \log \sigma(\varepsilon)}{\partial E}\right\}_{E_F}$$

Any mechanism enhancing ($d\sigma/dE$) will enhance S

(i) increasing the energy dependence of the conductivity close to the Fermi level

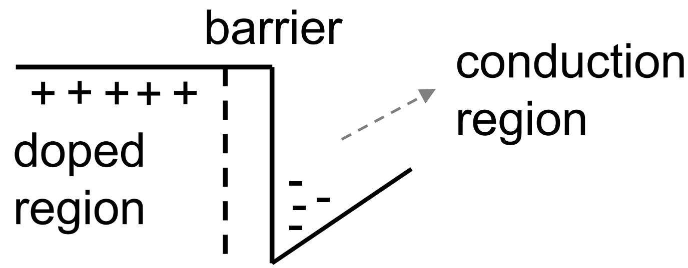
As *σ(E)=n(E)*e*μ(E)* ⟹ Variations of n(E) and mobility μ(E)

(ii) increasing the energy dependence of n(E) can be done by enhancing the energy dependence of DOS on energy, i.e. lowering the dimensionality



# Modulated doping

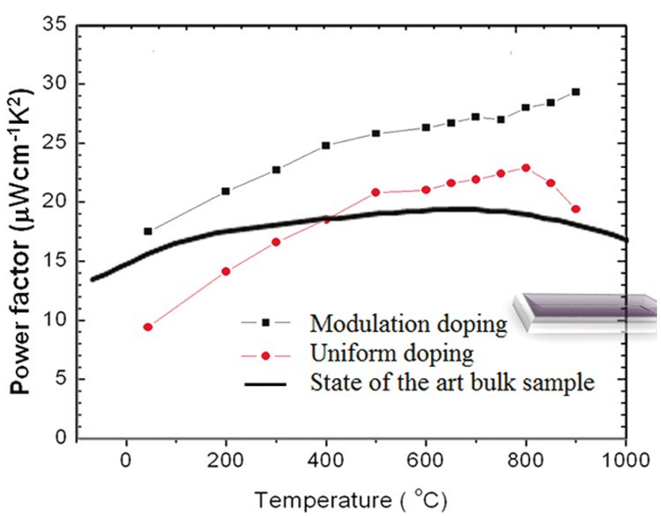
charge carriers are spatially separated from their parent impurity atoms to reduce the influence of impurity scattering increasing the electrical conductivity.

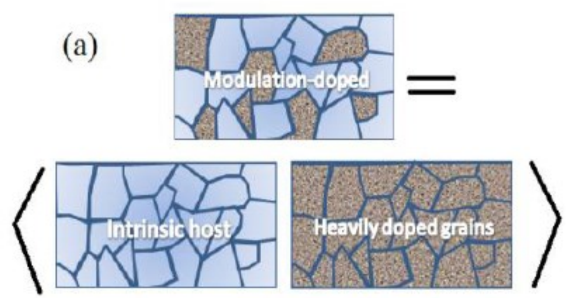



Mixing two types of SC NPs (20 nm):

undoped $(Si_{80}Ge_{20})_{70}$- doped$(Si_{100}B_5)_{30}$ or doped$(Si_{100}P_3)_{30}$

+ Compaction two types of nanoparticles to form a bulk composite.




doping

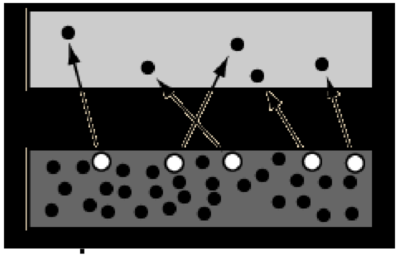
$2.6x10^{20}$ $cm^{-3}$.

Mobility

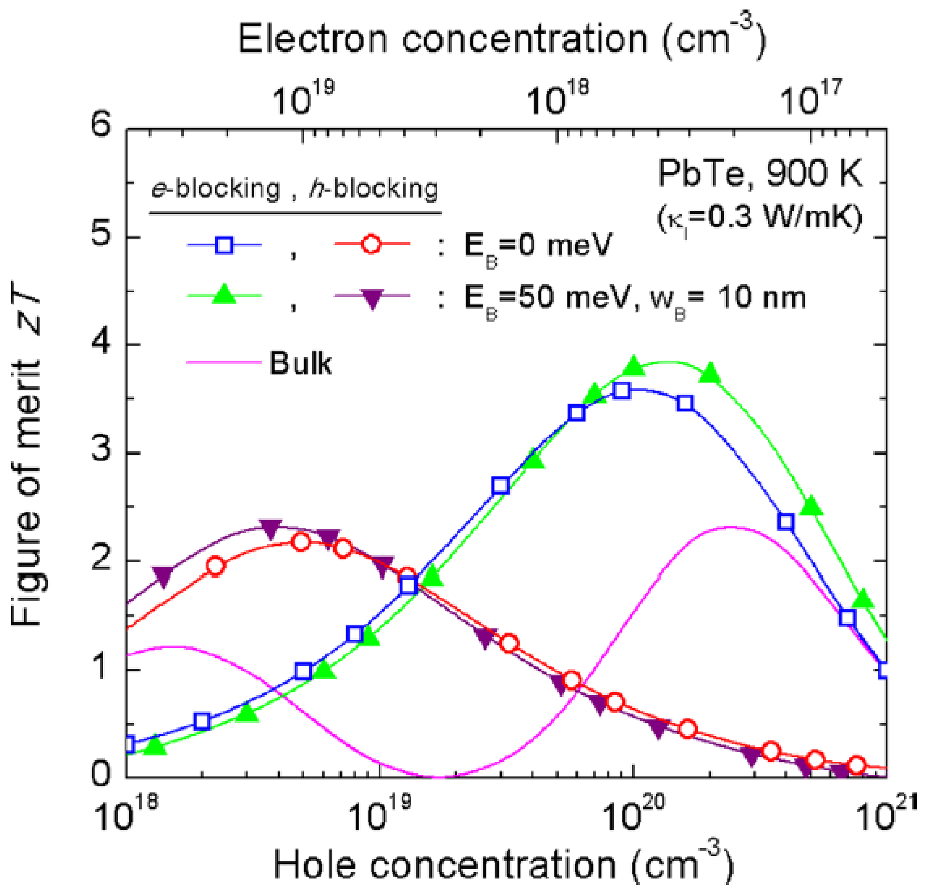
30% > in modulated sample

Zebarjadi et al. Nano Letters 2011

# Energy Filtering (I)   Minority carrier blocking



As T increases bipolar *k* increases lowering S

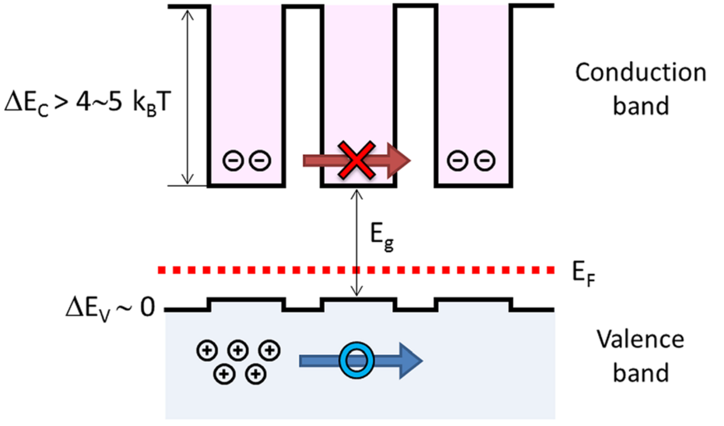



In the intrinsic regime

$$\kappa_{\mathrm{bi}} \propto \exp\left(-\frac{E_g}{2k_BT}\right)$$

## Concept

Blocking minority carriers




SLs or NP embedded in matrix

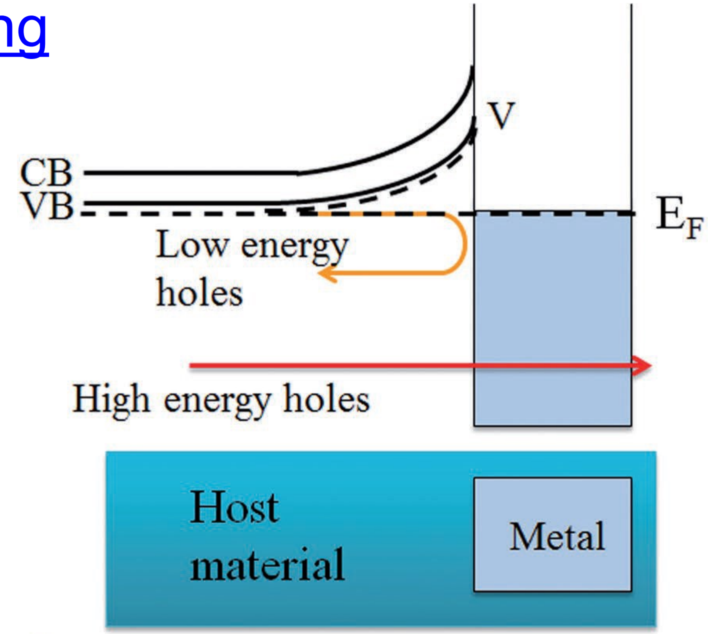
p-type PbTe:SrTe system.

Relevant for small $E_g$ materials at high T

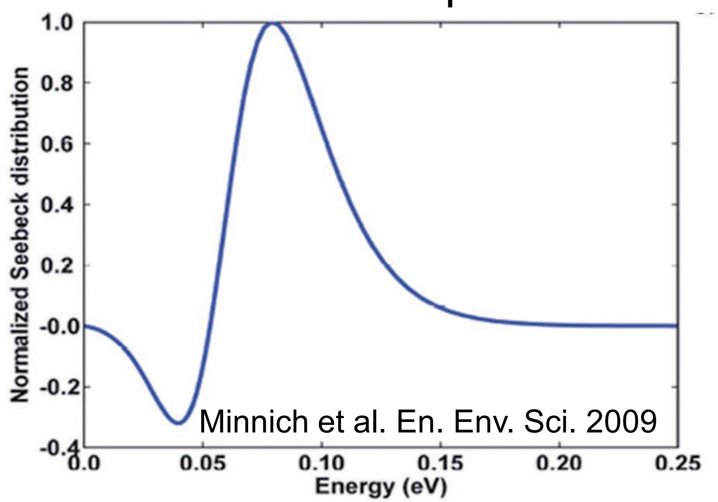
Shakouri et al. APL 2014

# Energy Filtering (II)    Hot carrier filtering

Second-phase NPs or specific barriers (gb & others) can serve as potential barriers that prohibit low energy carriers from passing through the barriers



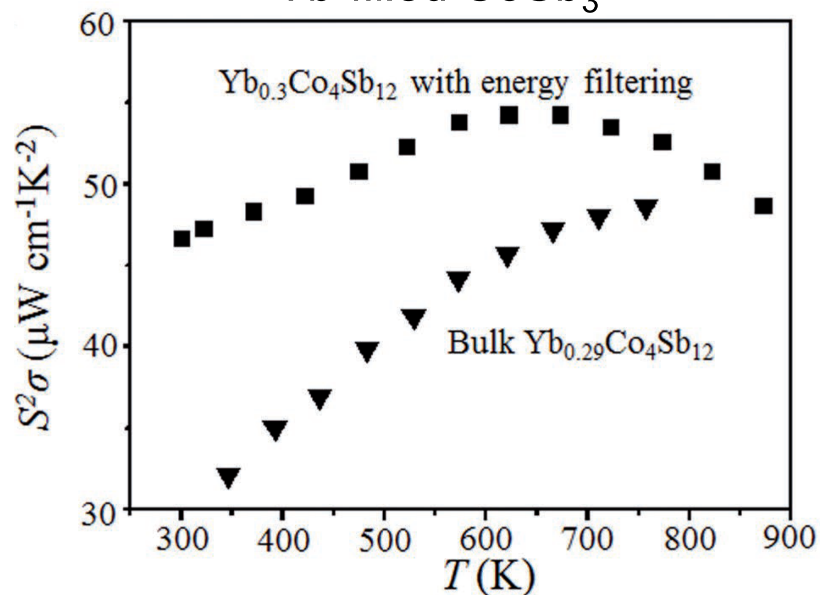

Calculation for p-SiGe




By filtering low-energy carriers average carrier energy increased

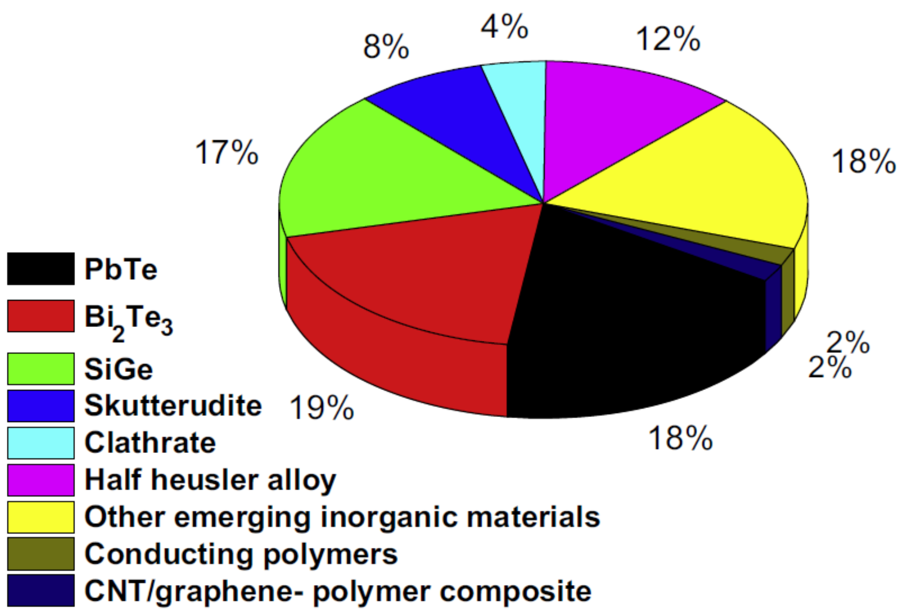
increase Seebeck coefficient

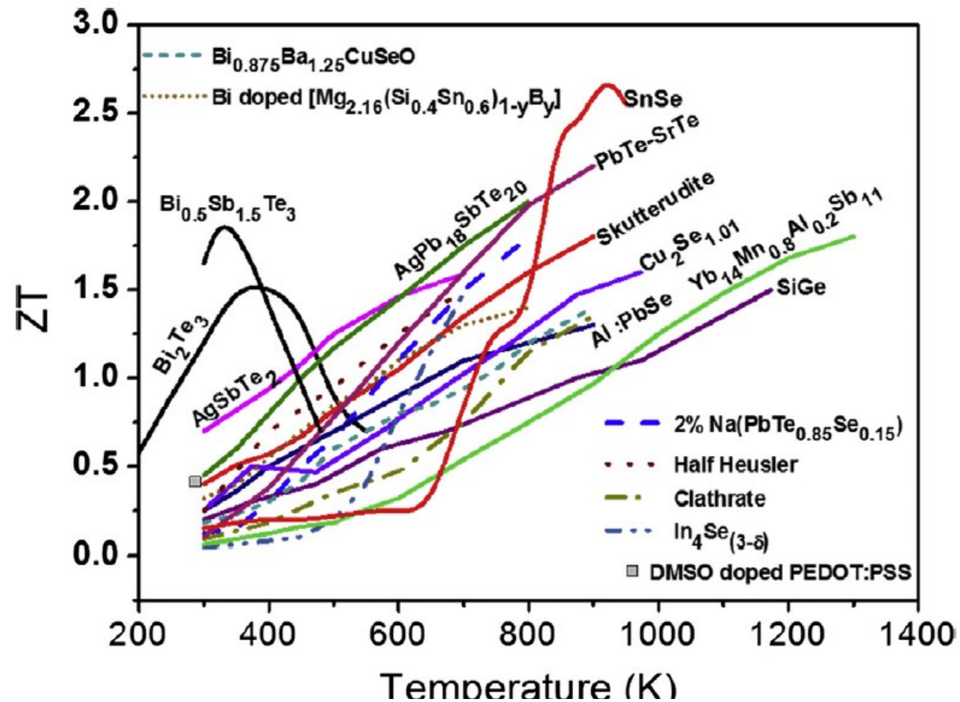
Yb-filled $CoSb_3$

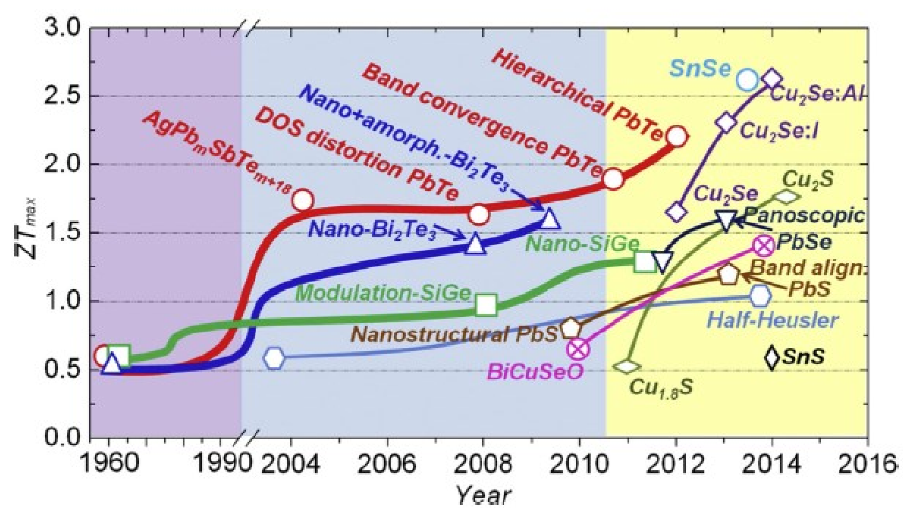


# TE MATERIALS

- Bulk tellurides
- SiGe
- Half-Heuslers
- Skutterudites
- Zintl phases, group 14 clathrates
- Metal oxides
- Nanostructured materials
  - Superlattices



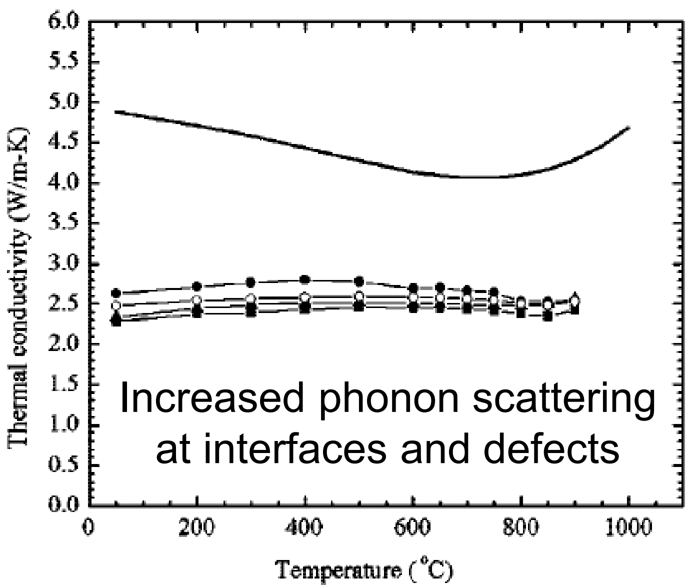

Gayner, Kar, PMS (2016)

# Nanostructured materials. Case of SiGe

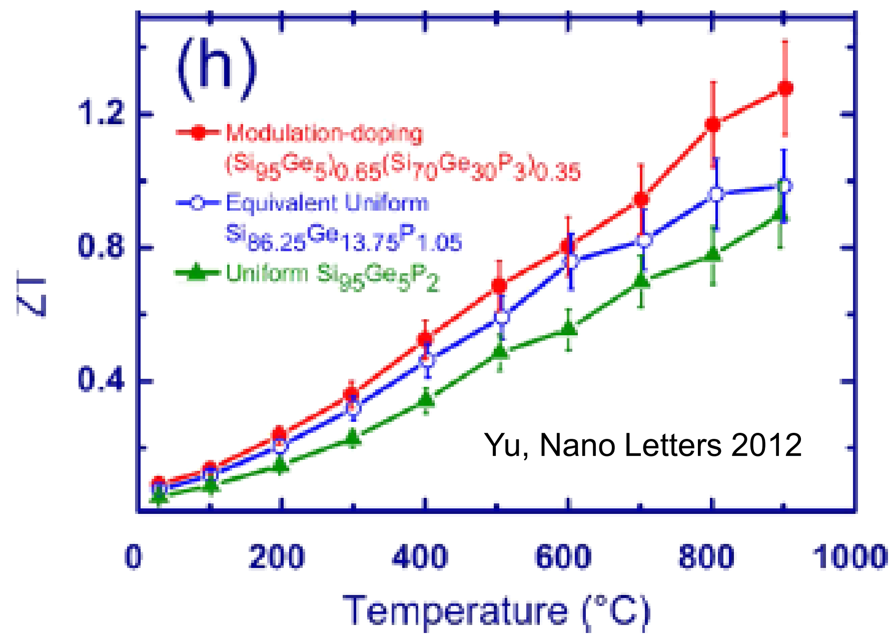
SiGe alloys: traditional material for high T Applications (T>800°C)

Can be doped n- and p-type enabling complete TE devices in one platform

Fabrication: BM + HP




$Si_{80}Ge_{20}$ with grain sizes about 20 nm




n-type ZT up to 1.5 at T=1173 K
p-type ZT up to 0.95

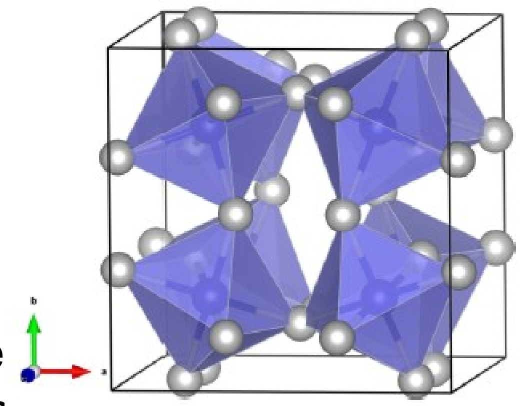
Increase ZT is a general feature in nanograin materials

Joshi et al. Nano Letters, 2009

# Skutterudites

"skutterudite" refers to naturally occurring mineral $CoAs_3$, first discovered in Skutterud, Norway.
Cubic structure composed of 32 atoms per unit cell

$CoAs_3$ exhibits a distorted version of the $AB_3$-type perovskite structure, that is, MX3 (M = Co, Rh, Ir is a group 9 transition metal and X a group 15 nonmetal P, As, Sb), with an octahedral structure and a void at its center.



$CoSb_3$ ($Im$-3)

**Key aspects:**

Filling the void fulfills PGEC-concept such as in $CeFe_4Sb_{12}$

The void-filling atom can act as an electron donor or electron acceptor.
Strong phonon scattering centers reduce *k*.

Good thermal and mechan. properties of both n- and p-type operating at medium T

| Material | | n/p | $ZT_{MAX}$ | Typical operating $T$ (°C) | Max operating $T$ (°C) |
|---|---|---|---|---|---|
| $CoSb_3$ | PF=6.5 μW/cmK$^{-2}$, k=10 W/mK | n | 0.8 | 500–600 | 700 |
| $CeFe_4Sb_{12}$ | | p | 0.8 | 500–600 | 700 |

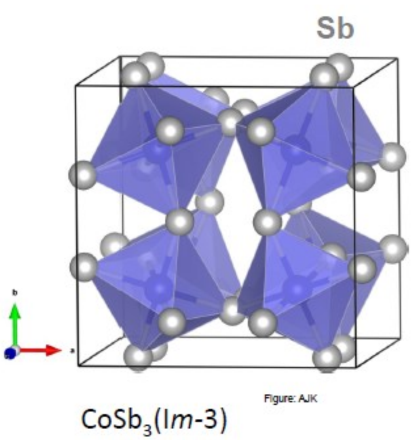
# Skutterudites

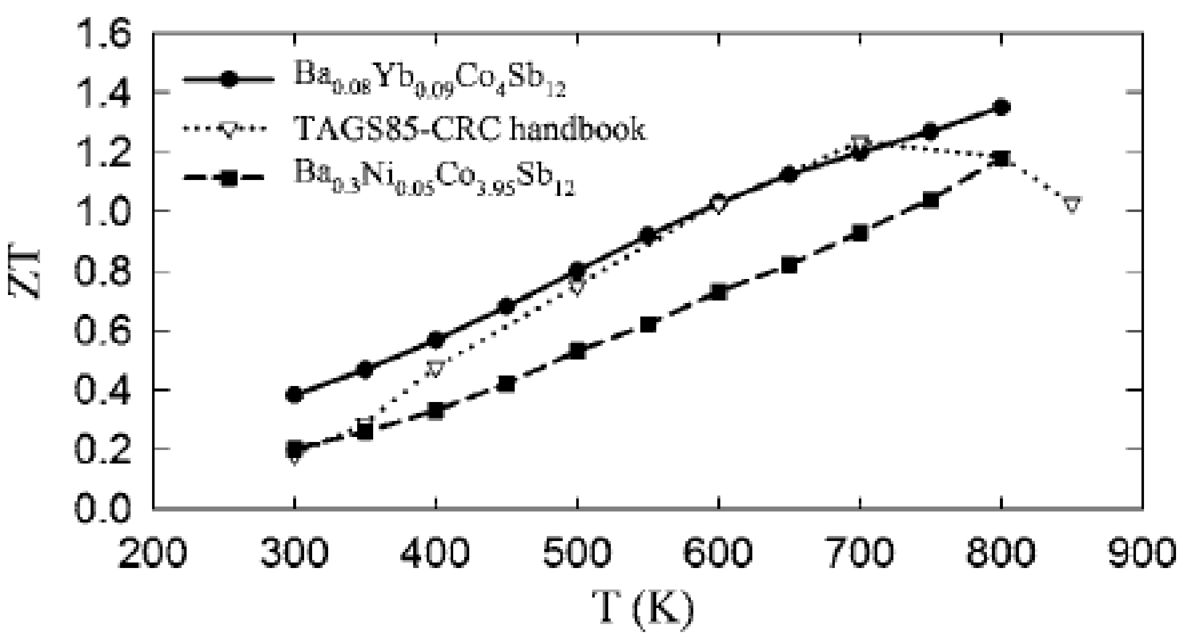
**Multiple filling of voids**

A ZT value of 1.36 is obtained for n-type $Ba_xYb_yCo_4Sb_{12}$ at 527 C.
The multiple-filled skutterudite $Ba_{0.08}La_{0.05}Yb_{0.04}Co_4Sb_{12}$ exhibits a ZT of 1.7 at 577$^o$C.

Filler ions form phonon resonant scattering centers with its own frecuency.

Multiple choice of filling atoms facilitates that different normal mode phonons of the lattice can scatter with the filler decreasing k



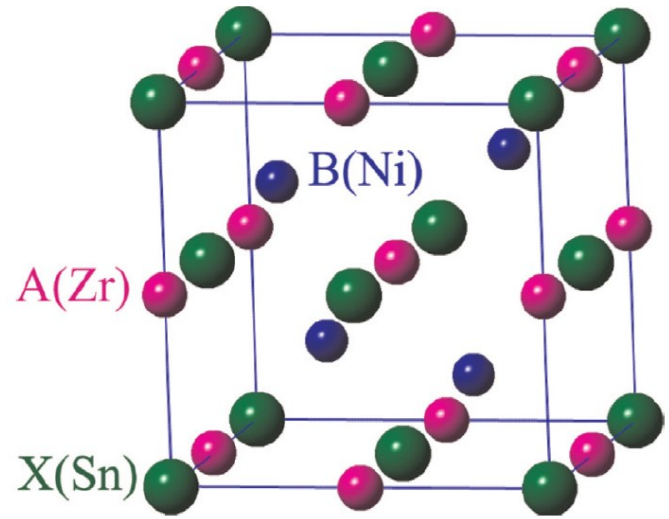

Shi et al. APL 2008

# Half-Heusler alloys (potential for high T)

Intermetallic phases with formula ABX formed by 3 interpenetrated fcc sublatices and one vacant sublattice

MCoSb and MNiSn with M=Ti, Zr, Hf

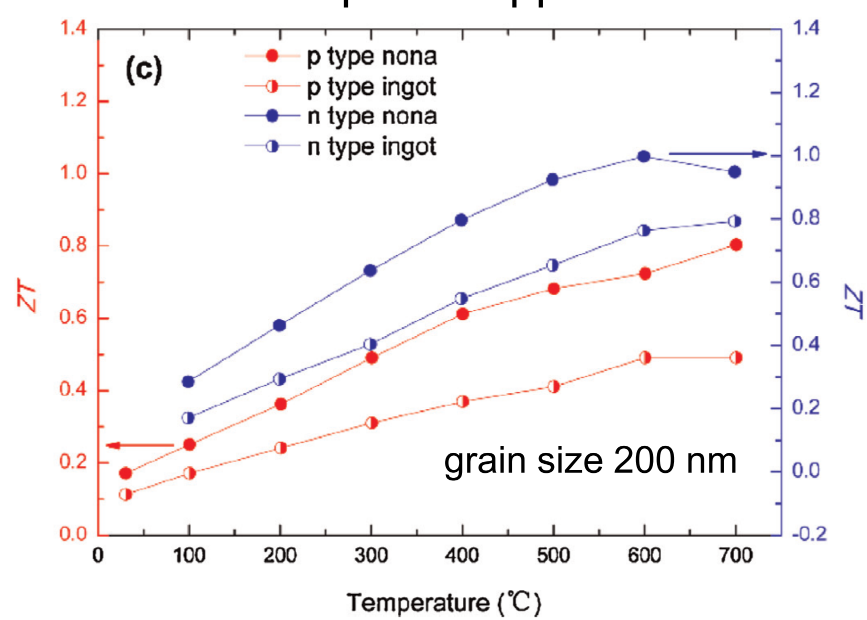
high S, high σ, high *k*




Substitution of A,B sites to reduce k due to mass fluctuations and strain fields

Substitution of X sites to tune carrier density and therefore increase σ

Nanocomposite approach in HH




$k_{lat}$ decreases 30% for p-type $Hf_{0.5}Zr_{0.5}CoSb_{0.8}Sn_{0.2}$

$k_{lat}$ decreases 25% for n-type $Hf_{0.75}Zr_{0.25}NiSn_{0.99}Sb_{0.01}$

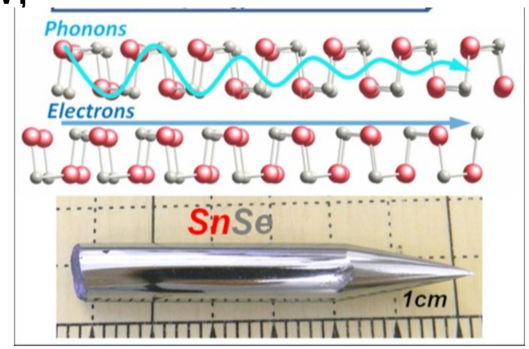
Hf and Ti reduces *k* compared to Hf and Zr

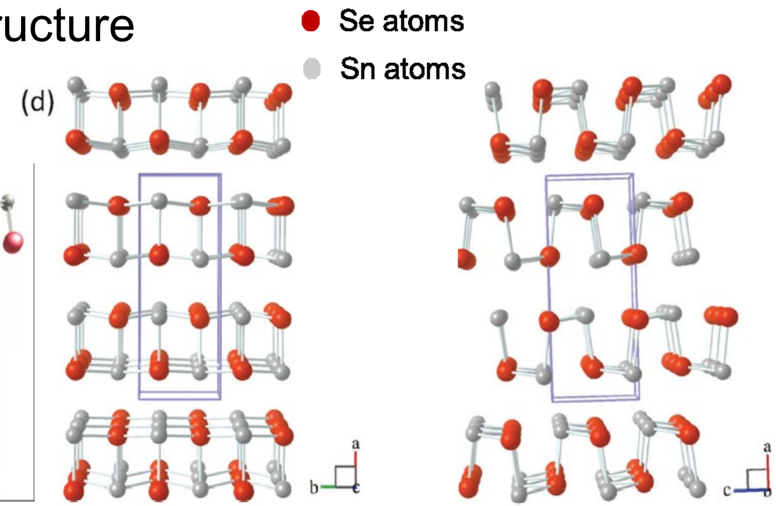
# Single-Crystal SnSe

ZT=2.6 at 973 K

Simultaneous low k and higher power factor

Orthorombic structure

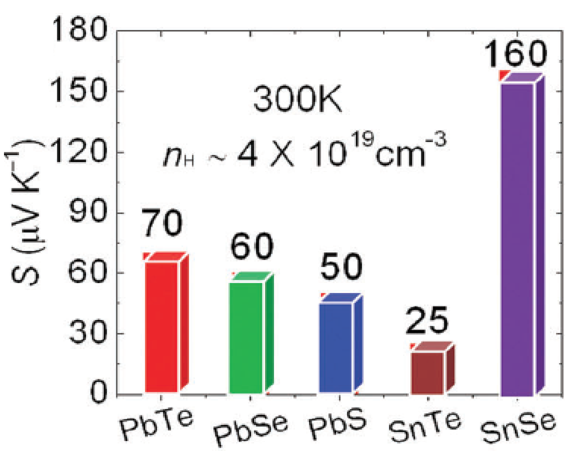


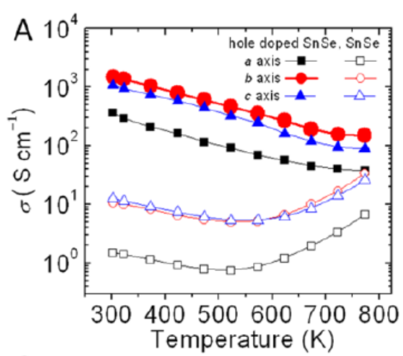




SnSe does not have high MW, nanostructuring, a complex crystal structure or a large unit cell.

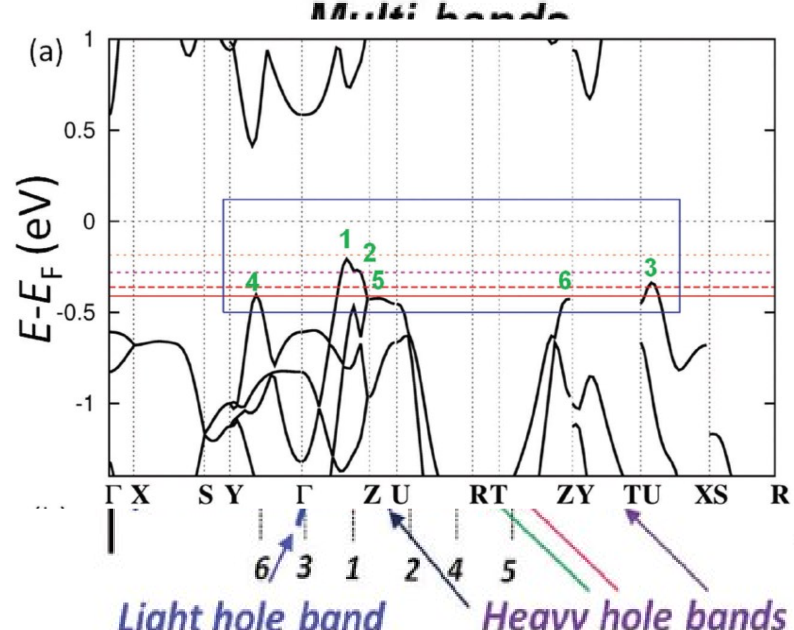
Power factor increase to 40 μW $cm^{-1}$ $K^{-2}$

$$S = \frac{\pi^2}{3} \cdot \frac{k_B^2 T}{e} \cdot \left\{ \frac{\partial \log \sigma(\varepsilon)}{\partial E} \right\}_{E_F}$$



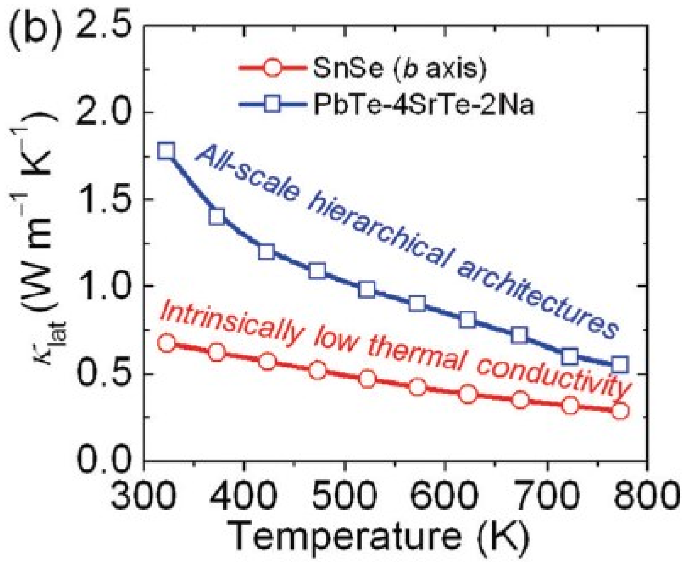

Complex electronic structure

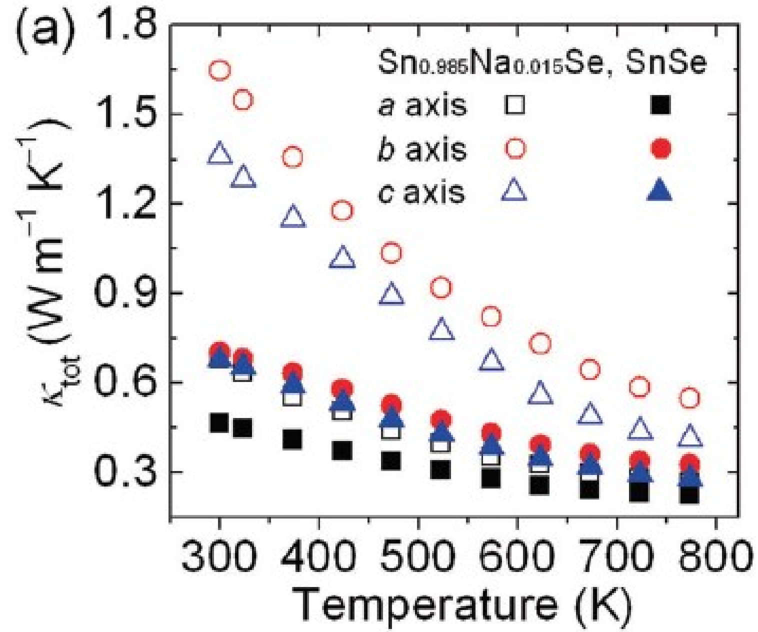



Zhao et al. Nature 2014, Science 2015 and En. Environ. Sci. (2016)

# Single-Crystal SnSe

Low lattice thermal conductivity (SnSe)

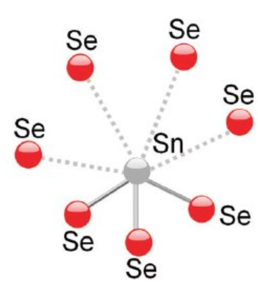


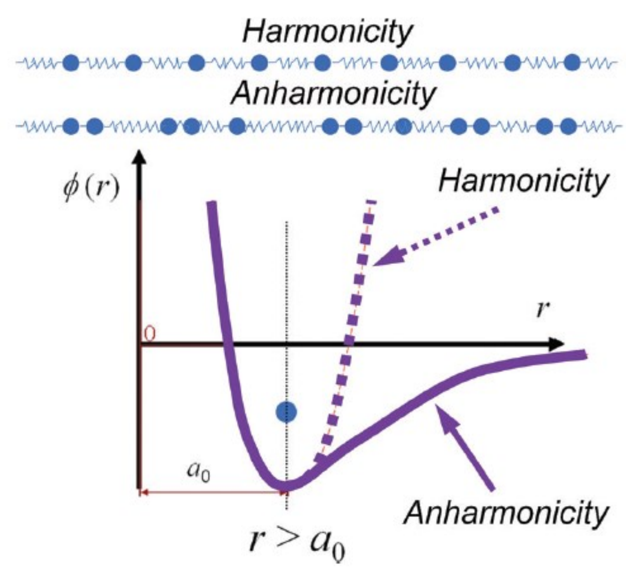




Low value of k partly comes from the 2D nature of the material
but other effects should be invoked

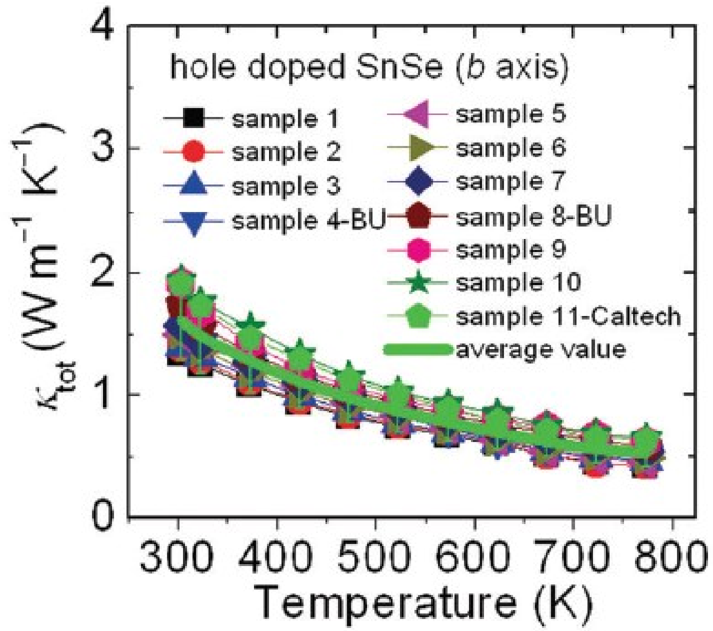
High anharmonicity results in strong ph-ph scattering reducing *k*

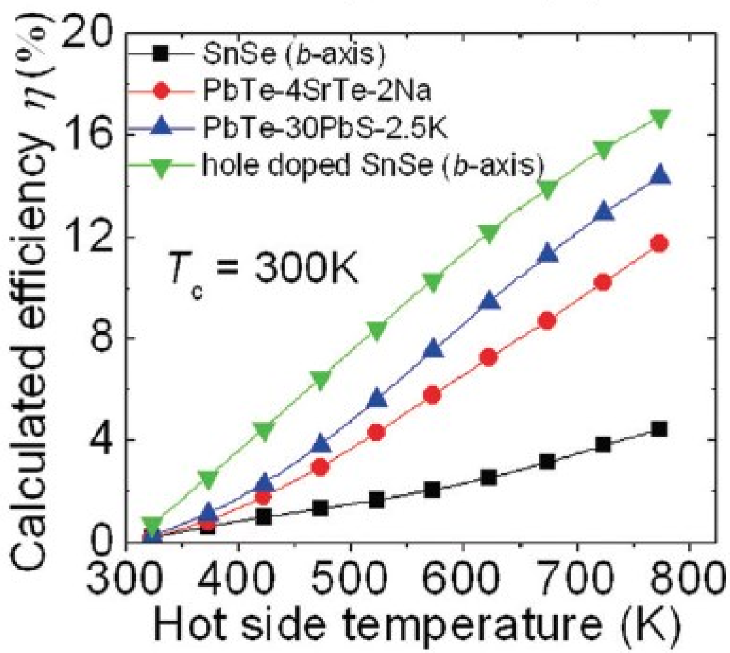
Heavily distorted SnSe7 polyhedra



# Single-Crystal SnSe

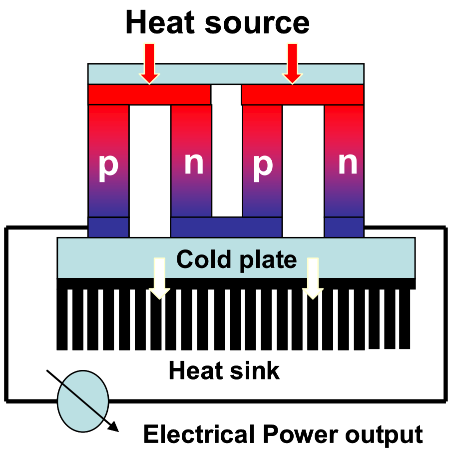


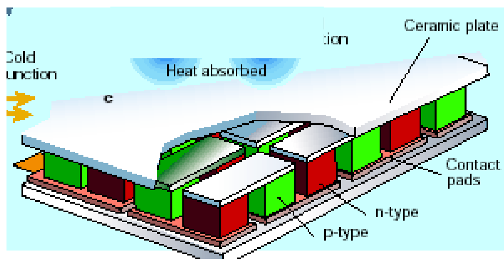



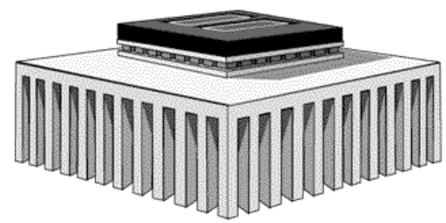

The physics of thermal and charge transport in SnSe is unusual and fascinating. The high thermoelectric performance of SnSe crystals suggests that single phase materials with strongly anharmonic bonding and ultralow thermal conductivity are promising candidates for achieving high thermoelectric performance.

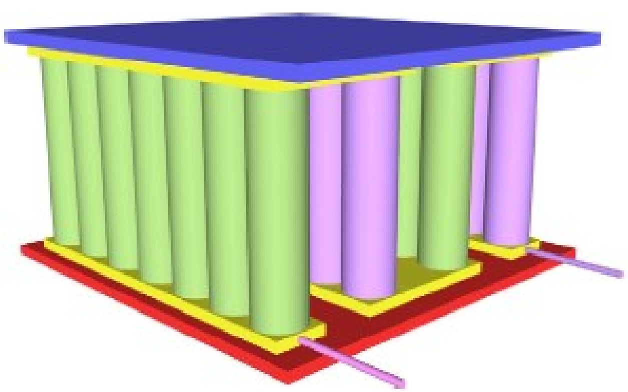
# APPLICATIONS

TE generators: Set of n,p legs electrically connected in series and thermally in parallel



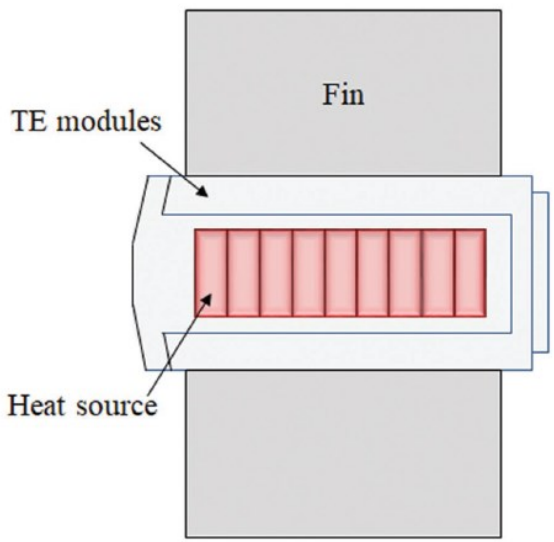



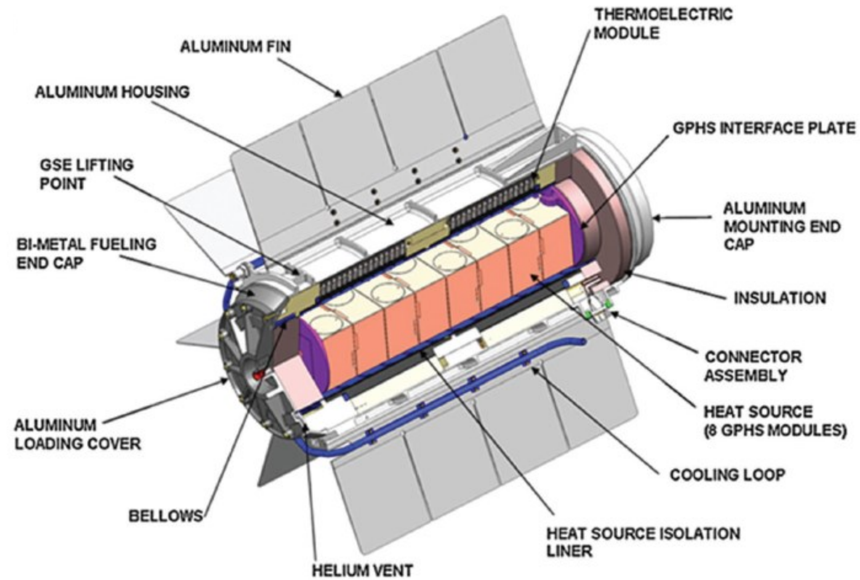





Apart from thermoelectric materials, contact materials also play a key role in TE devices. The semiconductor–metal junction exhibits a greater electrical resistance than a metal–metal junction, which affects the performance of the device

# Radioisotope thermoelectric generators, RTGs

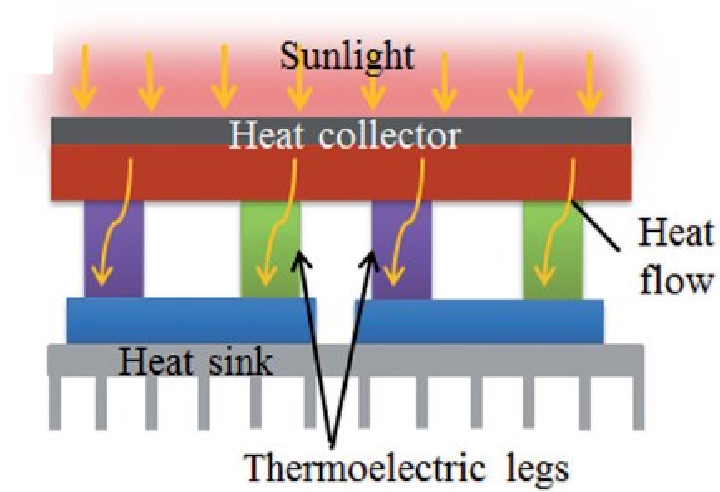


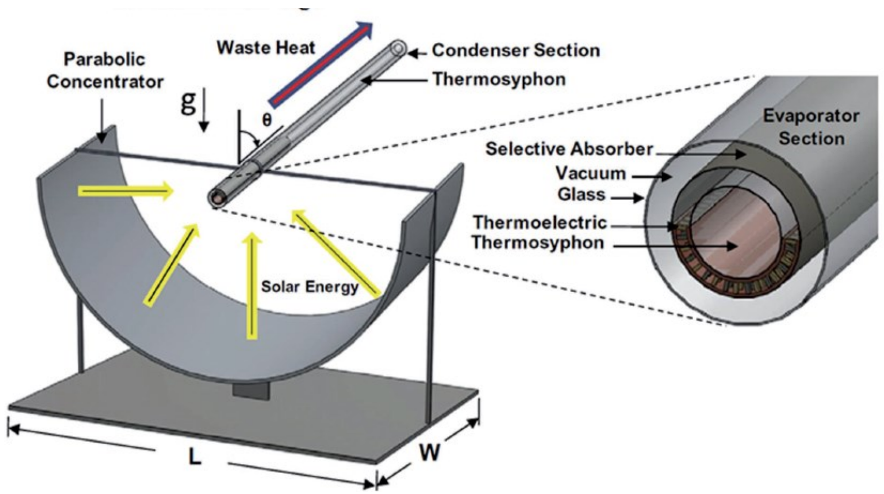




Yang, Adv. Energy Mat. 2017

ZT of 0.5 (p-type) and 0.9 (n-type)

# Solar Thermal Power Generation (STEG's)

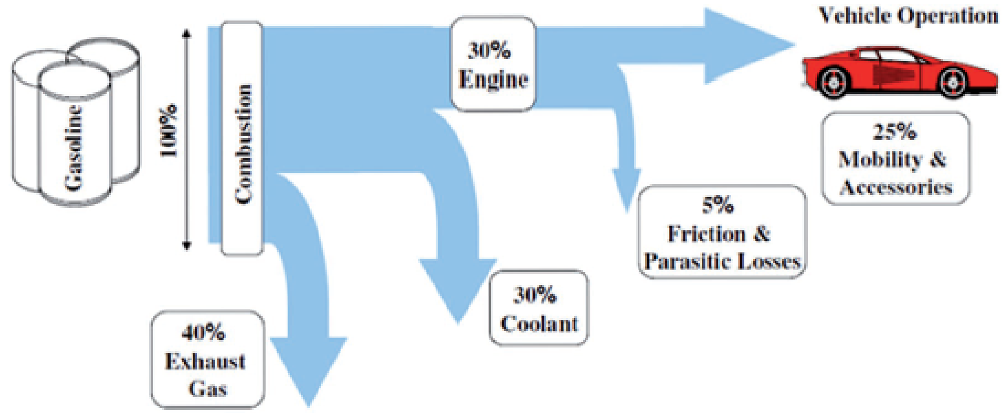


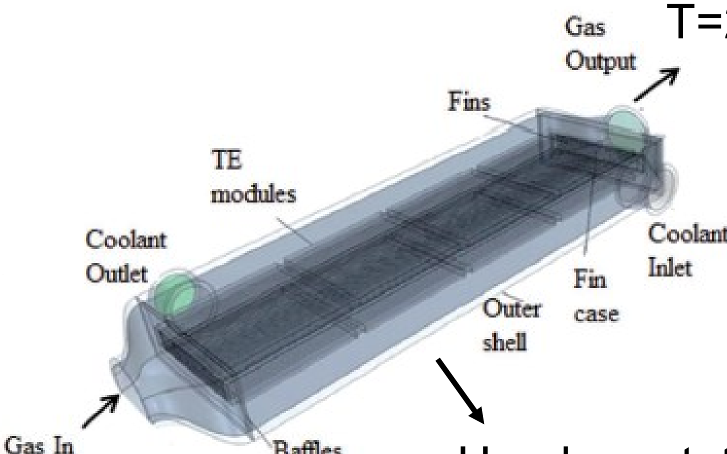

| Materials | | $\Delta T$ [K] | $N$[a)] | $P_{max}$[b)] [W] | $\eta_{max}$ [%] |
|---|---|---|---|---|---|
| p-type | n-type | | | | |
| Bi–Te alloy | Bi–Te alloy | 92 | 6 modules | 4.7 | 1.2 |
| $(Bi_2Te_3)_f$(CdTe) core–shell nanostructured thin film | | | | 16.66 mA $cm^{-2}$ | 4.8 |
| $Bi_{0.5}Sb_{1.5}Te_3$ thin film | $Bi_2Te_{2.7}Se_{0.3}$ thin film | 100 | | $80 \times 10^{-6}$ | |
| Commercial GM-200-127-14-16 | | ≈10 | 127 | $4.7 \times 10^{-3}$ | 0.23 |
| TGM-127-1.4-2.5 | | 155 | | 3 | 4 |

Yang, Adv. Energy Mat. 2017

# AUTOMOTIVE TEG's


T=200°C




T=800°C

Still in concept stages

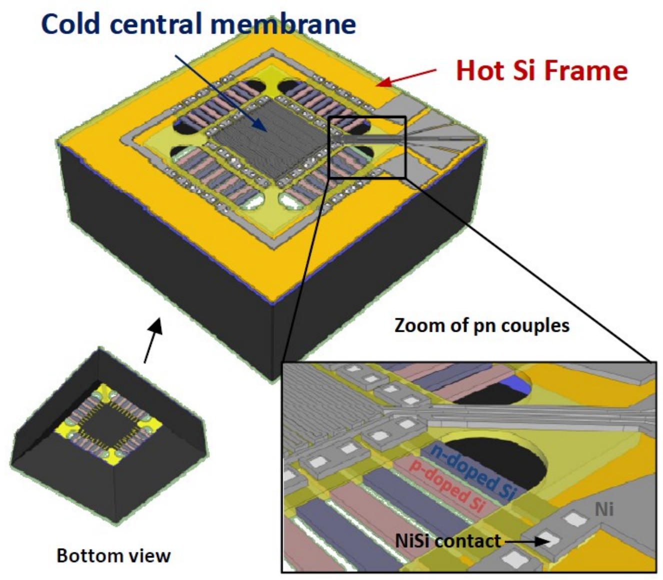
Goal total of 750 W from 20 W TEGs

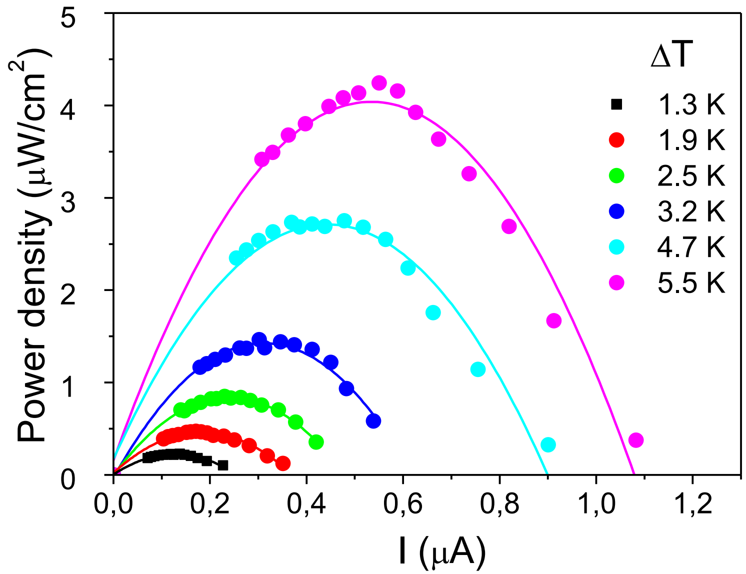
400 W with 4.6 kg of TE material

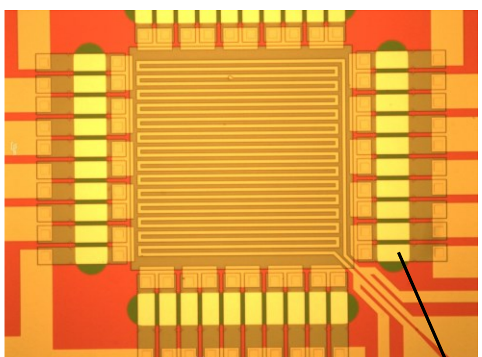
Honda prototype with líquid cooler gives 500 W
32 30 mmx 30 mm TEGs

Orr et al. App. Thermal Eng. 2016

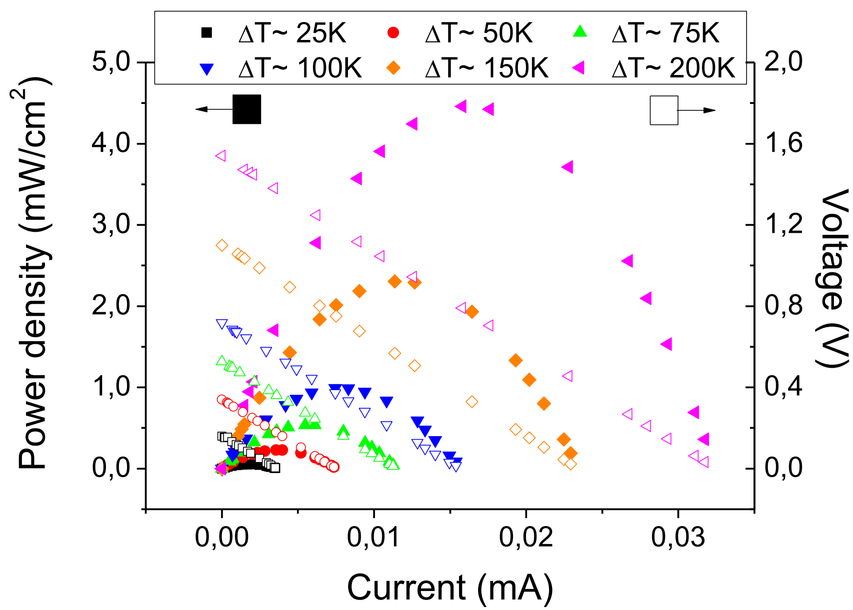
# Microthermoelectric TE-based generators/sensors



UAB, Nano Energy 2015



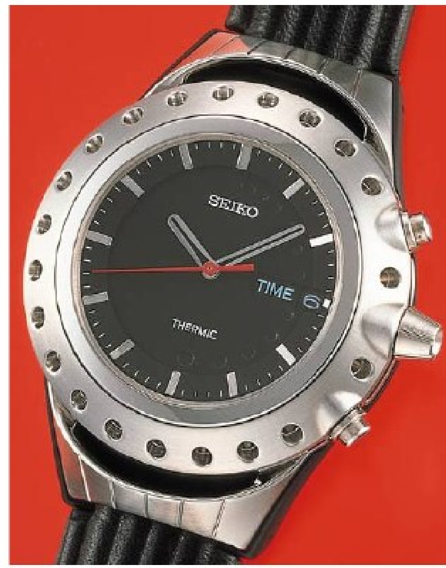

Size: 3x3 $mm^2$

Low-d Si thermopiles

# Low Power: using body heat

## Thermoelectric watch

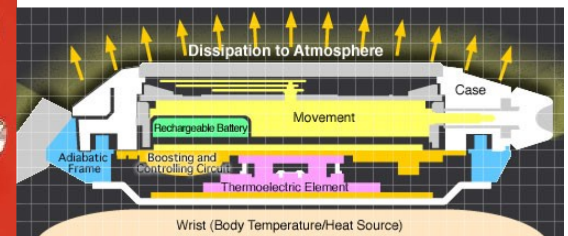

Bulova Thermatron (1982). Unreliable technology. The company went bankrupt.

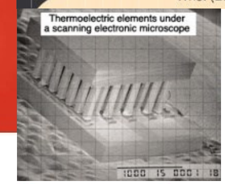



Seiko Thermic

http://www.watchonista.com/2914/watchonista-blog/news/bulova-thermatron-%E2%80%93-thermal-revolution

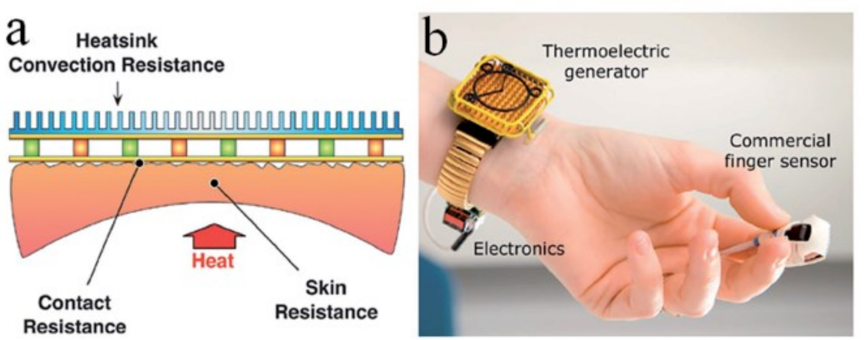
Seiko Thermic (1998). This one actually worked. The watch still needs a battery.



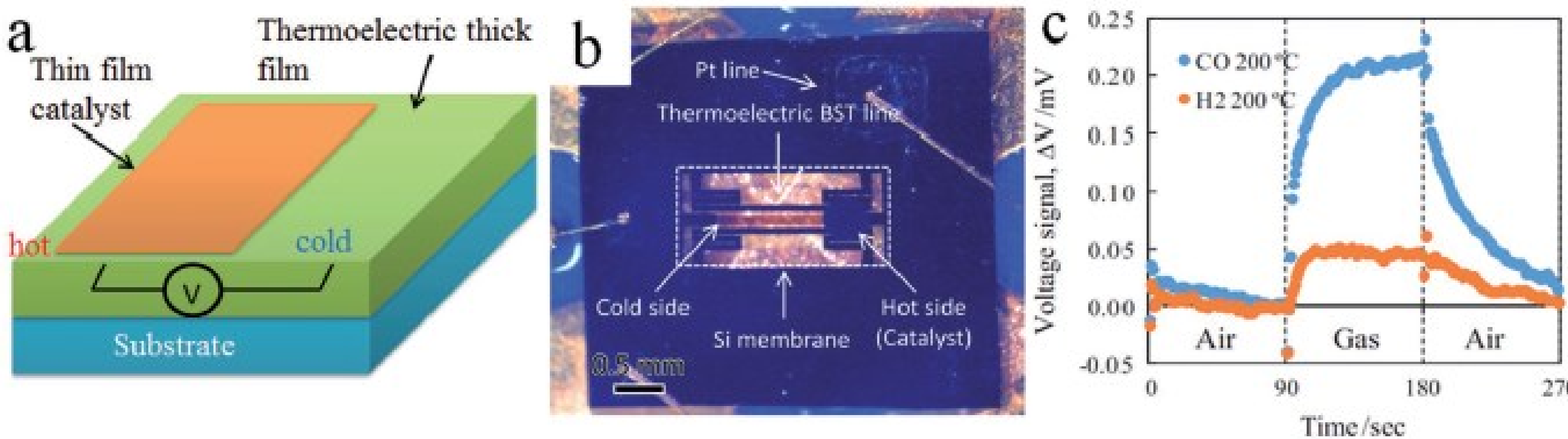

TE watches refuse to die: MATRIX PowerWatch crowdfunded at Indiegogo (2016)

https://www.indiegogo.com/projects/smartwatch-powered-by-you-matrix-powerwatch-watch-fitness

# SENSING APPLICATIONS

## Detecting heat signals from catalytic reactions



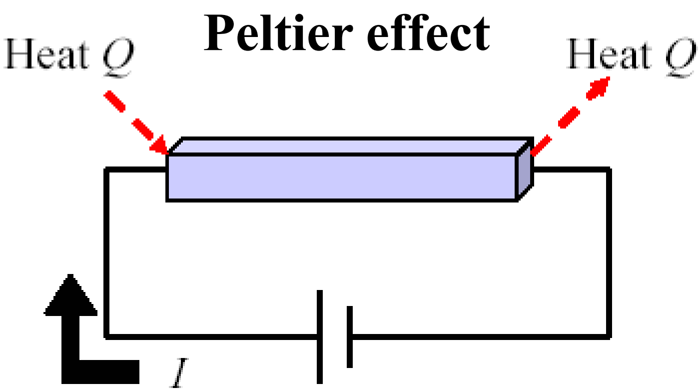

Pt thin film acts as a catalyst for the reaction with $H_2$, releasing heat amd creating a T difference

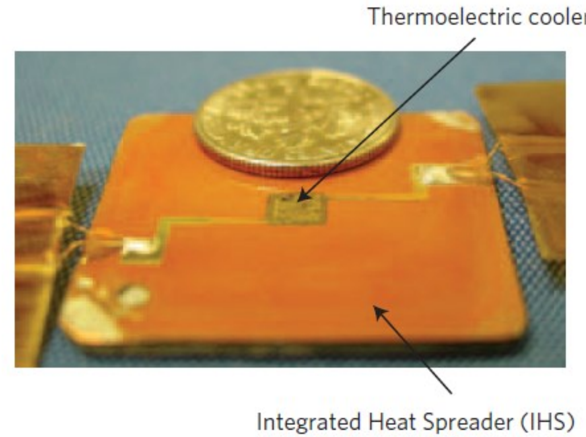
Good sensitivity and short response time

Other catalyst can be used for other gases

Yang, Adv. Energy Mat. 2017

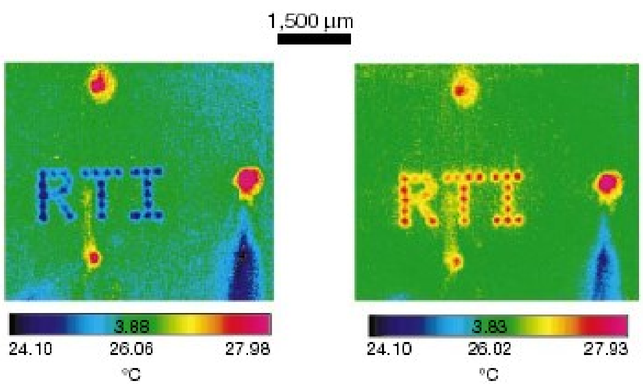
# On-chip cooling using SL's



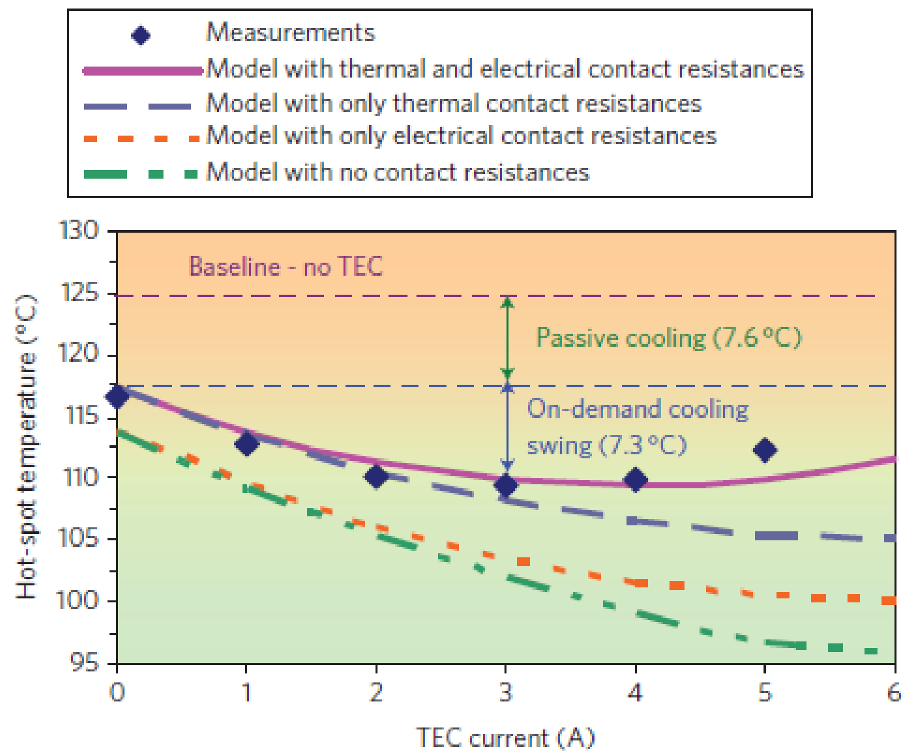




Creation of a heat difference from an electric voltage

$\Pi = Q / I$ Heat carried by carriers




Venkatasubramanian et al. Nature, (2001) 597-.




Choudhury et al. Nat. Nanotech 2007

# Thermoelectric refrigerators

- Electric current generates a temperature gradient
  - Can be used for cooling (or heating!)
- Thin-film Peltier coolers do actually possess high cooling power densities
- They can be utilized in scenarios where compressor-based cooling is impossible

Figure: alphageek.fi

USB-powered Peltier refrigerator

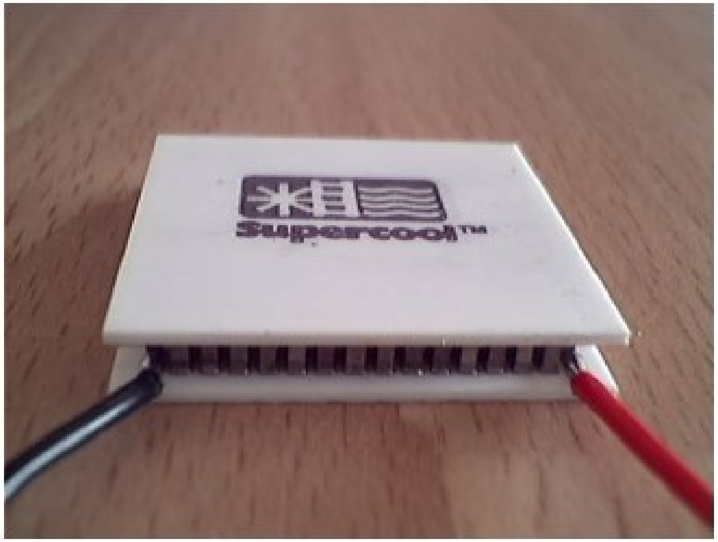



Figure: blog.novaeletronica.com.br

# CONCLUSIONS

- Reducing k below the alloy limit may require new strategies such as reduction of the phonon group velocity or reducing the number of phonon modes that propagate.
  Anharmonicity may play a significant role for decreasing $_k$.

- Many of strategies to increase ZT. However, ZT above 3 in both n- and p-type materials (required for some dreamed applications of energy harvesting) still far to be realized.

  Still PLENTY of ROOM for IMPROVEMENT

- In spite of this there are many opportunities for low-power applications to power sensor or low-consumption devices.

THANK YOU