Intermétalliques thermoélectriques d'hier, d'aujourd'hui... et de demain

Collège de France
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Clathrate

Half-Heusler

Skutterudite (C. Uher 15/05 seminar)

Higher Manganese silicides (HMS)

CdI_2 based sulfides and selenides

Bi_2Te_3

PbTe

Zintl Phases

SiGe

Oxyselenides (D. Bérardan/N. Dragoe, ICMMO, Orsay)

$La_{3-x}Te_4$

Borides

Pseudo-Hollandites

Mg_2Si

Chevrel Phases

$A_xMo_9Se_{11}$ (M.Potel URennes1)

$FeSi_2$

TAGS

Oxides (S. Hébert, CRISMAT)

Zn_4Sb_3

Tetrahedrites ($Cu_{12}Sb_4S_{13}$)

Plan du séminaire

1) Introduction
    a) Definitions
    b) Figure of merit
    c) Thermoelectric phenomenon and materials

2) Old thermoelectric materials
    a) Bi_2Te_3
    b) PbTe
    c) SiGe

3) New processes, new techniques in the quest for materials of the future…

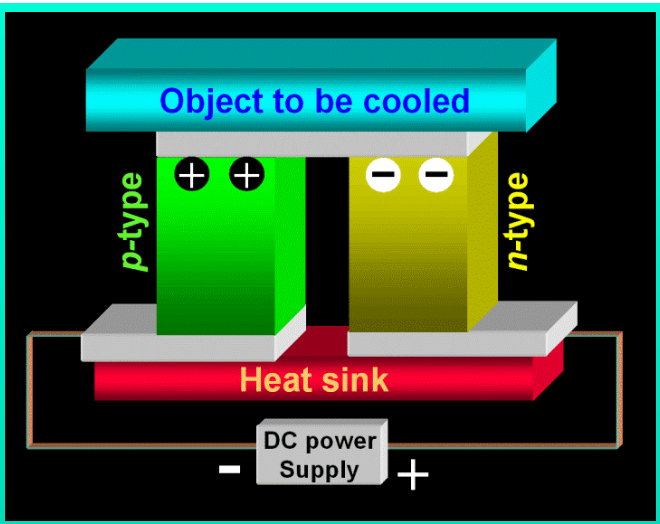
…or how to disrupt the phonons without affecting the charge carriers…

4) Strategy for new TE materials research
    a) Discovery of new TE materials?
    b) Few « good » examples: Zintl, Hollandite, $TiS_{2-x}Se_x$
    c) One bad example: $AgCrSe_2$

Definitions

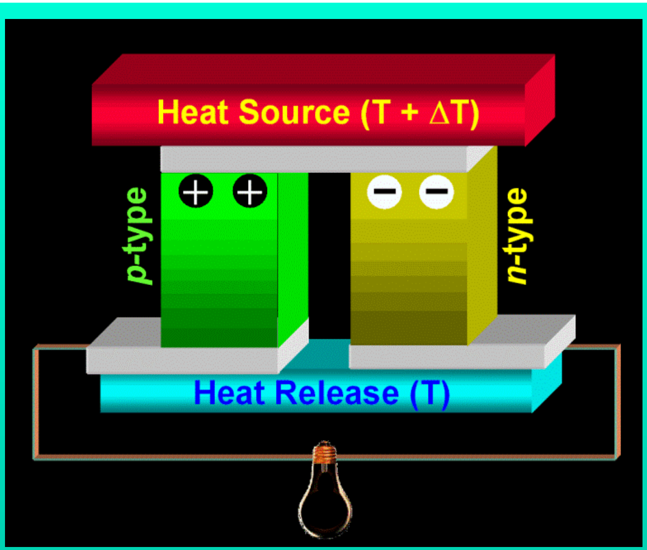
Thermo-Electric Conversion

Refrigeration mode
“Peltier effect”



When a current passes through the circuit, electrons and holes carry heat.

Generation mode
“Seebeck effect”



An applied temperature difference make the materials generate a voltage.

Thermoelectric figure of merit

S → High Seebeck coefficient (V/K)

High voltage/power needed !

ρ → Low electrcial resistivity (Ω.m)

Limit the thermal loss by Joule effect

κ → Low thermal conductivity (W/(m.K))

Maintain a temperature gradient ΔT high enough

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

Thermoelectric figure of merit

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

α → coefficient de Seebeck (V/K)
ρ → conductivité électrique (Ω.m)
κ → conductivité thermique (W/(m.K))

$$\alpha = \frac{\pi^2 k_B{}^2 T}{3e} \times \frac{8m^*}{h^2} \times \left(\frac{\pi}{3n}\right)^{2/3}$$

$$\sigma = \frac{1}{\rho} = ne\mu$$

$$\kappa = \kappa_r + \kappa_e$$

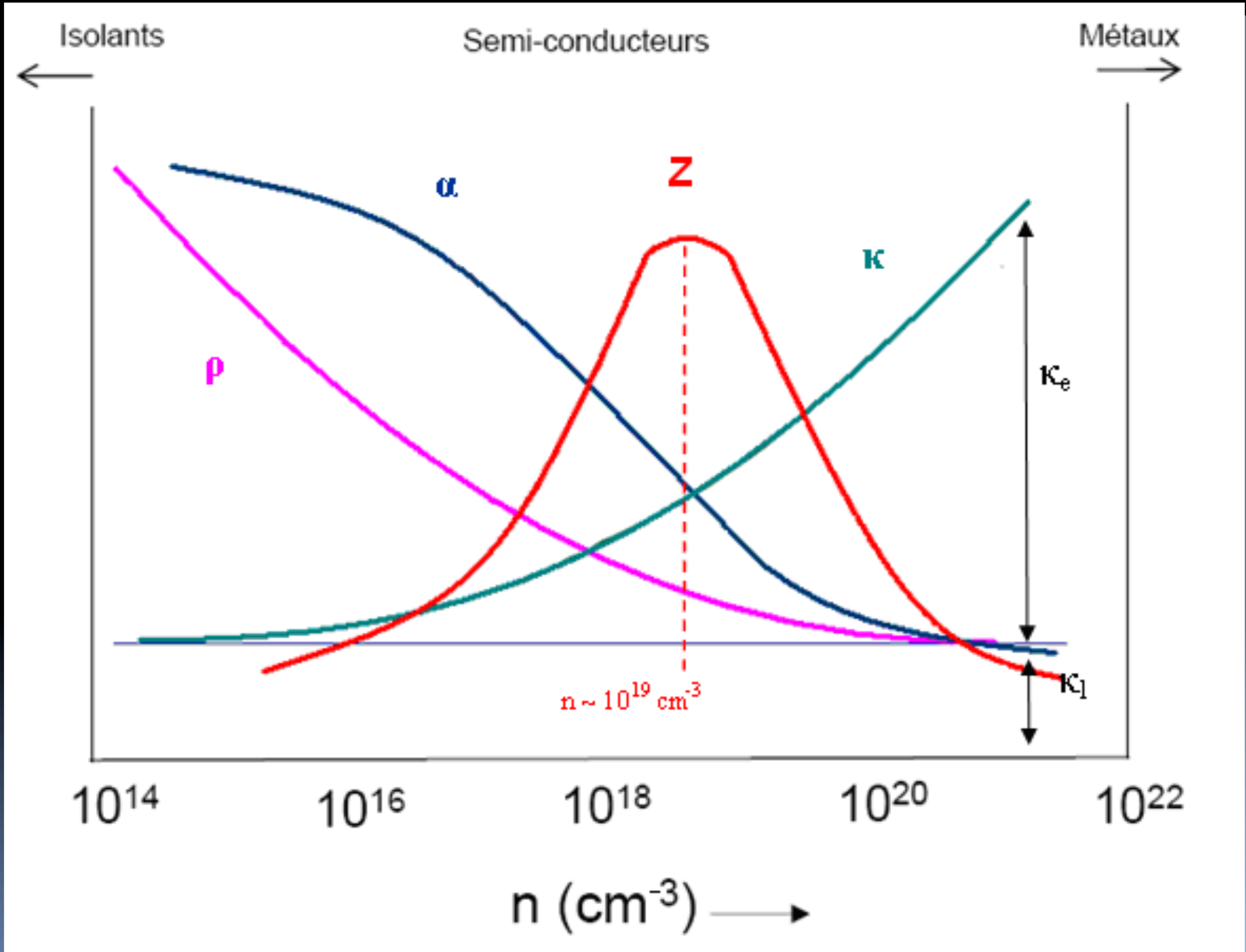
Wiedeman Franz Lorenz law

$$\kappa_e = \frac{LT}{\rho}$$

κ_e → contribution des porteurs de charge
K_r → contribution du réseau
k_B → constante de Boltzmann
e → charge de l'électron
m* → masse effective
h → constante de Planck
n → Charge carrier concentration
μ → mobilité des porteurs
L → facteur de Lorenz

$$ZT = \frac{\alpha^2}{L + \frac{\rho \kappa_r}{T}}$$

Variation with charge carrier concentration



A bit of histoiry…

1823: Seebeck

1835: Peltier

1851: Thomson

1930s: semiconductors with Seebeck > 100μV/K

1947: Telkes Thermogenerator with 5% efficiency

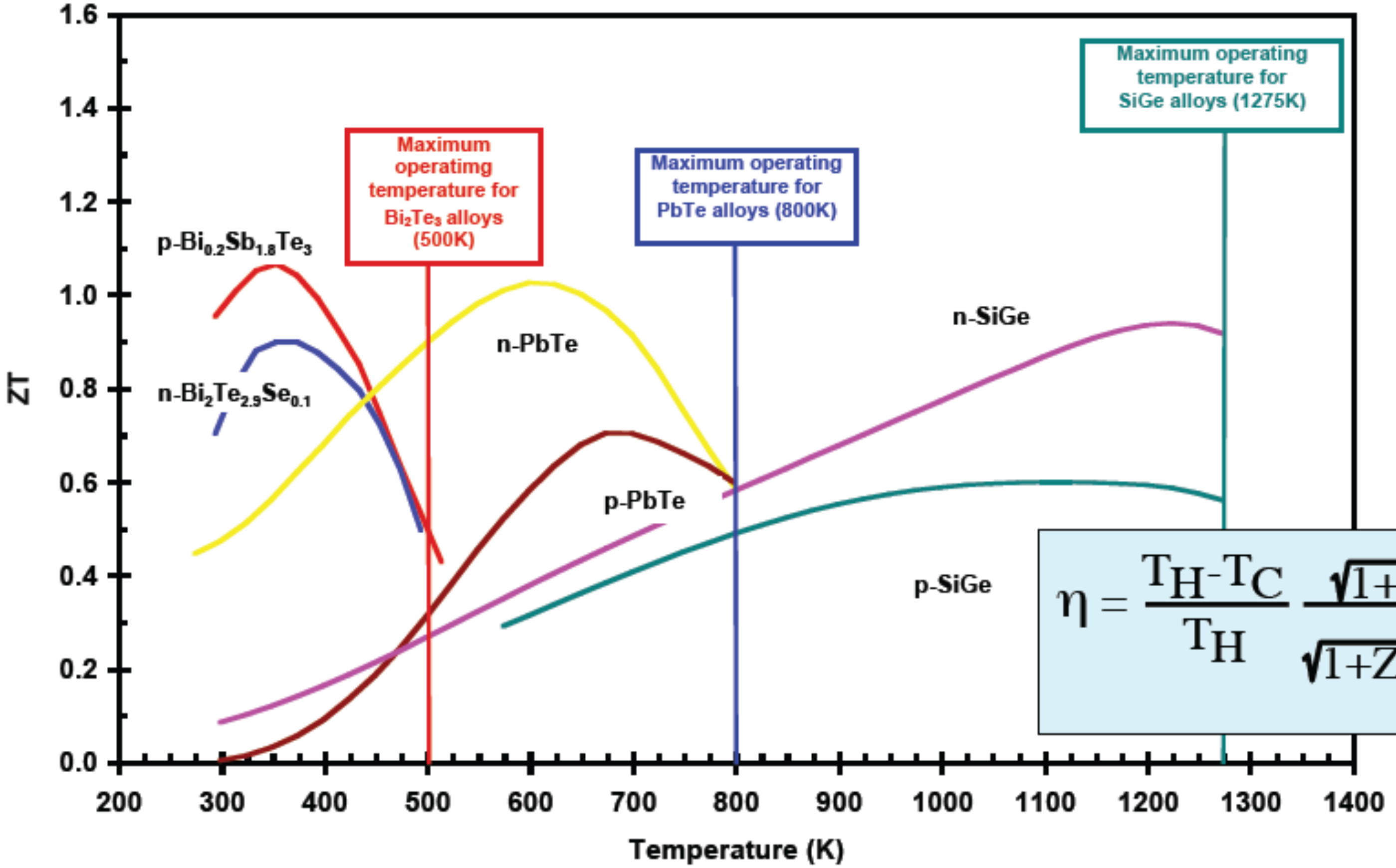
1977: NASA _ Voyager 2 (RTG / SiGe)

2020: NASA _ RTG (n-$La_{3-x}Te_4$ / p-$Yb_{14}MnSb_{11}$) ?

Today:

ONLY commercially available modules made of n and p Bi_2Te_3

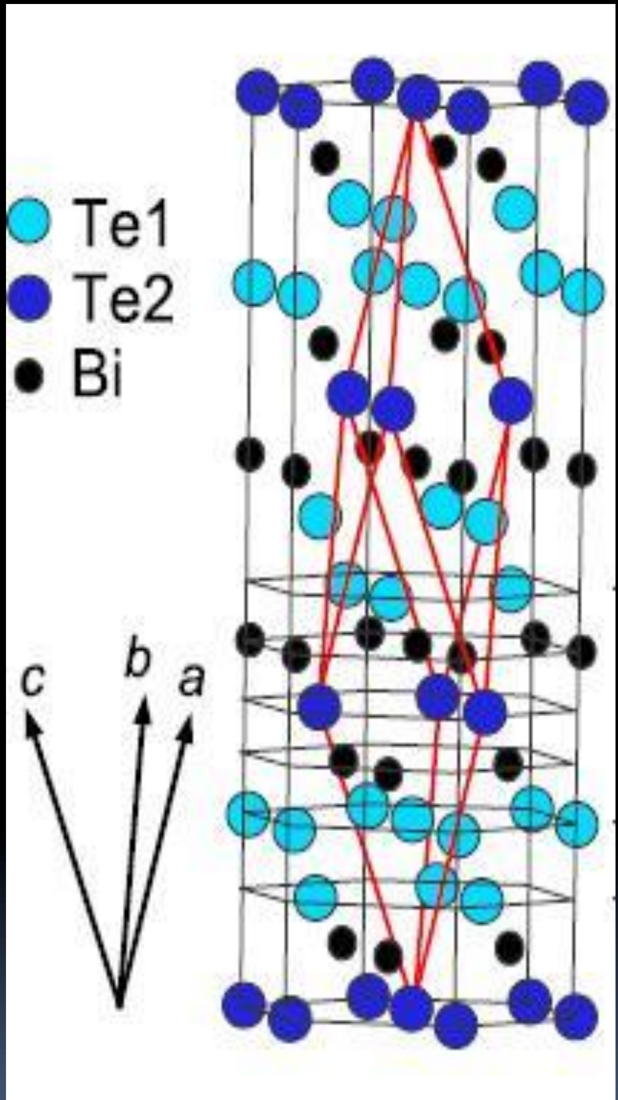
Historique des matériaux thermoélectriques

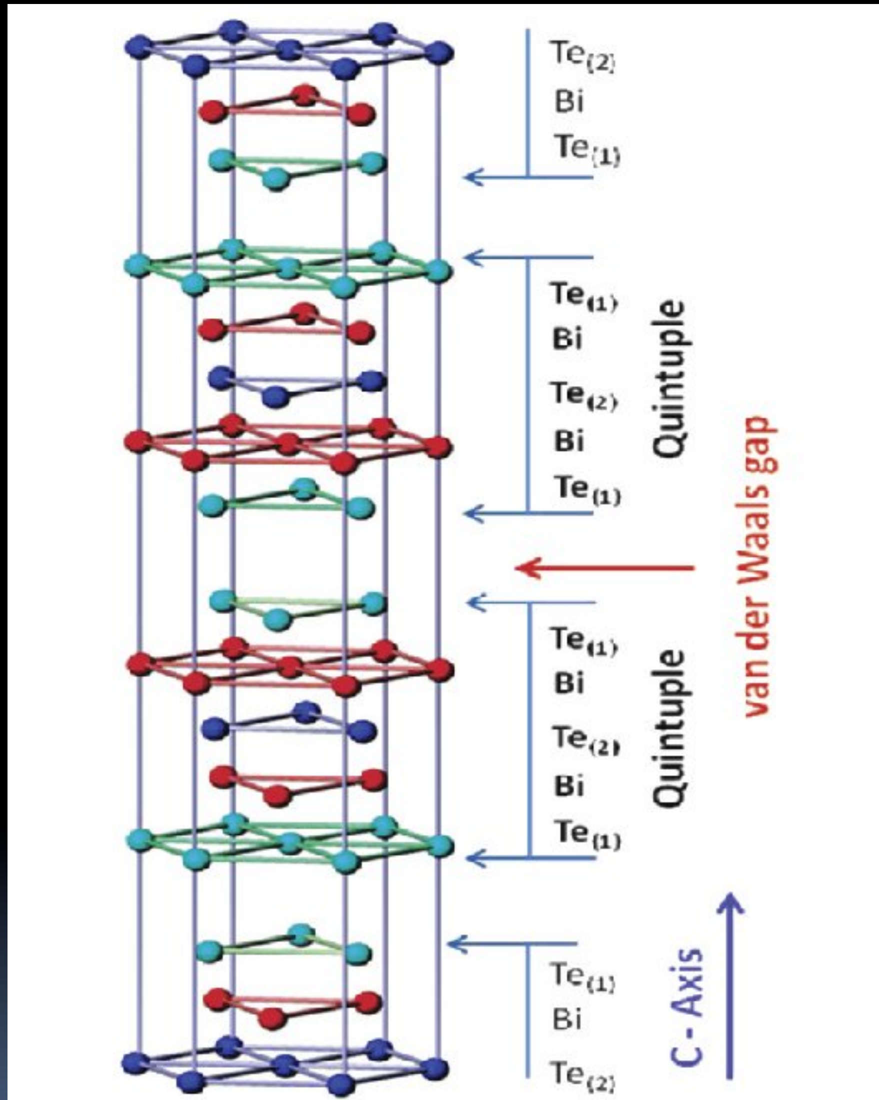


$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_C}{T_H}}$$

TE materials used in commercial applications were discovered in the 1960's

Bi_2Te_3 - structure



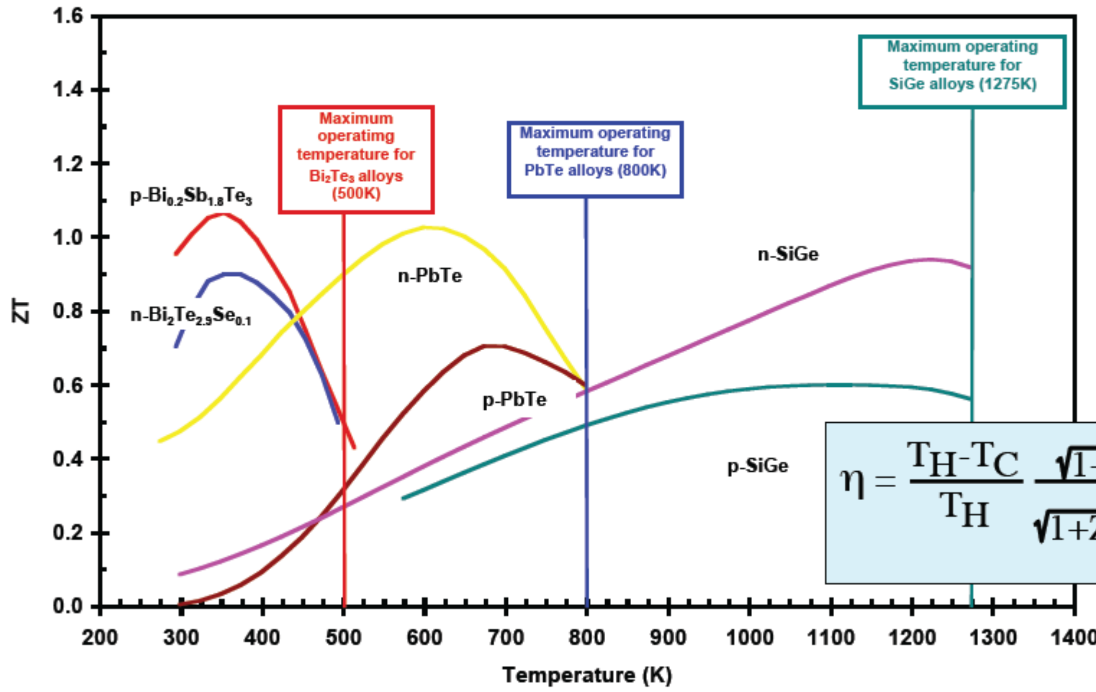


lamellar structure: **# Clivage plans (mechanically fragile)**
 # Anisotropy of transport properties

Bi_2Te_3 - dopage

p-type : solid solution $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$ ou $Bi_{2-y}Sb_yTe_3$

n-type : Solid solution $(Bi_2Te_3)_x(Bi_2Se_3)_{1-x}$ ou $Bi_2Se_yTe_{3-y}$



$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}}$$

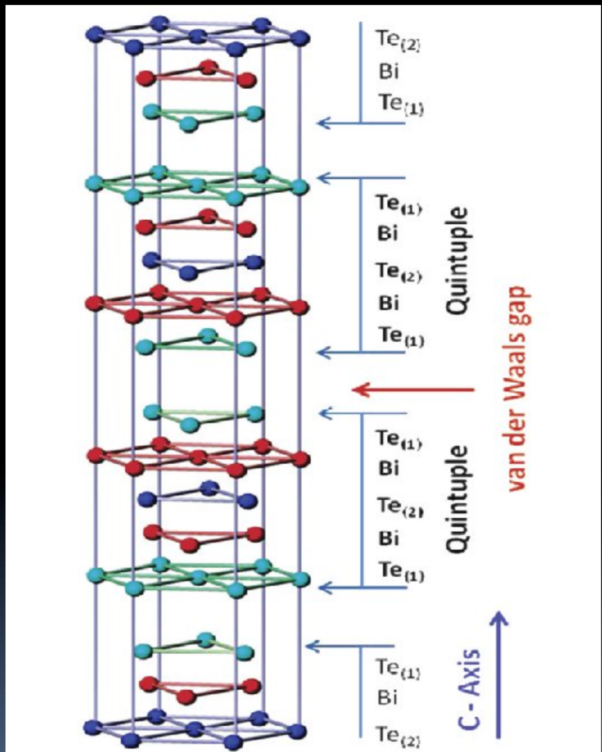
TE materials used in commercial applications were discovered in the 1960's

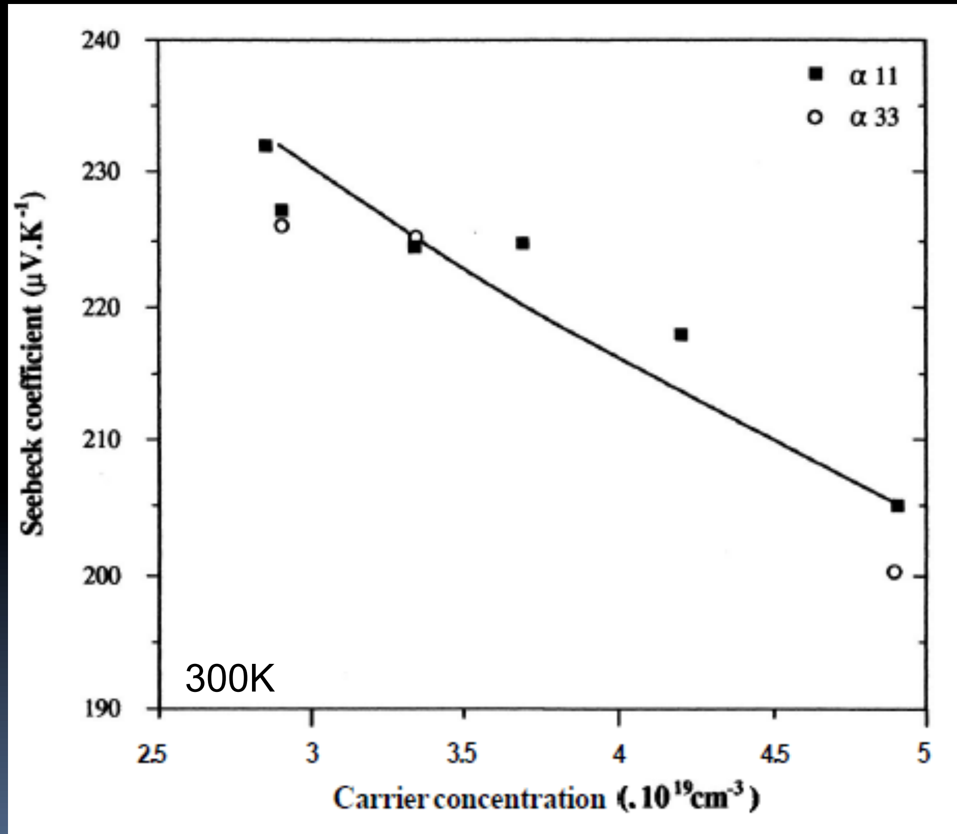
Bi_2Te_3 - Anisotropy of transport properties

In single crystals !

EXAMPLE: ComposItion : p- $Bi_{10}Sb_{30}Te_{60}$

properties TE measured in the ab plan (11) and along the c direction (33)

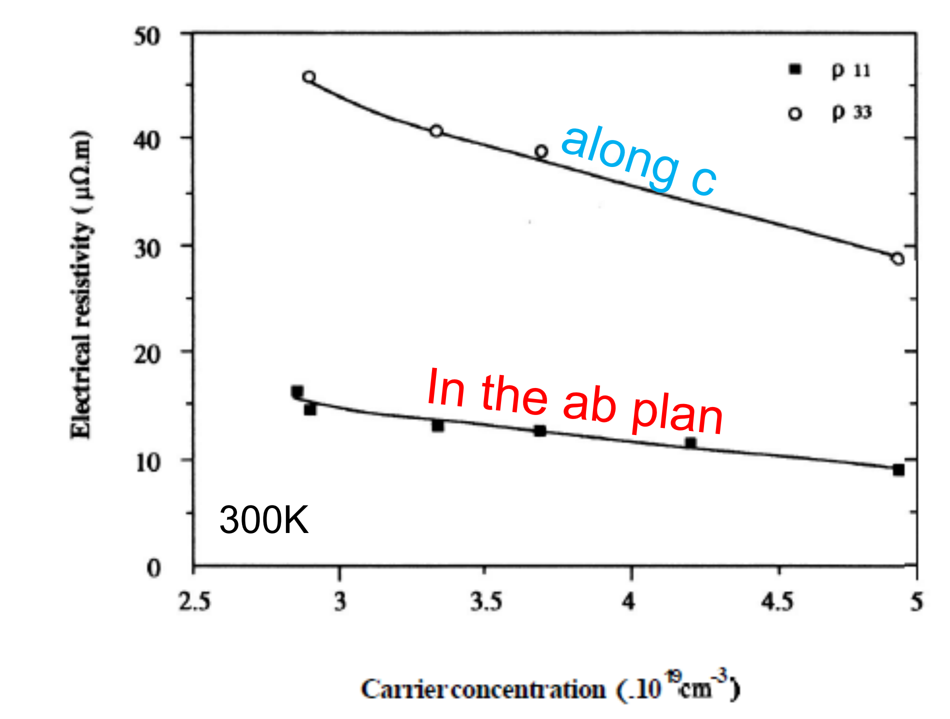


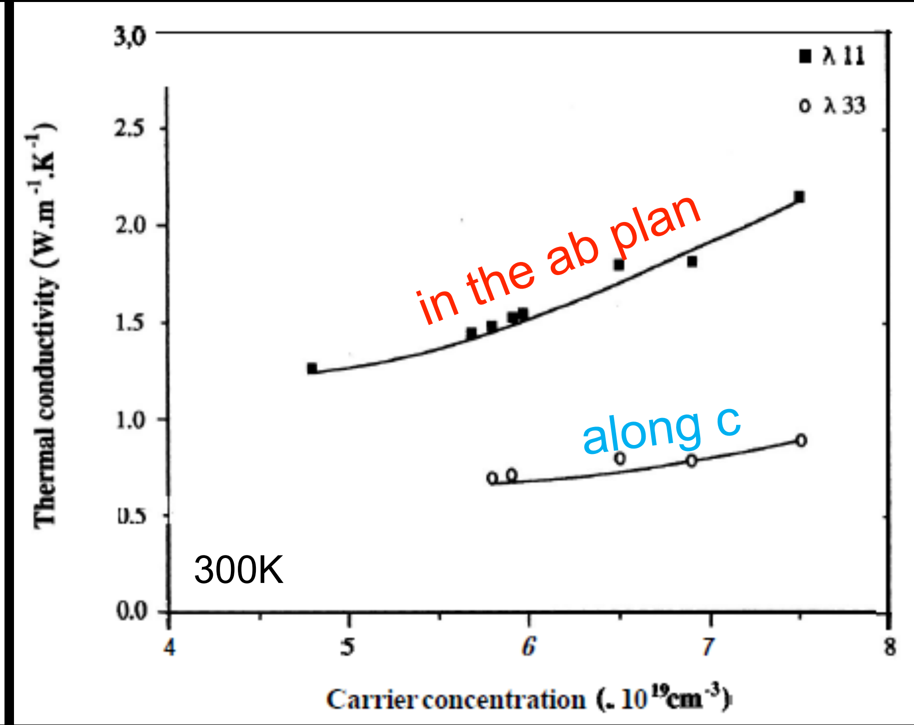


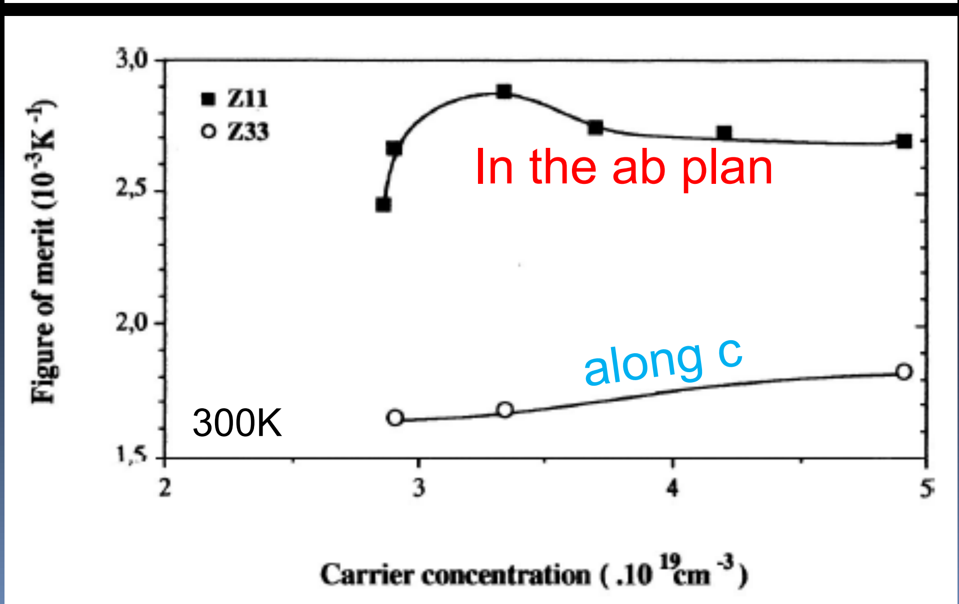
Seebeck is isotropic

Bi_2Te_3 - Anisotropy of transport properties

In single crystals !







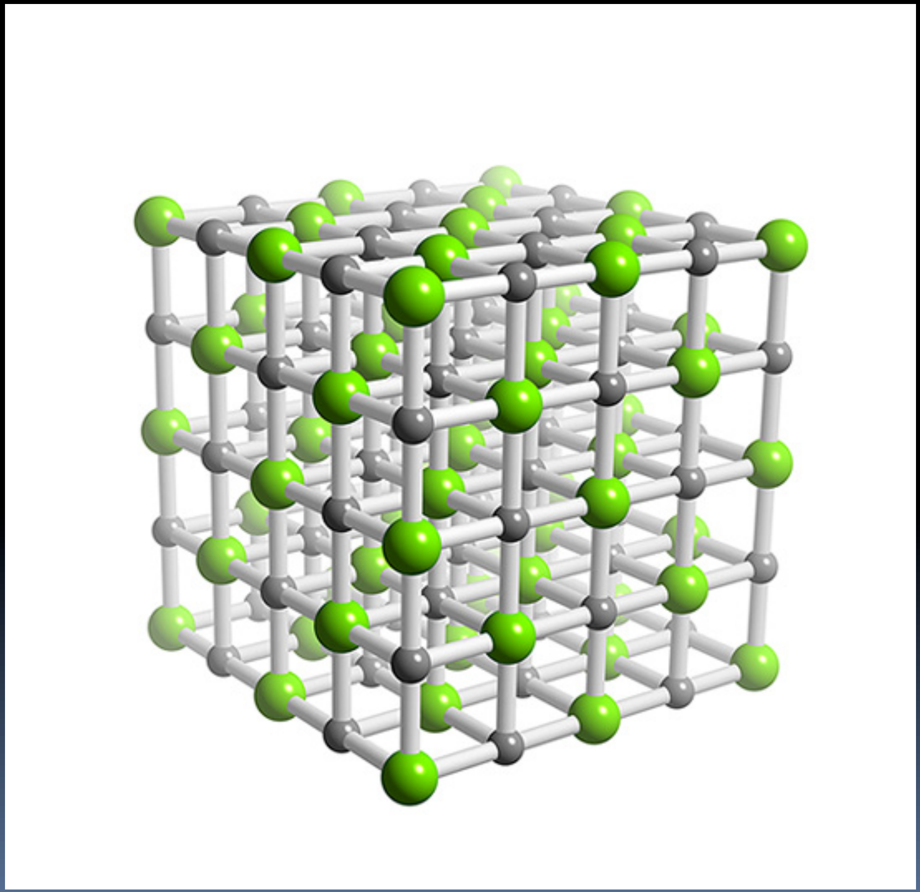
For n or p: ZT (ab) > ZT(along c) !

Must orient the TE legs when making a module
(commercial module : ZT_p~1-1,1 and ZT_n~0.9)

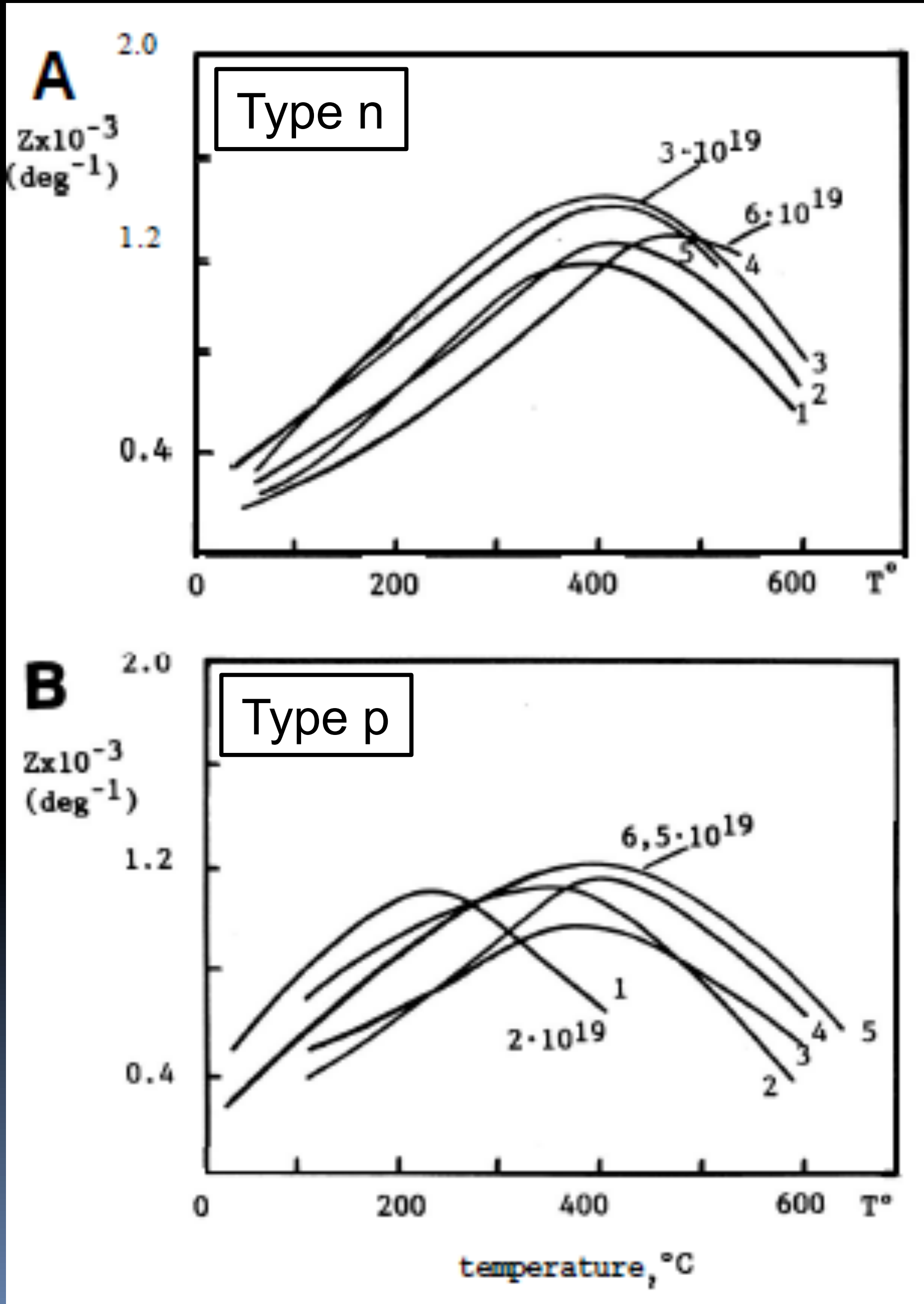
The most studied TE material
…still today…
(Cf 2^{ième} partie)

PbTe

\# a simple cubic structure Rock salt type
\# n and p type depending on the dopants
\# single cristals and polycrystalline samples



PbTe: variation of Z with the carrier concentration and temperature



p or n type depending on dopant(s)

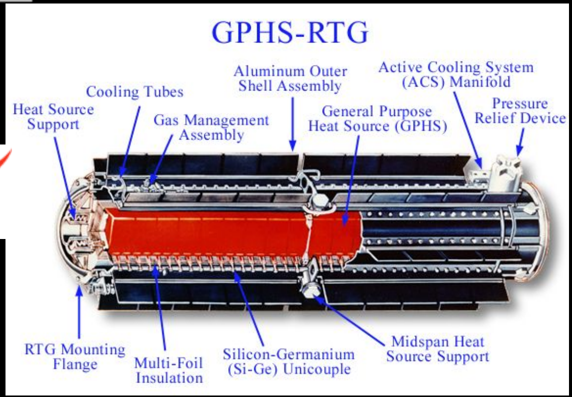
ZT about 1 at 800K

Very easy to synthesize

Pb: Forbidden in Europe (REACH…)

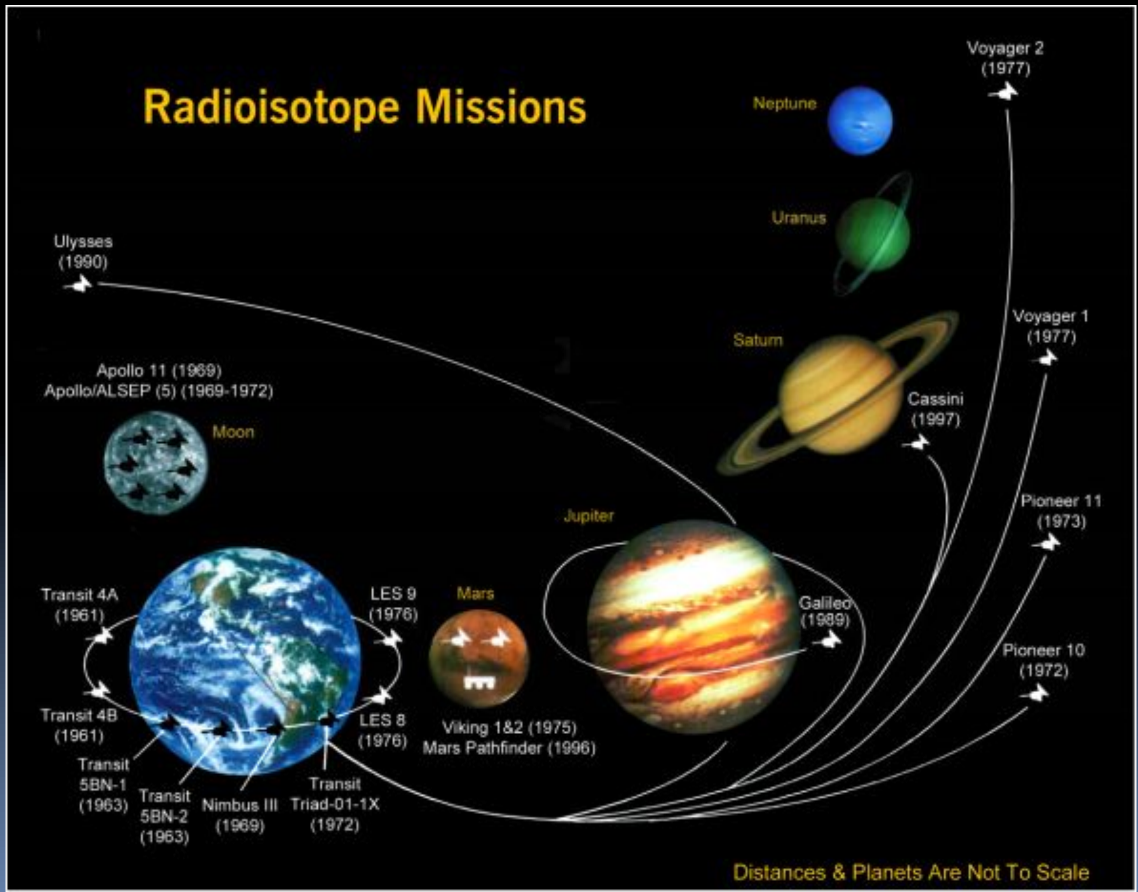
Much research underway in the USA
(Cf 2ième partie)

SiGe



Used in GPHS RTG since the 70'

n-type : highest ZT~0,9 à 1000°C
p-type : highest ZT~0,6 à 1000°C



Average ZT = 0.53
(couple over the range 473-1273K)

Efficiency ~8.5%

TE materials research strategy

To improve the performances of known TE materials

To find new thermoelectric materials

Improve the TE performances of known TE materials

Example: Bi_2Te_3, PbTe, SiGe…

$$\alpha = \frac{\pi^2 k_B{}^2 T}{3e} \times \frac{8m^*}{h^2} \times \left(\frac{\pi}{3n}\right)^{2/3}$$

$$\sigma = \frac{1}{\rho} = ne\mu$$

$$\kappa = \kappa_r + \kappa_e$$

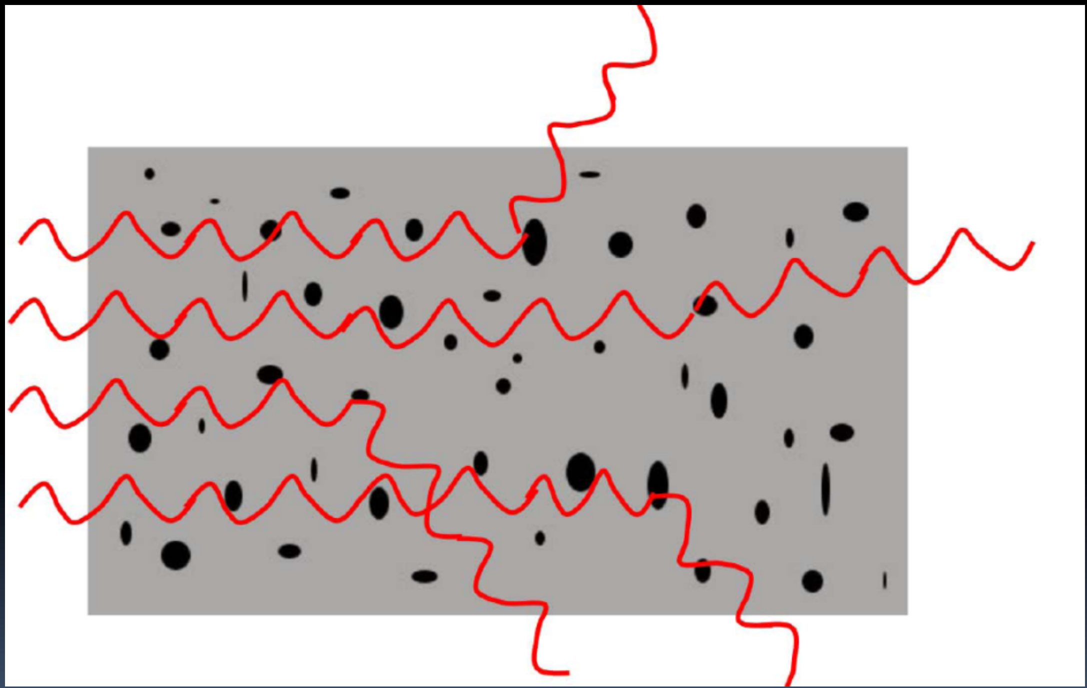
Chemically optimized! *(in termes of charge carrier concentration),*

-BUT κ_r can (maybe) be lowered (?)

-BUT can't we decouple the Seebeck coefficent and the resistivity?

How to decrease the lattice thermal conductivity?

= How to disrupt the phonons path ?
= How to decrase their mean free path ?



Disrupting the phonons displacement

Structural disorder
Mixed occupations
Positional disorder
"impurities"
Vacancies

Increase the number of grain boundaries
(Decrease the grain size (towards nano…?))

Increase the disorder at the grain boundary

Make (nano) composites

PbTe new generation…

$$2\ Pb^{2+} = Ag^{+} + Sb^{3+}$$

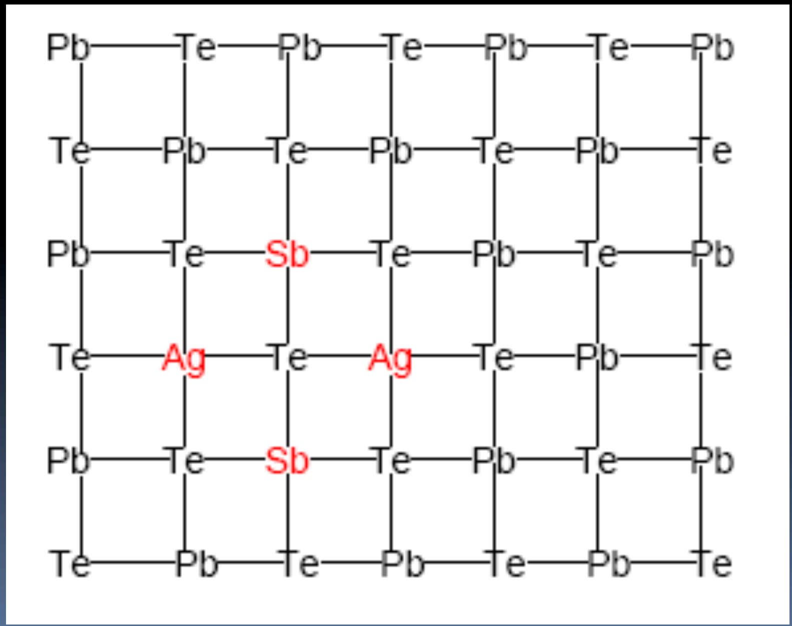
Substitution that leads to the family of LAST (M. Kanatzidis)

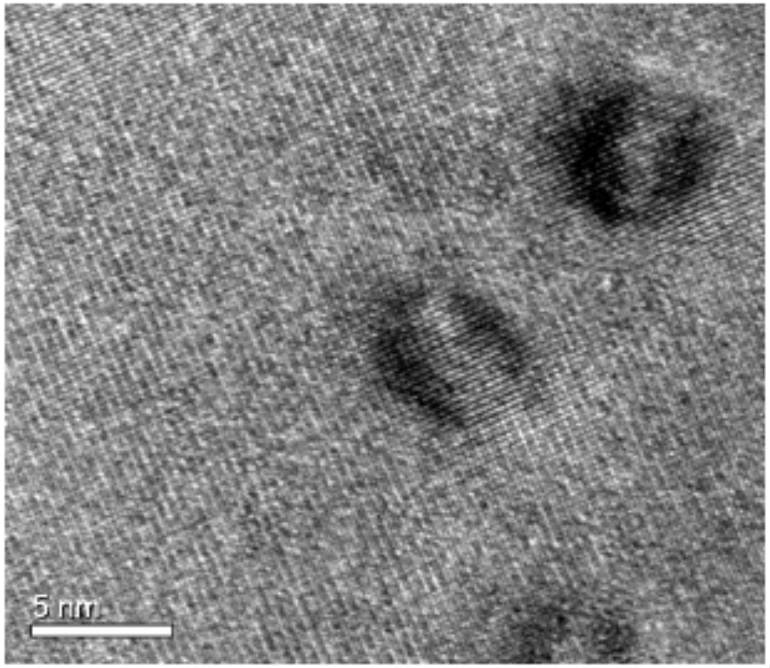
(LAST : Lead Antimony Silver Telluride)

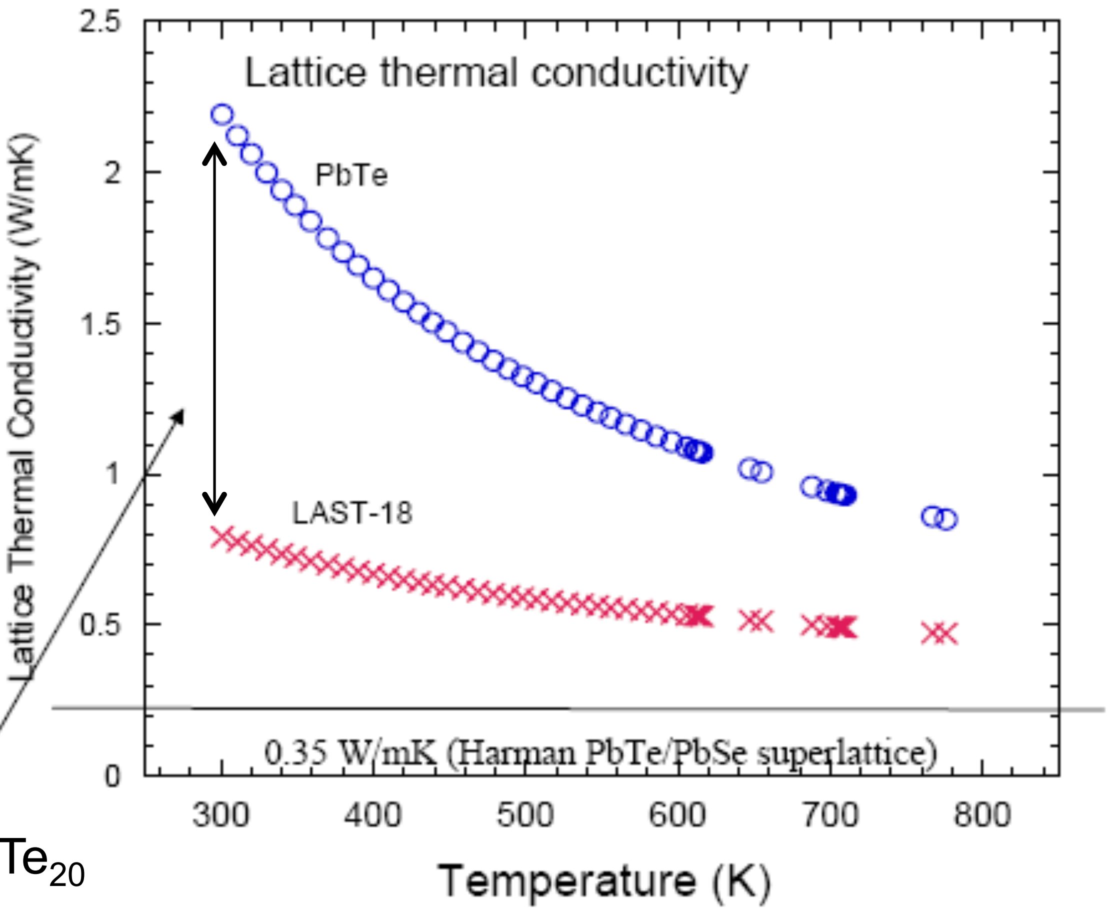
$AgPb_{n-2}SbTe_n$

Ag-Sb pockets formed by electrostatic attraction

Synthesis: fusion followed by slow cooling

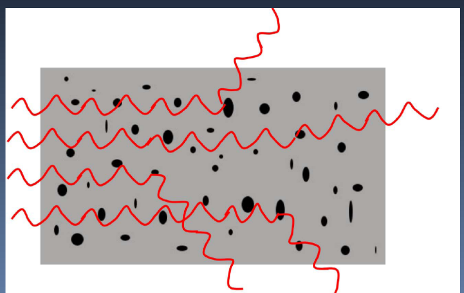






LAST-18 = $AgPb_{18}SbTe_{20}$

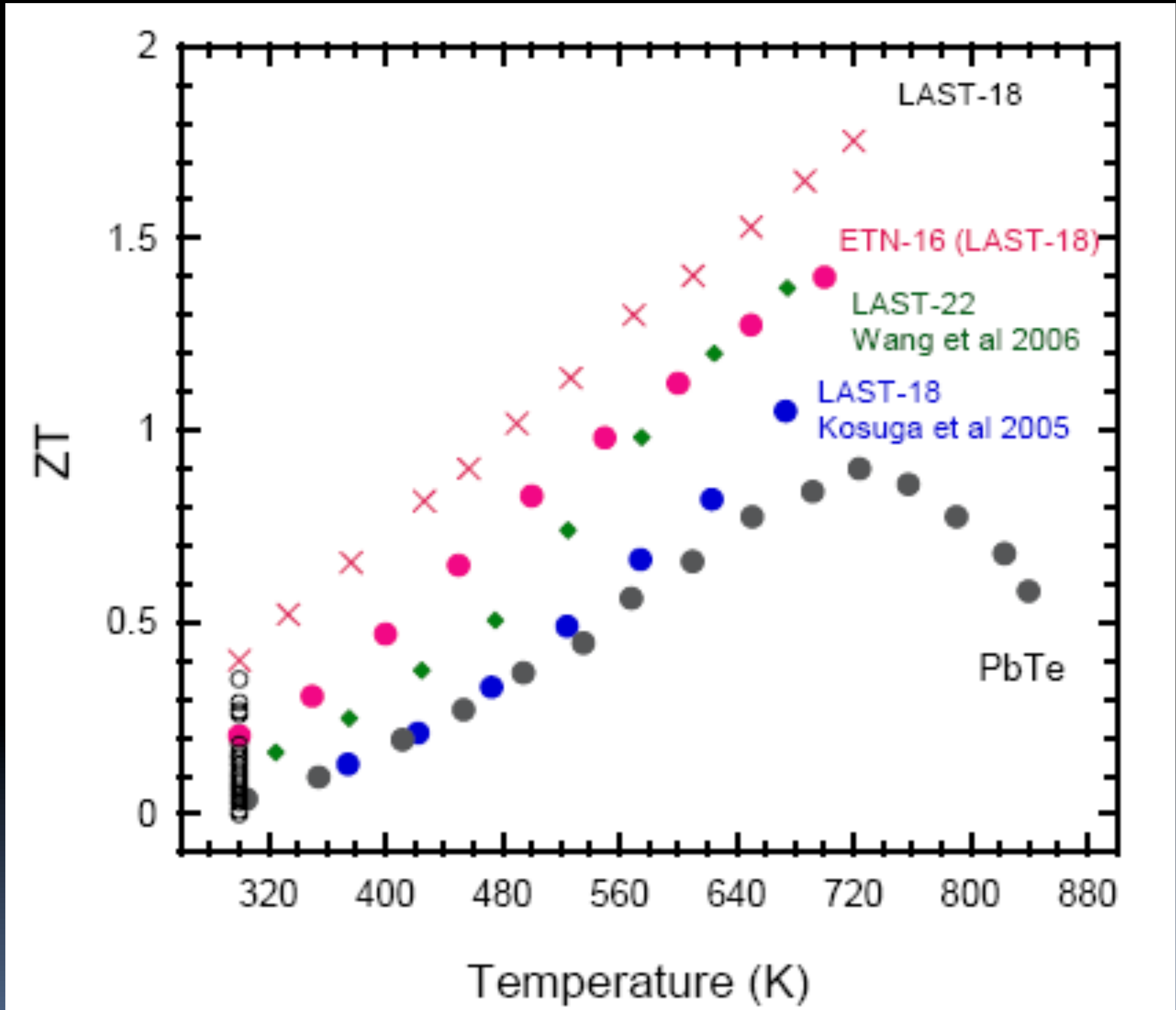
In situ formation of nano-domains Ag-Sb rich.



Decrease of the lattice thermal conductivity

Evident consequences on the ZT !

PbTe new generation…



References: Kanatzidis website @ : http://chemgroups.northwestern.edu/kanatzidis/greatthermo.html

Bi_2Te_3 new generation…

~Benefit from the anisotropy

Must utilize the (ab) direction !

~Avoid single crystals

Difficult synthesis

Poor mechanical properties

Synthesis of polycrystalline samples

Hot pressing (conventionnal or SPS)

Partial alignement of the grains perpendicularly to the axis of pressing

Measure the properties in both directions

Bi_2Te_3 nouvelle génération…

Synthesis: mechanical alloying (broyage réactif)

Fast
Reproducible
Small grain size
Low temperature (no evaporation)
Fine control of the stoichiometry
generate defects formation
easy to scale up

Typical parameters:

30 minutes
700 rpm } 15 grams of Bi_2Te_3

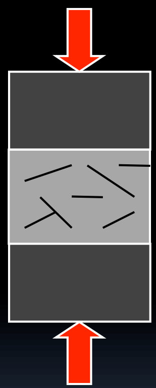
Bi_2Te_3 nouvelle génération…

Controling the degree of texturation is necessary in order to optimize the TE properties

__Step 1:__

Graphit die : Φ15mm

No preferred orientation

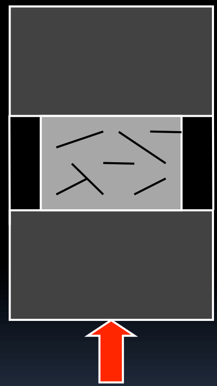


SPS1

__Step 2:__

Same pellet

Graphit die : Φ20mm



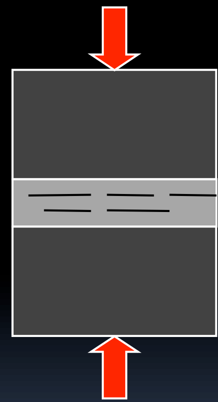
SPS2

__Step 3:__

Heat and pressure applied

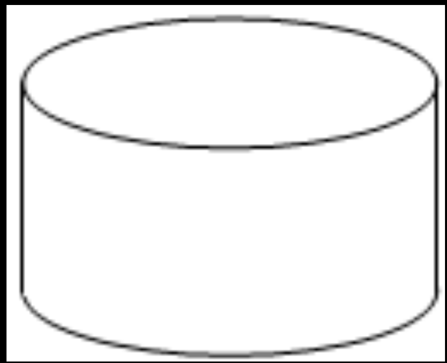
Strains are released

Flowing and texturation of the grains

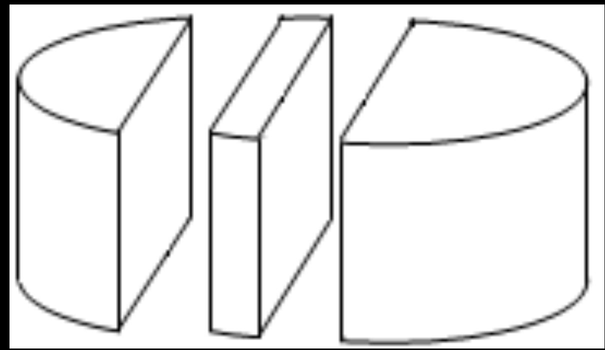


SPS2

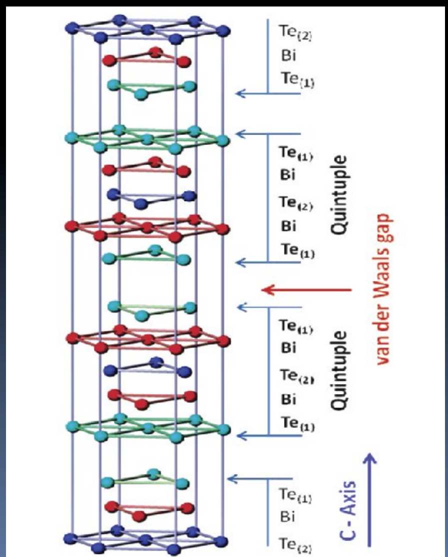
Bi_2Te_3 nouvelle génération… densification et découpes

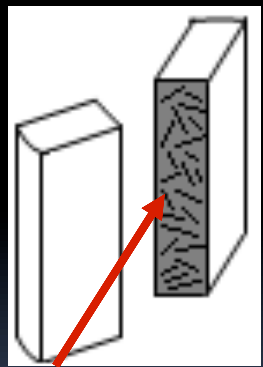


1. Puck after SPS

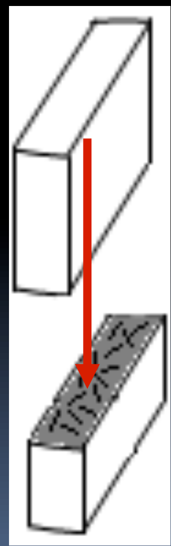


2.slicing



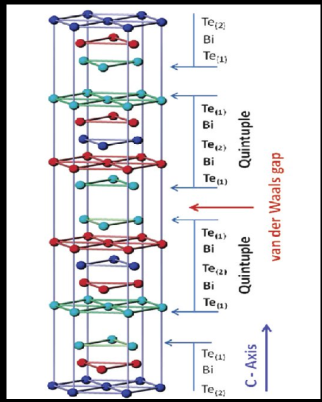


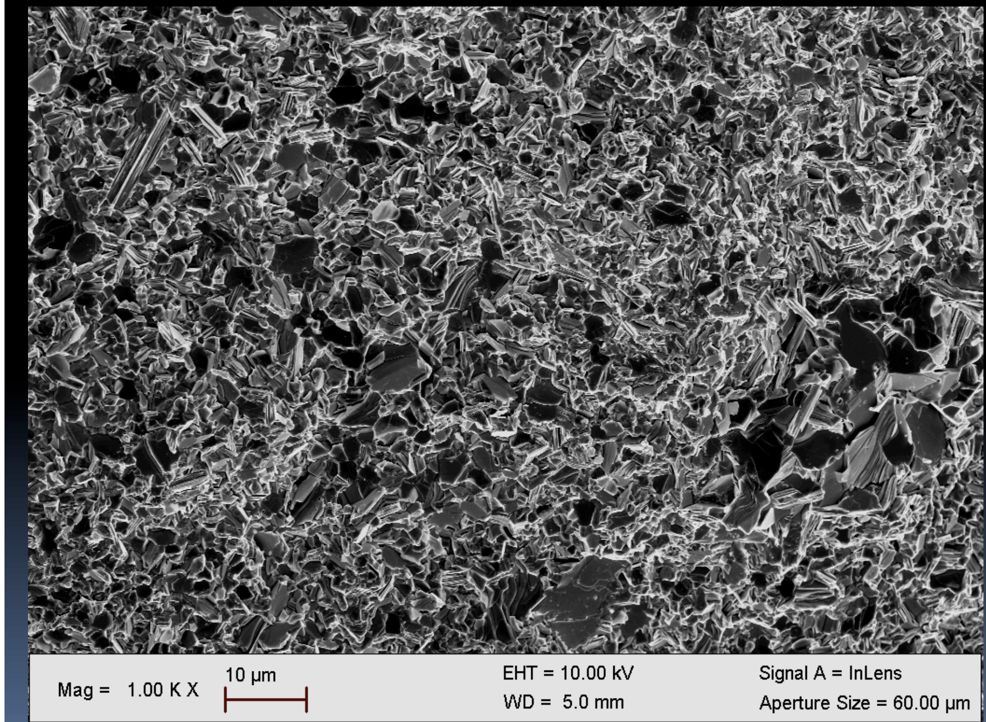
Echantillon coupé verticalement: in plane (ab)



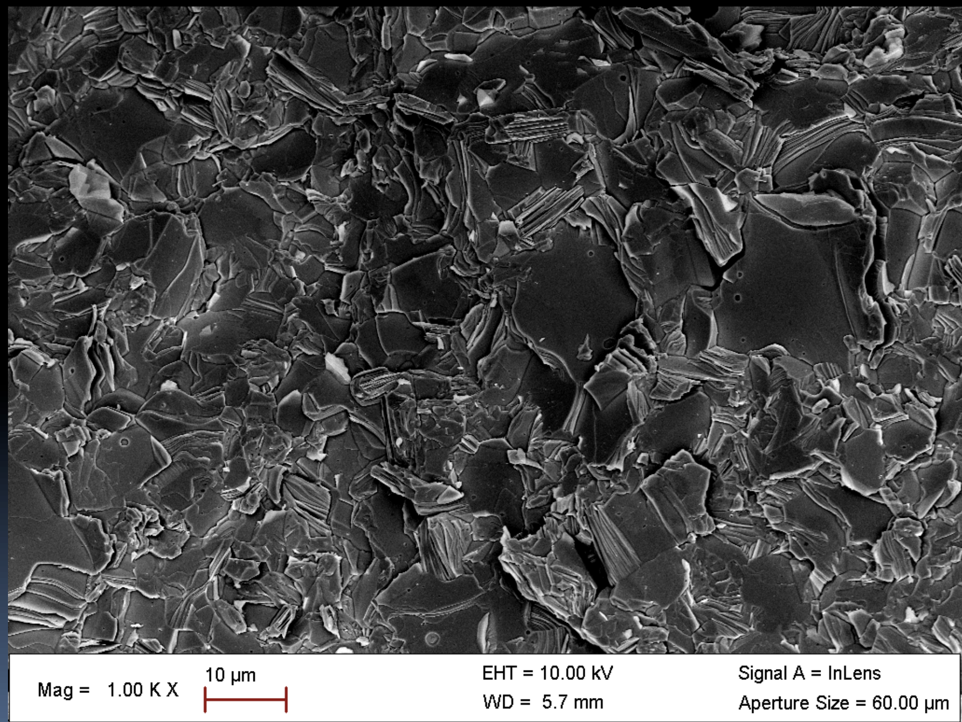
Echantillon coupé horizontalement: cross plane

Bi_2Te_3 nouvelle génération… microstructure



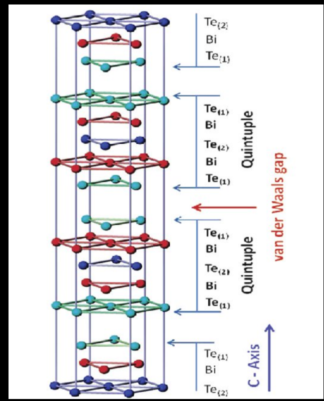


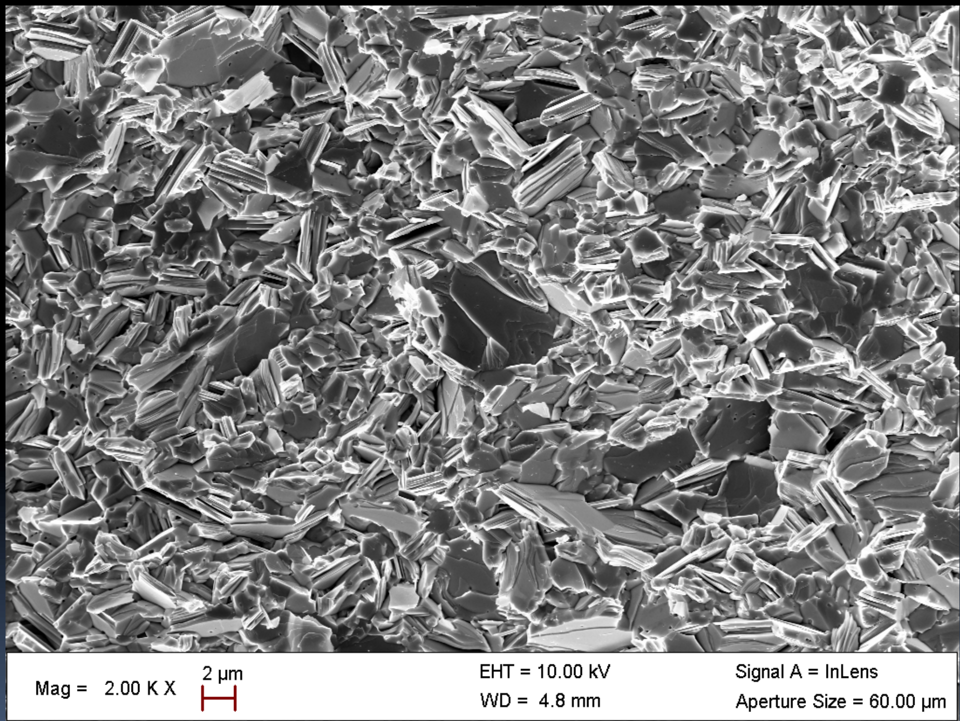
After first SPS densification



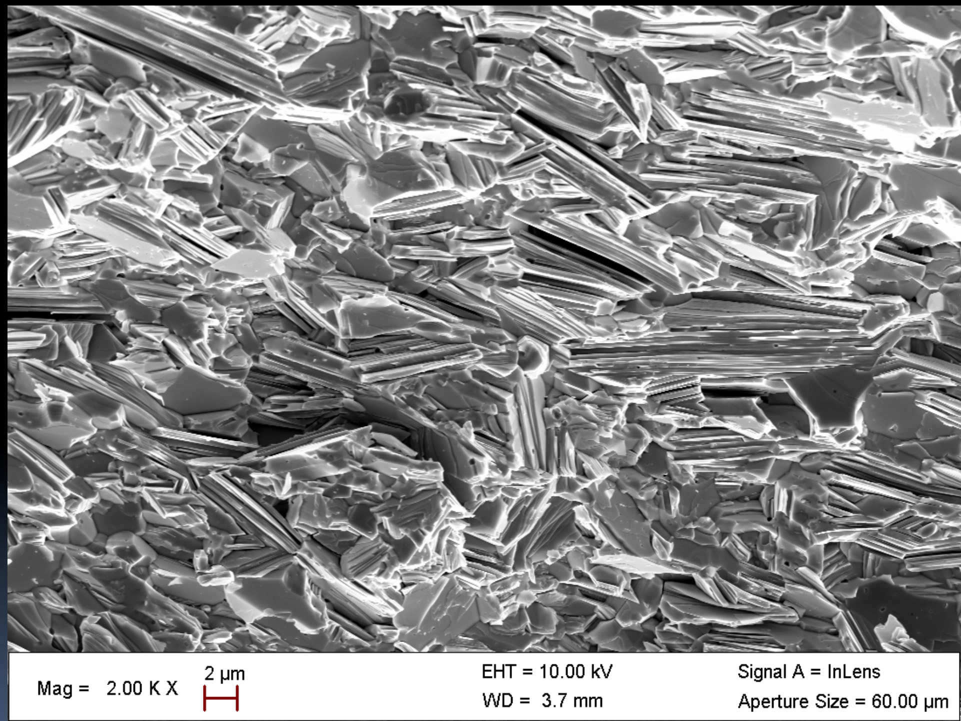
After second densification

Bi_2Te_3 nouvelle génération… microstructure





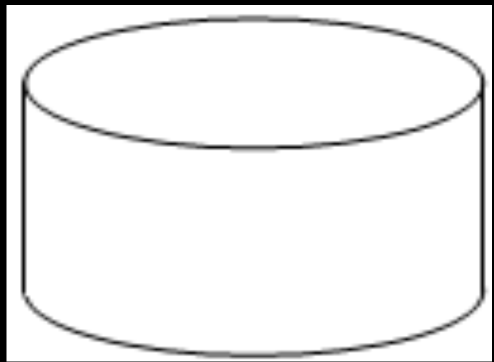
After first SPS densification



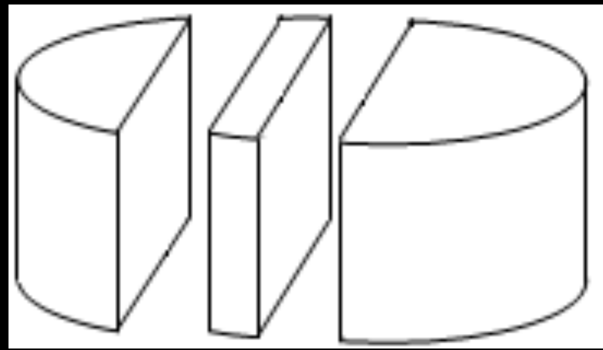
After second densification

Grains plus gros et mieux orientés

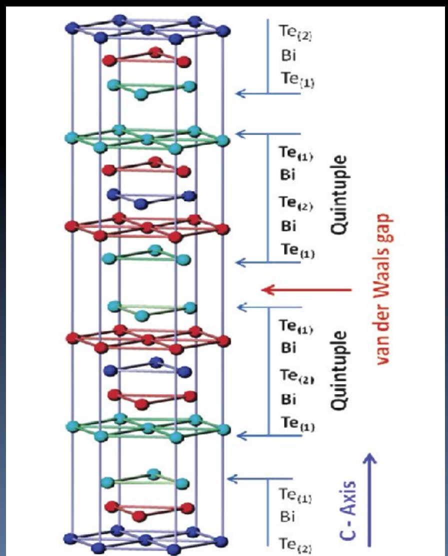
Bi_2Te_3 nouvelle génération… propriétés de transport

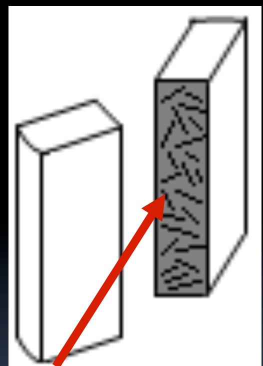


1. Puck aprés SPS

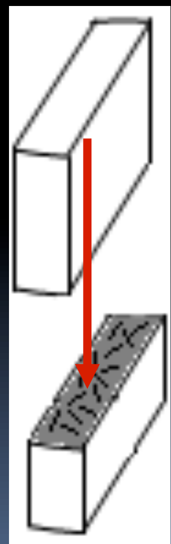


2.Découpe



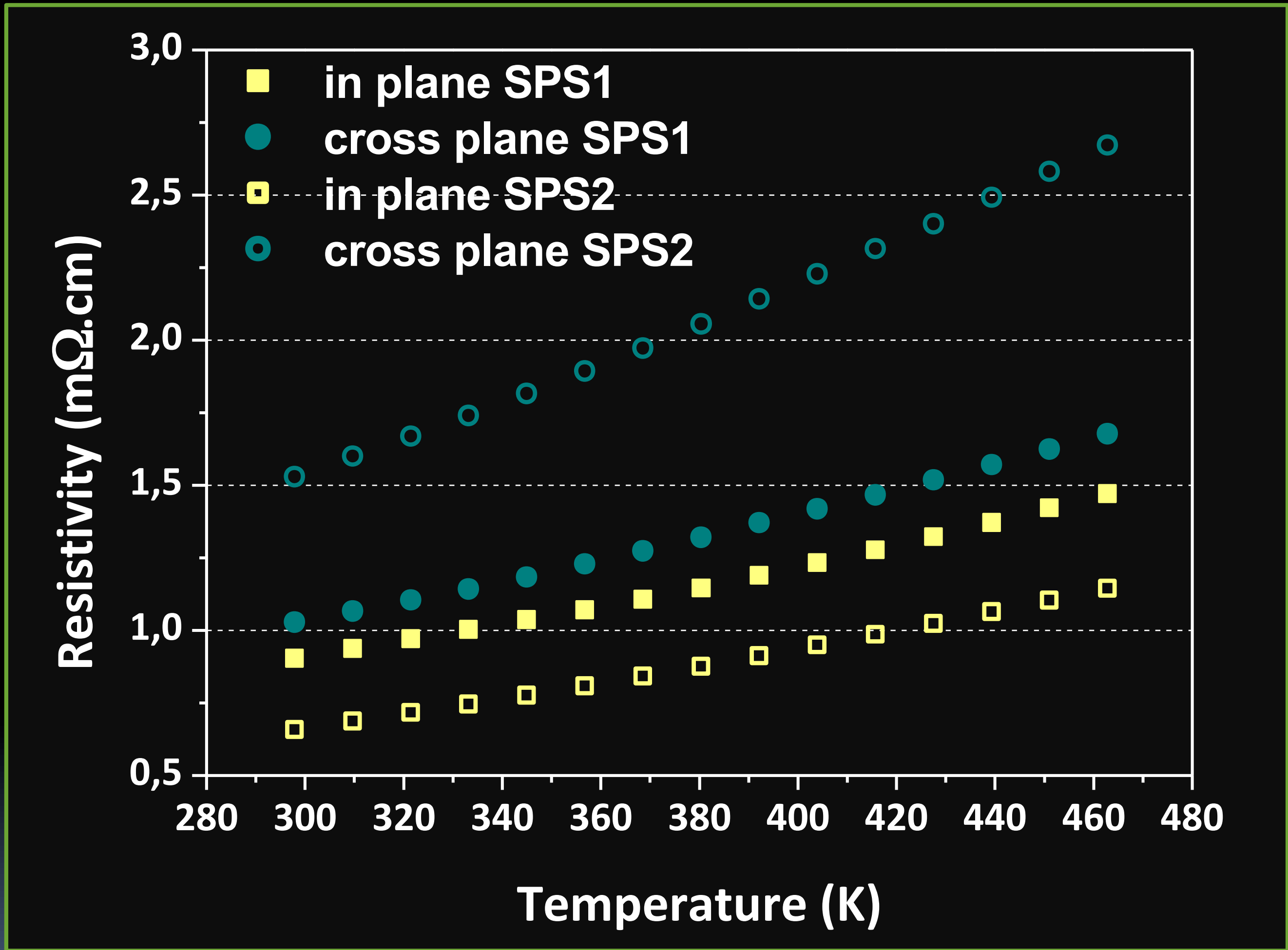


Echantillon coupé verticalement: in plane (ab)

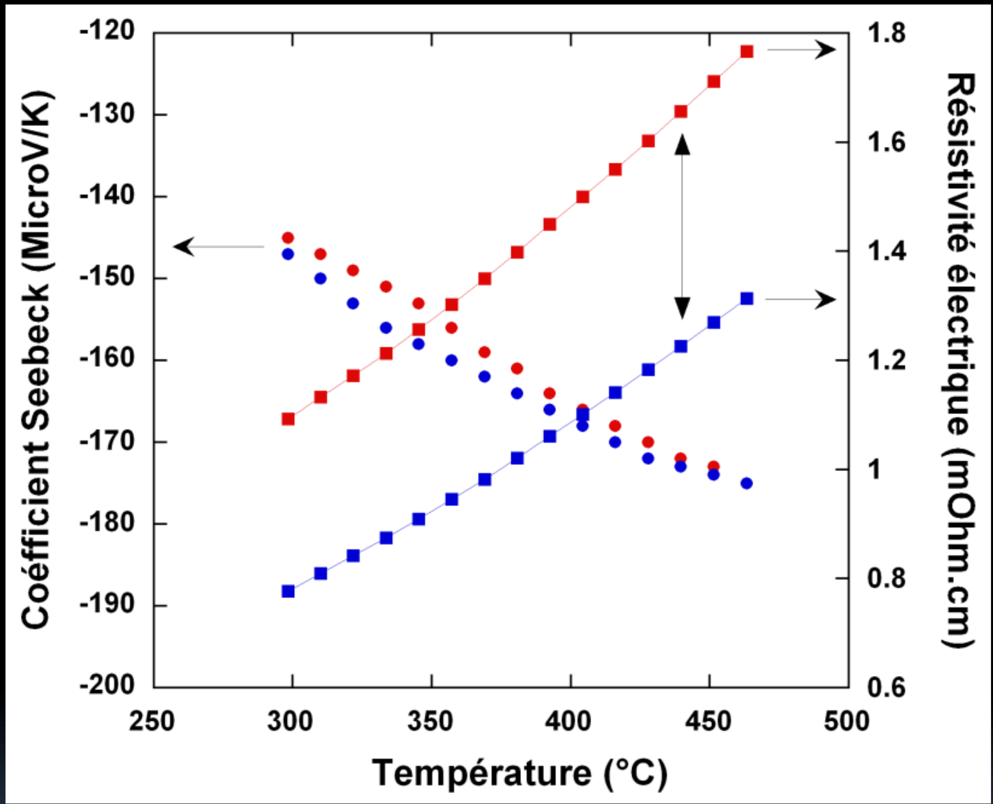


Echantillon coupé horizontalement: cross plane

Bi_2Te_3 nouvelle génération… propriétés de transport



Bi_2Te_3 nouvelle génération… propriétés de transport



Seebeck is isotropic
(like in single crystals

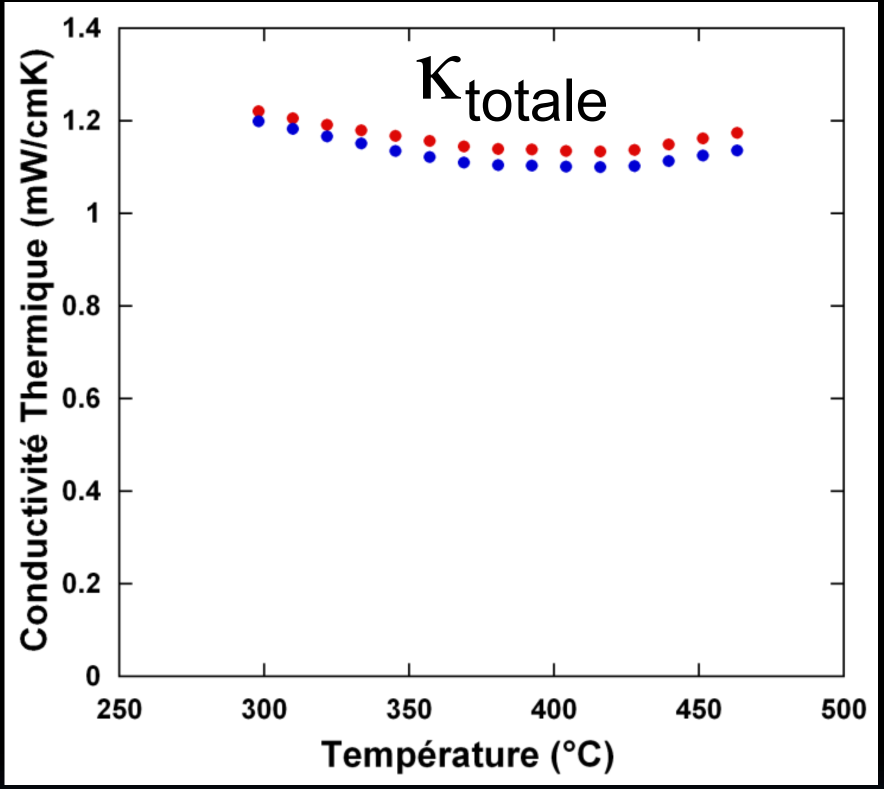
Resistivity decreases…

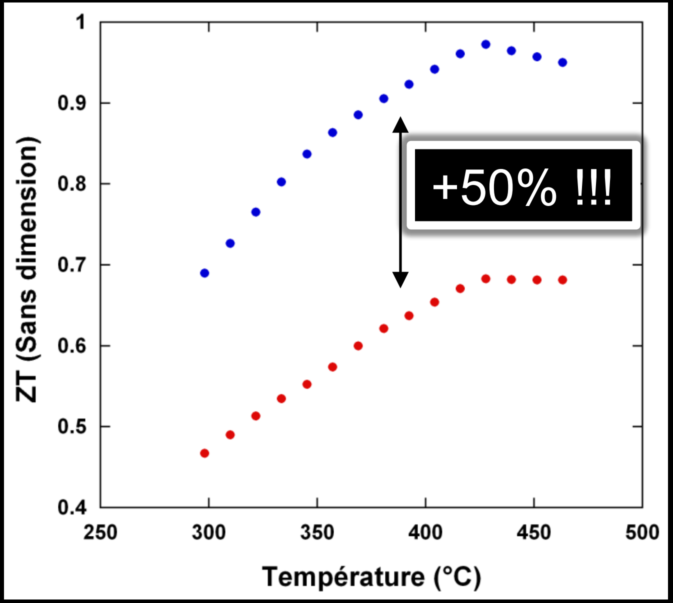
So we expect:

An increased κ_{el}
(WF law: $\kappa_{el} = LT/\rho$)

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

Bi_2Te_3 nouvelle génération… propriétés de transport



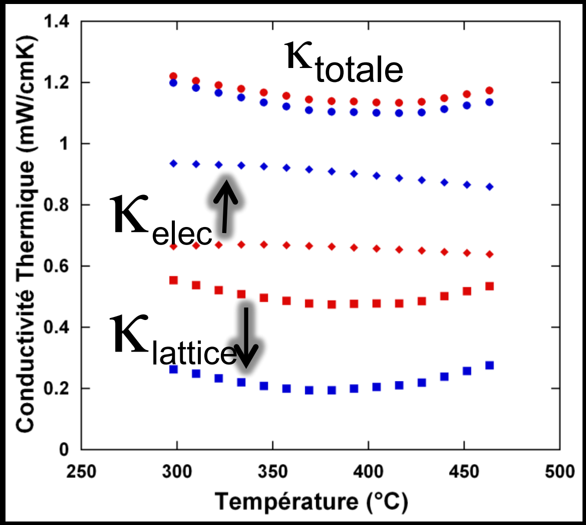


ρ decreases, α is constant, κ unchanged… ZT increase indeed !!!

Bi_2Te_3 nouvelle génération…

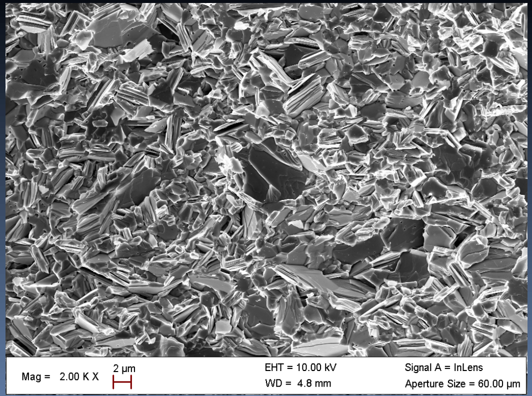
$$\kappa_{totale} = \kappa_{électronique} + \kappa_{réseau} = LT/\rho + \kappa_{réseau}$$

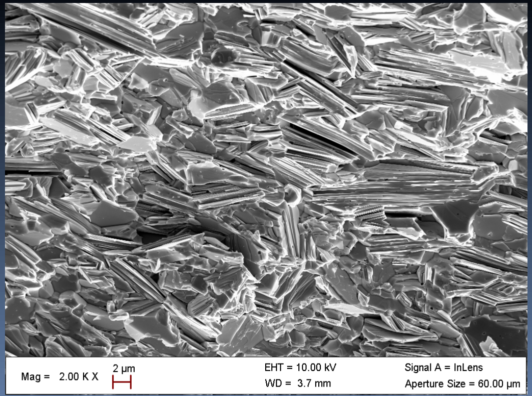
(Loi de Weidemann Franz)
avec $L_{(Bi_2Te_3)} \sim 2\ 10^{-8}\ W\Omega/K^2$)



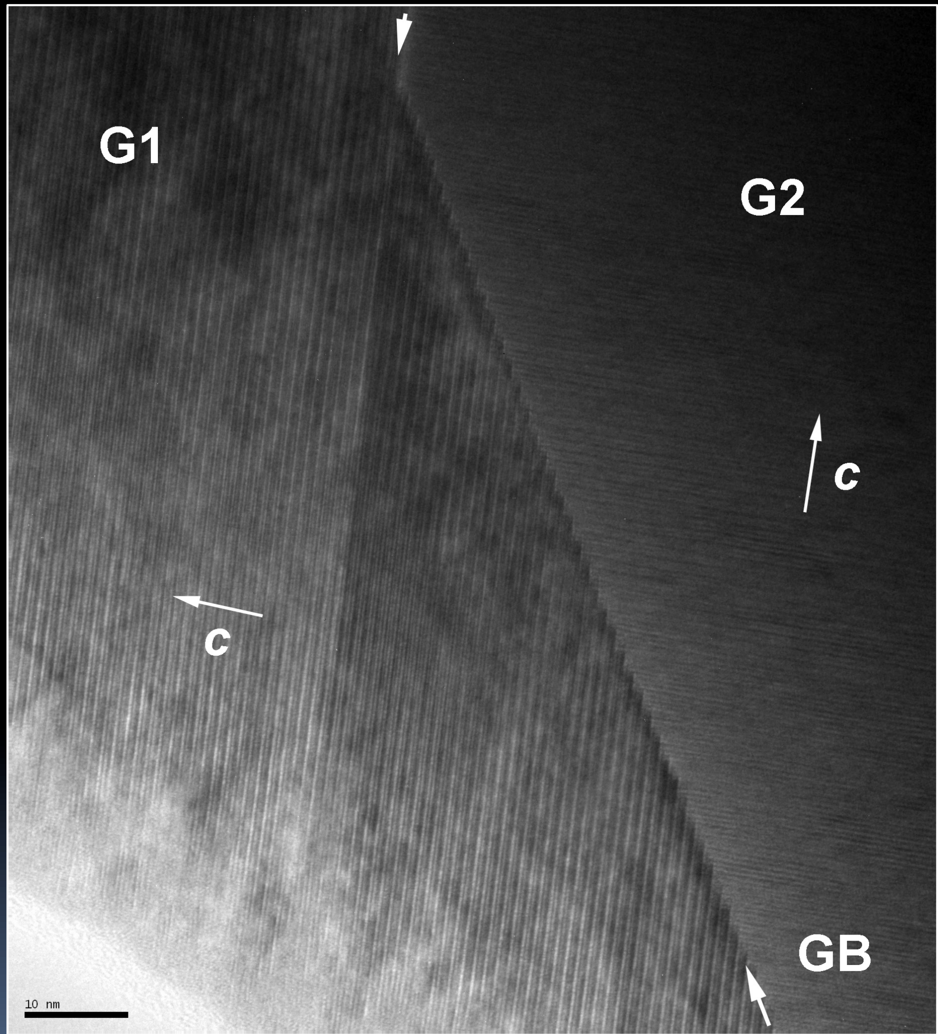
$\kappa_{réseau}$ …

Bigger grains should lead to an increase in $\kappa_{lattice}$ (less grain boundaries)



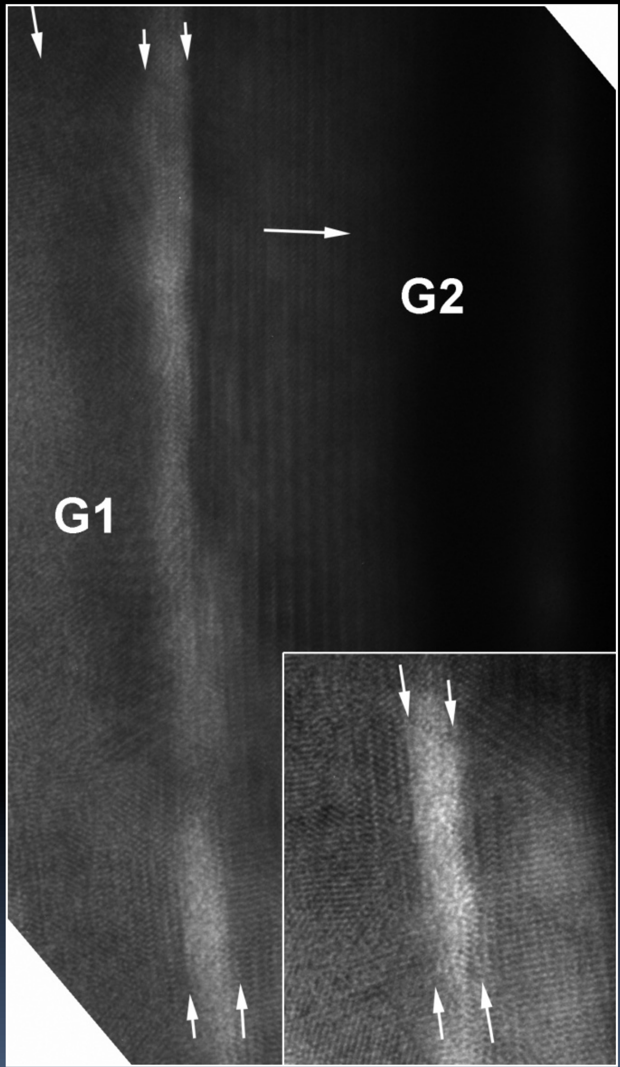


Bi_2Te_3 nouvelle génération… TEM after first SPS



Microscopie : Dr. Oleg Lebedev

Bi_2Te_3 nouvelle génération… TEM after second SPS



Amorphous, disordered grain boundaries…

Hypothesis:

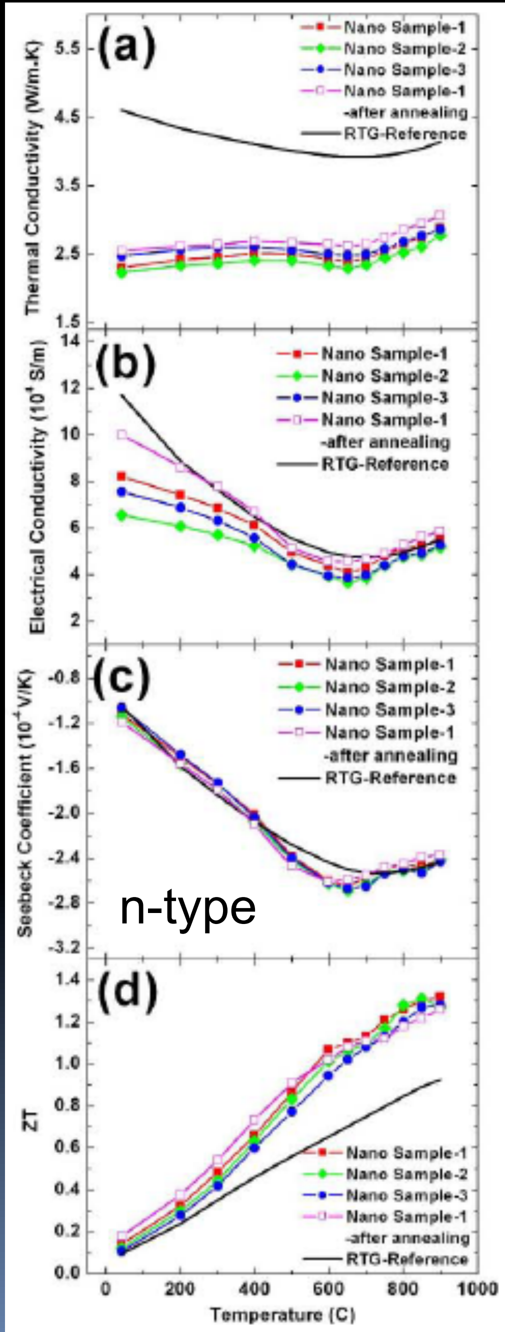
Results from the friction engendered by the second SPS, grains force to glide on each other.

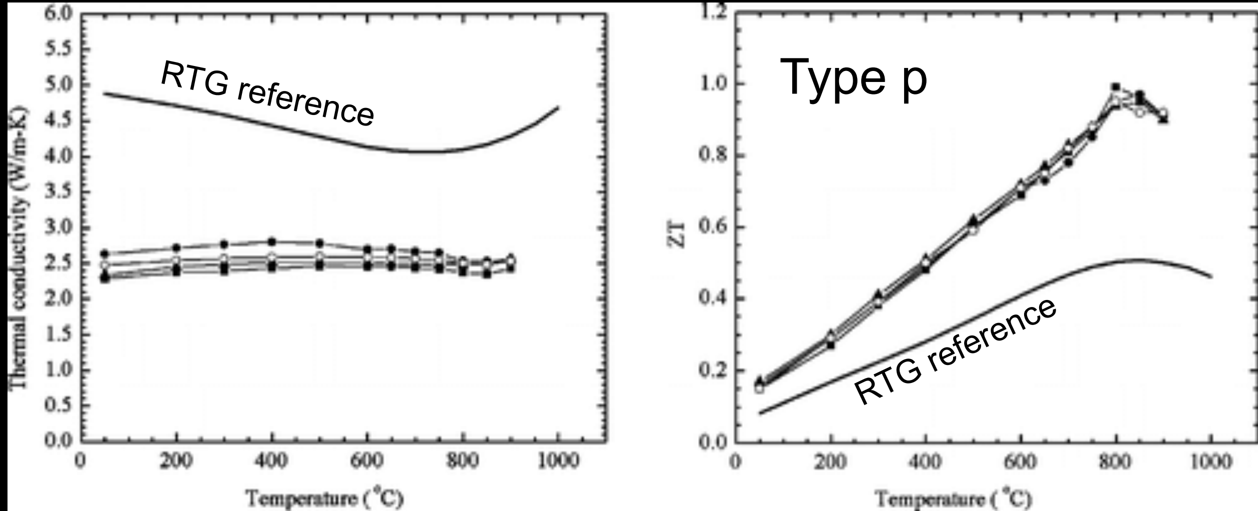
This result has been reproduced numerous times!

Mechanical process results in an increased thermoelectric figure of merit.

Microscopie : Dr. Oleg Lebedev

SiGe nanostructured





Prepared by mechanical alloying, n and p type SiGe have performances well above that of the heritage SiGe !

The existence of nano domains apparently explains this decreased thermal conductivity whereas the electrical resistivity is virtually unchanged…

Remarkably, this nanostructuration can withstand high temperature without evolving much.

Wang et al, APL 93, 193121, 2008

Thierry Caillat

Summary

- **To date, thermoelectrics has been mostly applied for niche markets**
  - Using TE materials developed in the 60's
- **New development in TE materials may open up new markets**
  - Automobile, industrial processes waste heat recovery
- **Both low cost and smart system engineering are needed to make these applications viable**
- **ZT ~ 3 cooling materials would open larger markets**

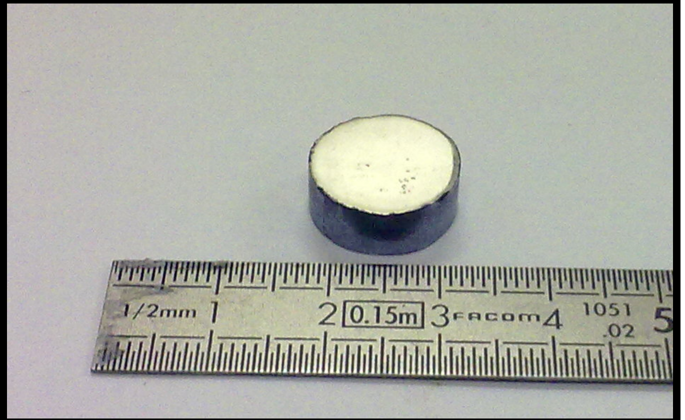
A le recherche de nouveaux matériaux TE …?

We need:

Low thermal conductivity
- Complex structure
- Heavy elements
- Possible (structural) disorder
  - Mixed occupancy
  - Positional disorder
  - Impurities
  - Vacancies
  - …

High Seebeck and electrical resistivity = Tunability of the carrier concentration
- flexible structure towards substitution, doping…
  - solid solution
  - flexible framework
  - Intercalation sites
  - Interstitial positions
  - …

A le recherche de nouveaux matériaux TE …?



We need:

To make the material pure in fairly large amount

To be able to densifiy it

The material to be mechanically sound

The material to be stable towards air and moisture

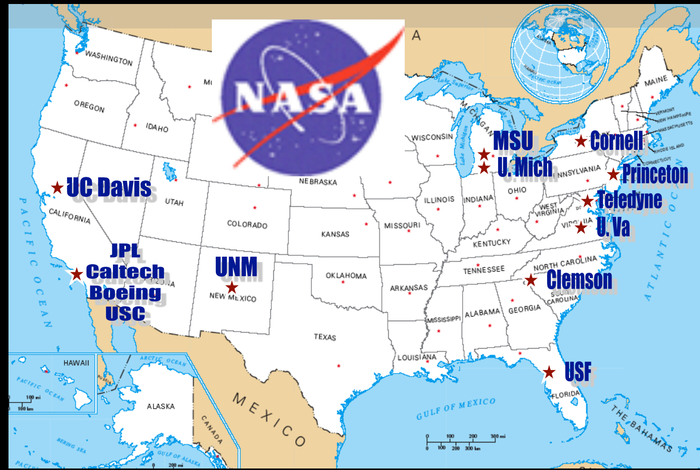
The constituting elements to be cheap enough, available and not toxic

Cost / effectiveness

A le recherche de nouveaux matériaux TE …?

Programme STMC

14 partners, 2 years… to find a solution replacement to the heritage SiGe



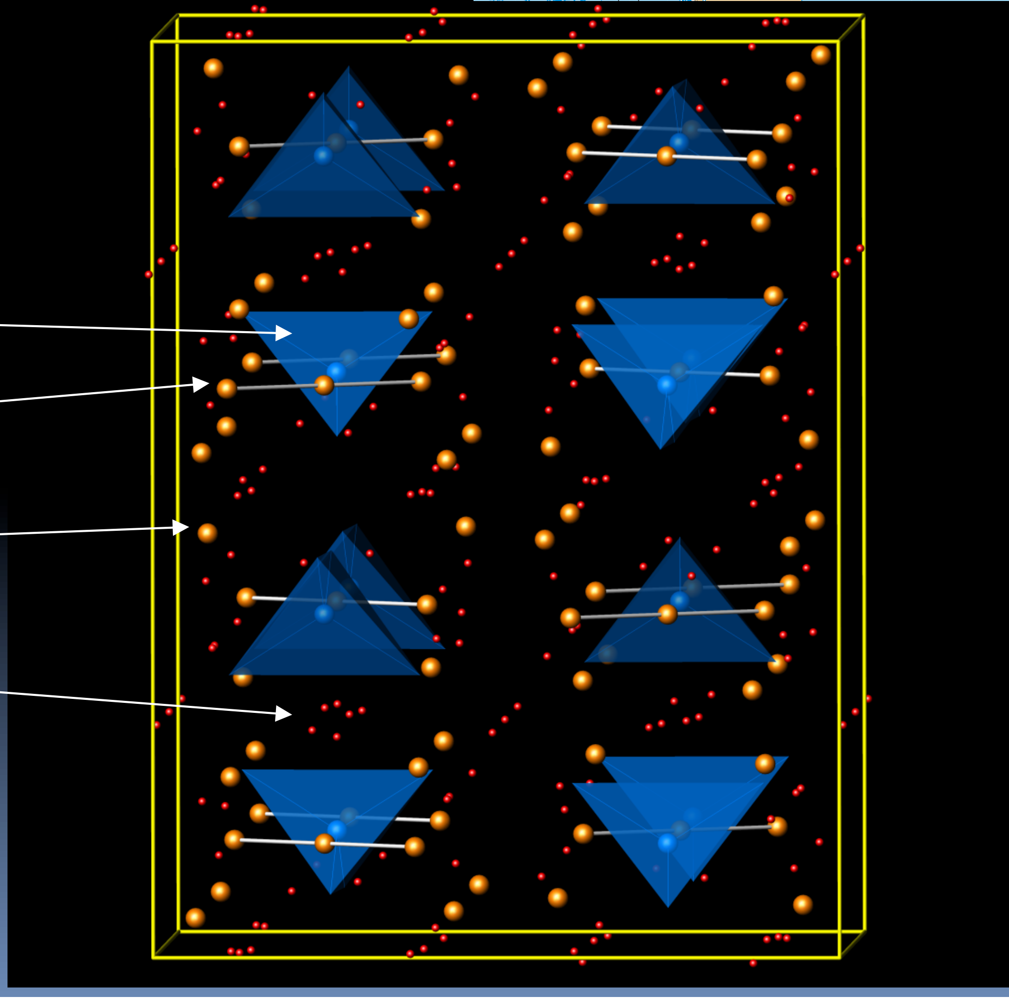
$Yb_{14}MnSb_{11}$

$[MnSb_4]^{10-}$

$[Sb_3]^{7-}$

$4Sb^{3-}$

$14Yb^{2+}$



$(10+7+4x3)^{-} + (14x2)^{+}$

$29(-) + 28(+) + 1h^{+}$

$Yb_{14}MnSb_{11}$ a naturally doped p-type HT TE material

Carrier concentration:

Calculated $[h+] = 8/6000\ 10^{-24} = 1.33\ 10^{21}$ cm-3
Measured $[h+] \approx 1.1 \pm 0.3\ x10^{21}\ cm^{-3}$

ρ and α OK !

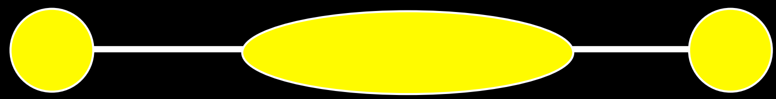
Complex 0D structure

Lattice parameters:

$I4_1/acd$
a = 16.562(3) Å
c = 21.859(2) Å
V = 6000 $Å^3$
Z = 8

\+

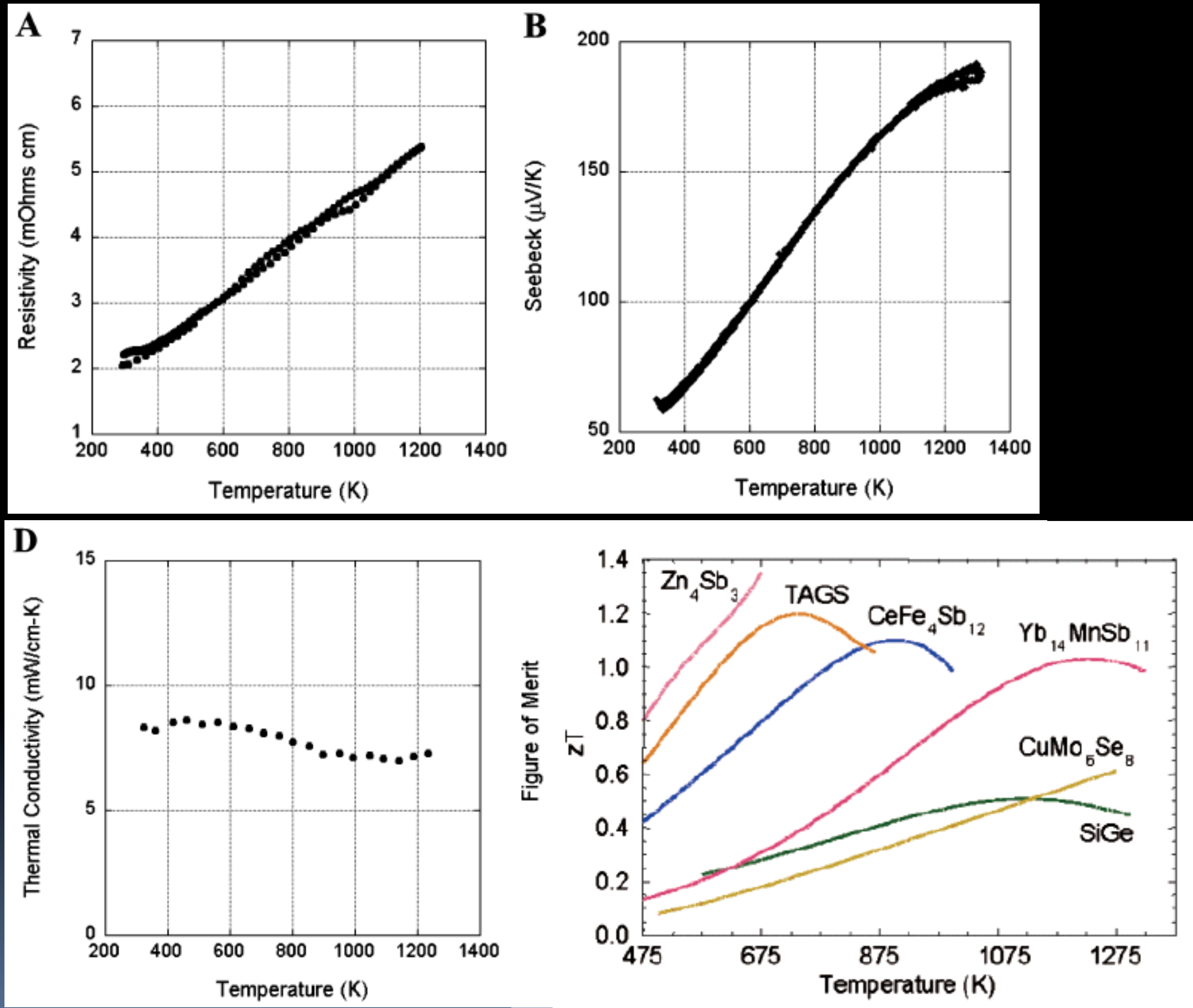
Highly disordered Sb_3 trimer



Sb_3^{7-}

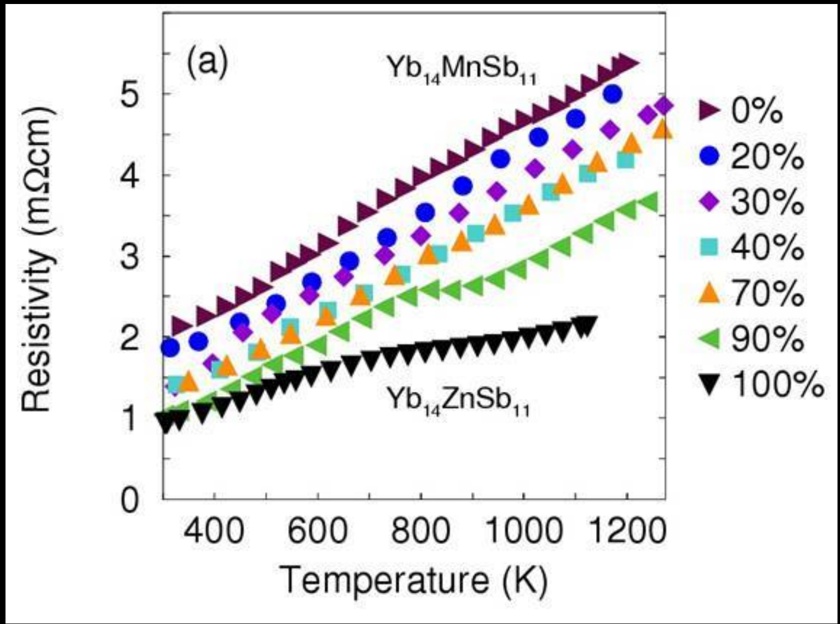
= Low K

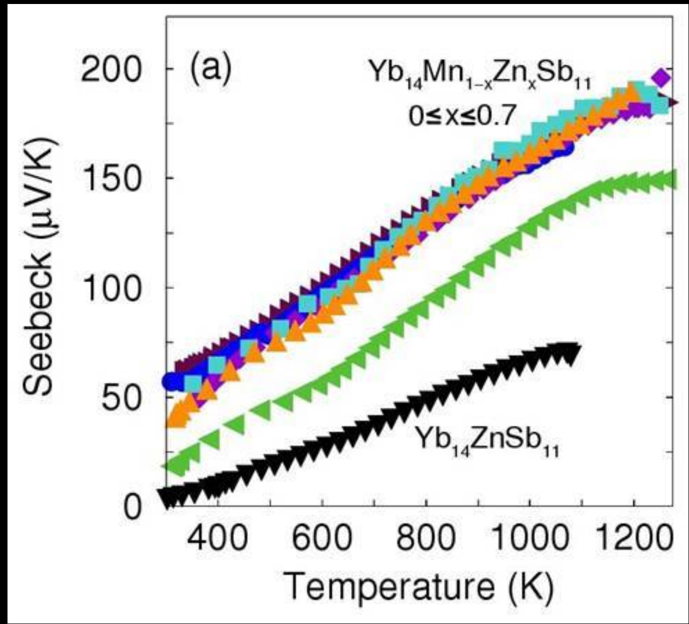
$Yb_{14}MnSb_{11}$ a naturally doped p-type HT TE material



S. Brown, F. Gascoin, G. J. Snyder, S. M. Kauzlarich, *Chemistry of Materials*, 2006, *18*, 1873.
U.S. Patent. Application Serial No. 11/470, 998

$Yb_{14}Mn_{1-x}Zn_xSb_{11}$





Mn and Zn both divalent → No Seebeck variation up to x = 0.7
No variation of $[h^+]$

Mn d^5, Zn d^{10} → lower spin concentration

→ lower spin disorder scattering

→ Lower Electrical resistivity

Transition metal chalcogenides as TE materials…

Pseudo Hollandite

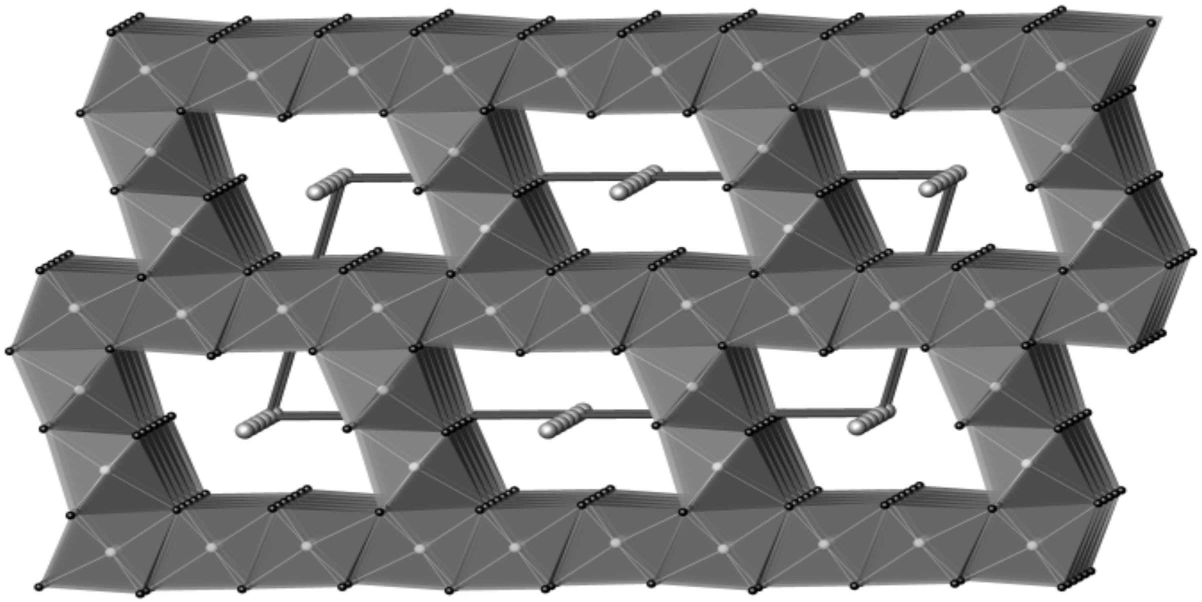
CdI_2 type layered : TiX_2 or $ACrX_2$

Large families of compounds, ideal playground for tuning the transport properties

Two disctinct subnetworks
Intercalation / Insertion
Solid solutions (TM and S/Se/Te)
Insulator – Metal transition likely…

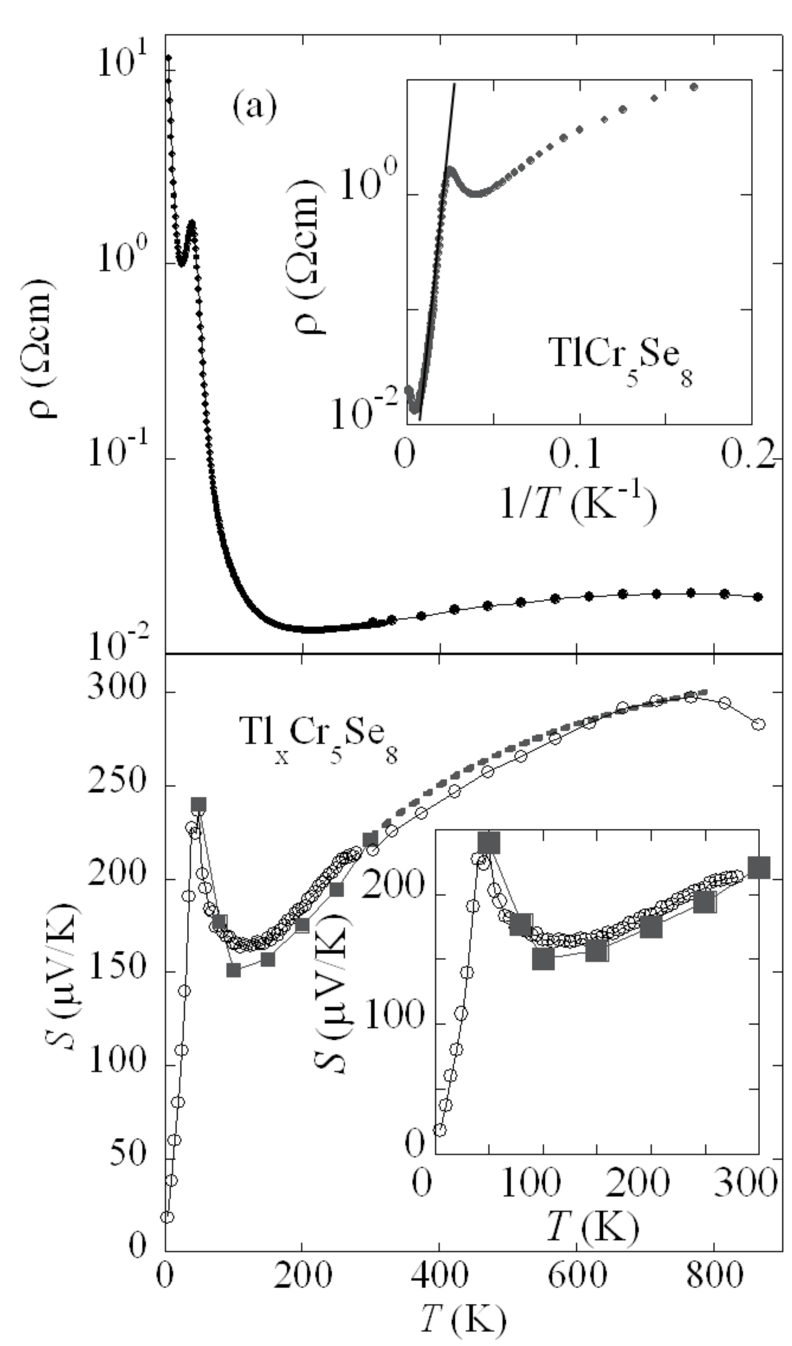
Transition metal chalcogenides as TE materials…

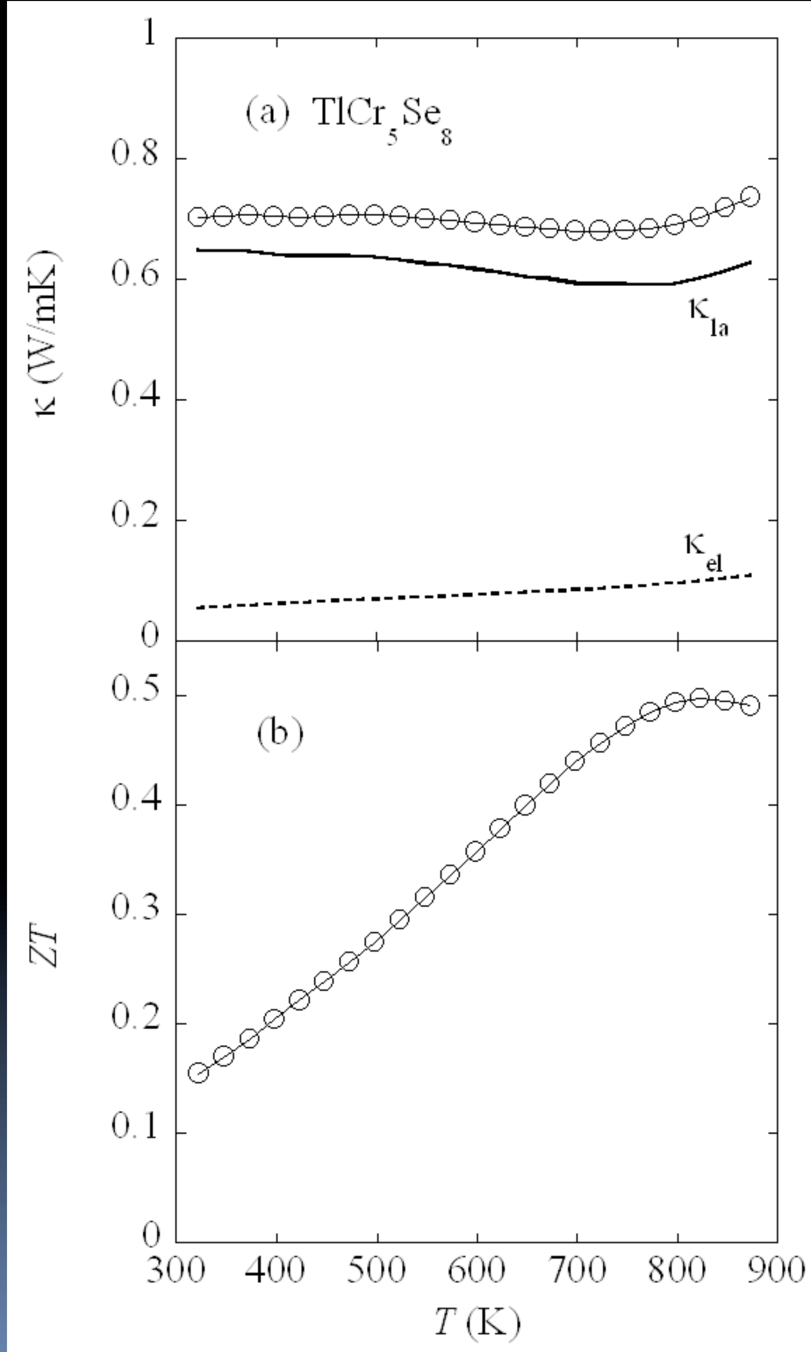
Pseudo-Hollandite



general formula $A_xB_{10}X_{16}$ with $x \leq 2$

Pseudo hollandite: $Tl_XCr_5Se_8$ with x<1

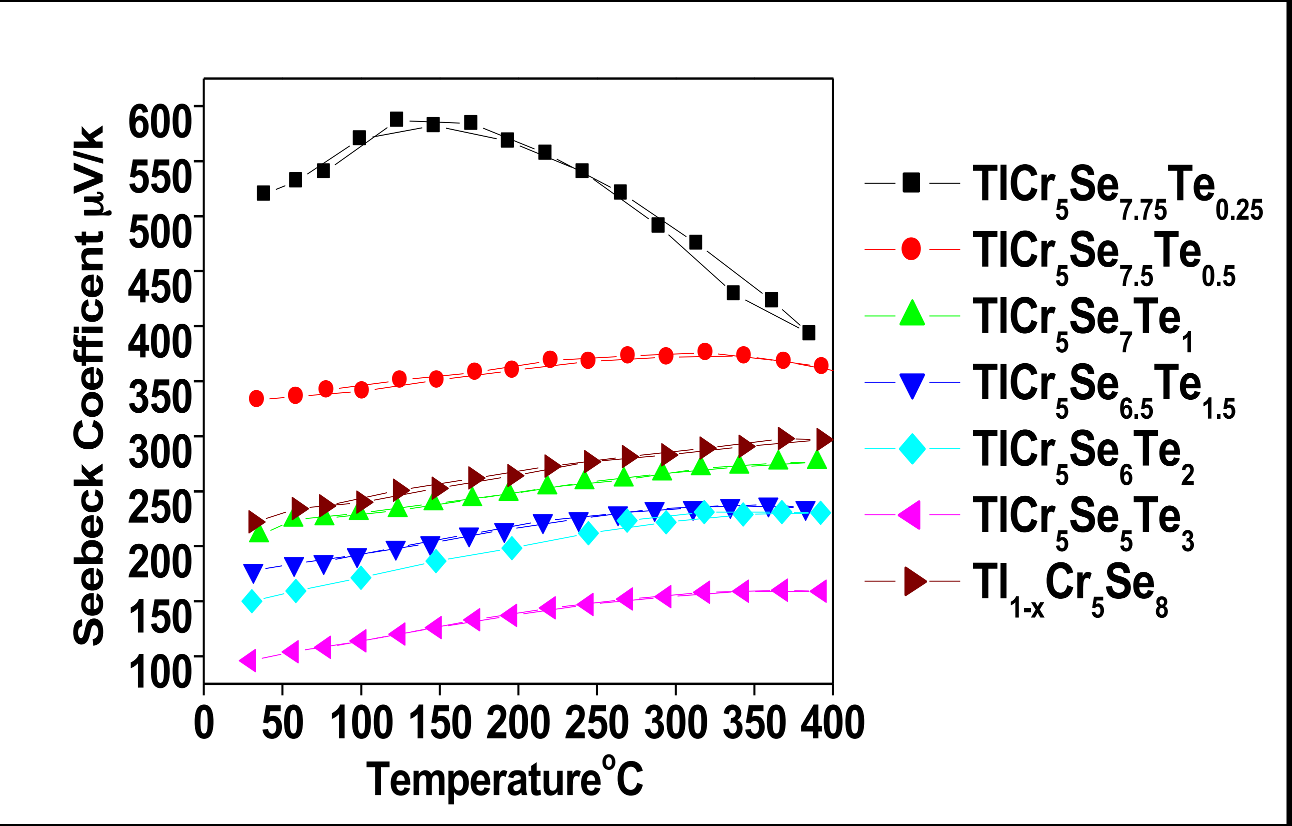




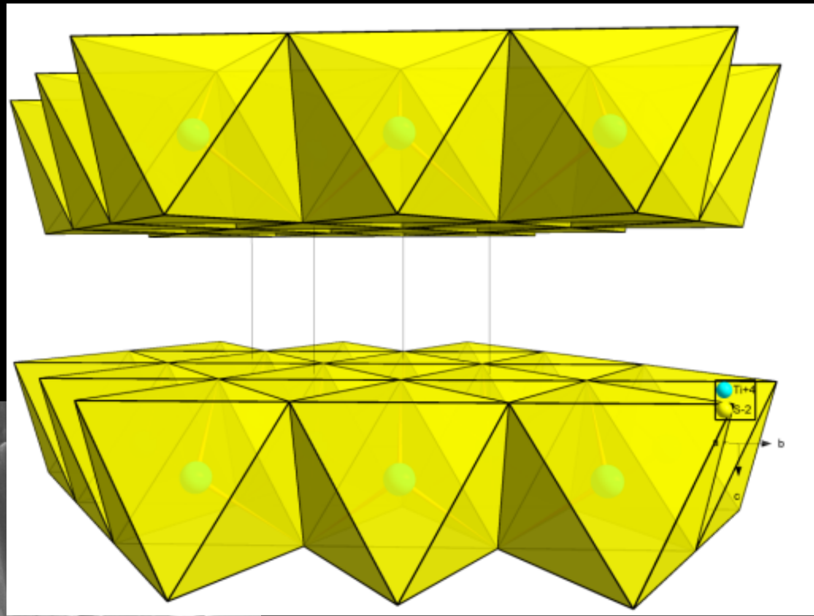
Pseudo hollandite: $Tl_xCr_5Se_{8-y}Te_y$

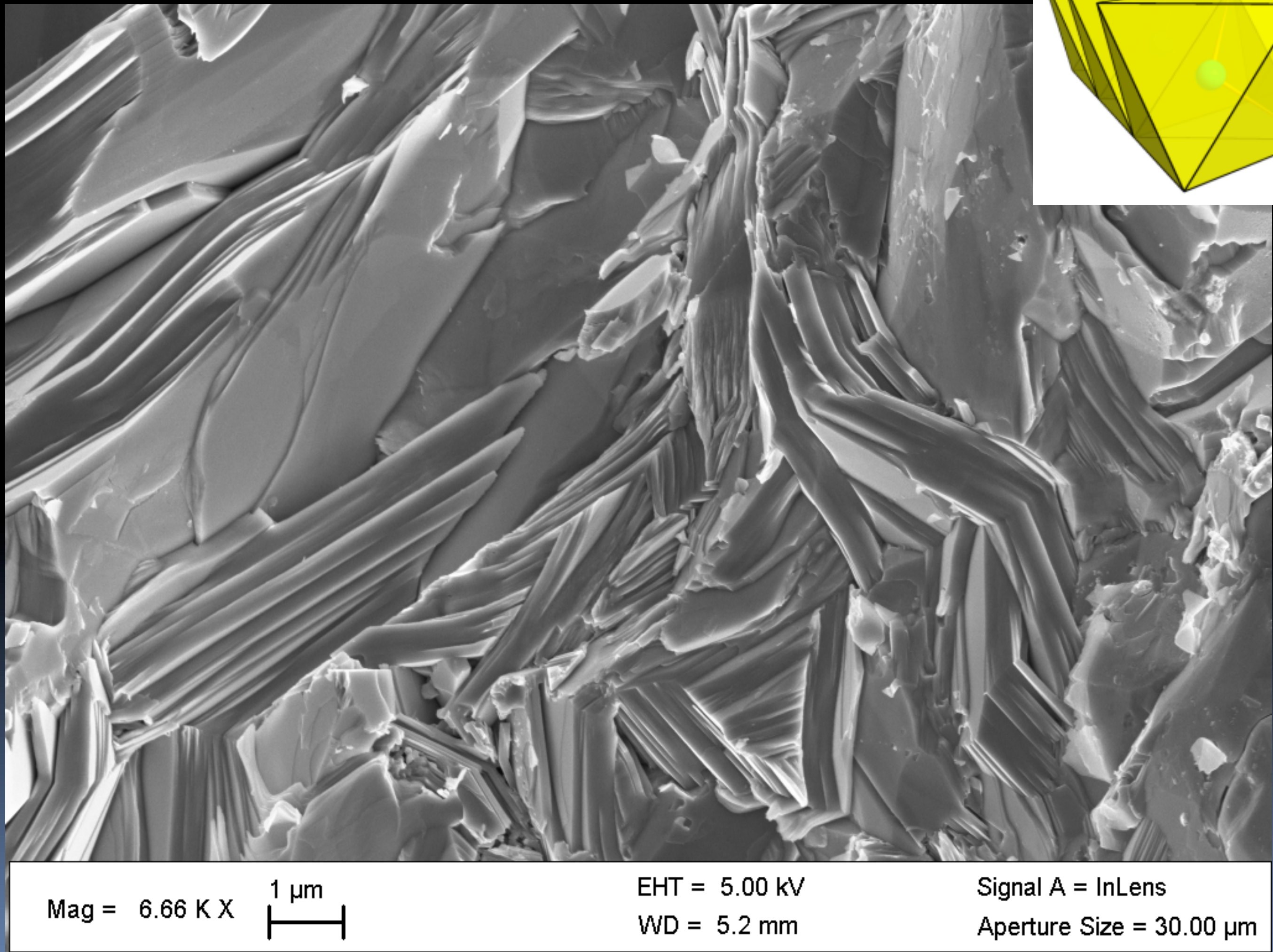
Going down the column, the metallicity increases…

O → S → Se → Te



Solid solution TiS_xSe_{2-x}





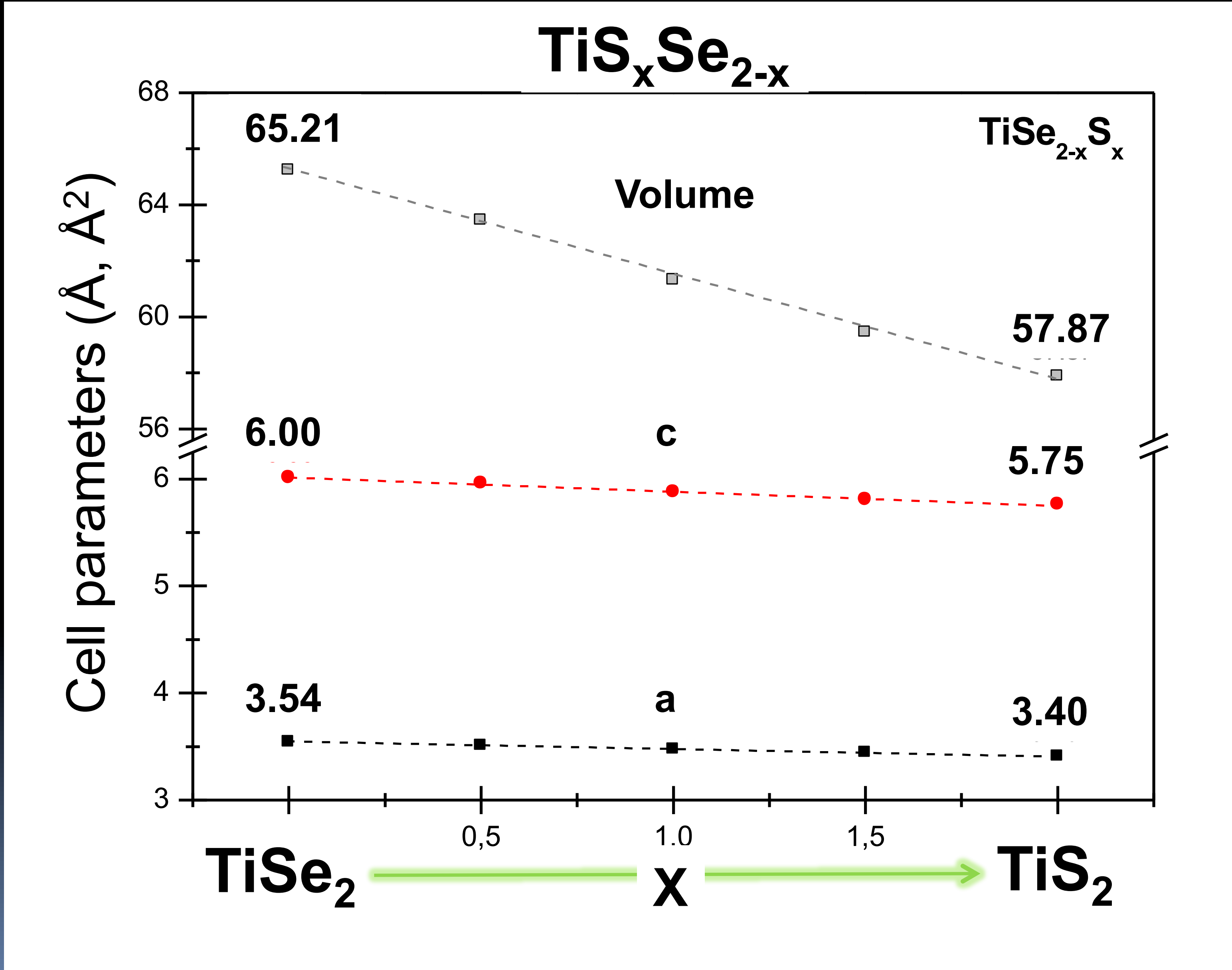
Synthesis:

Raw elements in sealed tubes

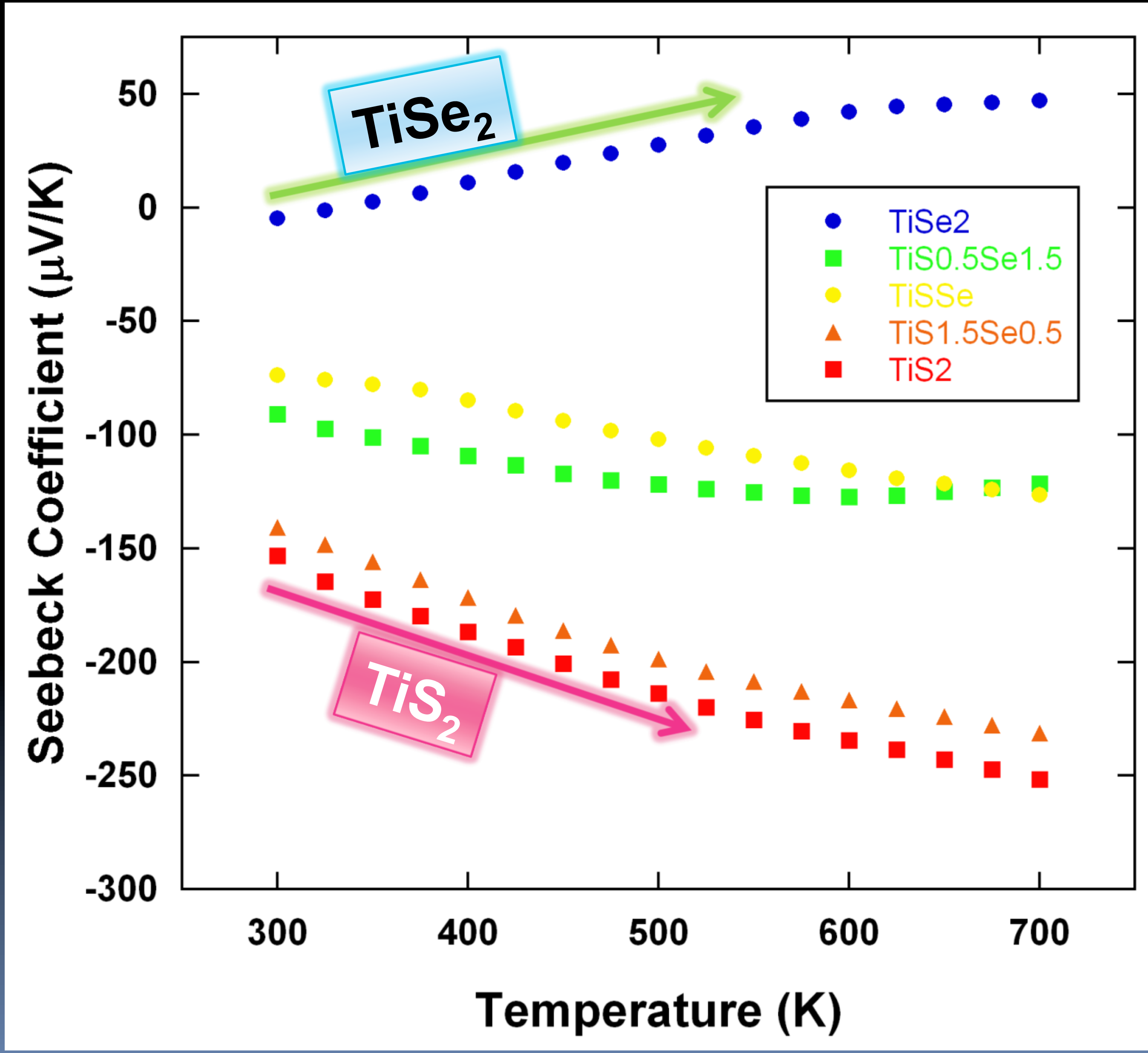
Processing:

SPS densification

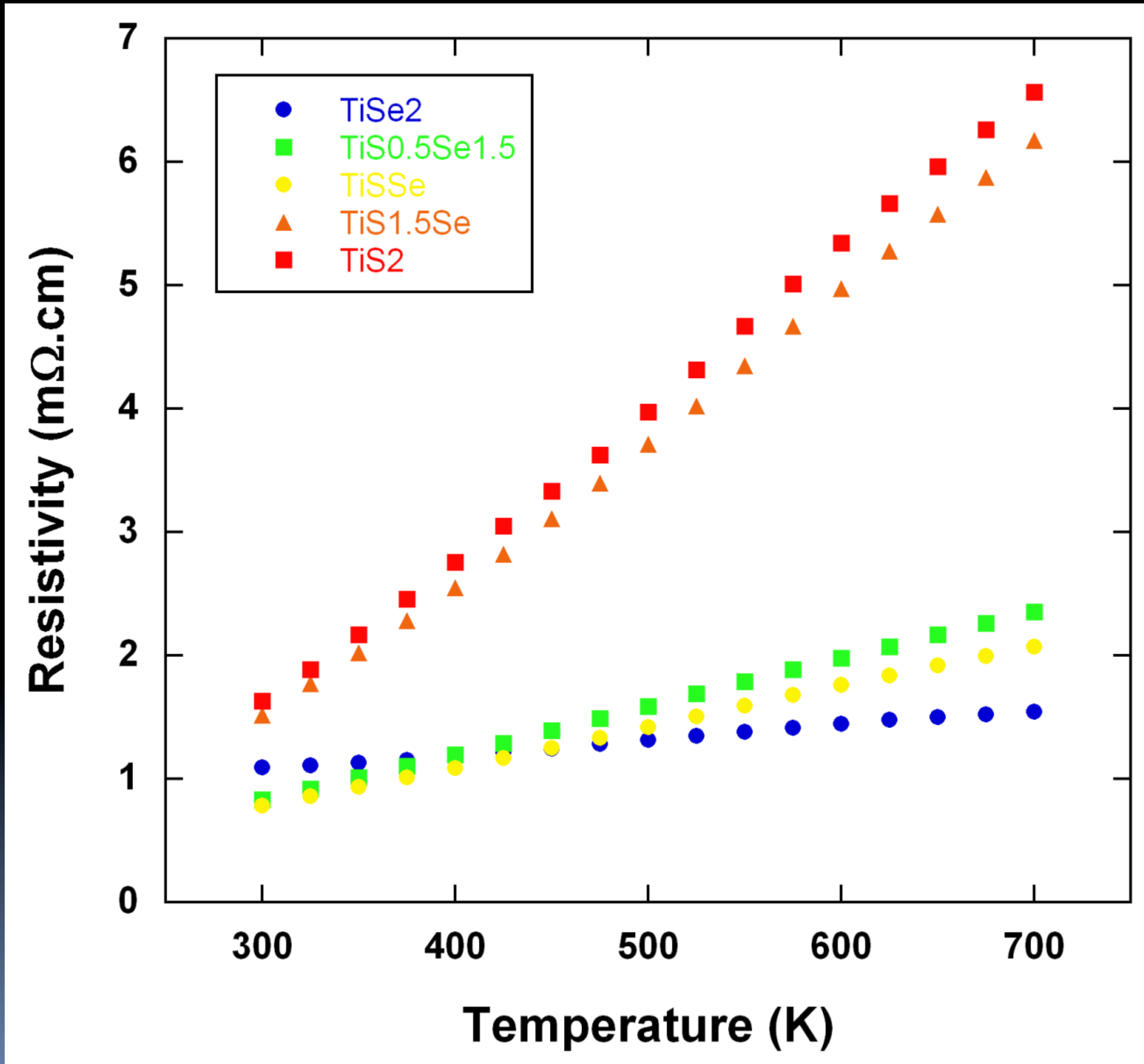
Solid solution TiS_xSe_{2-x}



Solid solution TiS_xSe_{2-x}



Solid solution TiS_xSe_{2-x}



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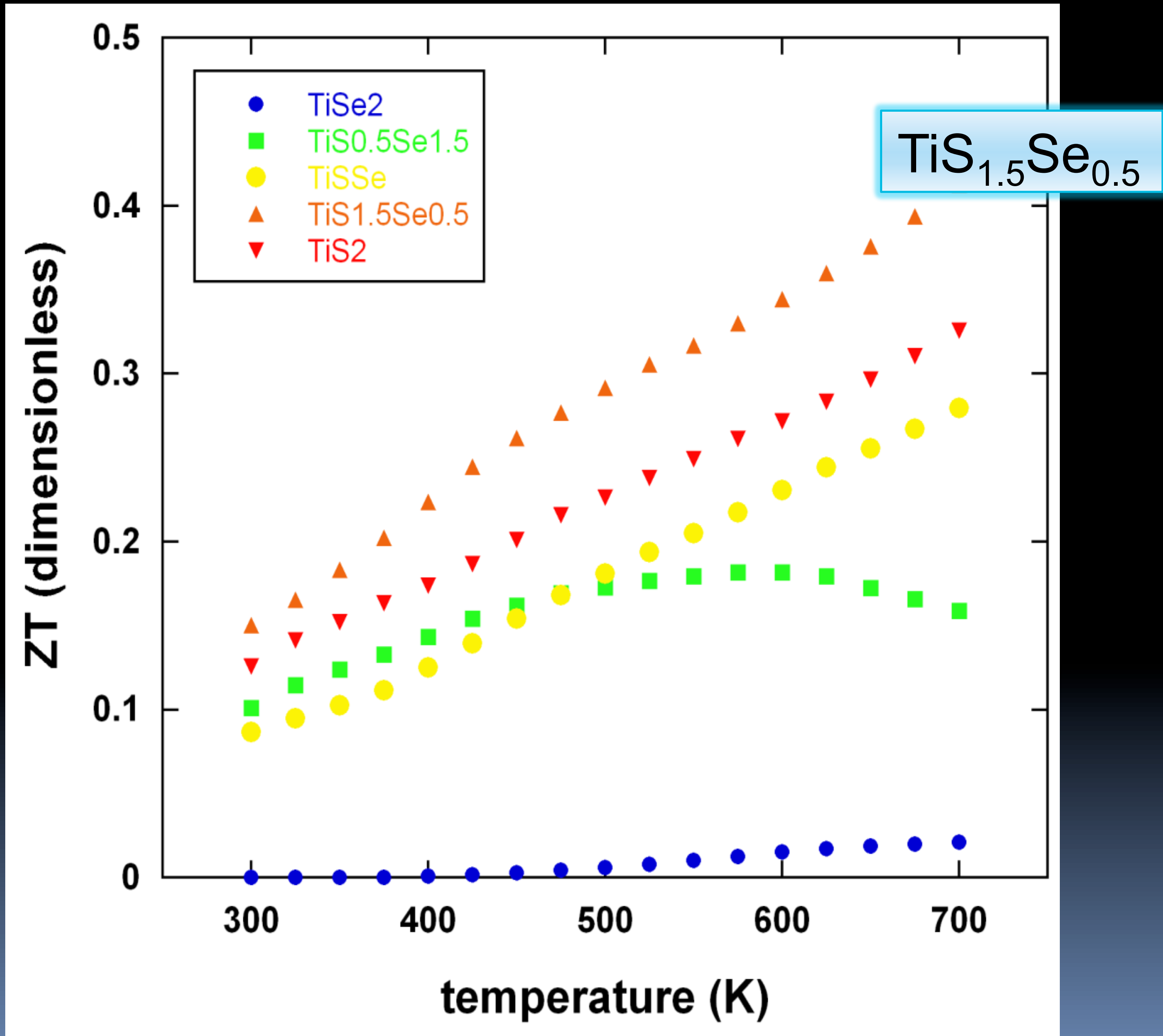
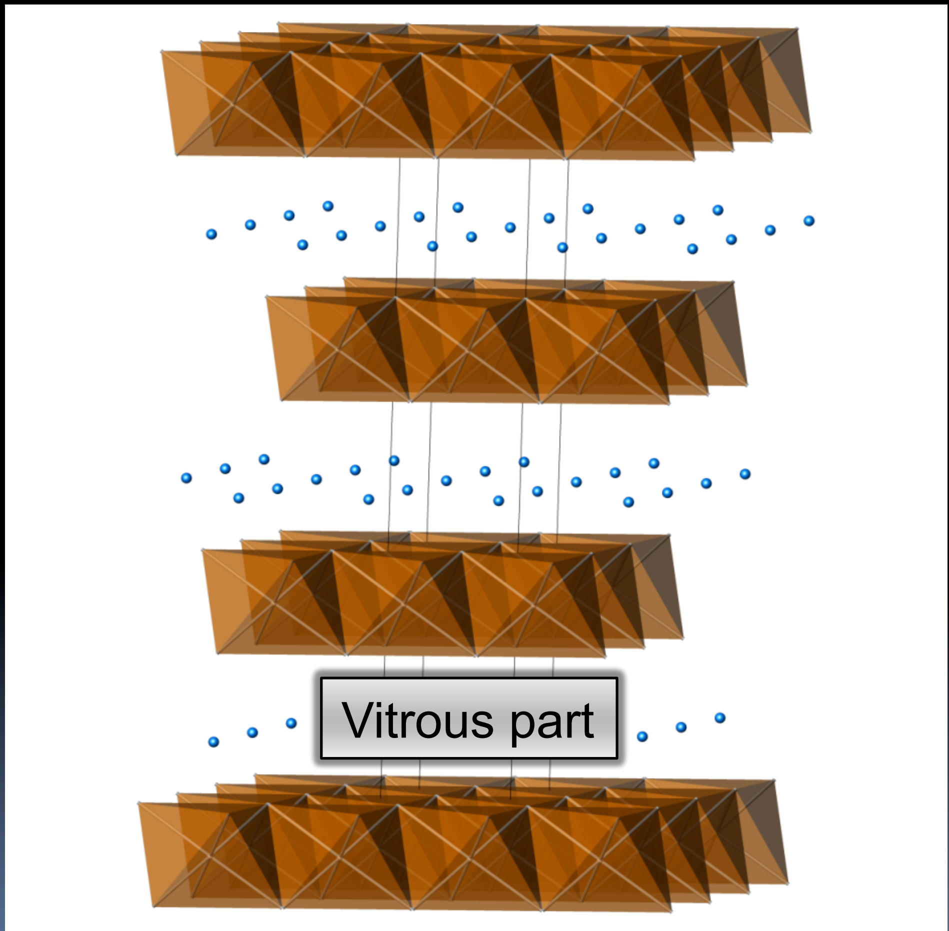


New ideas, new TE materials… ?

$AgCrSe_2$, *a priori* a good thermoelectric …



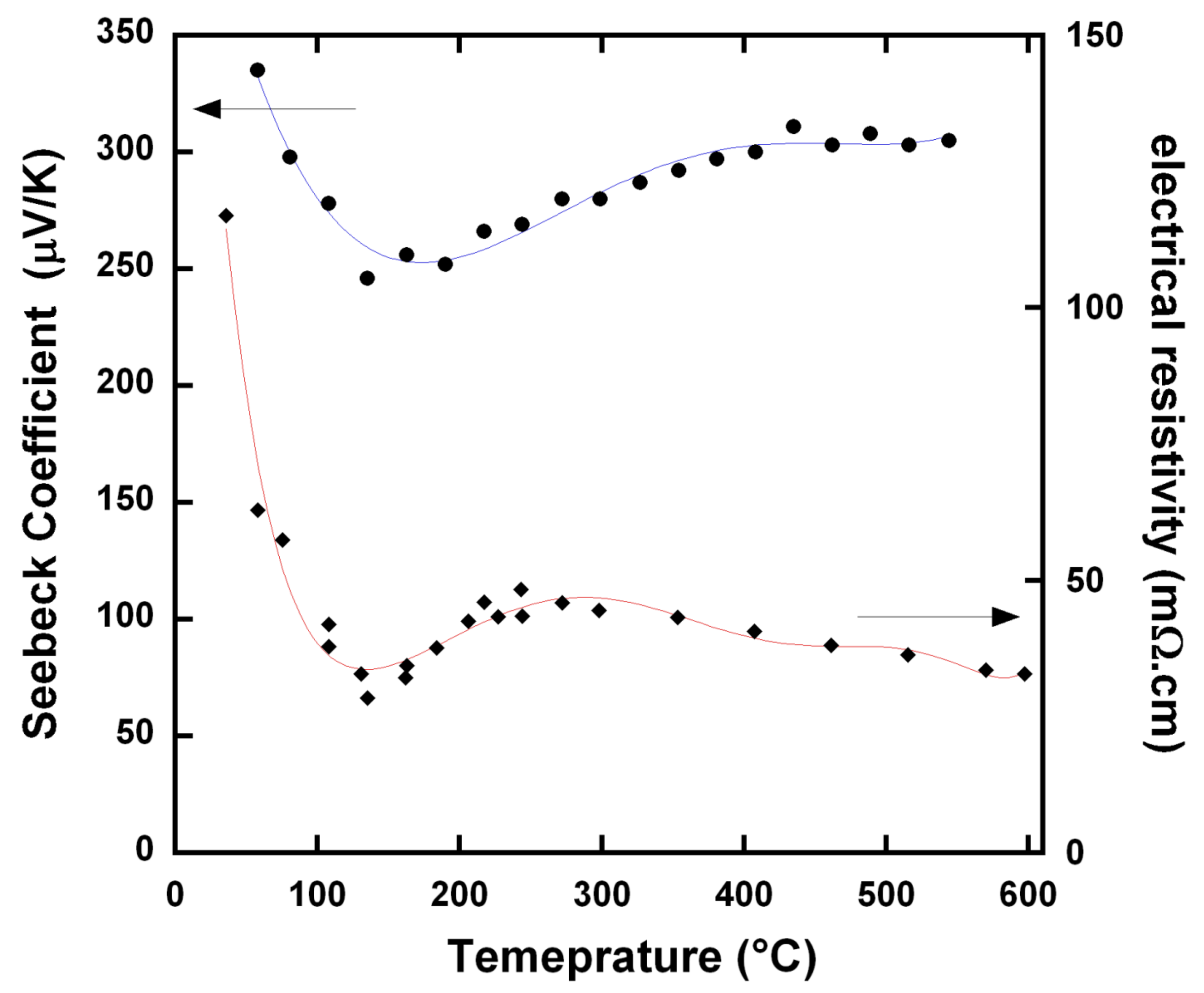
Electronic Conduction in the layer
+
Disorder between the layers
+
Many (!!!) compounds possible
=
Good choice for TE material …

CdI_2 type $CrSe_2$ layers

Highly dosrdered Ag atom in the interlayer spacing

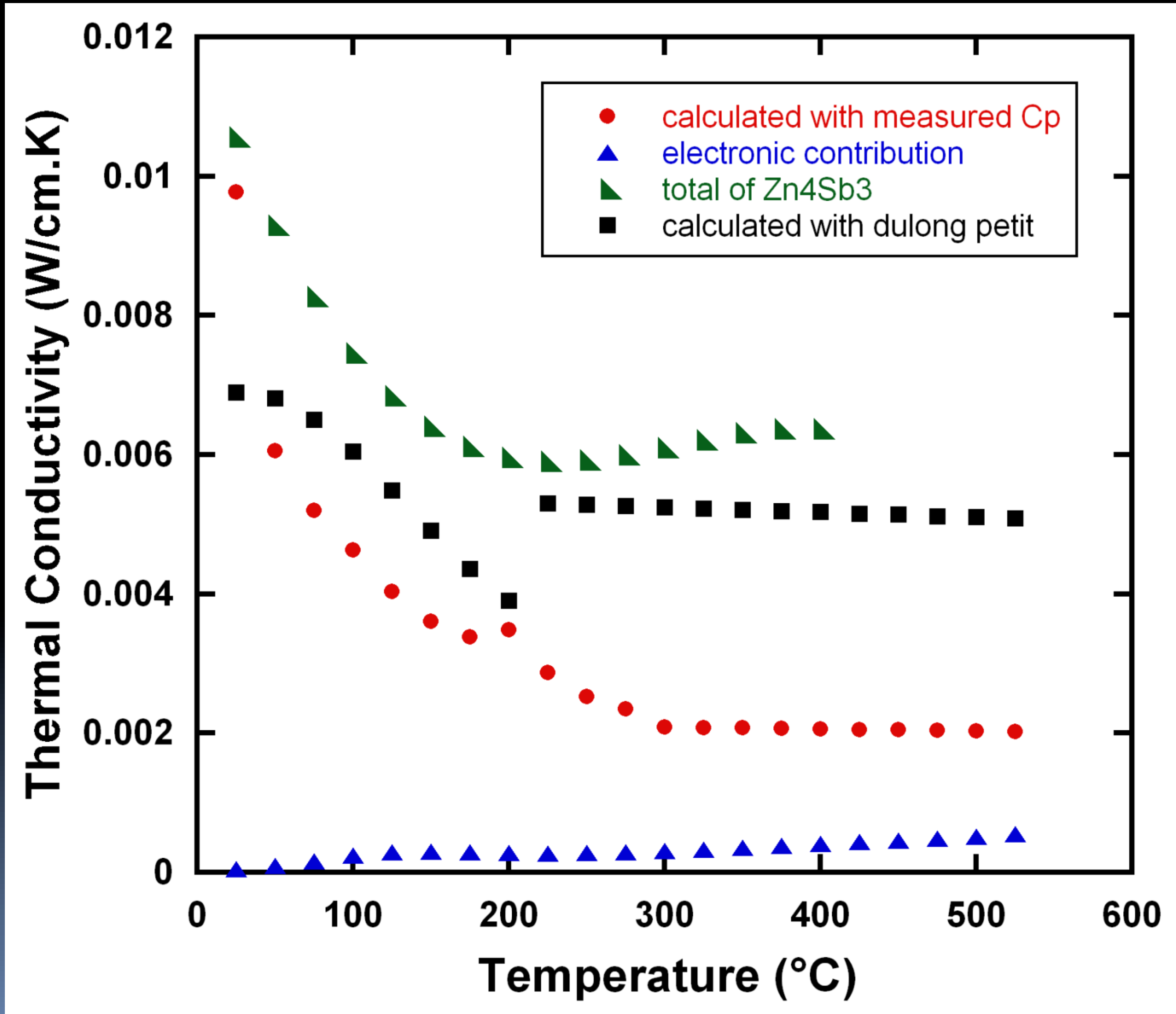
$AgCrSe_2$, *a priori* a good thermoelectric …

Huge Seebeck and « large » resistivity

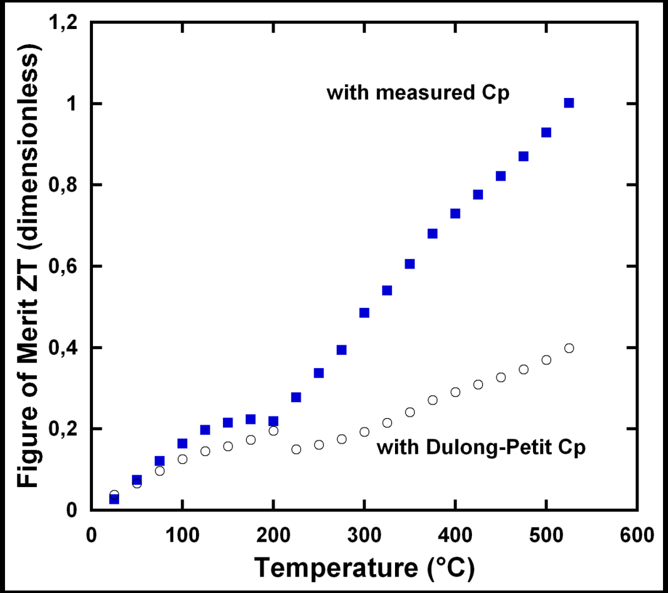


$AgCrSe_2$, *a priori* a good thermoelectric …

Extremely low thermal conductivity



AgCrSe$_2$, *a priori* a good thermoelectric …



As expected, very low thermal conductivity

(and that's this only think we could forecast !)

High Seebeck

BUT : Ionic conductor, hence impossible to use in a device…

However, the concept might be fruitful !?

To be continued…

Concluding remarks

There are good TE material out there … we just need to find them !!!

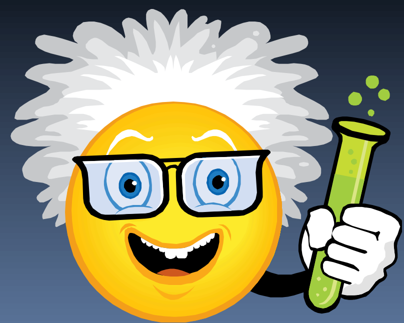
- $Yb_{14}MnSb_{11}$ out of the blue…

Known structure types hide special and interesting compositions (and chemists know crystallographic structures…)

- Transition metal chalcogenide and oxychalcogenides

New materials (structures!) must be looked for…

Applications/Industrials are waiting for us



Concluding remarks

TE Materials research must be accompanied by module conception and system design

For each (new) material, the making of a module has to be thought over!

A solution replacement for Bi_2Te_3 is far, very far !!! (ZT of 3 …???)

ZTs around 0.5 – 0.8 are easy to find, but not enough…

Cheap, non toxic, light, robust, long-life, efficient thermoelectric materials and device are the key to further viable applications