Summer School 2019

INTRODUCTION TO THERMOELECTRICS: FROM MATERIALS TO APPLICATIONS

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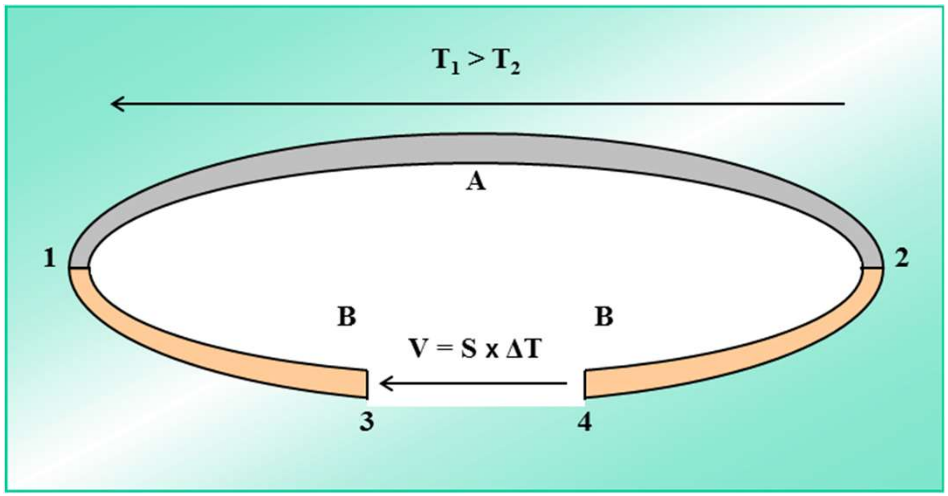
CONTENT

SOME YEARS AGO…

- **1821 :** *T. J. Seebeck* : a potential difference is created when a temperature difference is applied at the extremities of a material.



$$V = (S_A - S_B) \times (T_1 - T_2) = S_{AB} \times \Delta T$$

where S_i = Seebeck coefficient or thermoelectric power ($\mu V.K^{-1}$)

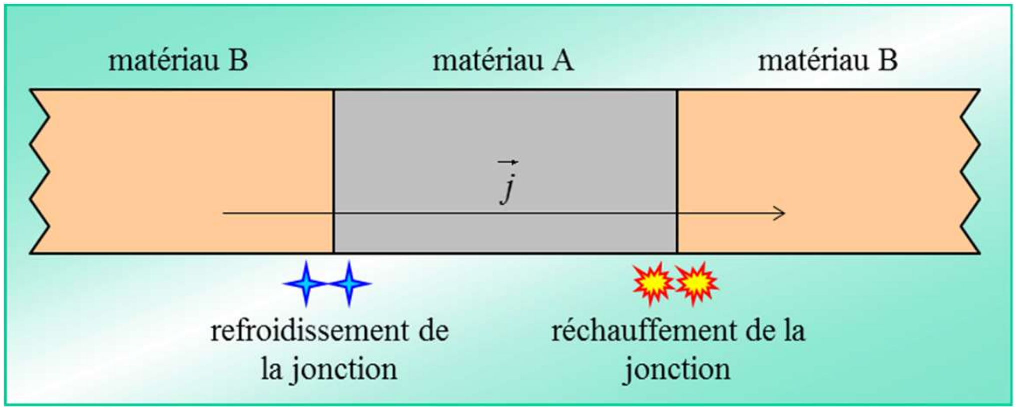
By convention : S < 0 for **n type** materials

S > 0 for **p type** materials

SOME YEARS AGO…

- **1834 :** *J.-C. Peltier* : when a current is applied through a solid, there is a heat transfer from one side to the other

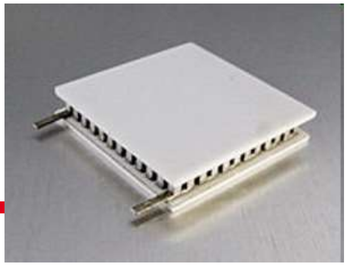
- **1838 :** *H. Lenz* : when a current goes through a material in contact with an other, there is a production, and vice versa, an absorption of heat at its extremities.



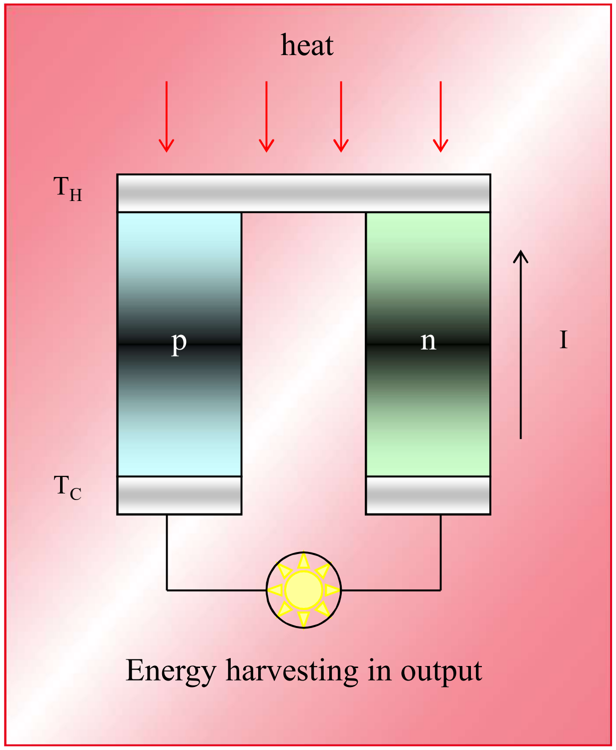
- **1851 :** *W. Thomson* : good definition of the three thermoelectric (TE) effects: Seebeck, Peltier and Thomson.

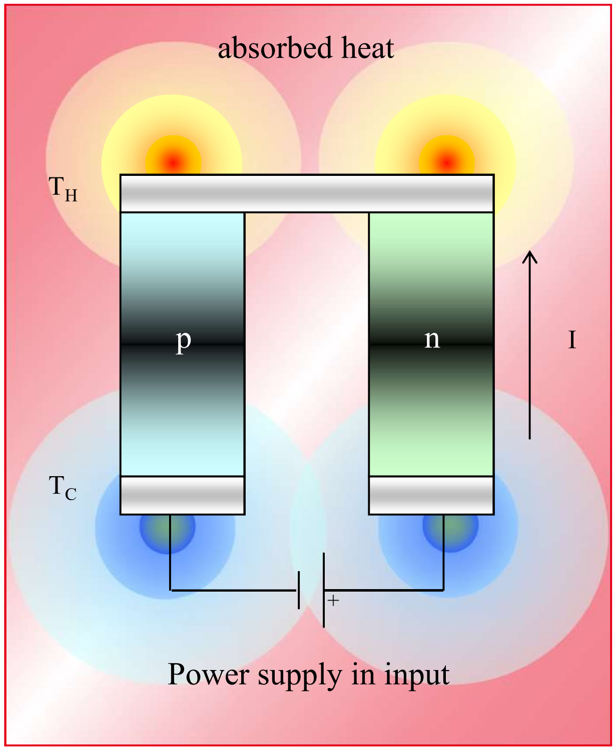
- **1950s :** *A. Ioffe* : discovery of TE properties of doped semiconductor materials.

THERMOELECTRIC CONVERTERS



- Two working modes:





Thermoelectric generator mode
Thermal gradient is imposed

→ **Seebeck effect: TE Generator**

Thermoelectric cooling mode
Electric tension is imposed

→ **Peltier effect: TE Cooler**

EFFICIENCY AND POWER FACTOR

- three important properties for TE materials :
  - S : TE power ($\mu V.K^{-1}$)
  - σ : electrical conductivity ($S.m^{-1}$)
  - λ : thermal conductivity ($W.m^{-1}.K^{-1}$)

- definition of the **dimensionless power factor ZT_m** :

$$ZT_m = \frac{\sigma \times S^2 \times T_m}{\lambda}$$

With $T_m = (T_c + T_f) / 2$

T_f = cold T
T_c = hot T

- definition of the maximum of conversion efficiency :

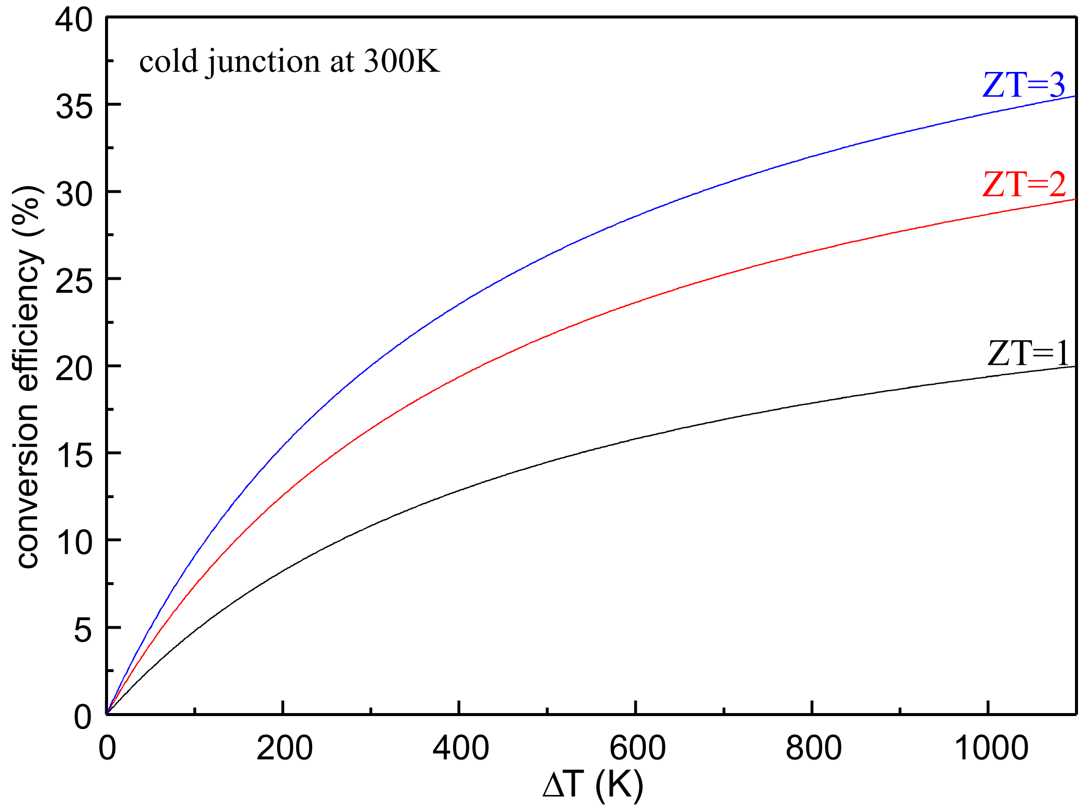
$$\Phi_m = \eta_c \times \eta_{th} = \frac{T_c - T_f}{T_c} \times \frac{\sqrt{(1 + ZT_m)} - 1}{\sqrt{(1 + ZT_m)} + \frac{T_f}{T_c}}$$

Carnot efficiency

TE system efficiency

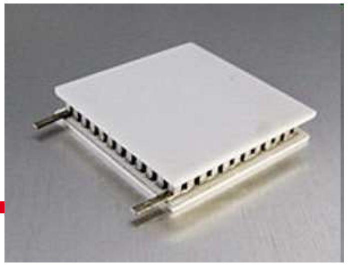
EFFICIENCY AND POWER FACTOR

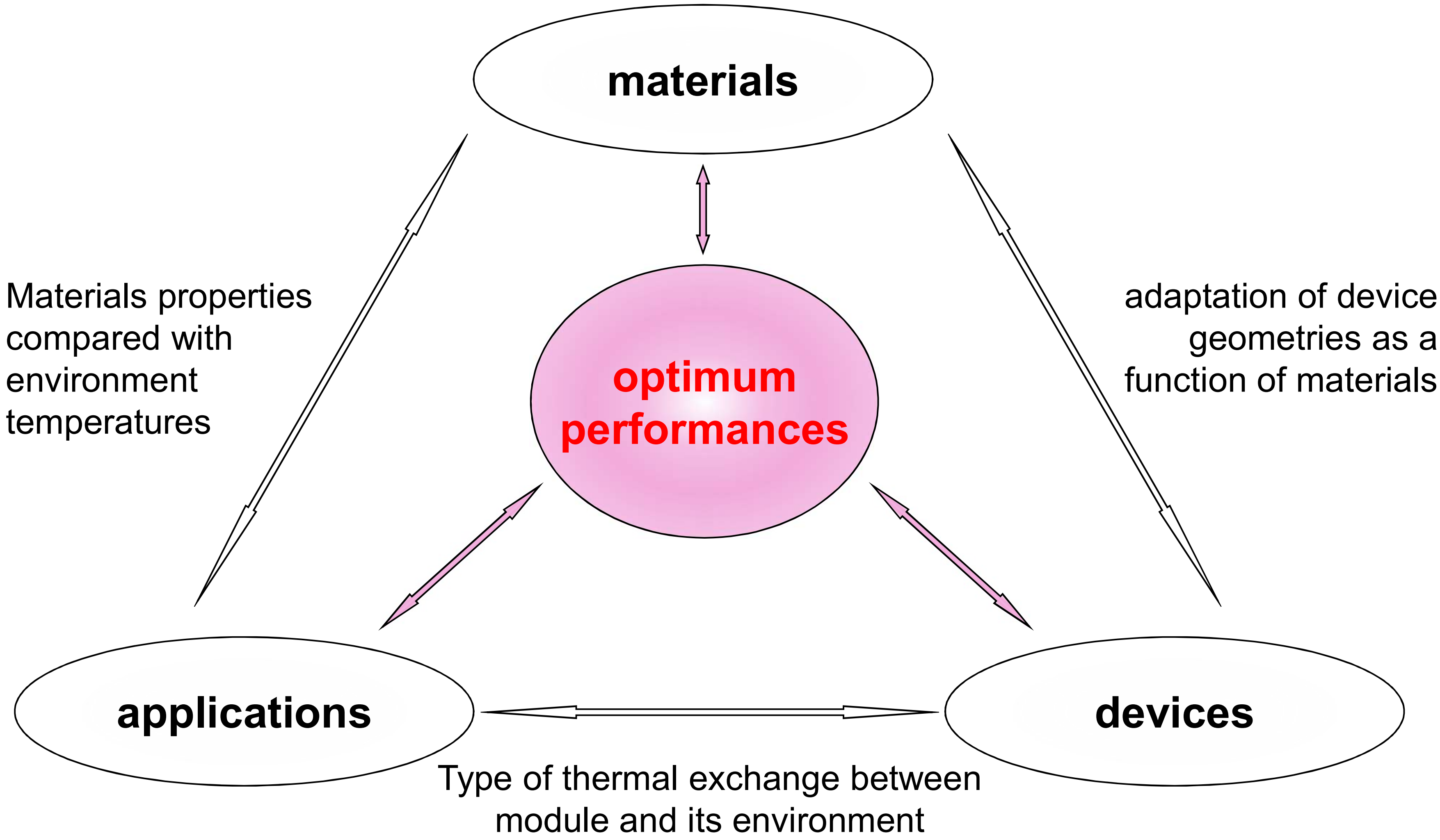
- Evolution of ZT as a function of temperature :



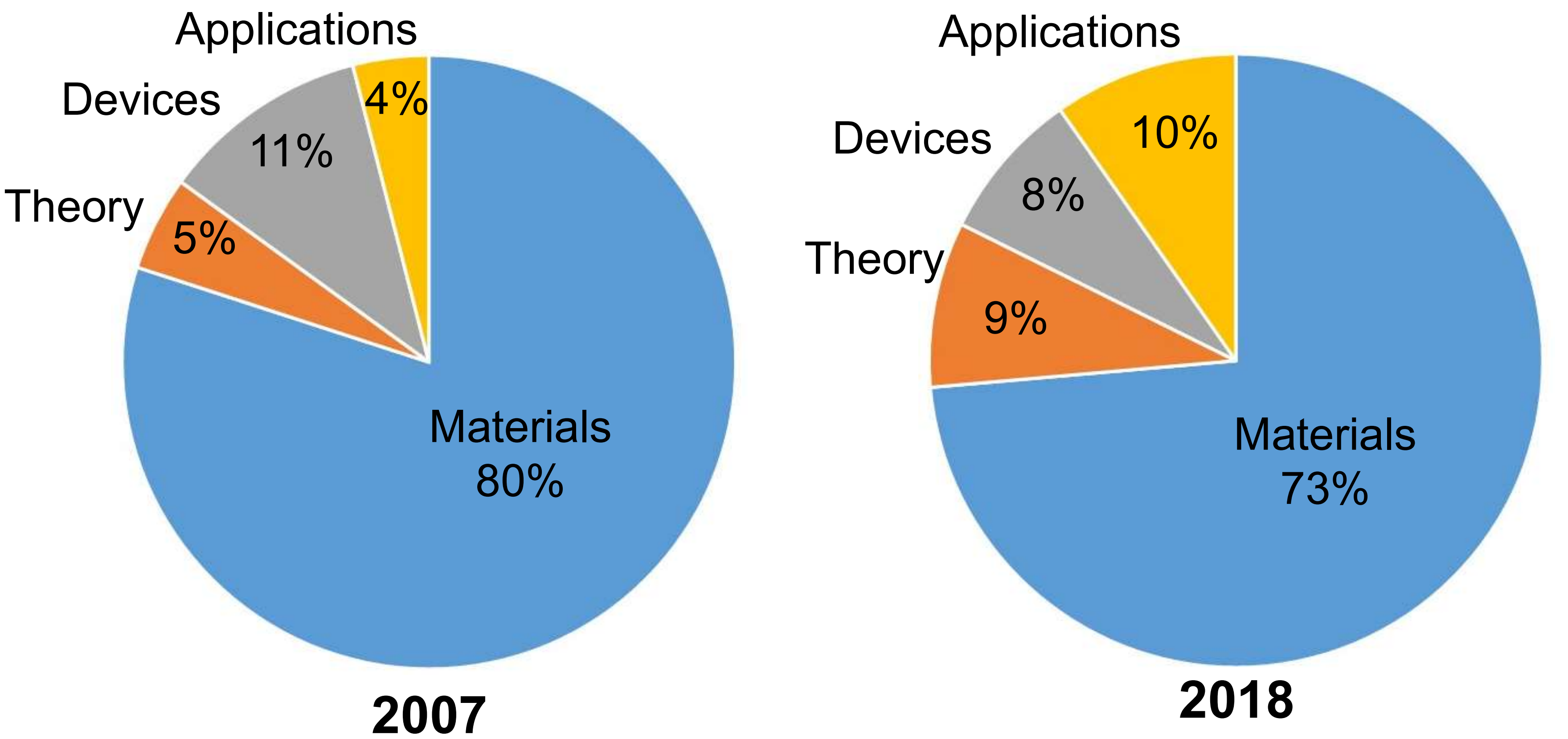
→ Goal : to obtain the highest value of ZT !

THERMOELECTRICS, A 3-LEVEL APPROACH





- Distribution of research areas:



(source : Int. Conf. Thermoelec., Jeju Island, South Korea, 2007)
(source : Int. Conf. Thermoelec., Caen, France, 2018)

THERMOELECTRIC MATERIALS

- Various families of TE materials :

  - semiconductors
  - oxides
  - skutterudites
  - silicides
  - etc.

- They differentiate themselves from each other by :

  - temperature range (ZT_{max} and thermal stability)
  - TE properties (σ, S and λ)
  - realization and integration technologies
  - criteria of abundance, toxicity

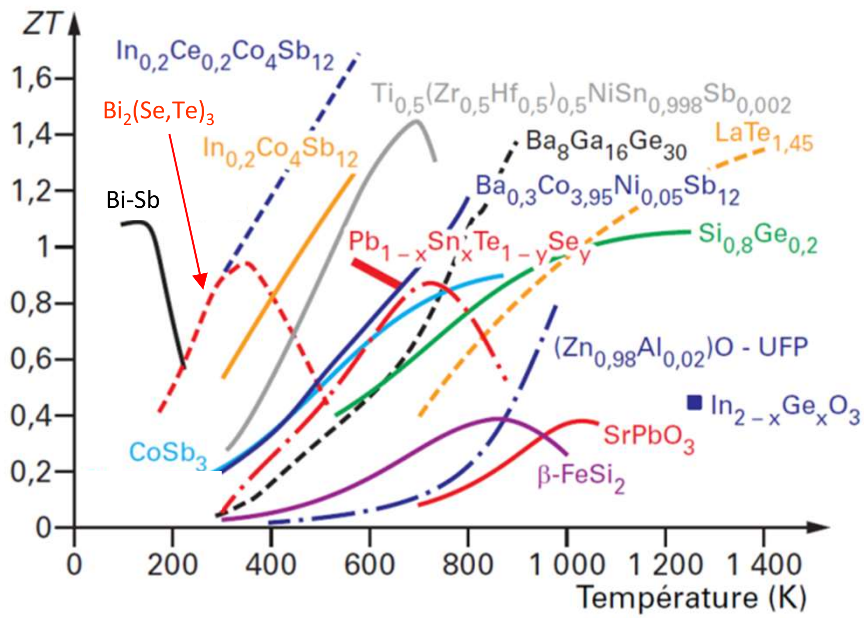
  } → economical and environmental considerations

  - structural properties → nanostructuration liten ceatech

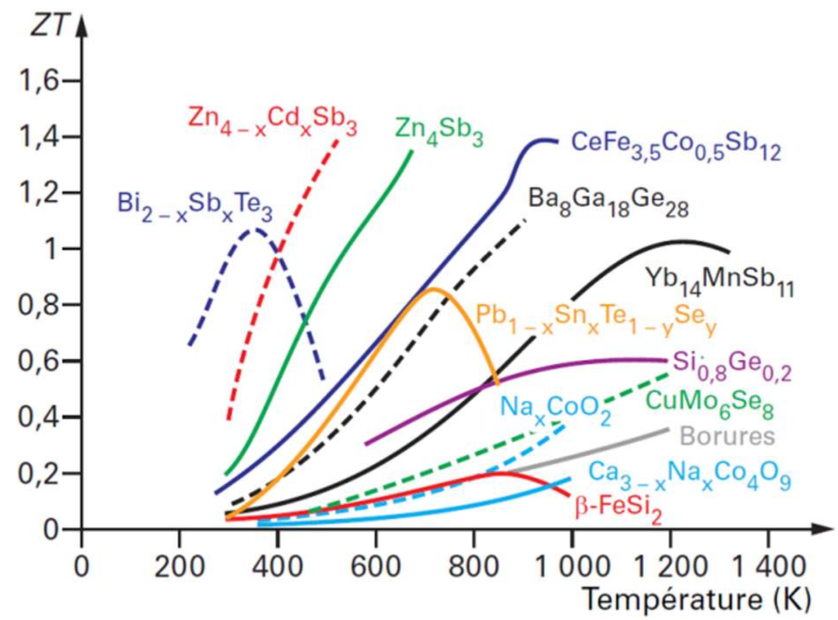
THERMOELECTRIC MATERIALS

- Performances of TE materials (non exhaustive list):

  → as a function of temperature



Type N



Type P

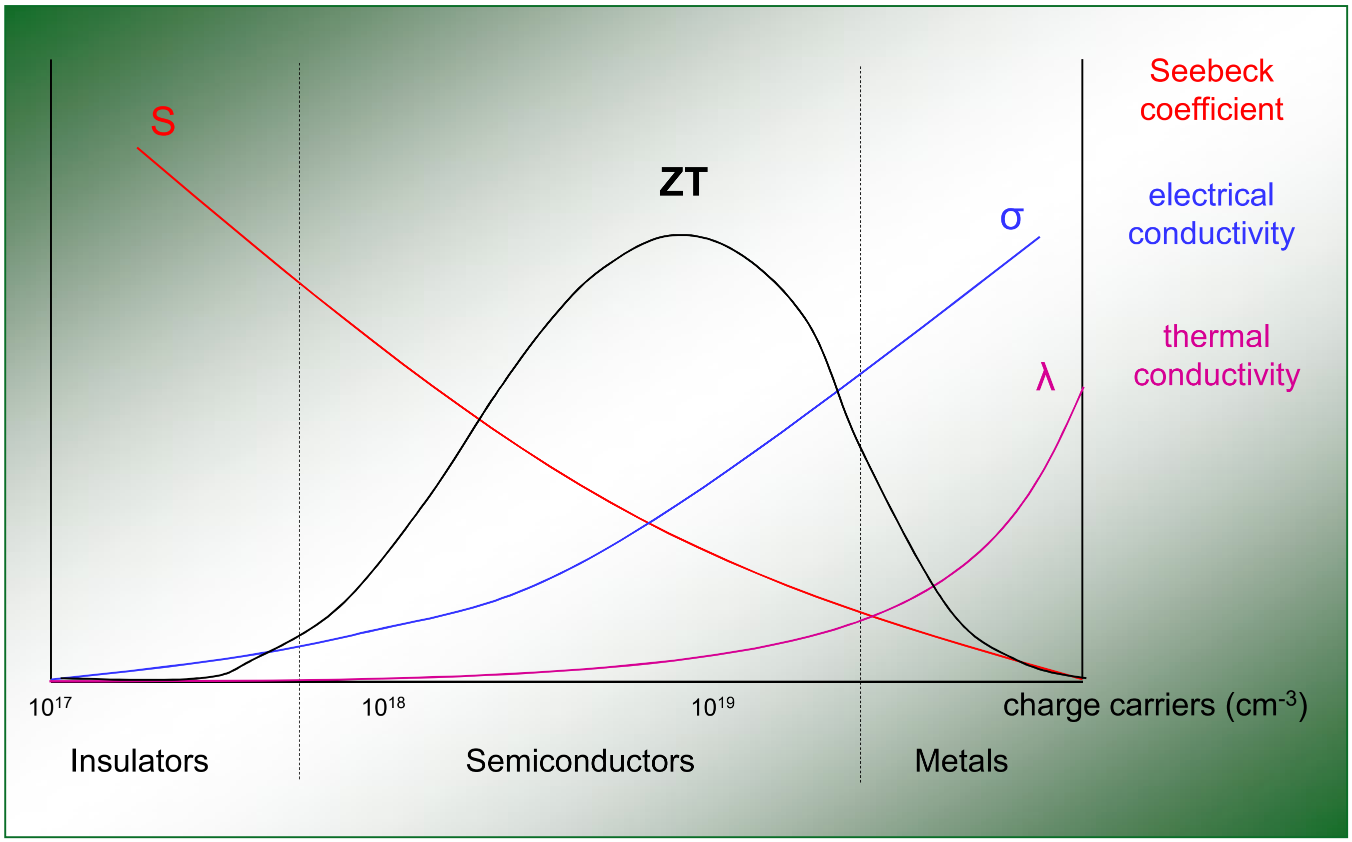
- H-H: TiNiSn & derivatives (430°C max)
- skutterudites: $CoSb_3$ & derivatives (530 °C max)
- clathrates: $Ba_8Ga_{16}Ge_{30}$ (630 °C max)
- $Pb_{1-x}Sn_xTe_{1-y}Se_y$ (530 °C max)
- $Si_{0.8}Ge_{0.2}$ (1000 °C max)
- Mg_2Si & derivatives (530 °C max)

- Zn_4Sb_3 & derivatives (400 °C max)
- skutterudites: $CeFe_{3.5}Co_{0.5}Sb_{12}$ (710 °C max)
- clathrates: $Ba_8Ga_{16}Ge_{30}$ (630 °C max)
- $Pb_{1-x}Sn_xTe_{1-y}Se_y$ (530 °C max)
- $Si_{0.8}Ge_{0.2}$ (1000 °C max)
- $MnSi_{1.75-x}$ (T_{max} not clear)

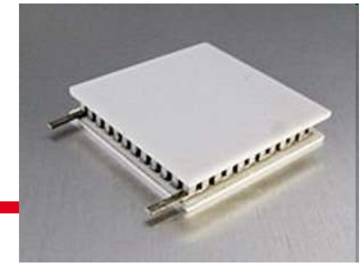
THERMOELECTRIC MATERIALS

- Performances of TE materials:
  - → as a function of nature of materials

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



THERMOELECTRIC MATERIALS



- **Bi_2Te_3**

  - since decades, THE thermoelectric material, the most performing at room temperature

- Advantages :

  - semiconductor with the two different kinds of doping:
    . doped with Sb for p type
    . doped with Se for n type

  - ZT ≈ 1 at 300 K
  (ρ = 1100 μΩ.cm, S = 210 μV.K^{-1} and λ ≈ 1.4 W.m^{-1}.K^{-1})

- Drawbacks :

  - scarcity, toxicity…

→ all commercial devices use Bi_2Te_3 as TE material!

- **Si / SiGe**

  - the most known of semiconductors…

- Advantages :

  - belongs to the world of microelectronics

  - both types of doping are obtained generally with:
    . B for p type
    . P or As for n type

  - performances at high temperatures (SiGe) :
    ZT ≈ 0.9 @ 1000 K (n type)
    ZT ≈ 0.6 @ 1000 K (p type)

  - abundant, not toxic

- Drawbacks :

  - performances at room temperature (SiGe) :
    ZT ≈ 0.1 at 300 K

- **Oxides**

  - ignored during a long time because of their very low electrical conductivity

  - advantages : non-toxicity, thermal stability, high resistance to oxidation

  - discovery in 1997 of Na_xCoO_2 : p-type material with a very high electrical conductivity (for an oxide) : 0.2 mΩ.cm

  - $S = 100\ \mu V.K^{-1}$ and $\lambda \approx 4$ à 5 $W.m^{-1}.K^{-1}$: so a $ZT \approx 0.3$ at 300 K

  - problem : to find competitive n-type materials

- More information :

  → I. Terasaki et al. "Large thermoelectric power in $NaCo_2O_4$ single crystals", Phys. Rev. B 56, (1997)

- **Skutterudites**

- identified in 1928 by Oftedal

- the name comes from Skotterud, a mining Norwegian town where cobalt is extracted

- binary compounds of MX_3 type where :
  - M = transition metal of column 9 (cobalt, rhodium, iridium)
  - X = element of column 15 (phosphorous, arsenic, antimony, bismuth…)
  - and also MX_6, M_4X_{12} types

- undoped, these binary compounds are p-type. But n-type compounds can be obtained by replacing a transition metal by an element from the column 10 (Ni, Pt, Pd), for example

- present high mobility and good Seebeck coefficient

THERMOELECTRIC MATERIALS

- **Skutterudites**

  - Complex compounds can be realized to obtain a low thermal conductivity

Materials	*Type*	*ZT (300K)*	*ZT (900K)*
$CeFeCoSb_3$	p	0.2	1.4
$Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$	n	0.08	1.25

- More information :

  → B. C. Sales et Al. Filled "Skutterudite antimonides: A new class of thermoelectric materials", Science 272, (1996).

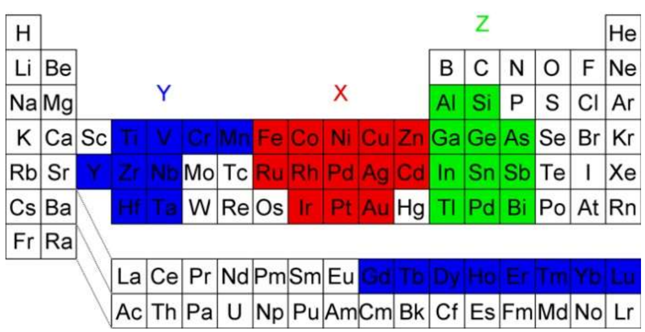
- **Half-Heusler**

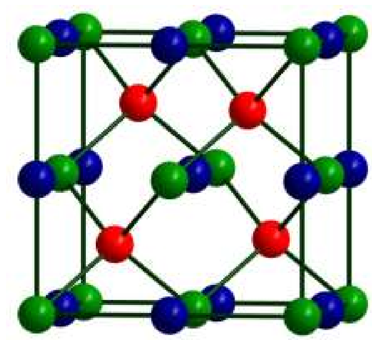
  - The term derives from the name of German mining engineer and chemist Friedrich Heusler, who studied such compounds in 1903.

  -Examples:

    - n-type : TiZrHfNiSn : ZT = 1.5 at 825 K
      ((V,Nb)-doped $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$)

    - p-type : $(Zr_{0,5}Hf_{0,5})_{0,33}Co_{0,33}(Sn_{0,2}Sb_{0,8})_{0,33}$: ZT = 0.4 at 873 K





XYZ composition

- More information :
  → G. Rogl, Acta Materialia 131 (2017)

•www.isabellenhuette.de

- **Silicides**

  - Compounds based on silicon and one (or more) metallic elements
  - Adapted for middle/high-range temperatures
  - Typical silicides: Mg2(Si,Sn), MnSi, etc.
    - n-type : Mg2(Si,Sn) : ZT = 1.55 at 773K
      (Bi-doped $Mg_2Si_{0.4}Sn_{0.6}$)
    - p-type : MnSi : ZT = 1.04 at 920K
      (doped with rhenium: $Mn_{30.4}Re_6Si_{63.6}$)

- More information :
  → P. Gao et al., Appl. Phys. Lett. 105, 202104 (2014)
  → A. Yamamoto et al., Jap. J. Appl. Phys. 55, 020301 (2016)

- **Zintl phase**

  - Polar intermetallic compounds of elements with large electronegativity differences

  - Obtained by reaction between a group 1 (alkali metal) or group 2 (alkaline earth) and any post-transition metal or metalloid (i.e. from group 13, 14, 15 or 16)

  - Named after the German chemist Eduard Zintl who investigated them in the 1930s

  - Examples: NaTl, NaSi, Cs_2NaAs_7, $K_{12}Si_{17}$

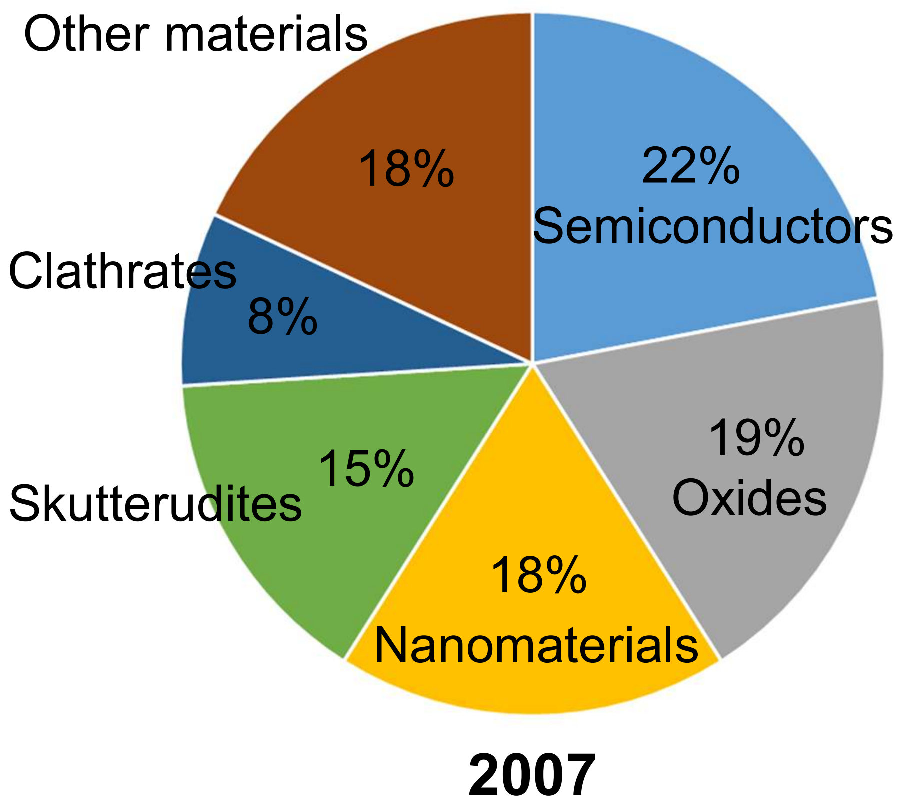
- **Clathrates**

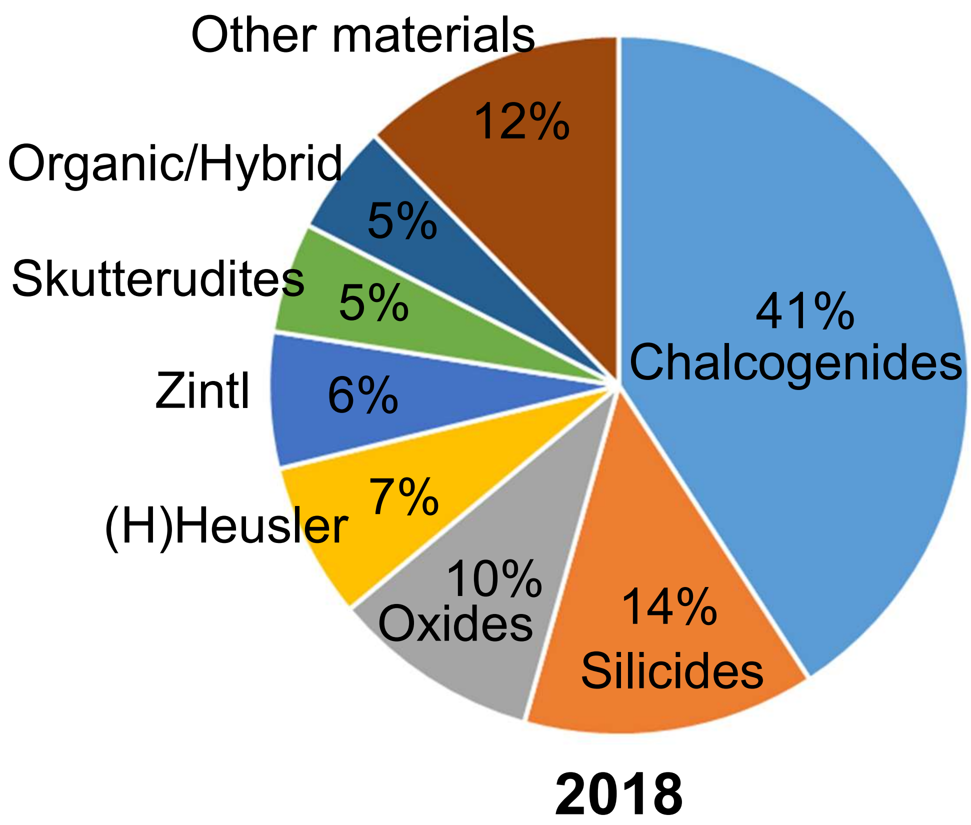
  - A clathrate is a chemical substance consisting of a lattice that traps or contains molecules

  - More information: https://www.sciencedirect.com/science/article/pii/S0927796X16300237

THERMOELECTRIC MATERIALS

- Distribution of materials research





(source : Int. Conf. Thermoelec., Jeju Island, South Korea, 2007)
(source : Int. Conf. Thermoelec., Caen, France, 2018)

- **Toxicity**

  → modernization of the European legislation for chemical substances

  → setting up of system REACH (since 2006), an integrated system of recording, estimates, permission and restriction of chemical substances.

- Objectives: improvement of the protection of human health and environment by maintaining a competitiveness and by reinforcing the innovation of the European chemical industry.

- A European agency for chemical products has been also created to manage the REACH program.

- Ex. of problematic TE material: lead telluride (PbTe)

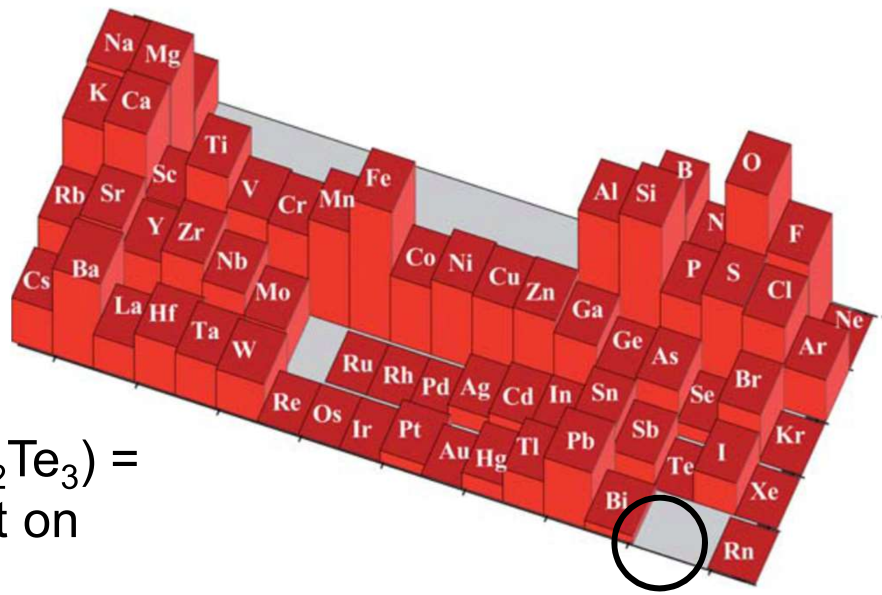
- More information :

http://europa.eu/legislation_summaries/internal_market/single_market_for_goods/chemical_products/l21282_fr.htm

THERMOELECTRIC MATERIALS

- **Scarcity**

→ relative abundance of main elements on Earth



→ Ex. : tellurium (Bi_2Te_3) = the 9th rarest element on Earth…

- More information :

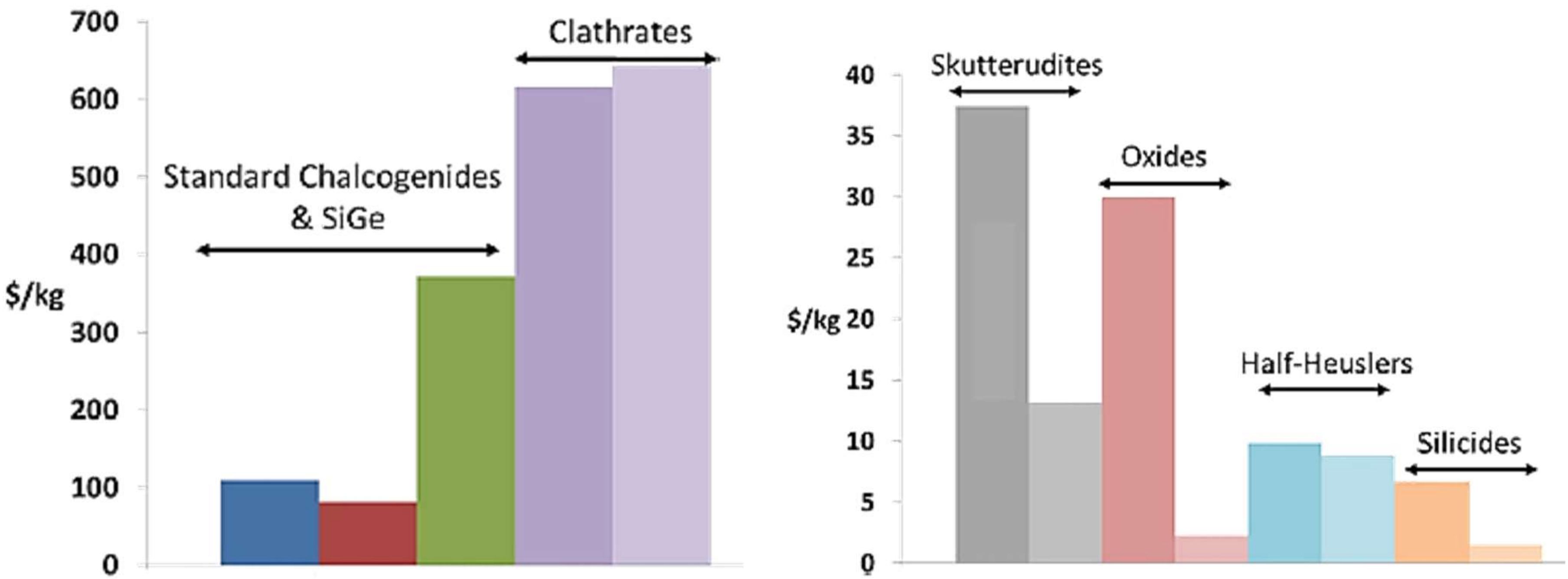
→ P. Vaqueiro et al., J. Mat. Chem. 20, (2010)

→ https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

THERMOELECTRIC MATERIALS

- **Cost** :

  → cost of TE materials based on untreated materials cost



- More information:

  → S. LeBlanc et al, Sust. Mat. Tech. 1-2, (2014)

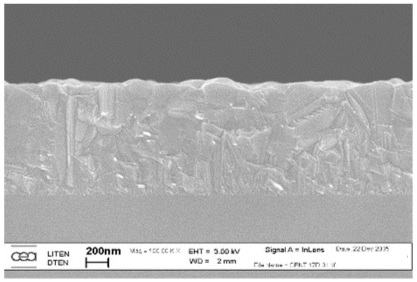
THERMOELECTRIC MATERIALS

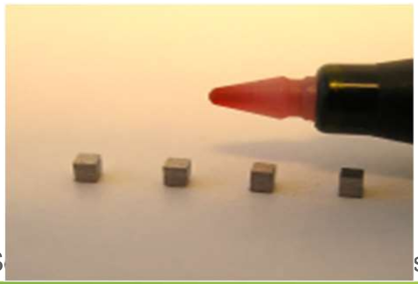
- TE materials can be obtained by different means

  → function of application, cost…

device thickness

e < 10 µm	10 < e < 500 µm	e > 500 µm
Thin film technologies Deposition CVD, PVD MoCVD, EJM, …	**Printing technologies** Ink jet, ink printing, spray, …	**Bulk materials technologies** Chemical and mechanical synthesis, HIP, SPS, …

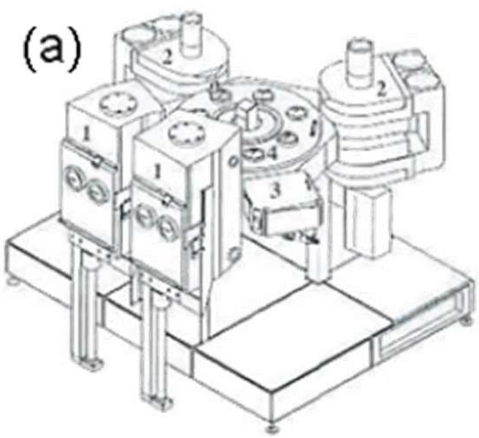


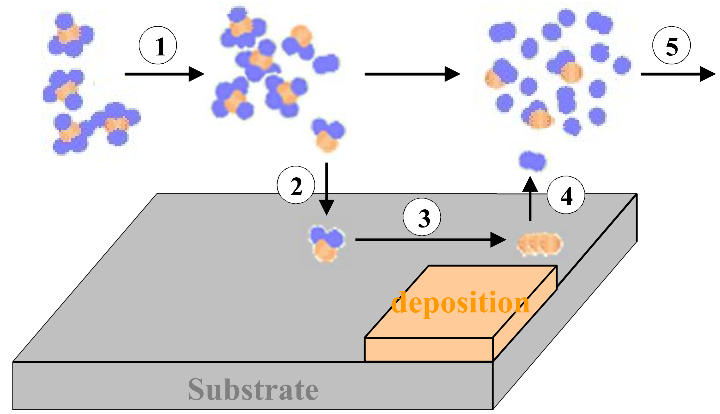


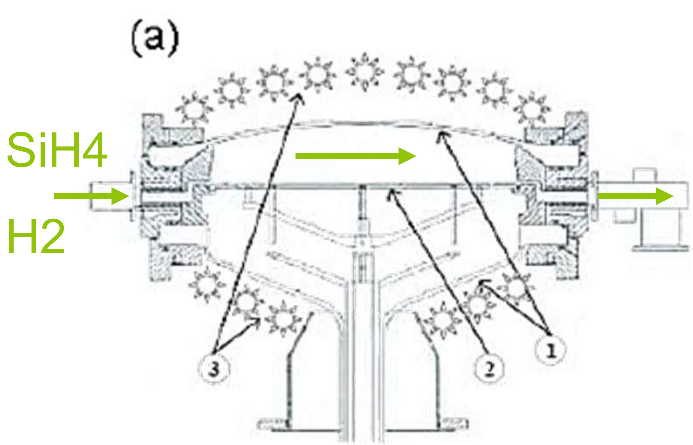
THERMOELECTRIC MATERIALS

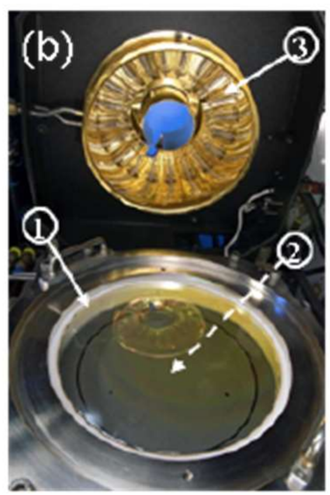
- Realization of TE materials in thin films technologies

  → ex : Si by CVD

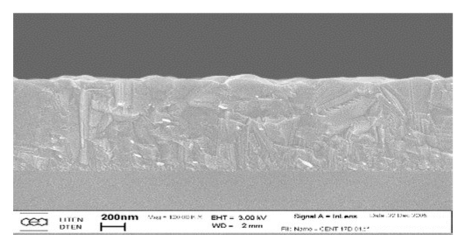








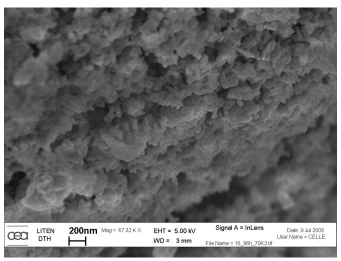
1 - **reactant transport** by forced convection
2 - **diffusion of reagent species** to the surface and adsorption ;
3 - **chemical decompositions of reagent species** ;
4 - **desorption of products** coming from the chemical reactions ;
5 - **evacuation of gaseous flow**



- Realization of TE materials in printing technologies

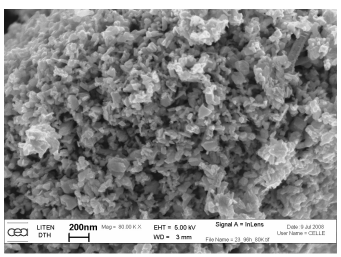
  → ex : Bi_2Te_3

p



TE powders

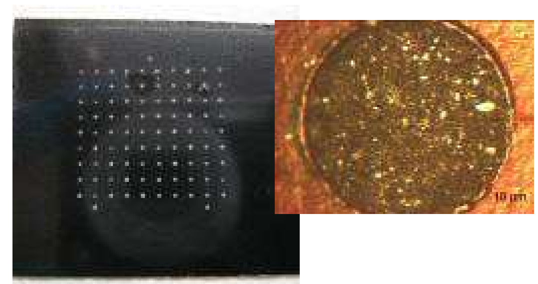
n

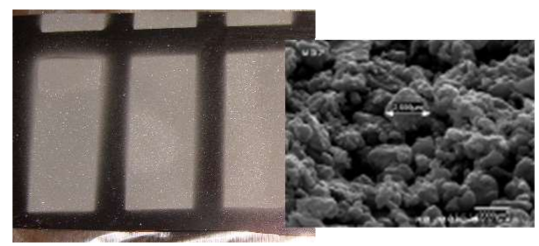


Formulation

TE ink / paste

printing



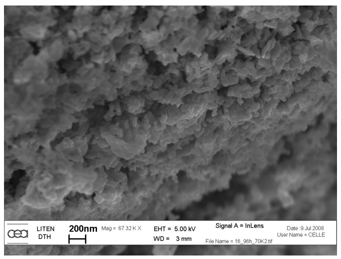


THERMOELECTRIC MATERIALS

- Realization of TE materials in bulk technologies

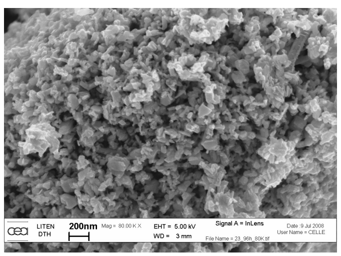
→ ex : Bi_2Te_3

p



TE powders

n



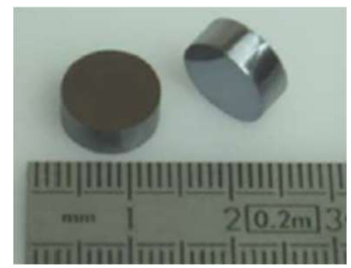
sintering

TE ingots

HIP, SPS, µwave

Cutting of discs

Functional discs



Cutting of legs

Thermolegs

Deposition of Ni - 2 µm

Functional thermoelements

1 - Thermoelectrics : some definitions and effects

2 - Thermoelectric materials

3 - Nanostructuration : why and how ?

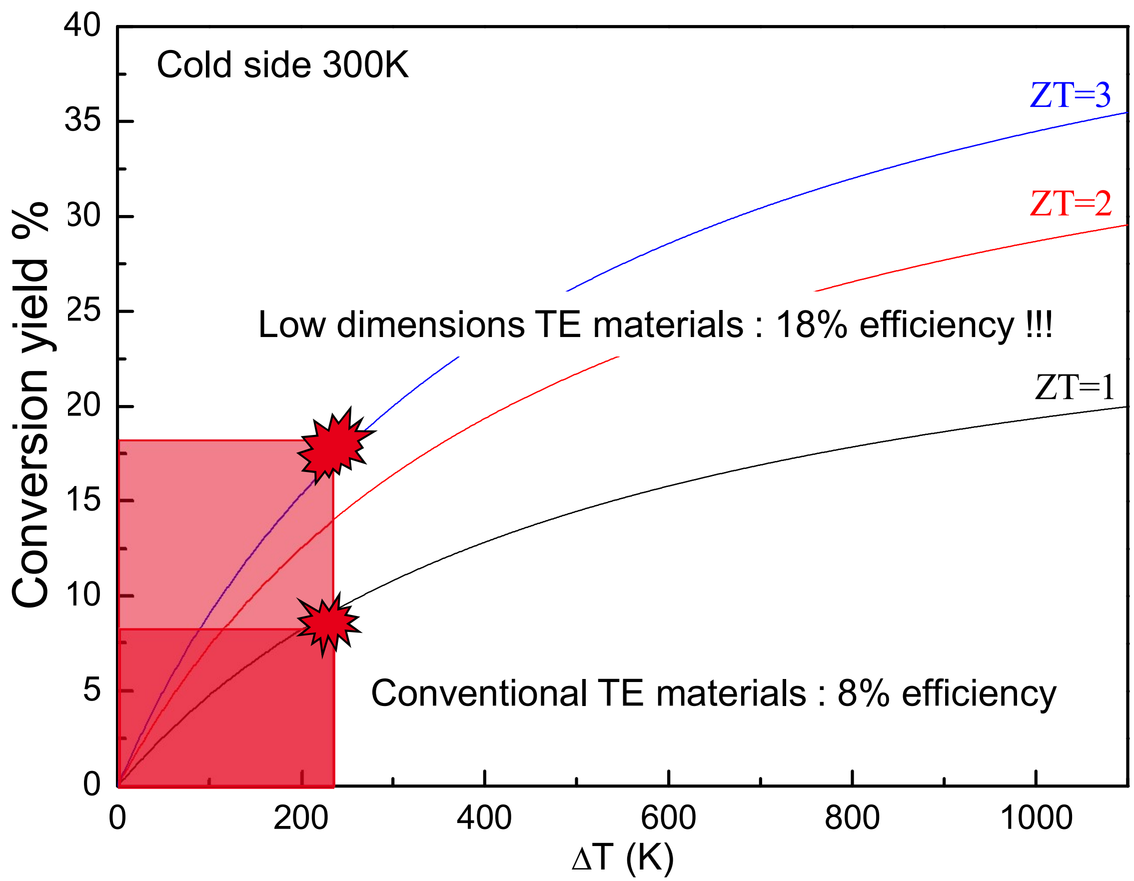
4 - Thermoelectric devices

5 - Applications

6 - Conclusions

THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- Best ZT for materials : ZT ≈ 1 at room temperature since tens of years
- To have a viable and competitive TE system, a ZT ≥ 3 is needed !
- How to increase ZT ?



THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- To increase $ZT = \frac{\sigma \times S^2}{\lambda} T$, two possibilities :

  - increase of power factor σS^2
  - decrease of thermal conductivity λ

- About fifteen years ago, Hicks and Dresselhaus have introduced the concept of electron and holes quantum confinement in low dimensional materials which could increase the ZT significantly.

- Originally to increase the power factor σS^2…

- In fact, to decrease the thermal conductivity λ !

→ Introduction of nanostructuration for TE !

- **Increase of power factor σS²**

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

  - Mott's equation : $S = -\frac{\pi^2}{3}\frac{k_B}{e}k_BT\left(\frac{\partial \ln \sigma(E)}{\partial E}\right)_{E_F}$

  - expression of σ : $\sigma(E) = \mu(E)n(E)e$

  - so : $S = \frac{\pi^2}{3}\frac{k_B}{e}k_BT\left[\frac{1}{\mu(E_F)}\left(\frac{\partial \mu(E)}{\partial E}\right)_{E_F} + \frac{1}{n(E_F)}\left(\frac{\partial n(E)}{\partial E}\right)_{E_F}\right]$

derivative in energy of state density

Derivative in energy of mobility

  - increase of the electron state density near Fermi level

    → increase of electron quantum confinement

  - by imposing judicious defaults at the electronic structure : by increasing the carriers number

THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- **Decrease of the thermal conductivity λ**

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

- Thermal conductivity : sum of two terms :

$$\lambda = \lambda_e + \lambda_p$$

with λ_e : electronic thermal conductivity
λ_p : lattice thermal conductivity (phonons)

- According to the Wiedemann-Franz law :

$$\lambda_e = L_0 \times \sigma \times T$$

with L_0 : Lorenz constant ($2{,}44.10^{-8}$ W.Ω.K^{-2})
σ : electrical conductivity
T : temperature

- Decrease of the lattice thermal conductivity λ_p

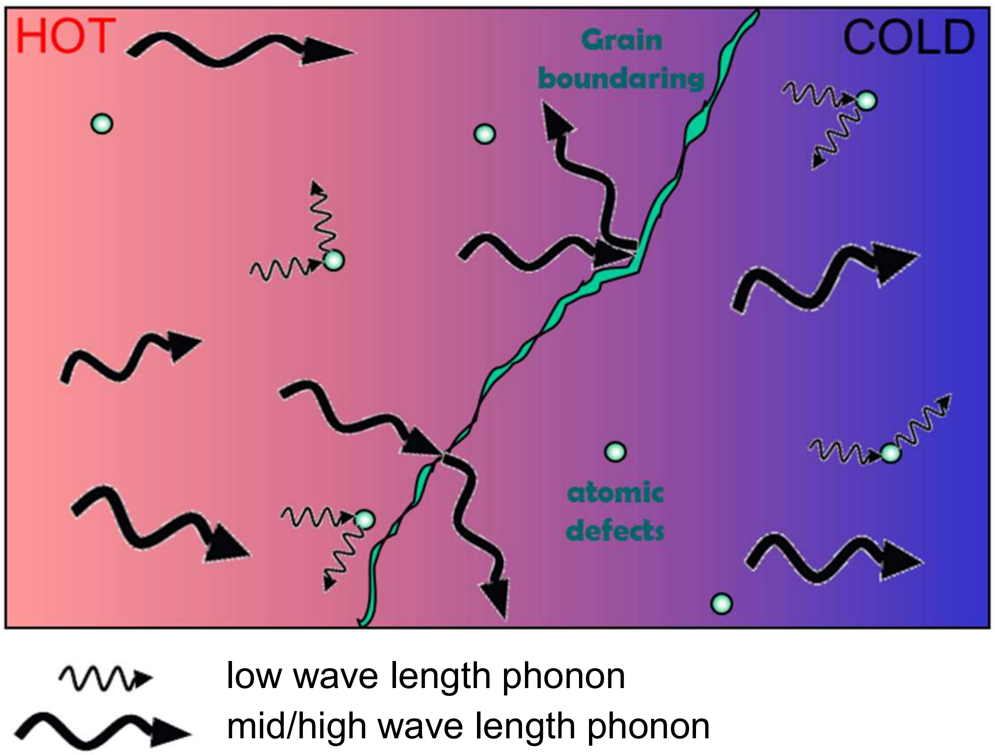
→ **phonons scattering !**

THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- Different mechanisms of phonon scattering:

→ “classical” scattering :

- grains boundaries diffusion (ex: polycrystalline materials)
- impurities diffusion



C. J. Vineis et al., Adv. Mat. 22, (2010)

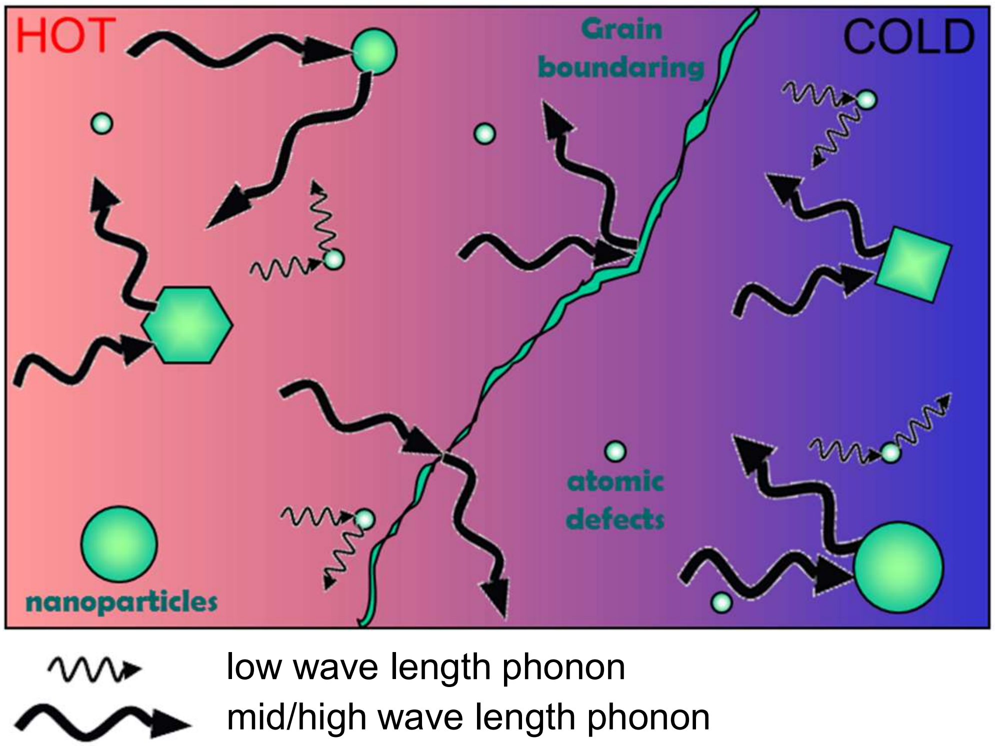
THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- How nanostructuration has an influence on phonon scattering ?

→ “addition” of phonon scattering mechanisms :

- scattering with interfaces
- scattering with nanoparticles

} → nanostructuration



C. J. Vineis et al., Adv. Mat. 22, (2010)

THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

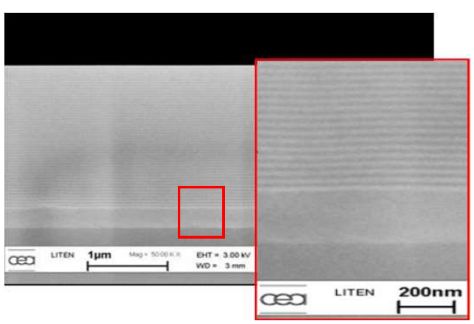
- The different kinds of nanostructuration :

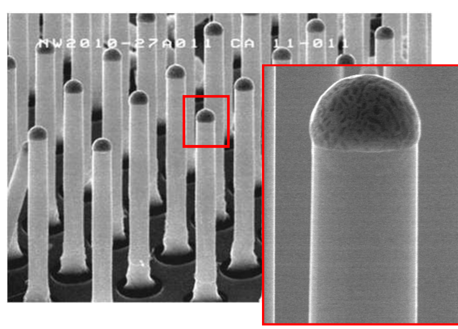
Device thickness →

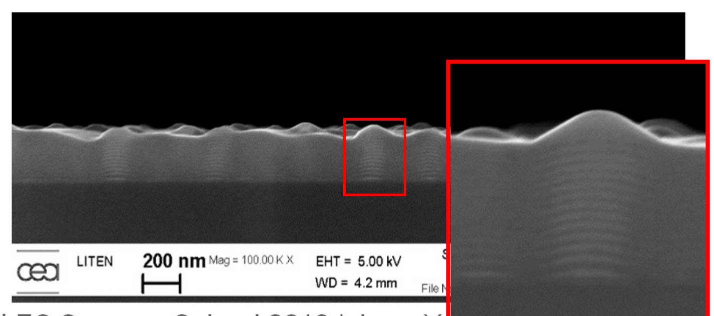
e < 10 µm	10 < e < 500 µm	e > 500 µm
Thin films technologies	**Printing technologies**	**Bulk materials technologies**

Thin films technologies →

Superlattices (SL)	**Nanowires (NW)**	**Quantum Dots Superlattices (QDSL)**







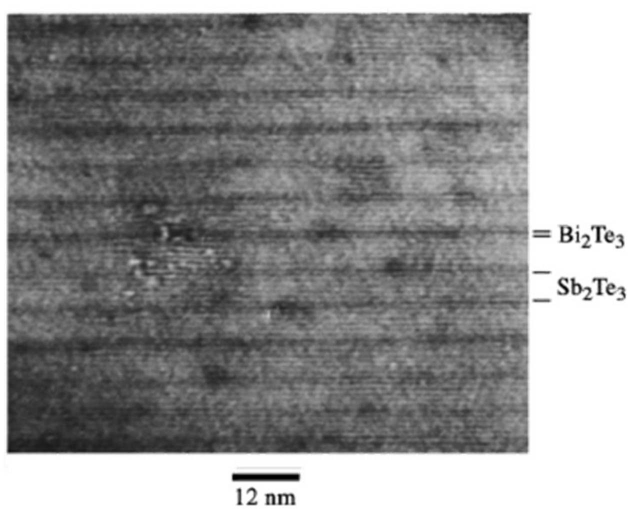
THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

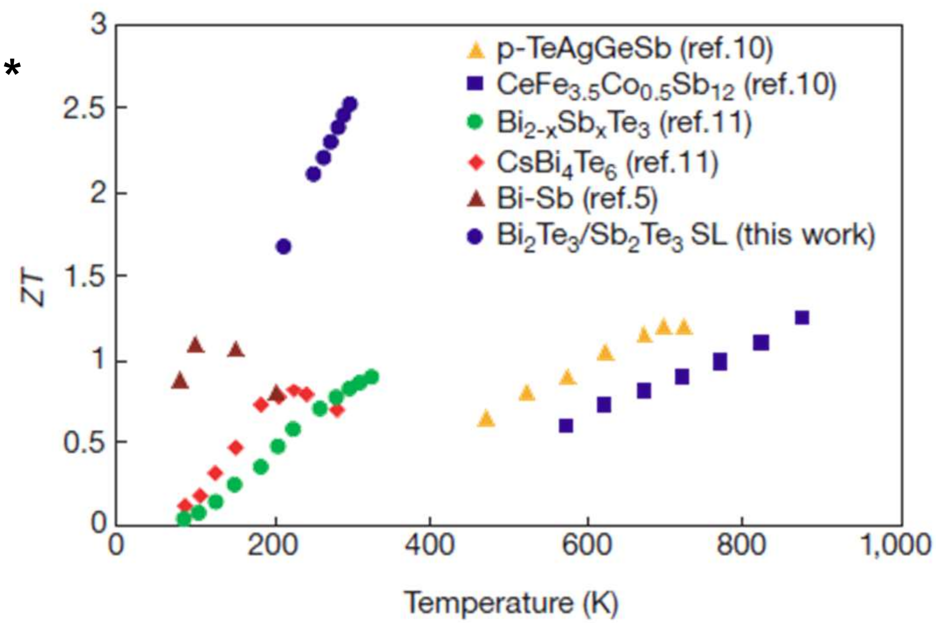
• Influence of nanostructuration on materials performances in thin films technologies : superlattices

→ these nanostructures are very studied for a lot of materials families such as Bi_2Te_3, PbTe, SiGe, GaAs… originally to increase σS^2, finally to decrease lattice thermal conductivity λ_p

• **Example 1: p-type Bi_2Te_3/Sb_2Te_3 SL ***

→ grown by low-temperature organometallic epitaxy





Evolution of ZT as a function of temperature for Bi2Te3 / Sb2Te3 SL (1 nm / 5 nm)

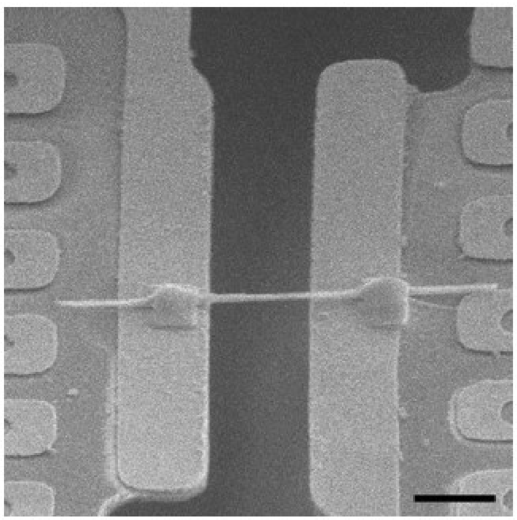
→ ZT record at room temperature : 2.5

* R. Venkatasubramanian et al., Nature 413, (2001)

- Influence of nanostructuration on materials performances in thin films technologies : nanowires

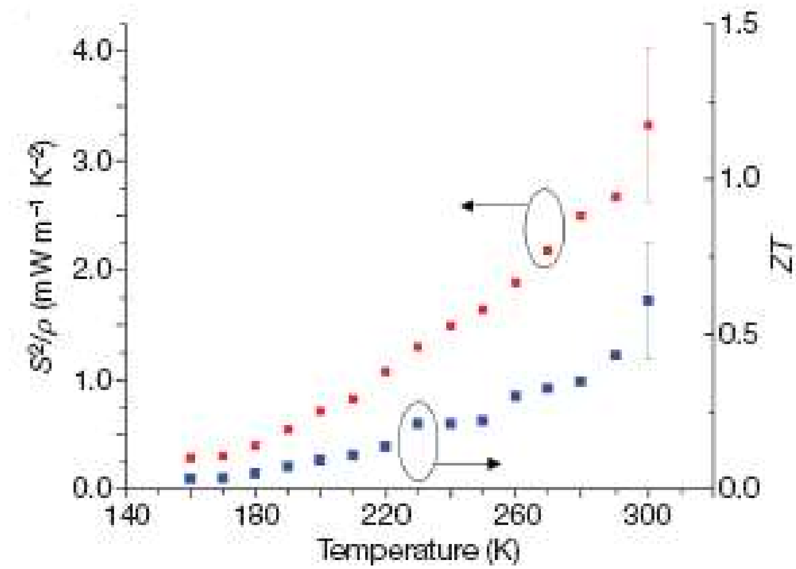
- **Example 2: p-type rough Si NW ***

  → grown by electroless etching (EE) method



SEM image of a Pt-bonded Si nanowire

→ ZT at 300 K : 0.6

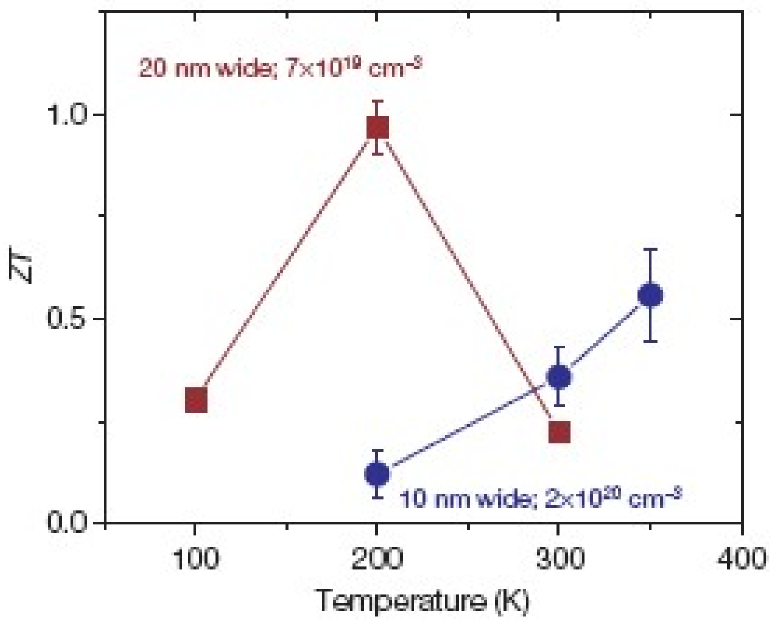


Single nanowire power factor (red squares) of the nanowire and calculated ZT (blue squares) using the measured k of the 52nm NW. By propagation of uncertainty from the ρ and S measurements, the error bars are 21% for the power factor and **31% for ZT**.

* A. I. Hochbaum et al., Nature 451, (2008)

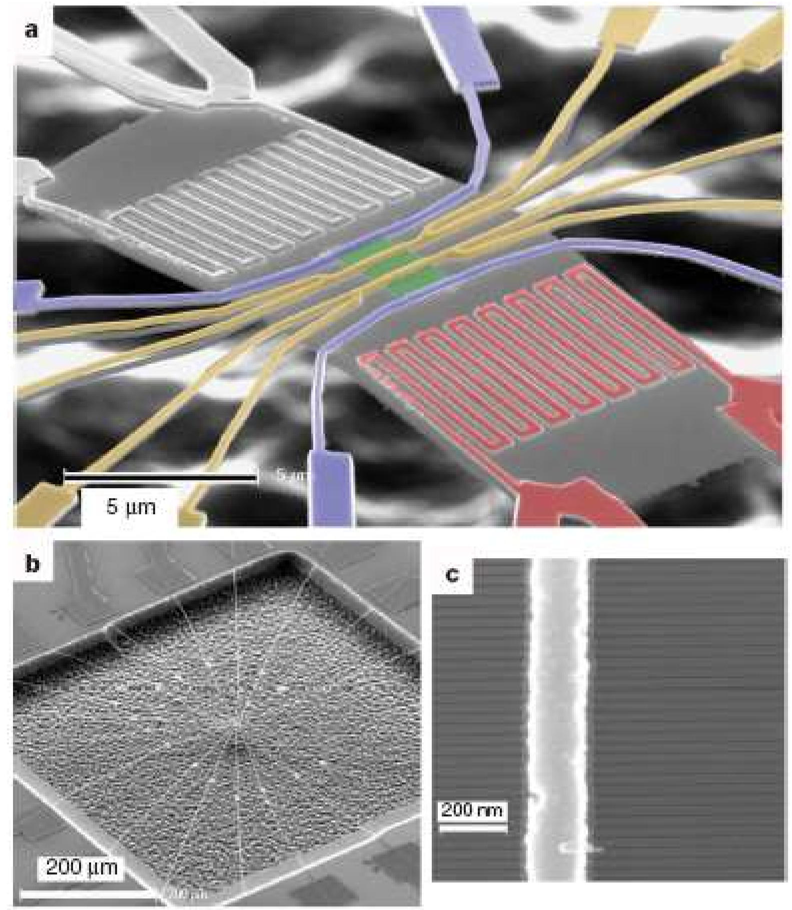
- Influence of nanostructuration on materials performances in thin films technologies : nanowires

- **Example 3: p-type Si NW ***



Temperature dependence of ZT for two different groups of nanowires

→ ZT at 200 K : 1



Scanning electron micrographs of the device used to quantify S, σ and λ of Si nanowire arrays

* A. I. Boukai et al., Nature 451, (2008)

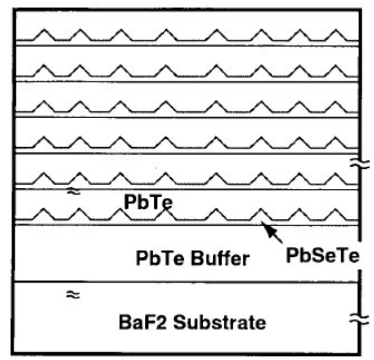
- Influence of nanostructuration on materials performances in thin films technologies : quantum dots superlattices

→ many studied systems, notably SRBQ with PbTe, SiGe, ErAs… All these nanostructures allow an important decrease of λ, rather than an increase of σS^2. The nanodots scatter high wave length phonons, and decrease slightly σS^2 (because of the scattering of charge carriers)

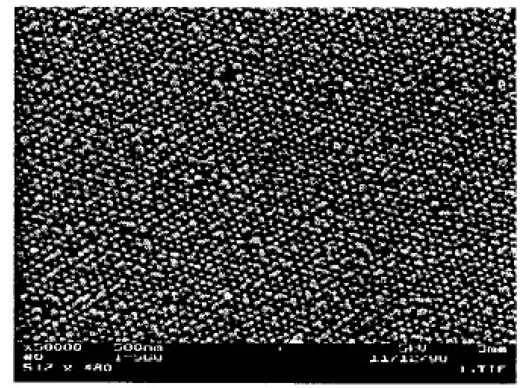
- **Example 4: n-type PbSeTe/PbTe QDSL ***

→ grown by MBE epitaxy

→ ZT at room temperature : 1.6



Schematic cross section of the QDSL structure investigated



SEM image of quantum-dot (top view)

Sample	S(μV/K)	ZT	Carrier conc. (cm^{-3})	Carrier mobility (cm^2/V-s)
n-QDSL A	−219	1.6*	1.2×10^{19}	370

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

THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

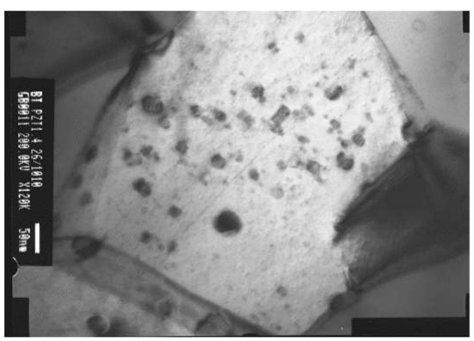
- The different kinds of nanostructuration :

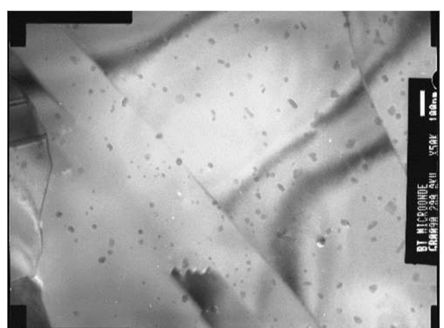
Device thickness

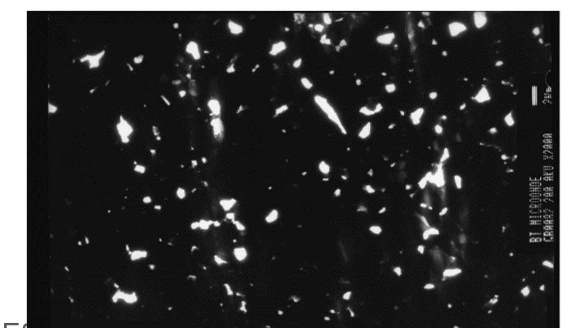
e < 10 µm	10 < e < 500 µm	e > 500 µm
Thin films technologies	**Printing technologies**	**Bulk materials technologies**

Printing technologies + Bulk materials technologies →

Nanopowders
Nanoinclusions



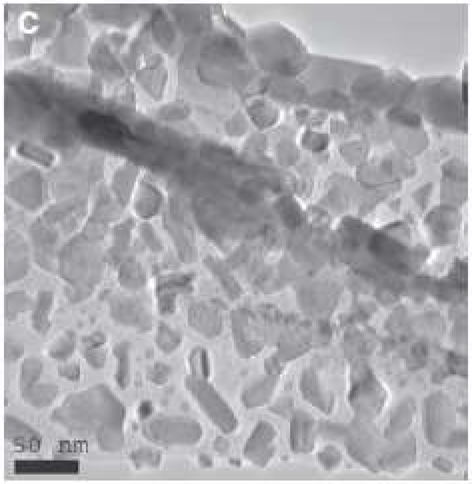




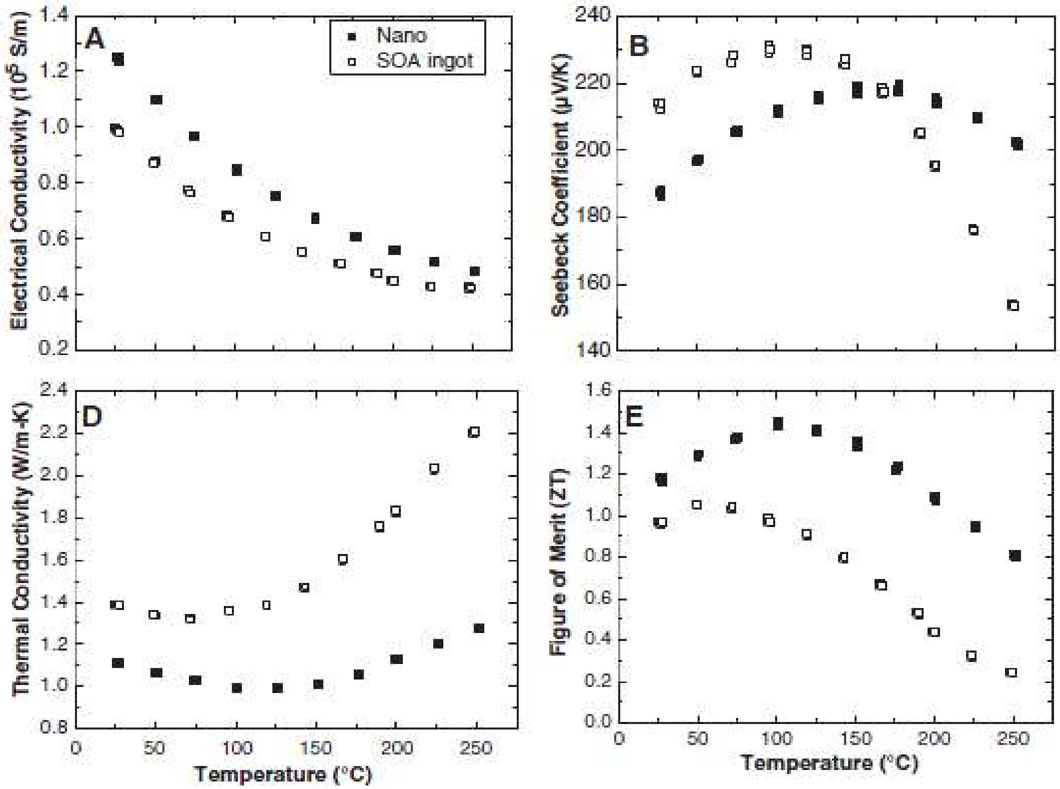
THERMOELECTRIC MATERIALS: NANOSTRUCTURATION

- Influence of nanostructuration on materials performances in bulk technologies

- **Example: Bi_2Te_3 (p) ***



Low-magnification TEM images of an as-ball-milled nanopowder.



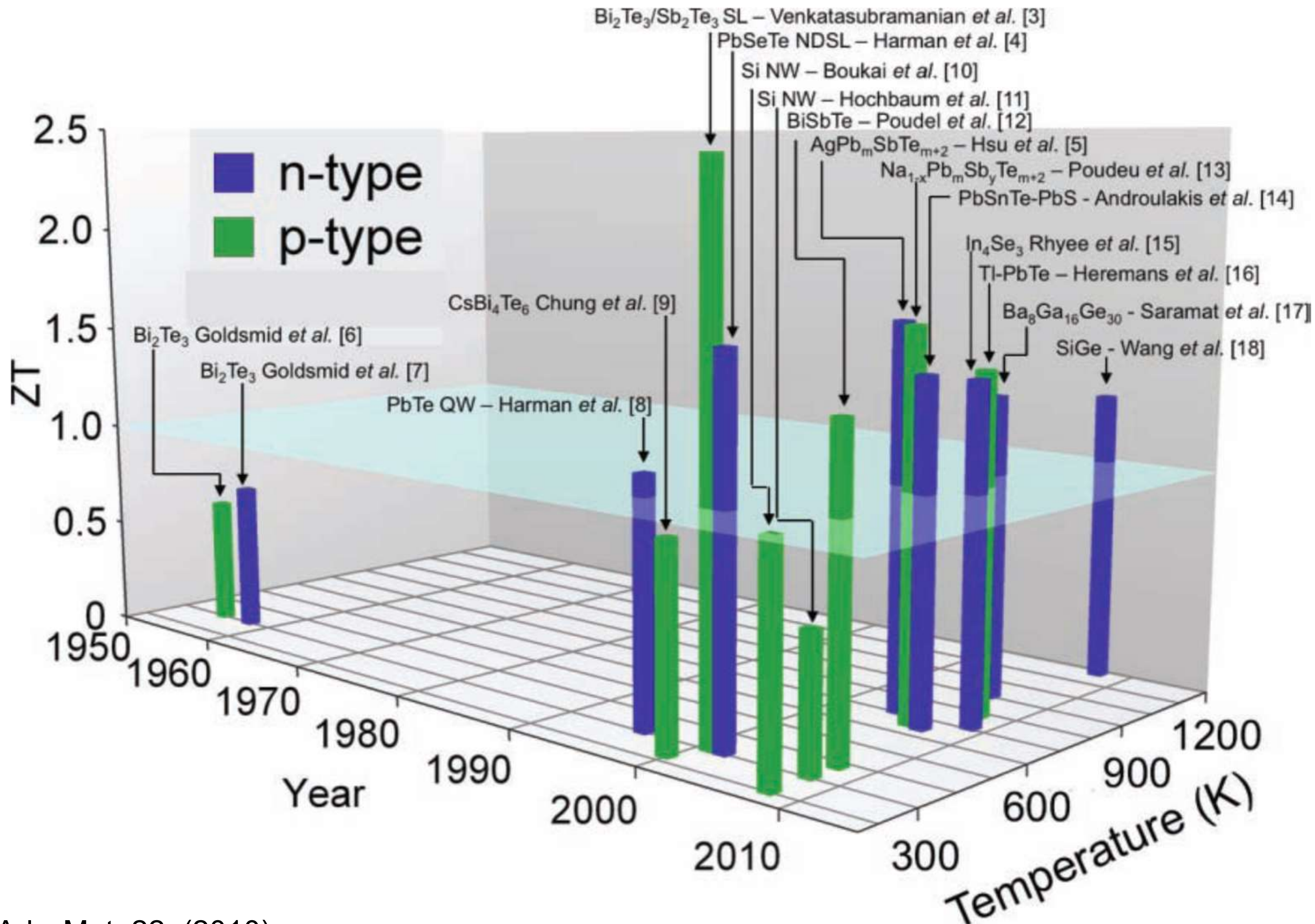
Temperature dependence of σ (A), S (B), λ (D), and ZT (E) of a hot-pressed nanocrystalline bulk sample (black squares) as compared with that of an SOA ingot (white squares)

→ ZT at 300 K : 1.2 (0.95)
→ ZT at 400 K : 1.4 (1)

→ Bi2Te3 (n) : 22% increase of ZT (0.9/1.04 at 25°C/125°C) compared to SoA (0.7/0.85 at 25°C/125°C)

B. Poudel et al., Sience 320, (2010)   X. Yan et al., NanoLetters 10, (2010)   M. S. Dresselhaus et al., Adv. Mat. 19, (2007)

- Nanostructuration: summary state of the art

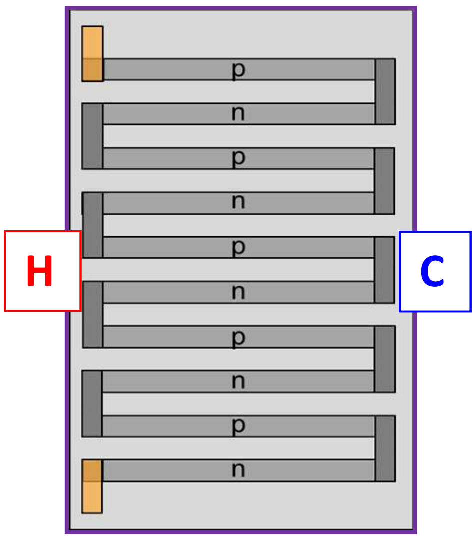


C. Vineis et al., Adv. Mat. 22, (2010)

THERMOELECTRIC DEVICES

- Three main architectures

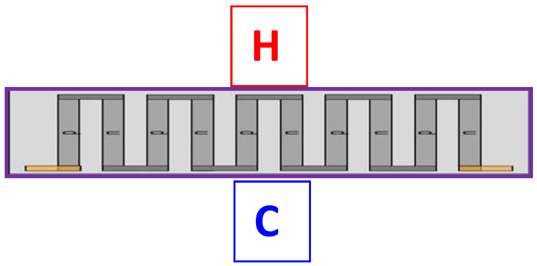
- **2D Architecture (planar)**



Top view of 2D architecture

→ modules made of lines
→ n or p lines
→ thermal and electrical flow in planar direction

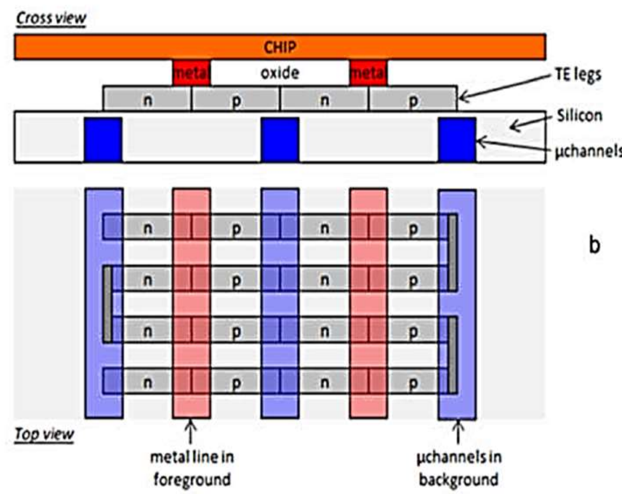
- **3D Architecture (cross-plane)**



Top view of 3D architecture

→ modules made of legs
→ n or p legs
→ thermal and electrical flow in cross plane

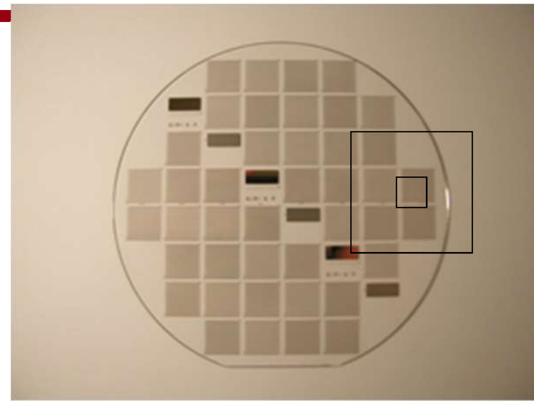
- **2.5D Architecture (combined)**

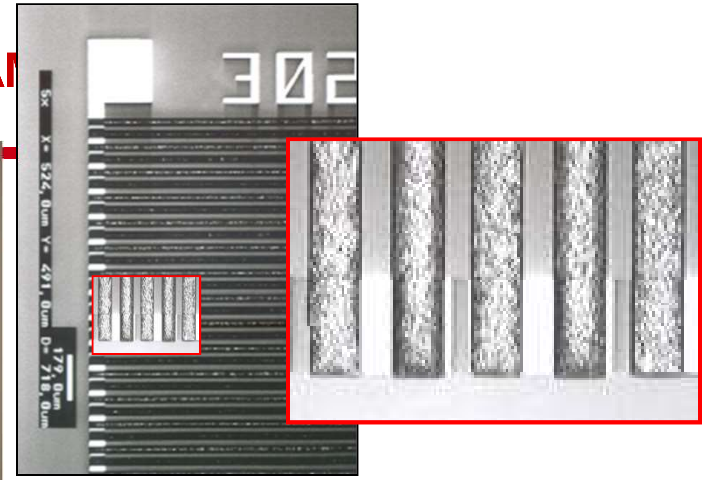


Cross view and top view of 2.5D architecture

→ modules made of lines
→ lines made of n and p segments
→ thermal flow in cross plane and electrical flow in planar direction

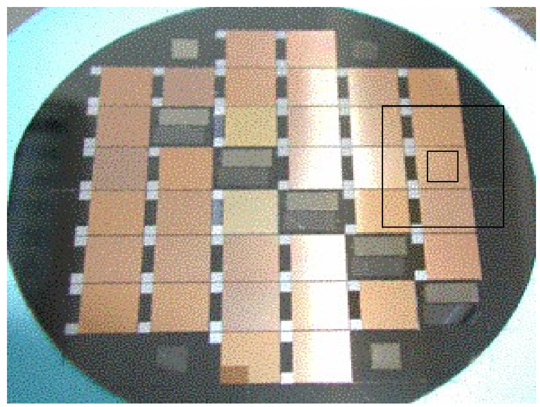
THERMOELECTRIC DEVICES: CEA EXA

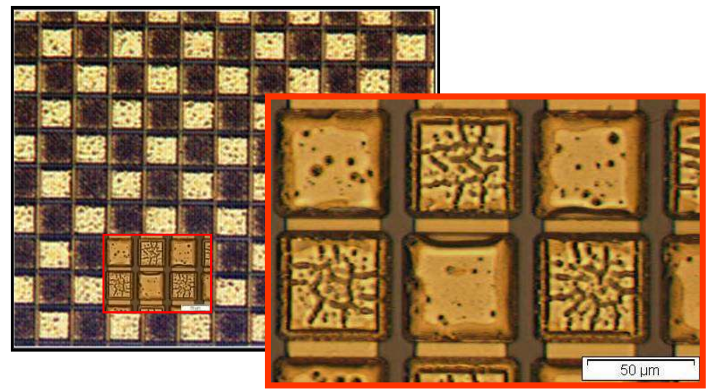




- **2D Bi / Sb devices**

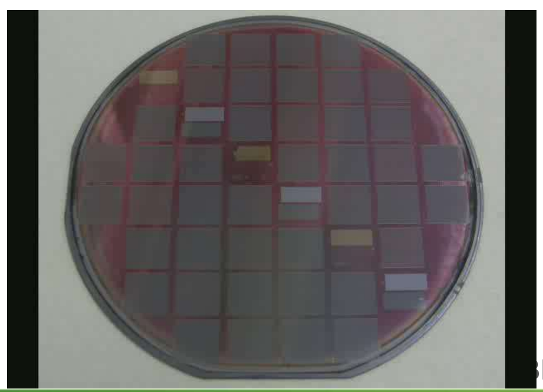
  Glass substrate 100mm
  Patterns: lines
  N = 100 to 160 junctions
  A_{te} = 1 cm²

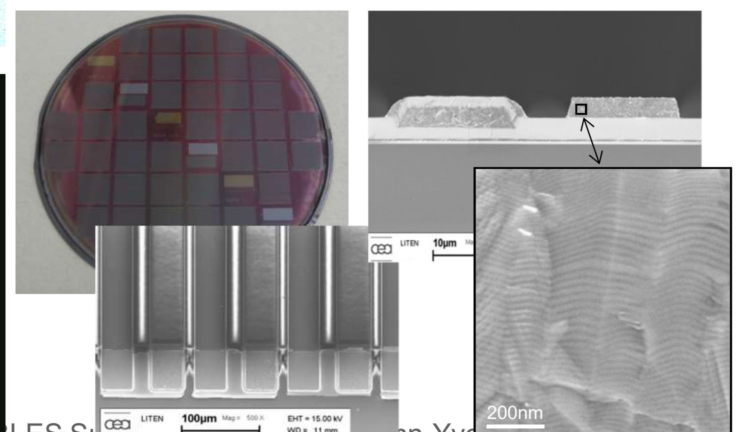




- **3D Bi / Sb devices**

  Si substrate 100mm
  Patterns: legs
  N = 9000 to 60000 junctions
  A_{te} = 1 cm²

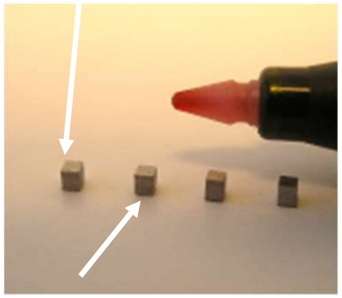




- **2D Si/SiGe SR devices**

  SOI substrate 100mm
  Patterns : lines
  N = 80 to 120 junctions
  A_{te} = 1 cm²

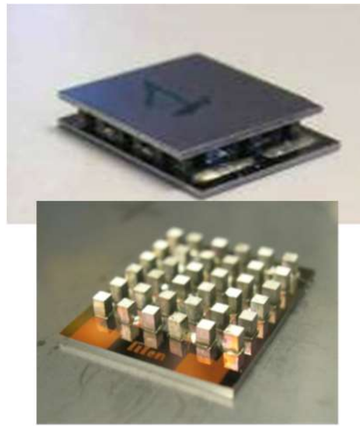
THERMOELECTRIC DEVICES: CEA EXAMPLES



Functionalized thermo-elements

Assembly

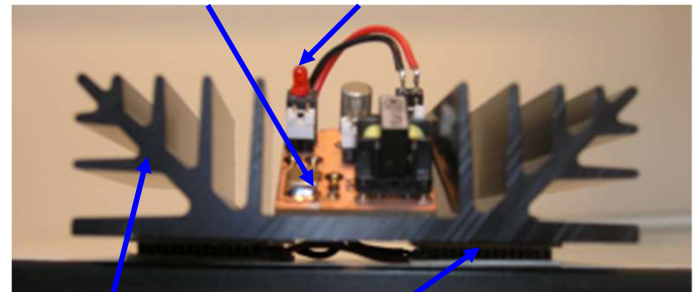
Connections



Thermoelectric generator

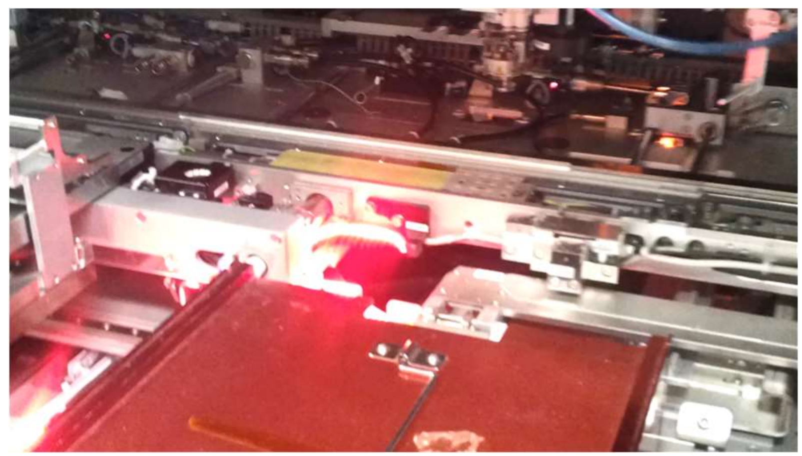
System integration

Heat spreader, converter



Final system

Semi-automatic manufacturing of bulk devices



Automatic manufacturing of bulk devices

THERMOELECTRIC DEVICES

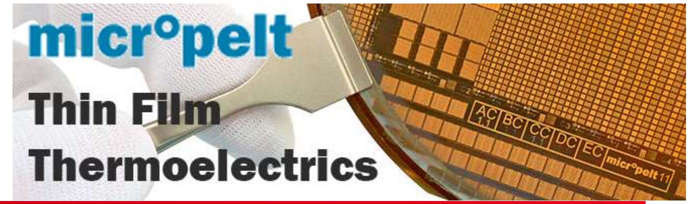
- Thin film technology devices

  - The main devices manufacturer for energy harvesting and cooling in thin film technology are:

    - Micropelt (Germany)

    - Laird (USA)

  - For these two manufacturers, devices are realized with Bi_2Te_3.



- **Micropelt Technology**

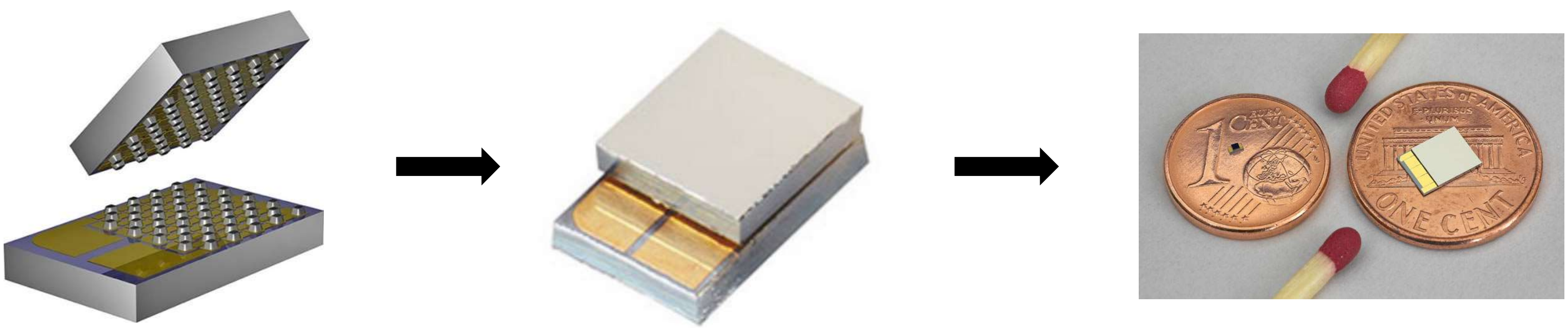
→ polycristalline Bi_2Te_3 deposited by sputtering on Si standard wafers with SiO_2 layer, with thickness around some tens of microns

→ n and p type materials deposited separately on two different wafers

→ wafers are then cut and n and p parts are pasted together

→ more than 100 junctions are integrable on 1 mm²

→ very small devices

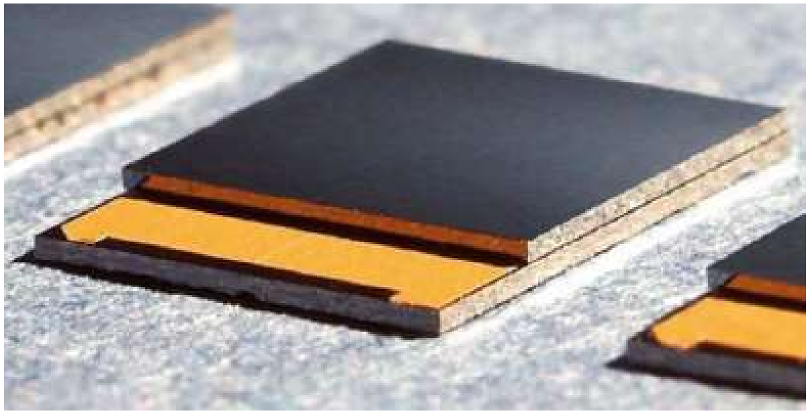


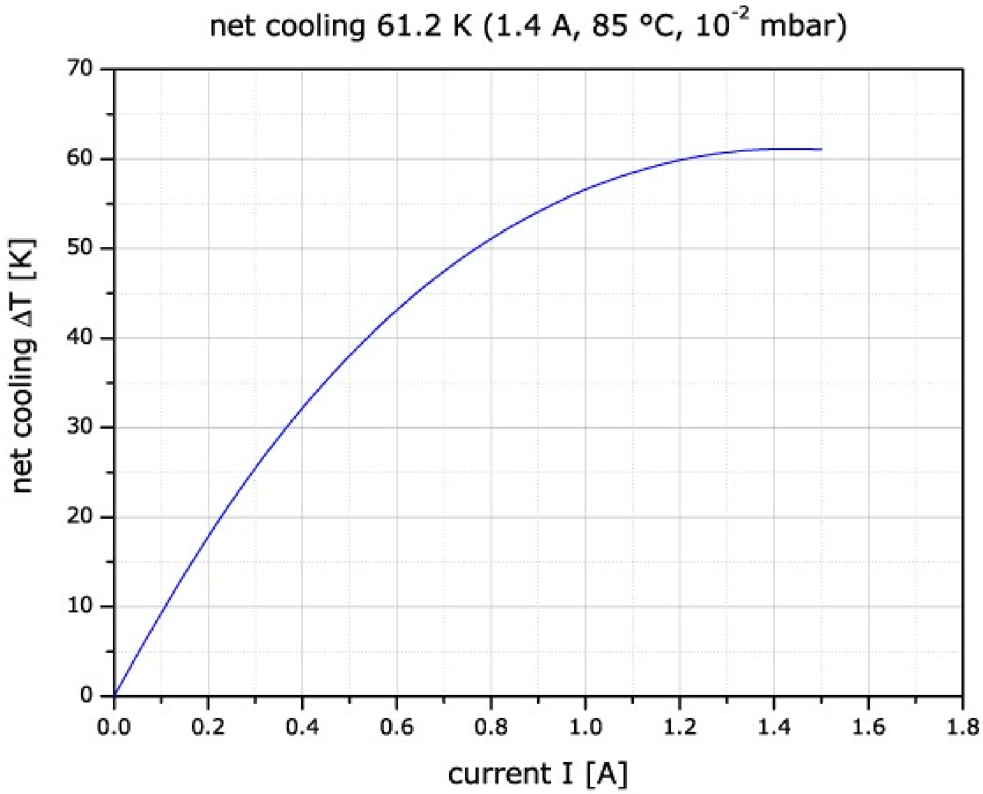
www.micropelt.com

THERMOELECTRIC DEVICES

micr°pelt

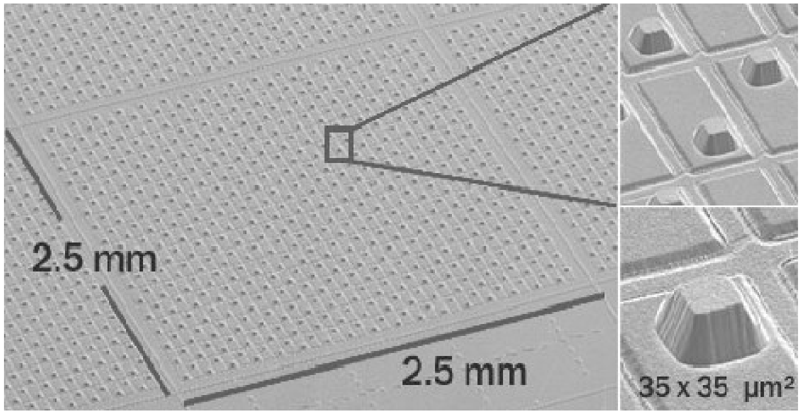
- Thin film technology devices
  - Micropelt : Peltier cooler

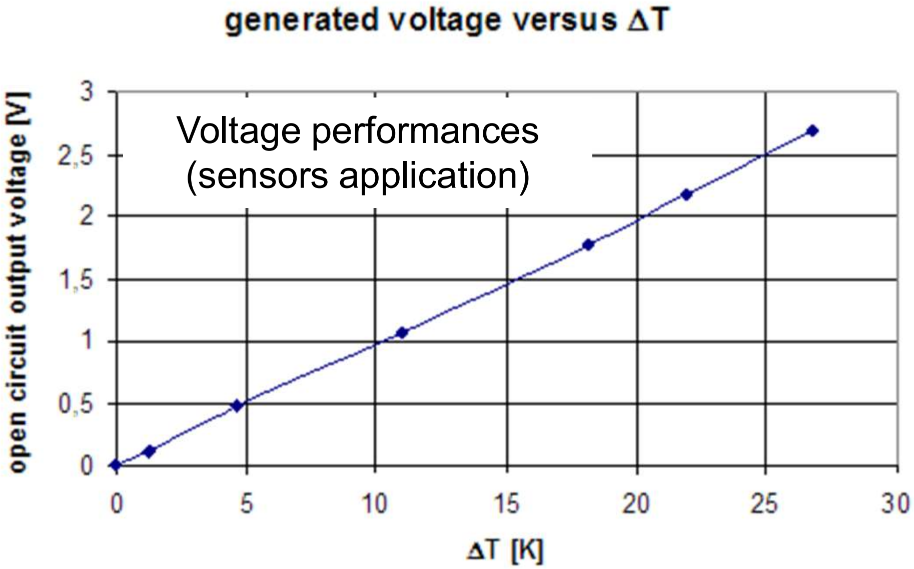


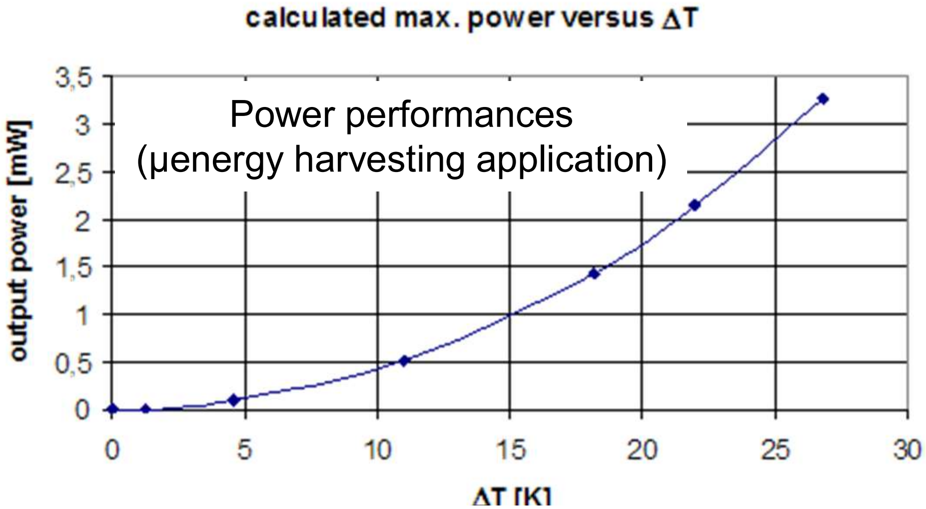


www.micropelt.com

- **µTEG Micropelt**



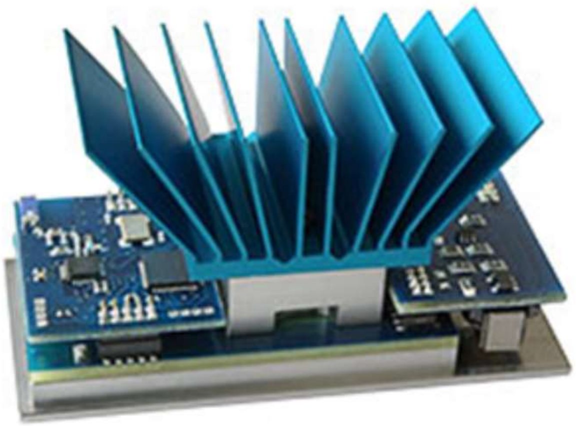




Ex : Performances of MPG-D602 device with 450 leg pairs

www.micropelt.com

- **µTEG Micropelt**



Micropelt thermoelectric generators				
Device	**Foot print x y Total thickness**	**Electrical resistance at 23 °C Thermal resistance at 85 °C**	**Net Seebeck Voltage at 23 °C**	**Features**
» MPG-D651 (PDF 1122 KB)	3375 µm 2500 µm 1090 µm	185 Ω 22 K/W	75 mV/K	High output voltage per degree ΔT Very fast response time Ideal for energy harvesting and heat energy sensing
» MPG-D751 (PDF 1122 KB)	4248 µm 3364 µm 1090 µm	300 Ω 12.5 K/W	140 mV/K	High output voltage per degree ΔT Very fast response time Ideal for energy harvesting and heat energy sensing

- **Applications**

  → Sensors
  → Wireless communication

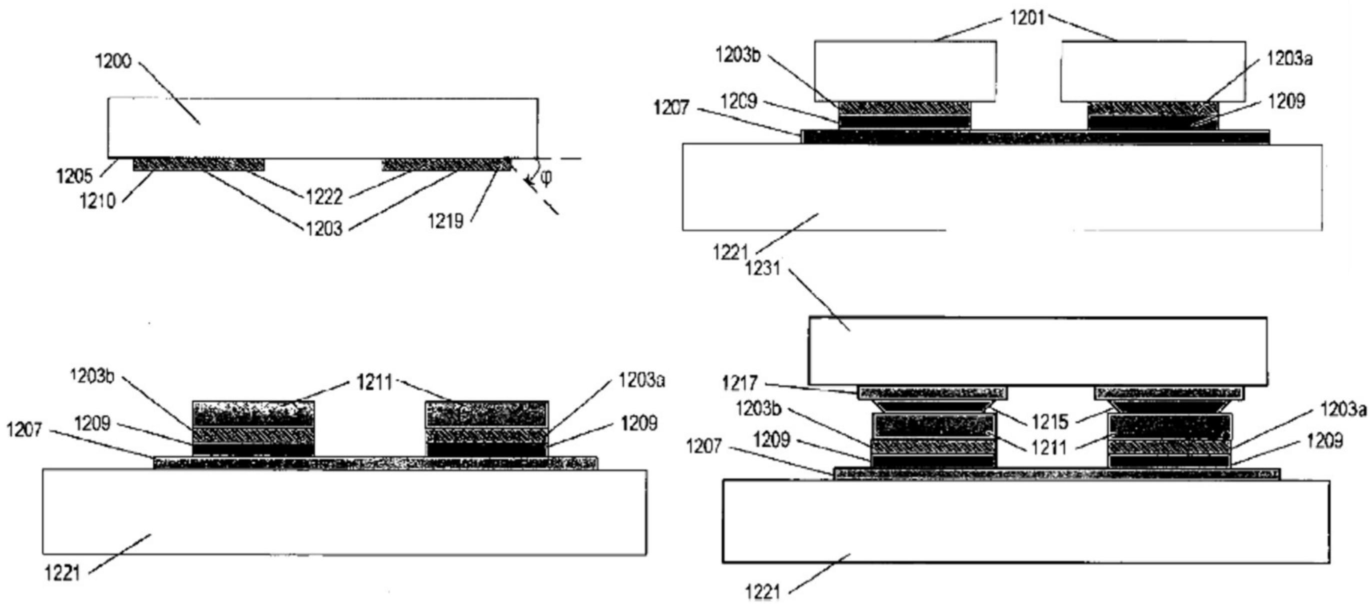
www.micropelt.com

- **Laird (Nextreme) Technology**

→ Laird Technologies, components and solutions manufacturer for thermal protection of electronic devices acquired Nextreme Thermal Solutions (US manufacturer of TE thin film technologies) in 2013

→ polycristalline Bi_2Te_3 deposited by MOCVD on GaAs sacrificial substrates

- **Laird (Nextreme) Technology**



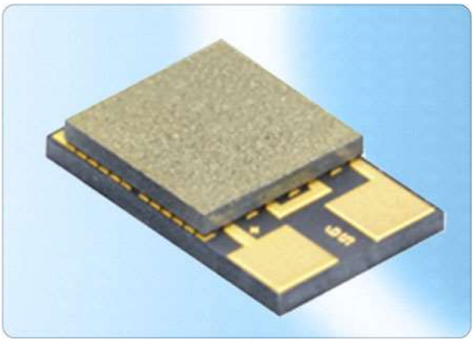
→ n and p type materials deposited separately on two different substrates

→ wafers are then cut and n an p parts are pasted on support (as thermal conductor ceramic)

→ metallic contacts are deposited by electrodeposition on n and p parts, and a second support is pasted with complementary metallic contacts

(extracted from patent n° EP2423990 A1 deposited by Nextreme Thermal Solutions, Inc.)

- **Laird Peltier µcooler**



Item #	ΔTmax (TH = 85°C)	Qmax	Imax	Vmax (TH = 85°C)	Qmax / area	Dimension A	Dimension B	Dimension E
HV14.18.F0.0102.GG	45 °C	1.3 watts	0.9 A	2.5 V	64 W/cm²	1.15 mm	2.04 mm	0.62 mm
HV37.48.F2.0202.GG	45 °C	3.7 watts	1 A	6.4 V	66 W/cm²	2.36 mm	2.36 mm	0.62 mm
HV56.72.F2.0203.GG	50 °C	6.8 watts	1.1 A	10.4 V	81 W/cm²	3.54 mm	2.36 mm	0.6 mm

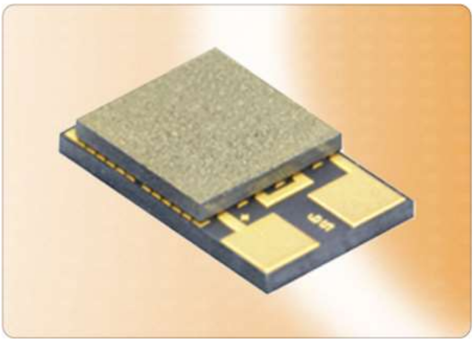
- **Applications**

→ Laser diodes
→ IR sensors

PowerCool Series Air-to-Air Thermoelectric Assembly

(extracted from patent n° EP2423990 A1 deposited by Nextreme Thermal Solutions, Inc.)

- **Laird µTEG**



Item #	Power	Voltage	Current	Voltage Open Circuit	Current, Short Curcuit
PG09.14.F0.0102.GG	8.6 mW	0.15 V	58 mA	0.3 V	115 mA
PG24.48.F2.0202.GG	24 mW	0.4 at 50°C V	60 at 50°C mA	0.8 V	115 mA
PG37.72.F2.0203.GG	1.5 mW	0.6 at 50°C V	60 at 50°C mA	1.2 V	115 mA

- **Applications**

→ Wireless sensors
→ LED lighting
→ Battery charger

Thermobility WPG-1

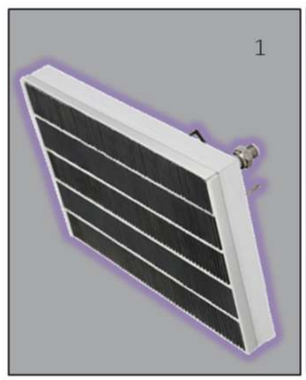
(extracted from patent n° EP2423990 A1 deposited by Nextreme Thermal Solutions, Inc.)

THERMOELECTRIC DEVICES

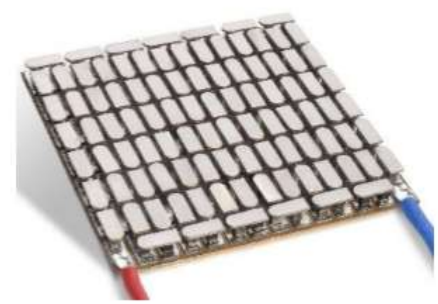
- Bulk technology devices

  - The main device manufacturers for energy harvesting and cooling in bulk technology are offering Bi_2Te_3-based products
  - A lot are based in USA, Russia, Ukraine, Japan, Korea, China…

  - European producers of GEN2 TE materials and TEGs are emerging:
    - RGS Development
    - Isabellenhütte
    - Hotblock Onboard



RGS Thermagy® panel

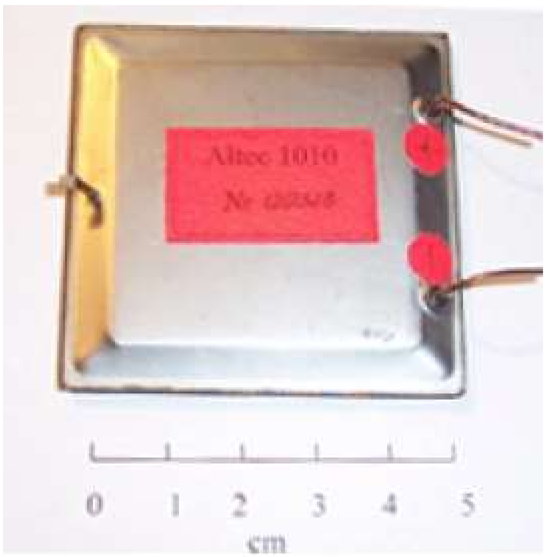


Isabellenhütte TE module

THERMOELECTRIC DEVICES

- Bulk technology devices

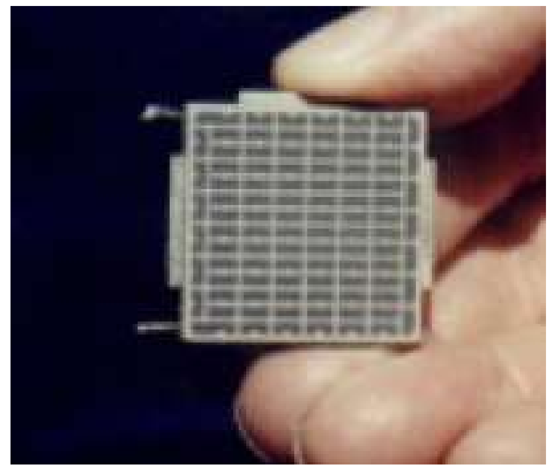
  - Altec 1010 device



- temperature range: 30 and 250 °C
- supply 6 W (4.4 V)
- efficiency 6 %

http://ite.cv.ukrtel.net

  - HZ-2 (Hi-Z) device

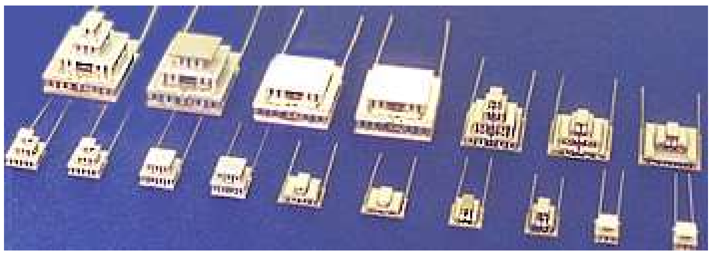


- temperature range: 30 and 230 °C
- supply 2.5 W (3.3 V)
- efficiency 4.5 %

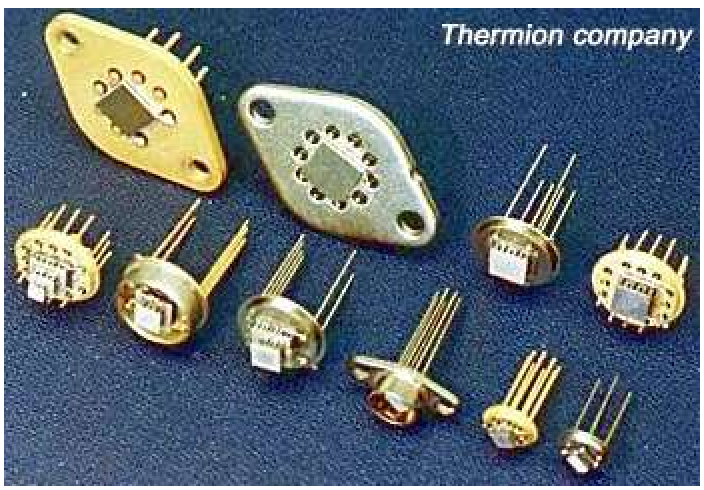
www.hi-z.com

THERMOELECTRIC DEVICES

- Bulk technology devices
  - Thermion device (Ukraine)
    → for cooling



- max current : from 0.3 to 5 A
- max deltaT :
  . 73 K (one level)
  . 130 K (multi-levels)



Applications :

- IR detectors cooling
- lasers
- photonic tools
- microchips
- scientific tools
- …

www.thermion-company.com

THERMOELECTRIC DEVICES: MAIN COMMERCIAL COMPANIES

Companies	Countries	Main applications
HOTBLOCK ONBOARD	FRANCE	Power generator
THERMOGEN-AB	SWEDEN	Power generator and Peltier module
RIF Corporation	RUSSIA	Peltier module
MicroPelt	GERMANY	Power generator and Peltier module
ALTEC	UKRAINE	Power generator and Peltier module
THERMION	UKRAINE	Peltier module
THERMIX	UKRAINE	Peltier module
KRYOTHERM	RUSSIA	Power generator and Peltier module
European Thermodynamics	UK	Power generator and Peltier module
CIDETE	SPAIN	Power generator and Peltier module
KOMATSU	JAPAN	Power generator and Peltier module
TAIHUAXING	CHINA	Power generator and Peltier module
NEXTREME	USA	Power generator and Peltier module
MARLOW	USA	Power generator and Peltier module
MELCOR	USA	Power generator and Peltier module
FERROTEC	USA	Power generator and Peltier module
Hi-Z	USA	Power generator

APPLICATIONS

- **Three kinds of TE applications:**

  → **sensors**

  → **cooling**

  → **energy harvesting**

SENSORS

APPLICATIONS

- **Thermal flow sensors**

  - Major applications (notably in thin films technologies) thanks to a high sensitivity in voltage !!
  - Autonomous marketable technology
  - New perspectives for embedded components:
    - Silicon based technology compatible with microelectronic technologies
    - performances given by integration conditions of device and used materials
  - Internet of Things (IoT, IIoT): wide networks of autonomous sensors

- **Thermal flow sensors**

→ applications area: mobile phones, laptop…

→ with the increasing number of applications, the integrated components number increases and the temperature too

→ need to control, manage thermal flow

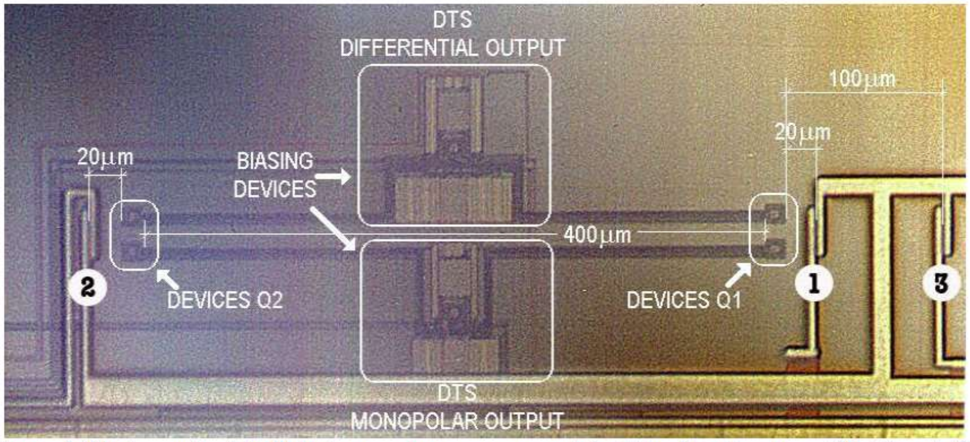


Figure 4: Photograph of built-in temperature sensors and 3 of the 4 heat sources (①, ② and ③).

E. Aldrete-Vidrio et al., Thermionic Conf., (2005)

- **Thermal flow sensors**

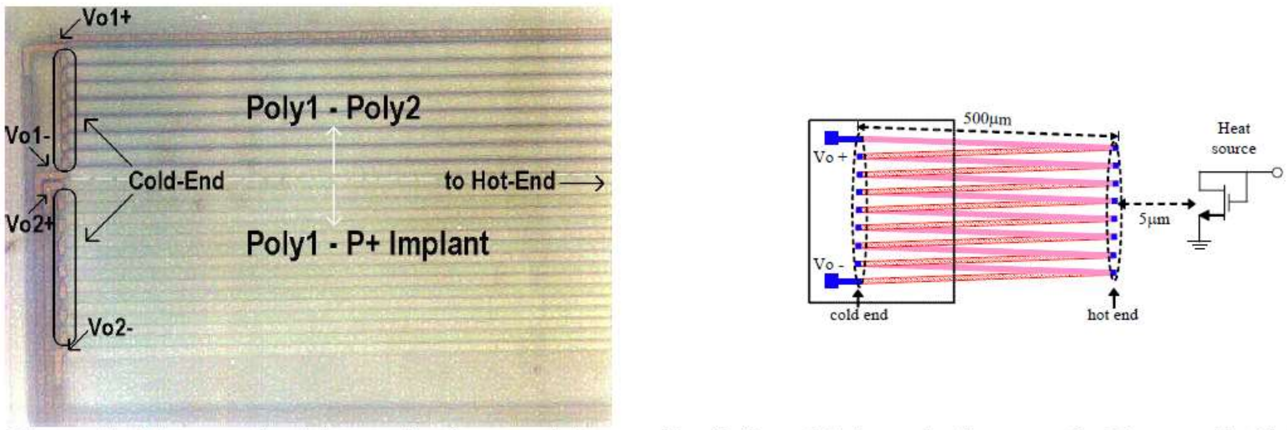


Figure 11: Photograph of the two implemented thermopiles (left) and Schematic diagram of a Thermopile (right)

→ excellent sensibility in voltage

→ free sensors in current

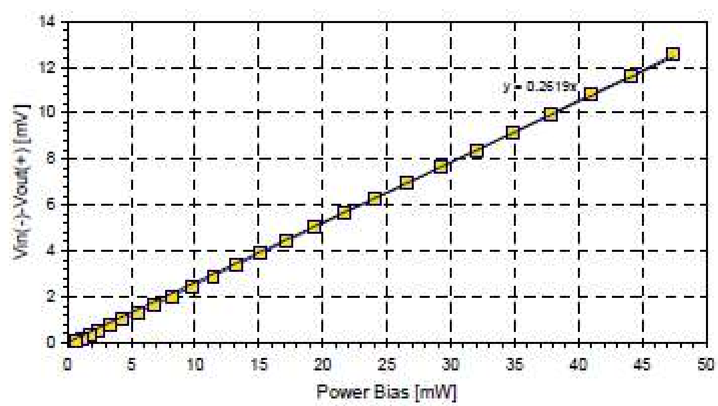


Figure 13: Output voltage of thermocouple Poly1-P+ as a function of the power dissipated by the MOS transistor.

E. Aldrete-Vidrio et al., Thermionic Conf., (2005)

- **Thermal flow sensors**

→ spin-off from ETH Zurich (Federal Polytechnic High School of Zurich) created in 2009

→ greenTEG develops, manufactures and commercializes thermal and radiative flow sensors (and TEG)

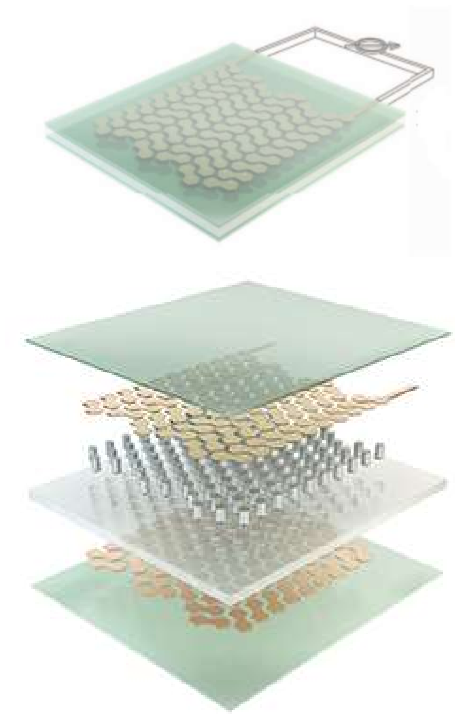
→ measures thermal flow (conductive, radiative, convective) quickly with a high accuracy

Pictures of different greenTEG sensors

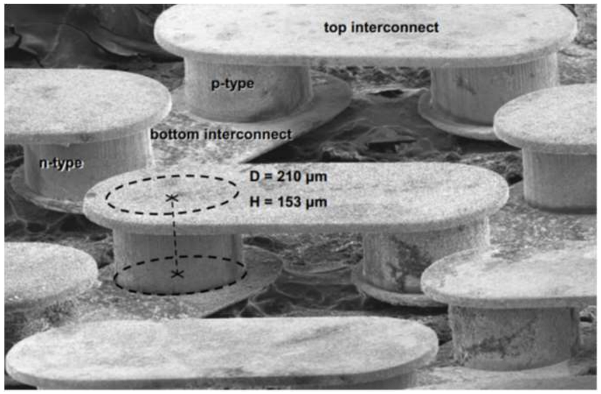
(data from http://www.greenteg.com/)

- **Thermal flow sensors**

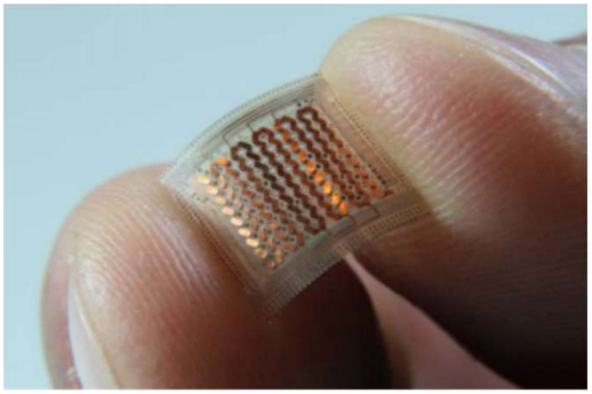
→ flexible devices from Bi_2Te_3 deposited by electrochemical process in micro-holes on polymer sheet (SU8)



Schematic structure of the greenTEG device



Microscope picture of pn junctions



Picture of flexible greenTEG device

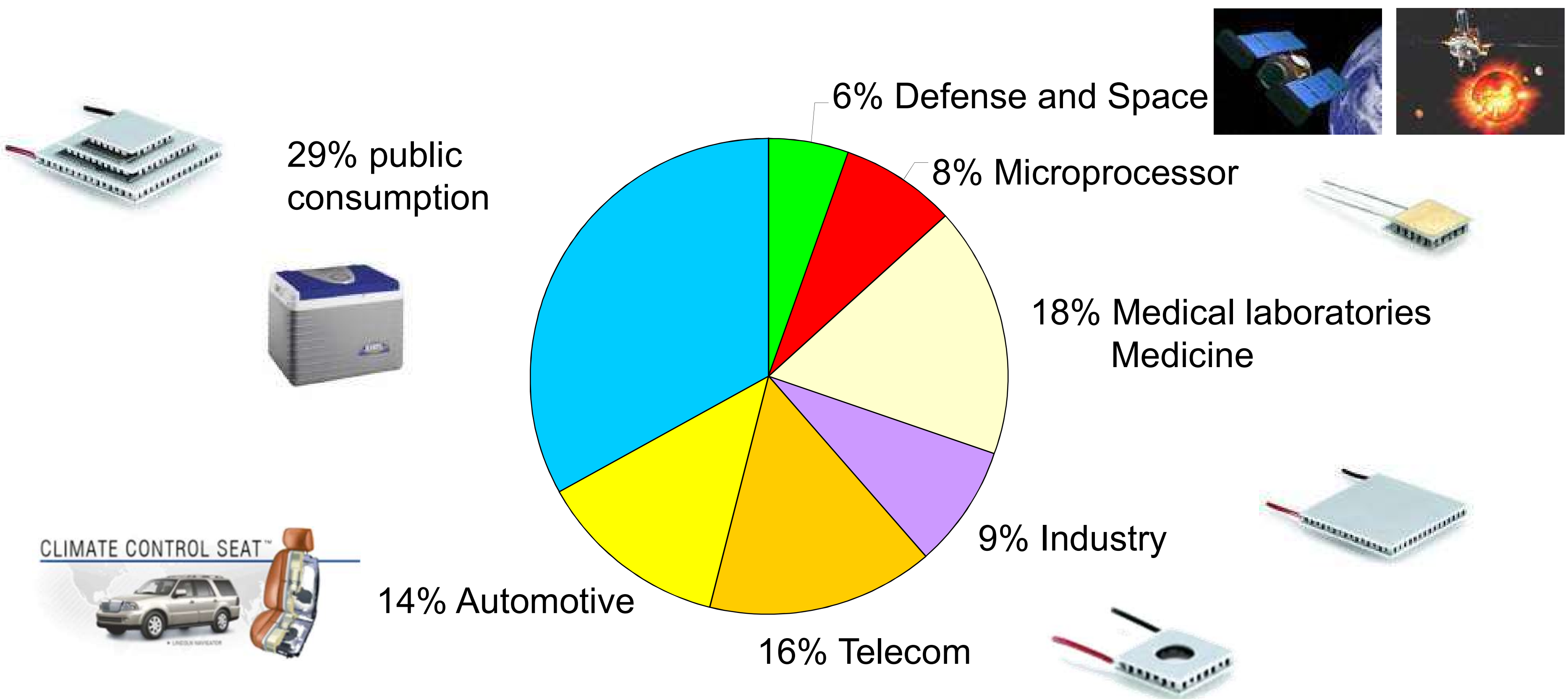
(data from http://www.greenteg.com/)

COOLING

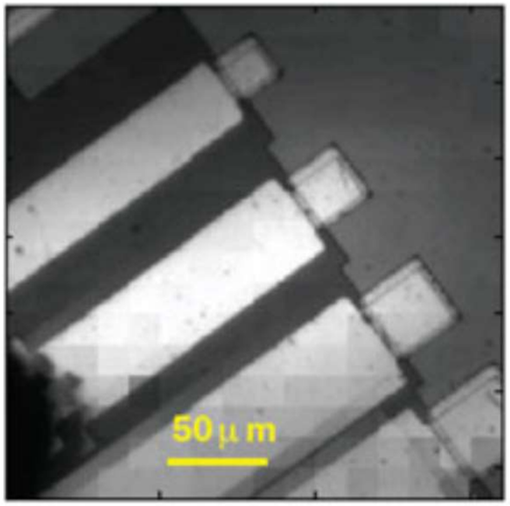
APPLICATIONS

- **Thermoelectrics market (Komatsu ECT2007)**

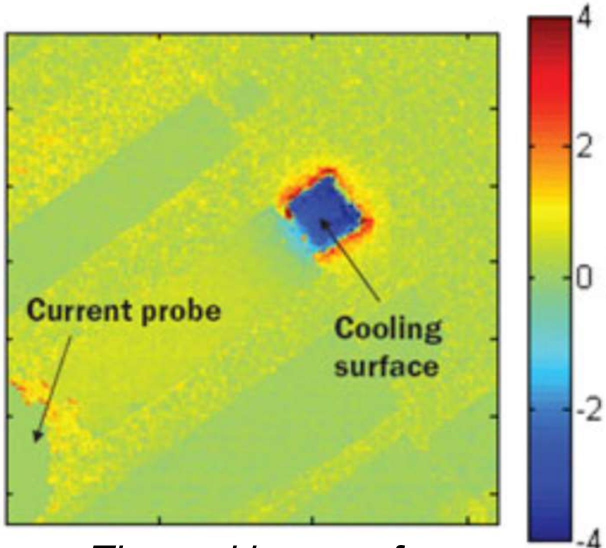
→ world market for Peltier devices (not final products, only TE devices)
≈ US$ 200-250 M/year



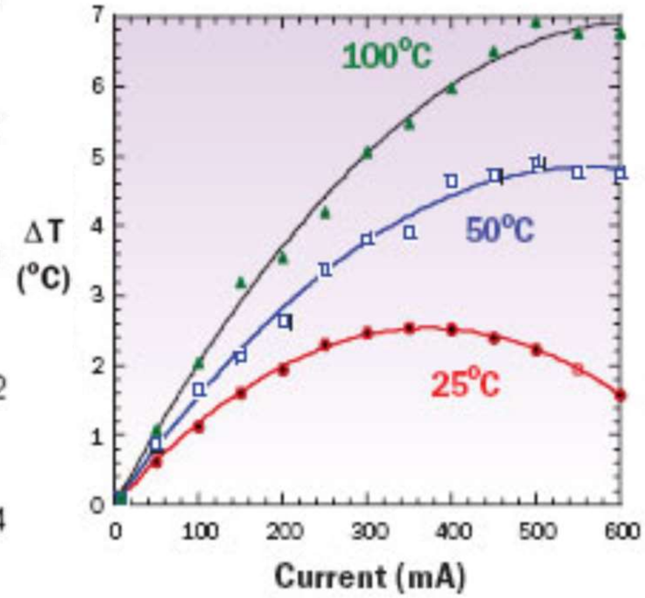
- **Peltier micro-cooling**
  - IC chips cooling
  - Micro-localized cooling
  - Embedded cooling in chips



Thin film SiGe/Si SL microrefrigerator



Thermal image of microrefrigerator under operation

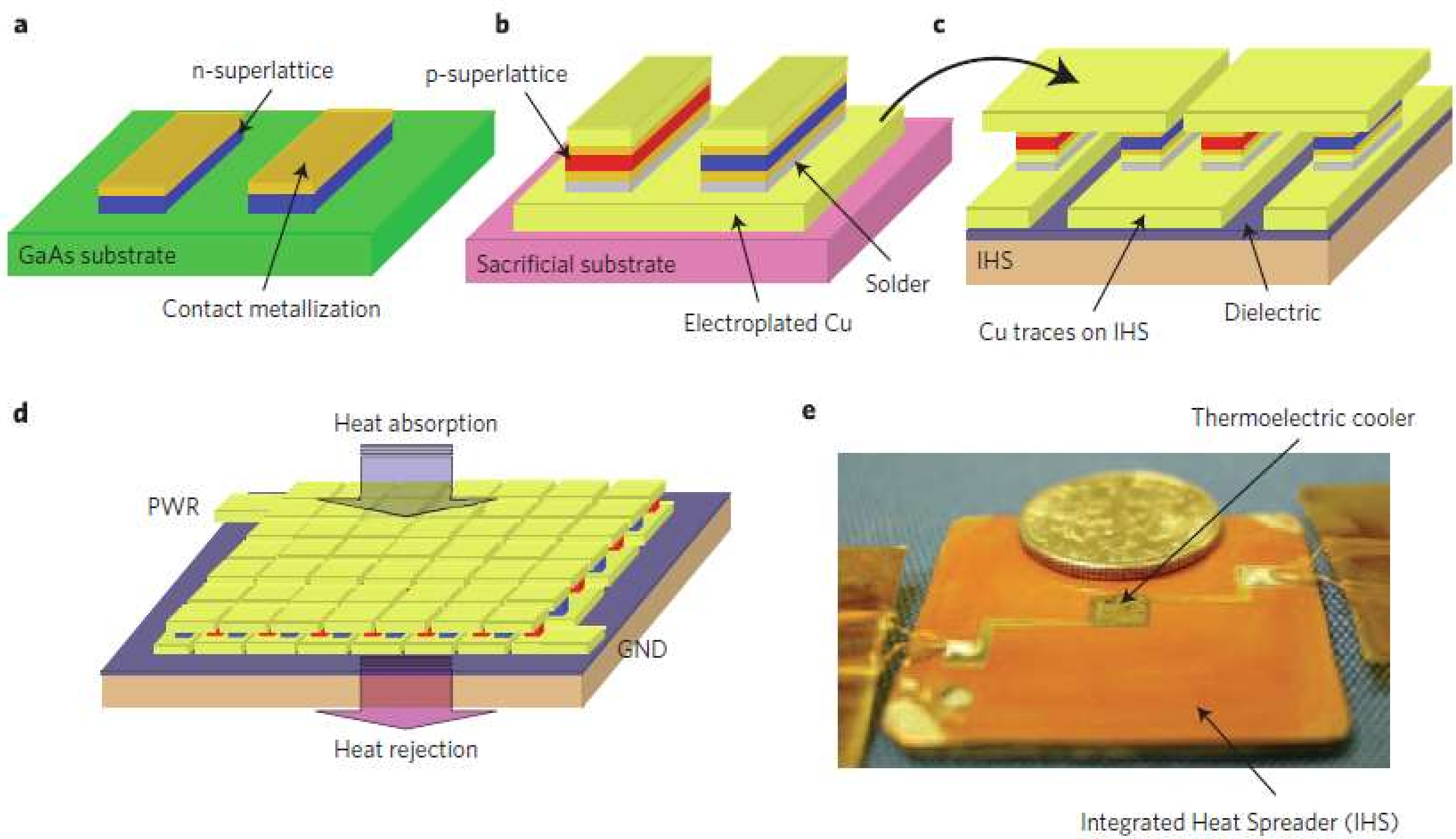


microrefrigerator's cooling versus supplied current

(data from K. Fukutani, Solid-State Microrefrigerator on a Chip, http://www.electronics-cooling.com/2006/08/solid-state-microrefrigerator-on-a-chip/)

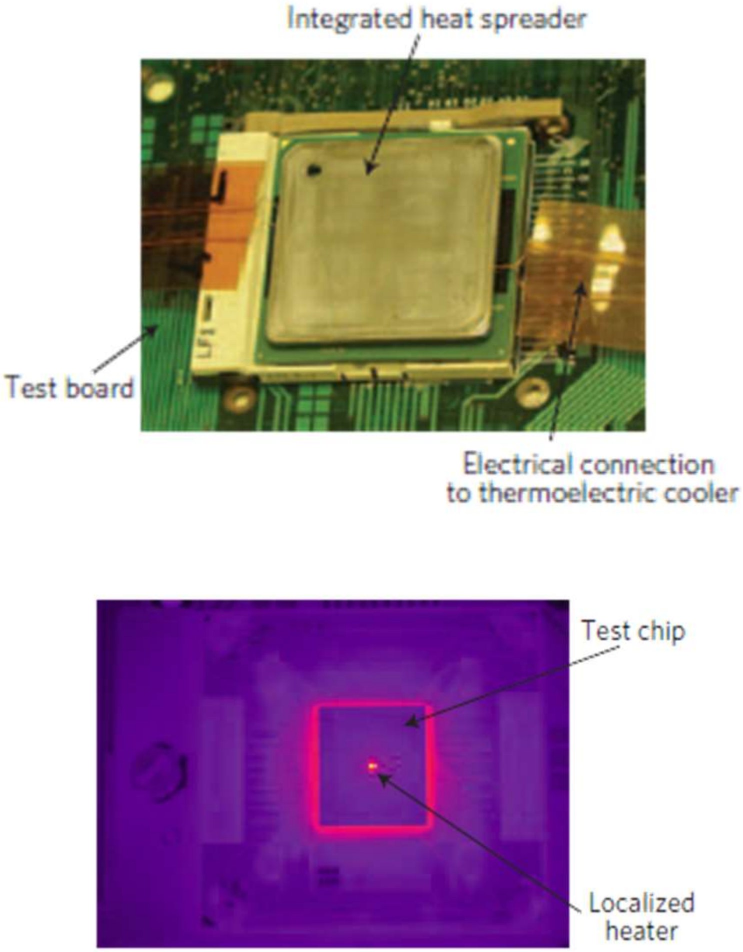
APPLICATIONS

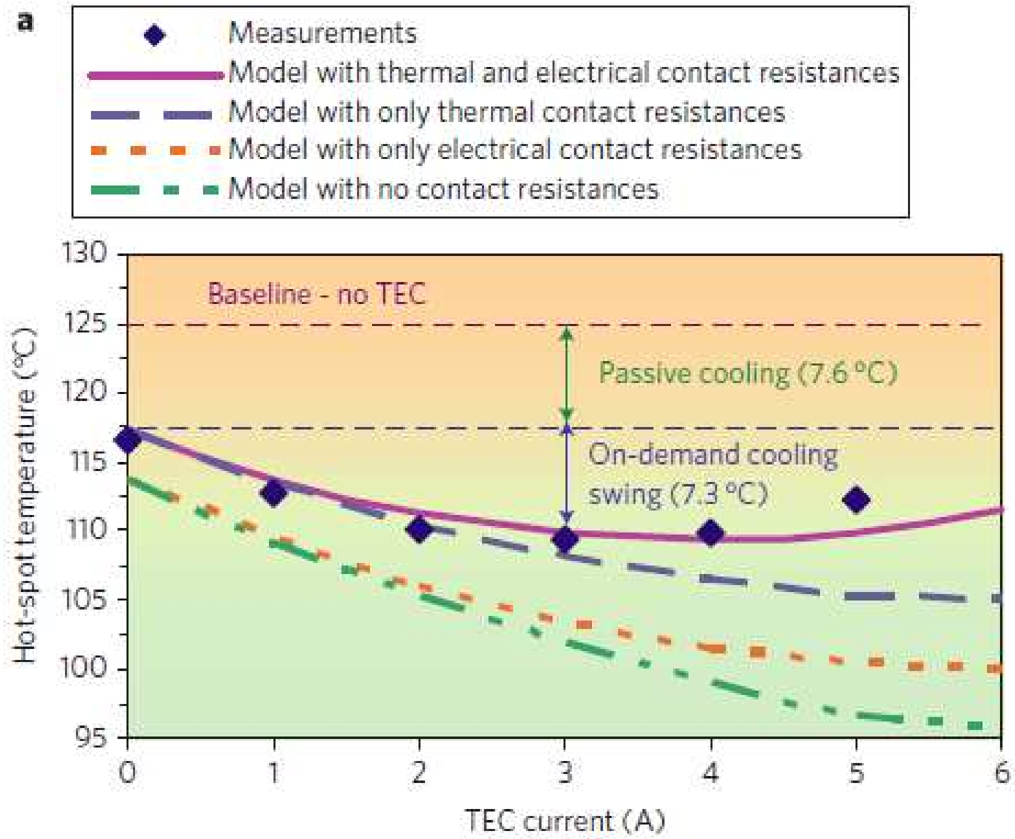
- **Localized TE micro-cooling (for ex, for electronic chips…)**



Intel Corporation, Nature Nanotech., (2009)

- **Localized TE micro-cooling (for ex, for electronic chips…)**





→ total cooling : 15 °C

Intel Corporation, Nature Nanotech., (2009)

- **Domestic consumption: mini-fridge**

Wagan EL6224 24 Liter Electric Car Cooler and Warmer

★★★★☆ 682

$61.99

Eligible for Shipping to France

More Buying Choices
$57.65 (8 used & new offers)

Igloo Iceless Thermoelectric Cooler

★★★★☆ 1,385

$72.52 - $426.99

More Buying Choices
$63.82 (35 used & new offers)

Wagan EL6206 - 6 Quart 12V Portable Electric Cooler/Warmer for Car, Truck, SUV, RV, Trailer DC Powered

★★★★☆ 63

$56.60 ~~$69.95~~

Eligible for Shipping to France

More Buying Choices
$48.59 (24 used & new offers)

APPLICATIONS

- **Automobile**
  - Cockpit air conditioning

    → HVAC : Heating, Ventilation and Air-Conditioning

    → TE systems localized near the dashboard, roof…

APPLICATIONS

- **Automotive**
  - Air-conditioned seats

    → Amerigon : US company producing air-conditioned seats for automotive market

    → TE devices supplier : BSST (USA)

→ Climate Control Seat (CCS)

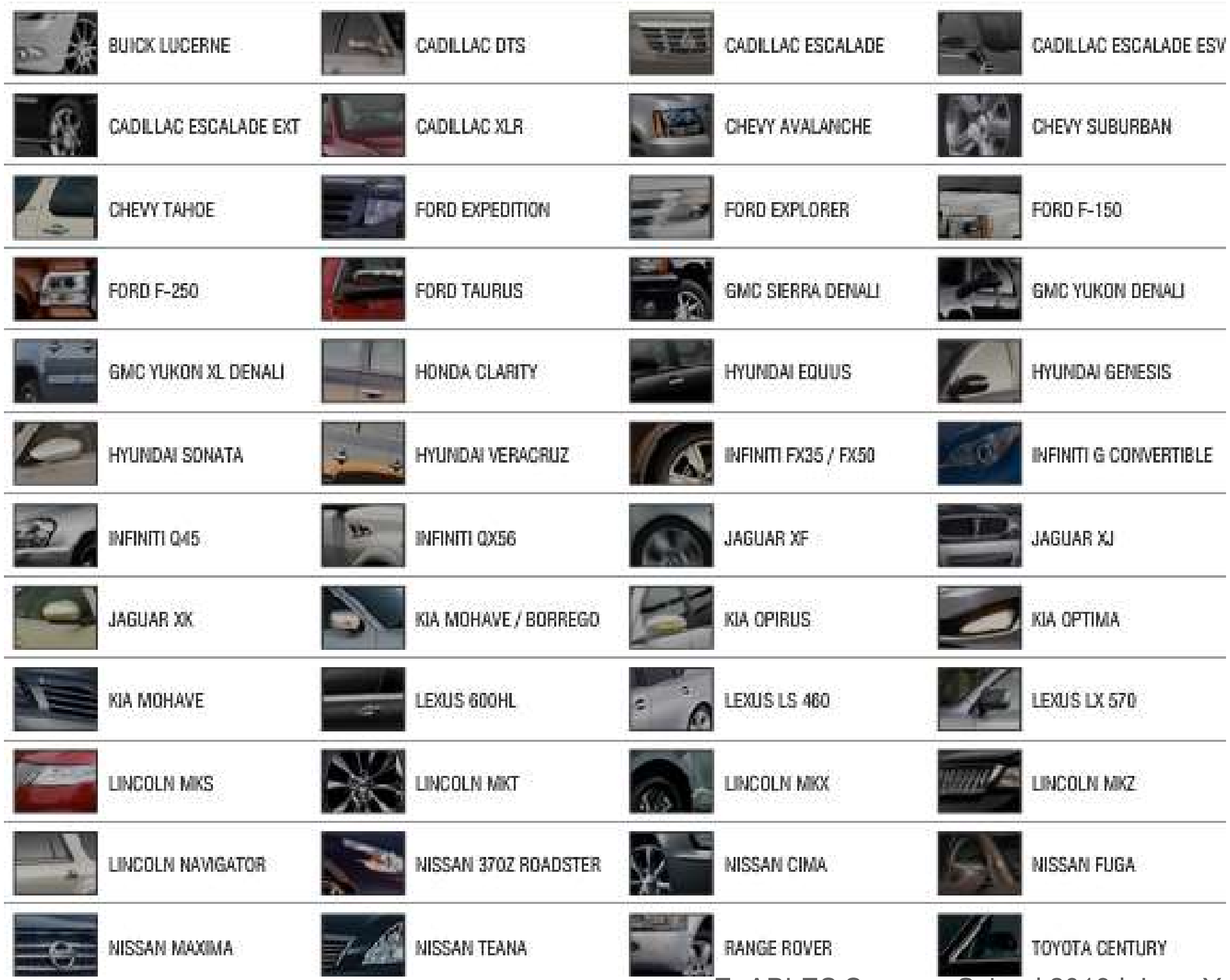
→ heating or cooling seats

→ for automotive and trucks companies

www.amerigon.com

APPLICATIONS

- **Automotive**
  - Air-conditioned seats



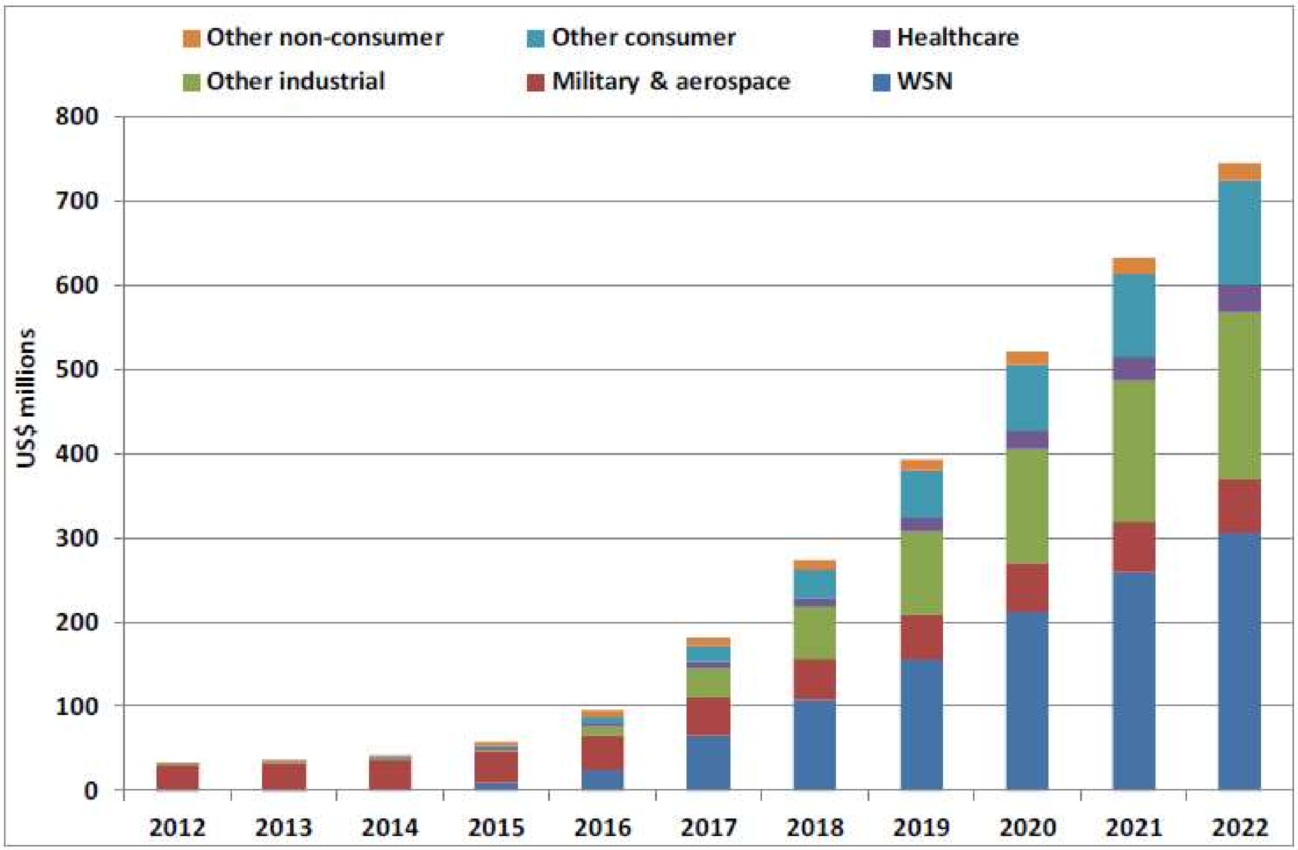
www.amerigon.com

THERMOELECTRIC GENERATORS

APPLICATIONS

→ world market for generators devices (final systems)
≈ US$ 25-50 M/year

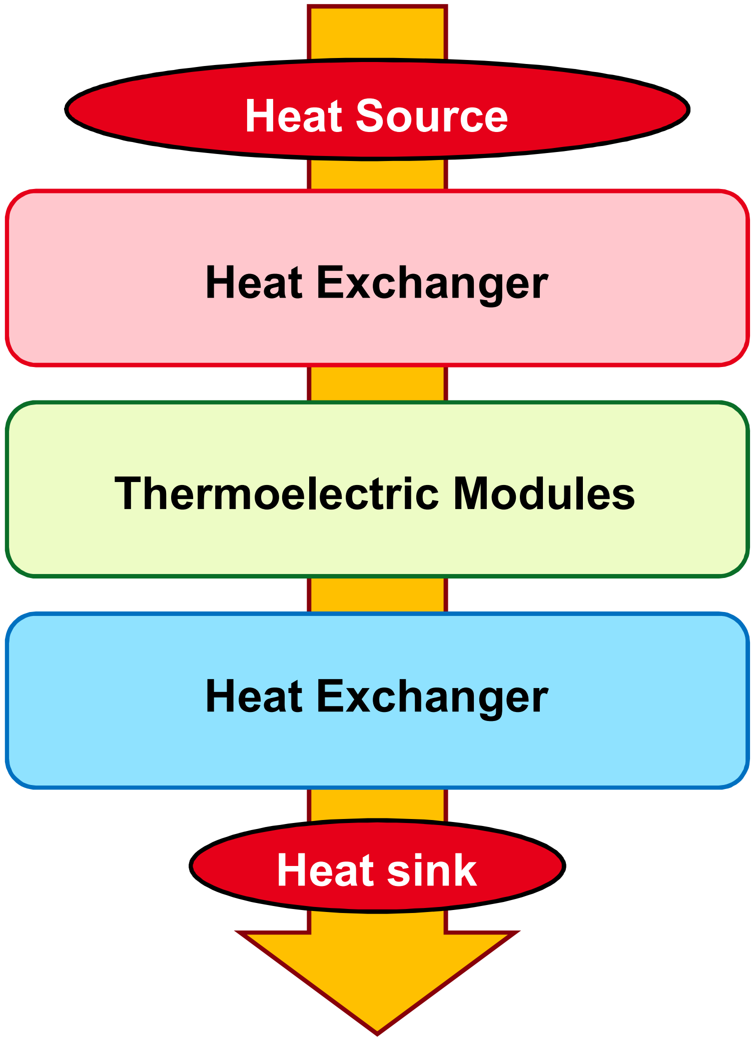
→ Forecasts for the next years :



Source IDTechEx

Requirements for a TEG

- Main elements:
  - TE Modules to convert heat into electricity
  - 2 heat exchangers to maintain heat flow and temperature gradient
- In addition a DC/DC or AC/DC converter / inverter to provide usable current, i.e. suitable voltage and intensity



Conditions for a performing TEG: to optimise all stages

- TE material level
- Device level
- System level

On top of this: make it price competitive

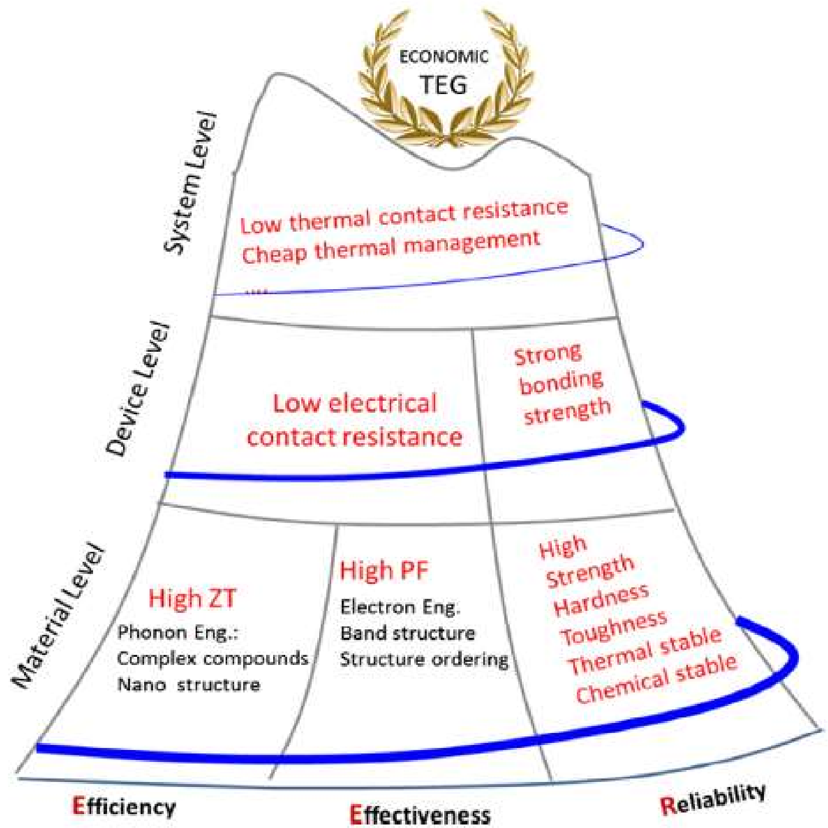
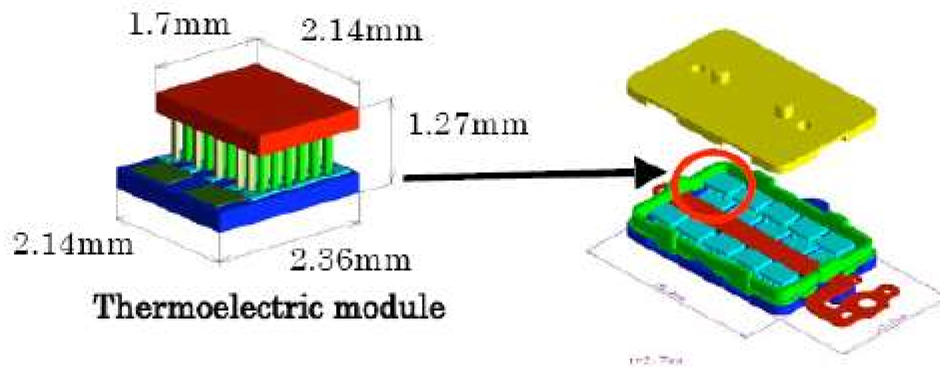


Fig. 15. Hierarchical requirements for TEG: the efficiency–effectiveness–reliability mountain.

Liu, W. (2015). Current progress and future challenges in thermoelectric power generation: From materials to devices. *Acta Materialia*, Vol. 87, pp. 357-376.

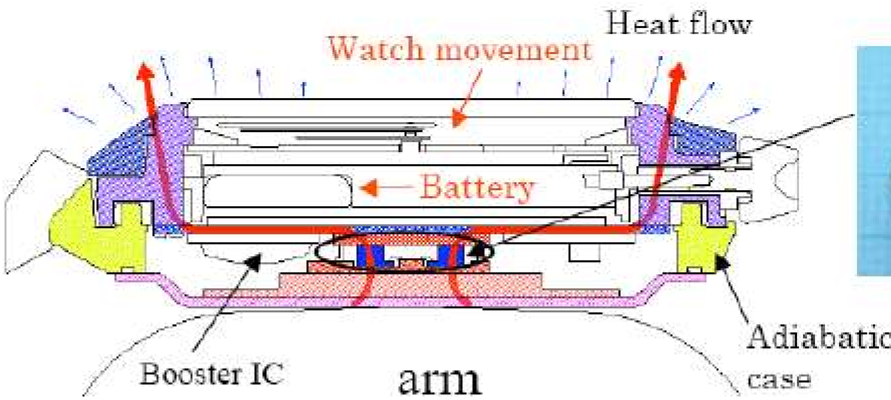
- **Seiko watches**

Thermal energy watch



Thermoelectric module

Thermoelectric unit



Thermoelectric (Photo)

source : SEIKO

→ legs in Bi_2Te_3
→ manufactured and commercialized in 1998
→ 1000 watches sold for 1100 €

M. Kishi, 18th ICT, (1999)

- **Citizen watches**

Fig. 10 Montre Citizen modèle CTY66-0341

→ TE generator made with 1242 junctions
→ power : 13.8 µW for a voltage 515 mV/K
→ manufactured and commercialized in 2001
→ price in Japan 500 €

www.citizen.co.jp/release/01/010815ec.htm

K. I. Uemura, private communication, (2001)

APPLICATIONS

- **Watches :**

→ the only commercialized application

→ a watch consumes between 1 and 2 μW

→ temperature difference available at wrist : only 1 K

→ Seiko TE generator performances : 22 μW (300 mV)

→ a voltage amplifier increases it to 1.5 V

Space Applications: RTG

- nuclear electrical generator producing electricity with heat from radioactive disintegration of radioisotope materials (typically ^{238}Pu)
- first applications for RTG : military and spatial (in particular, the missions: Apollo, Pioneer, Viking, Voyager, Ulysses, Galileo, New Horizons)

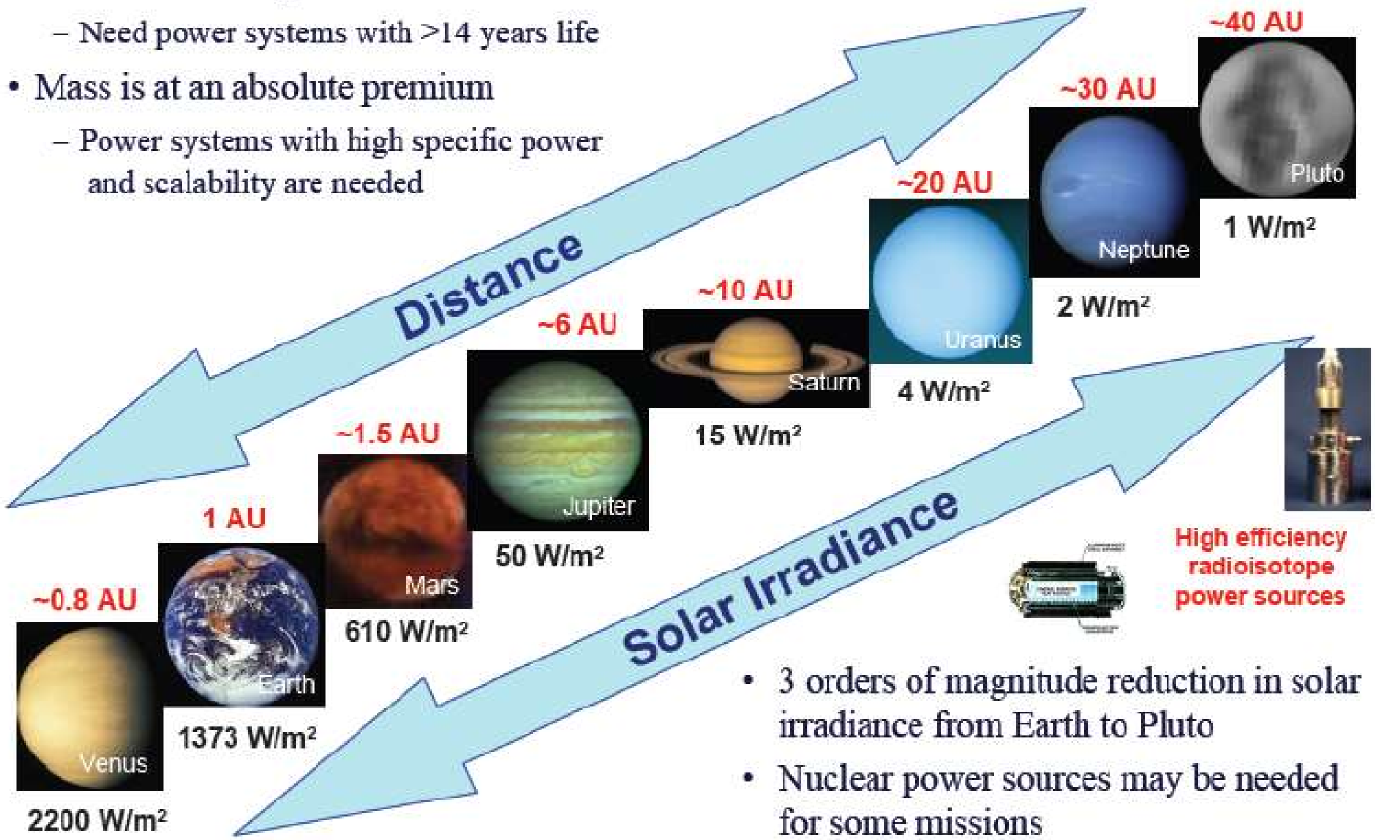
A. Pustovalov, 18th ICT, (1999)

Advantages:

- For the majority of these programs, supply in electricity for equipment which has to work continually for several years without human intervention
  - e.g. embedded generators for New Horizons probe : can provide 200 W for 50 years. After two centuries, power decreases to 100 W
  - Better resistance to cold conditions than a battery. On Mars: T_{avg}: -63°C / T_{min}: -143°C / T_{max} +20°C
  - Advantage over solar panels: less surface with same power, works at night and far away from the Sun, insensitive to dust.

APPLICATIONS

- Missions are long
  - Need power systems with >14 years life
- Mass is at an absolute premium
  - Power systems with high specific power and scalability are needed

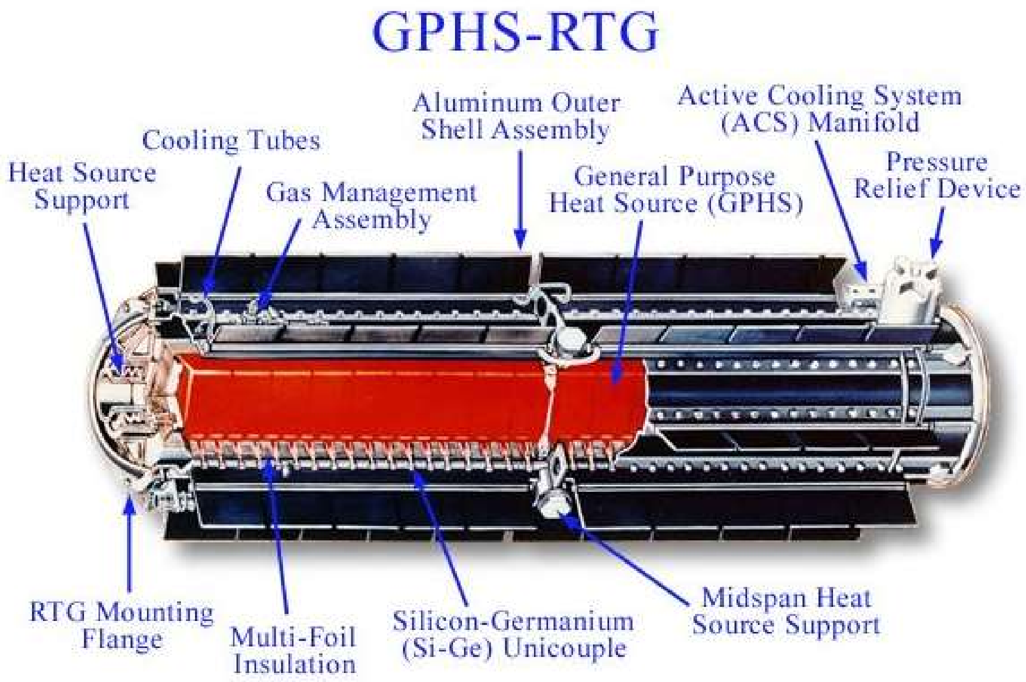


- 3 orders of magnitude reduction in solar irradiance from Earth to Pluto
- Nuclear power sources may be needed for some missions

* T. Caillat et al., 23rd rd Symposium on Space Nuclear Power and Propulsion STAIF 2006 Jet Propulsion Laboratory/California Institute of Technology

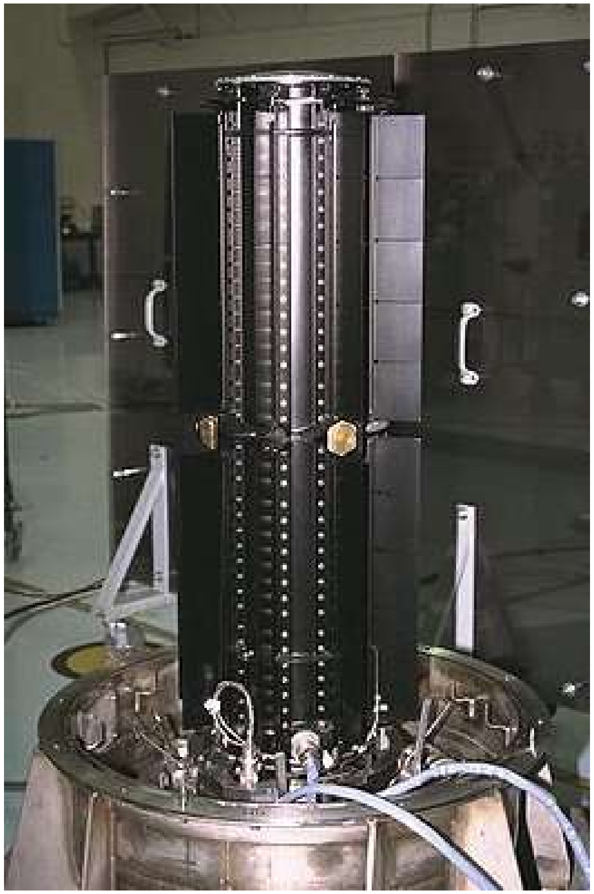
- **Applications for Space: RTG**

Glow of $^{238}PuO_2$ because of its own radioactive disintegration



GPHS-RTG diagram of Ulysses, Galileo, Cassini-Huygens and New Horizons probes

• **Applications for Space: RTG**



Picture of Cassini probe RTG

Assembly of the New Horizons probe (2005) integrating the RTG

APPLICATIONS

- **Other applications for RTG**

  → **Lighthouses**

  - Used by Soviet Union to supply isolated lighthouses
  - integrated with thousands of generators
  - today, no RTG anymore because of terrorism

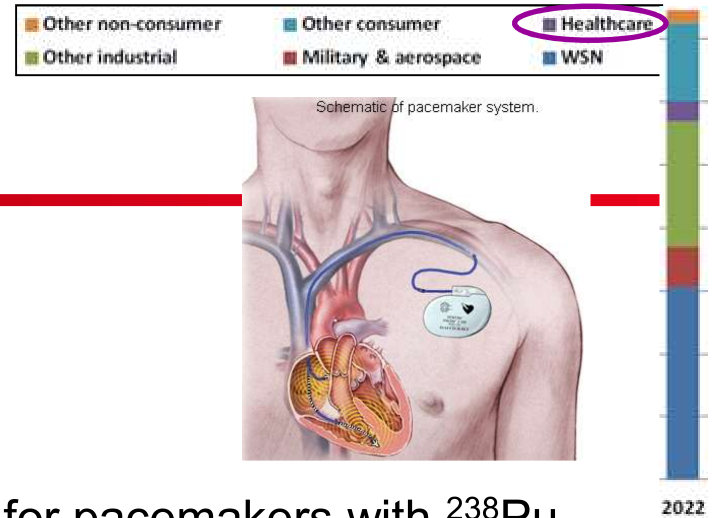
Dimensions of the cylinder	10 by 10 centimetres
Weight	5 kilograms
Capacity	240 watts
Concentration of strontium 90	1,500 TBq, or 40,000 curies
Temperature on the surface, centigrade	300-400 degrees
Exposition dose rate at the distance of 0,02 to 0,5 metres	28-10 Sv/h

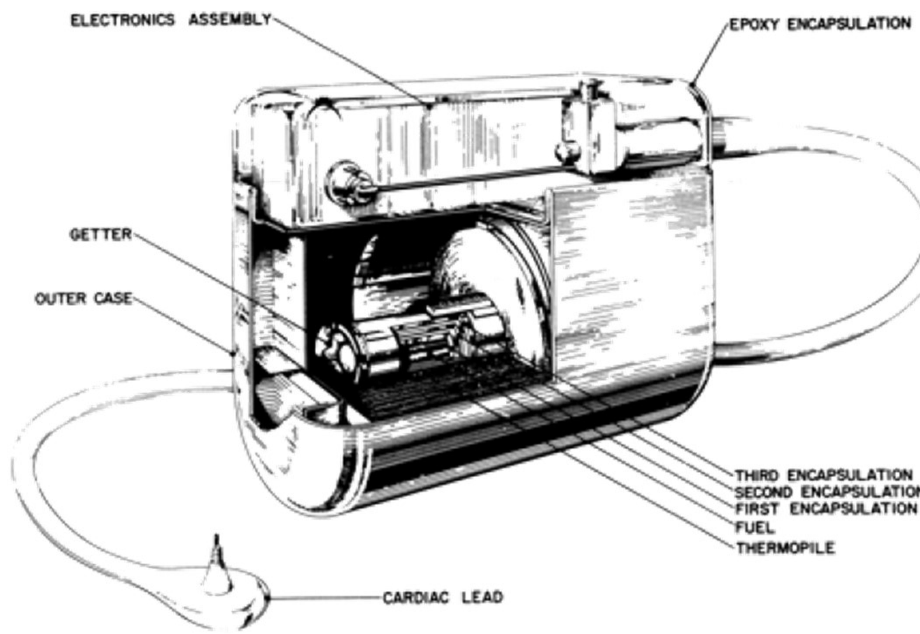
APPLICATIONS

- **Other applications for RTG**

  → **Pacemakers**

  - development of miniaturized generators for pacemakers with ^{238}Pu
  - generated power: 300 µW
  - first implantation in 1970 in Paris



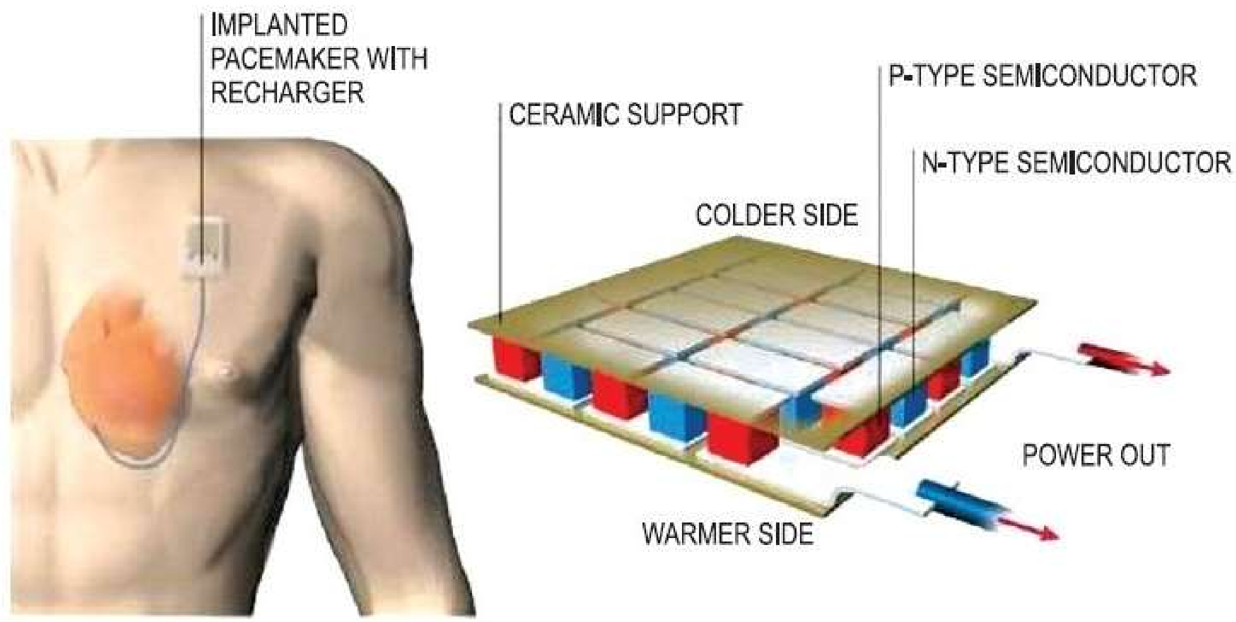


APPLICATIONS

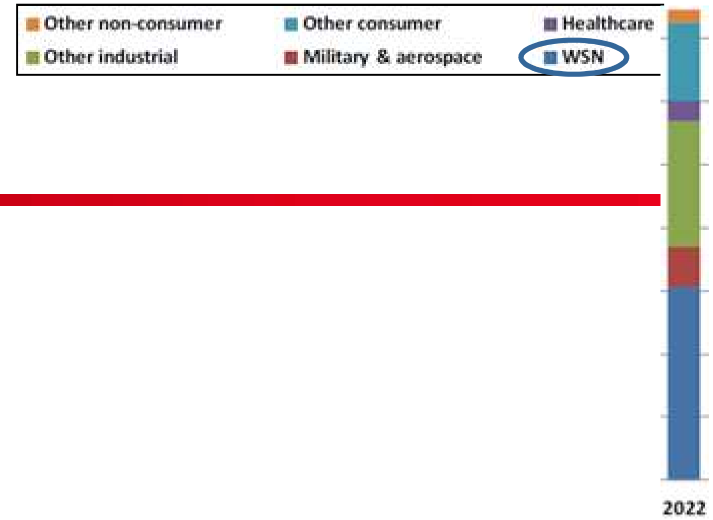
- **Other applications for RTG**

→ **Pacemakers**

→ today RTG for pacemakers have been substituted by green technologies based on lithium-ion batteries or even other TE systems
→ generated power: 100 µW and voltage 4 V with 4000 junctions and an 6 cm² area



(D. Bhatia, J Pharm Bioallied Sci. 2010)



- **Applications: WSN**

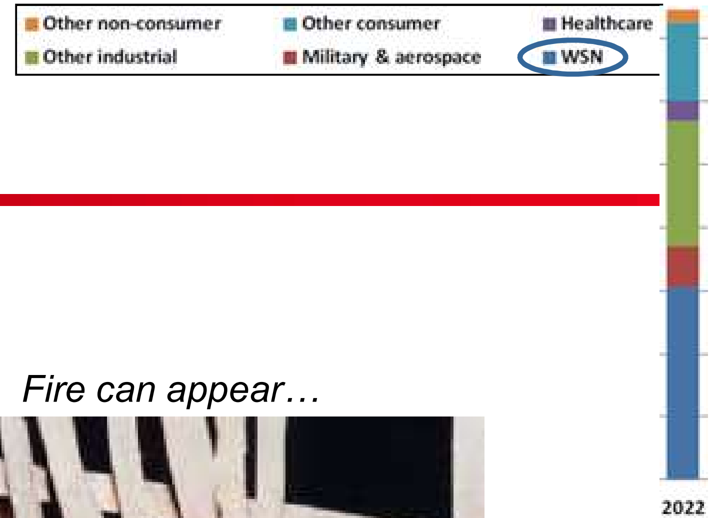
→ WSN : Wireless Sensors Networks

→ Sensors usually located in difficult environment with the goal to send information (temperatures, pressures, flow, etc.) to control rooms

→ **New potential with Industry4.0 and Internet of Things**

→ Transmission by RFID which needs power

→ Power needed:
- few µW in sleep mode
- few mW to several hundreds mW in transmission mode

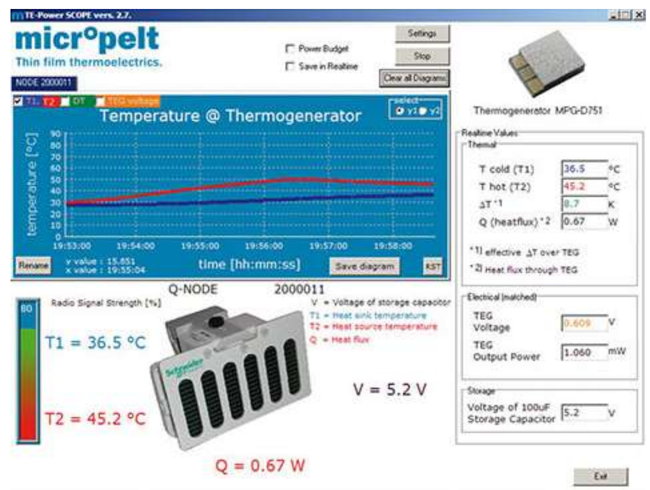


APPLICATIONS

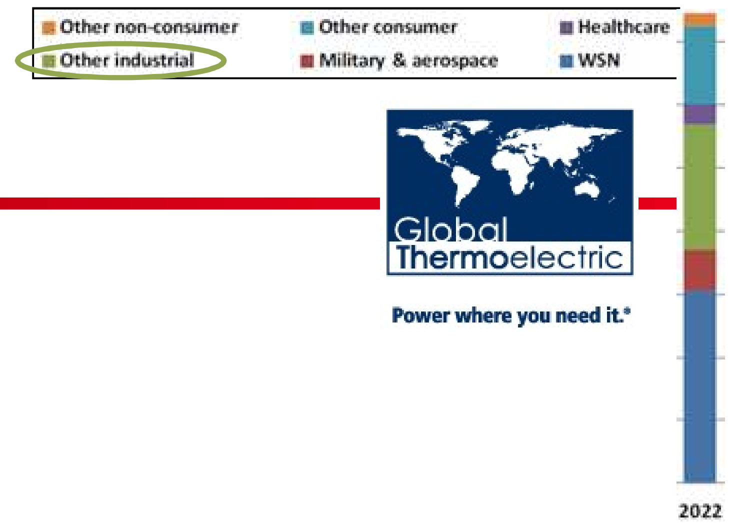
- **Applications: WSN**
  - → Example : bus bars in electrical installations

Fire can appear…


Information transmitted to control room



(http://www.micropelt.com)

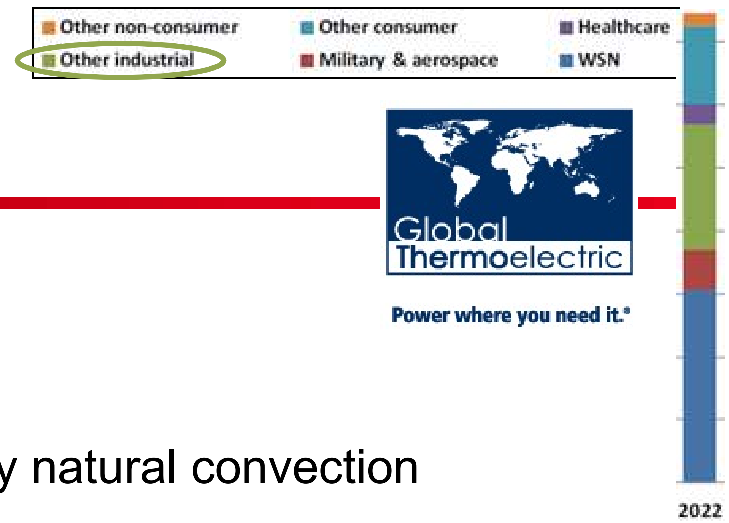


APPLICATIONS

- **TE generators: Global TE**

  → Specialized in very big TE installations

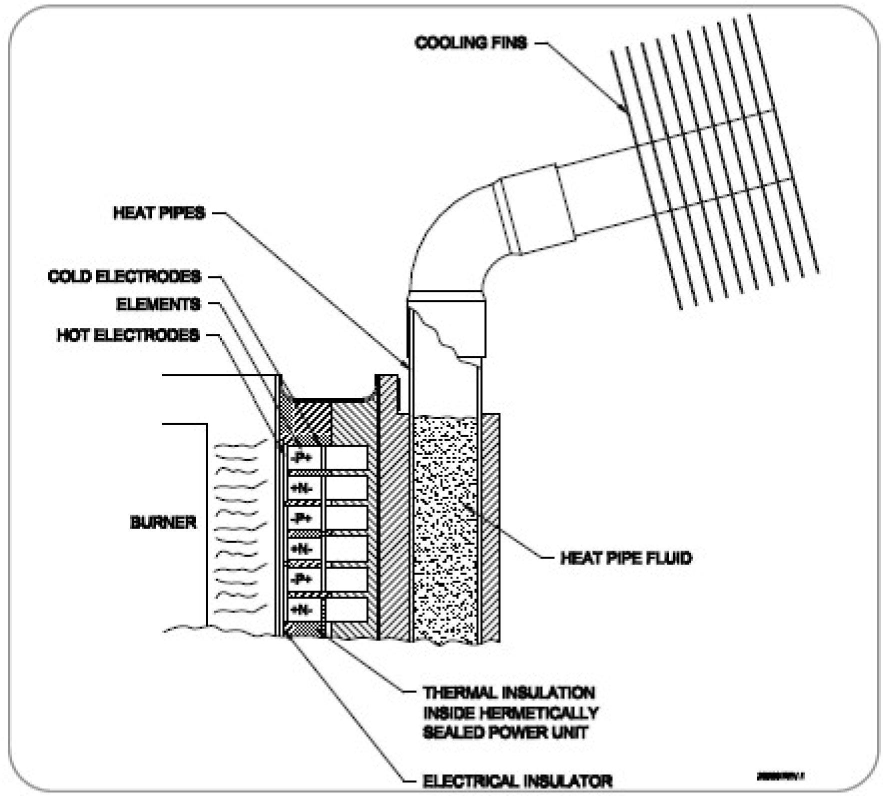
(http://www.globalte.com/products/GlobalTEGs/Model8550)



APPLICATIONS

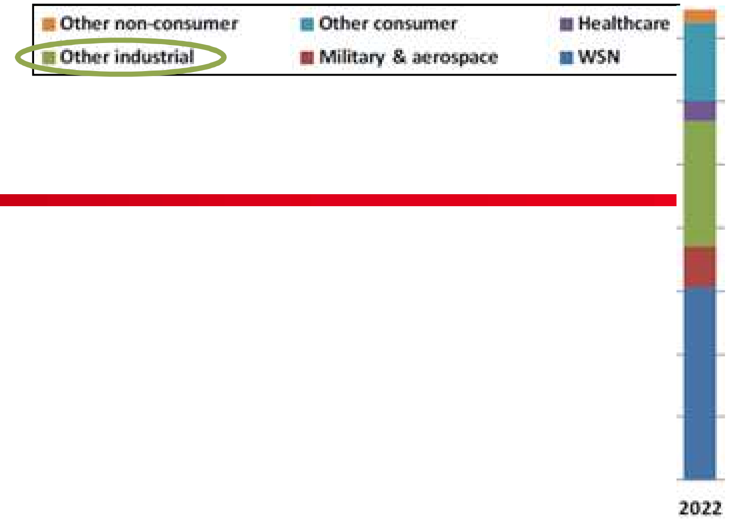
- **TE generators: Global TE**

→ T_{hot} = 538ºC (gas burner)
→ T_{cold} = 163ºC (cooling fins spreading heat by natural convection
→ Performances:
. 480 Watts at 12 Volts
. 550 Watts at 24 Volts



(http://www.globalte.com/products/GlobalTEGs/Model8550)

APPLICATIONS



- **Automotive**

  - Strong constraints for CO_2 emissions

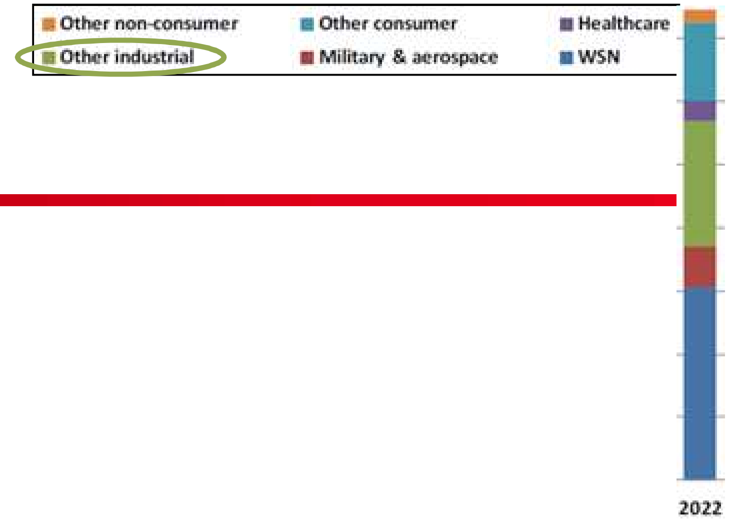
    → bonus/penalty system

    → commitment to decrease CO_2 emission for new cars

    → norm for greenhouse gas

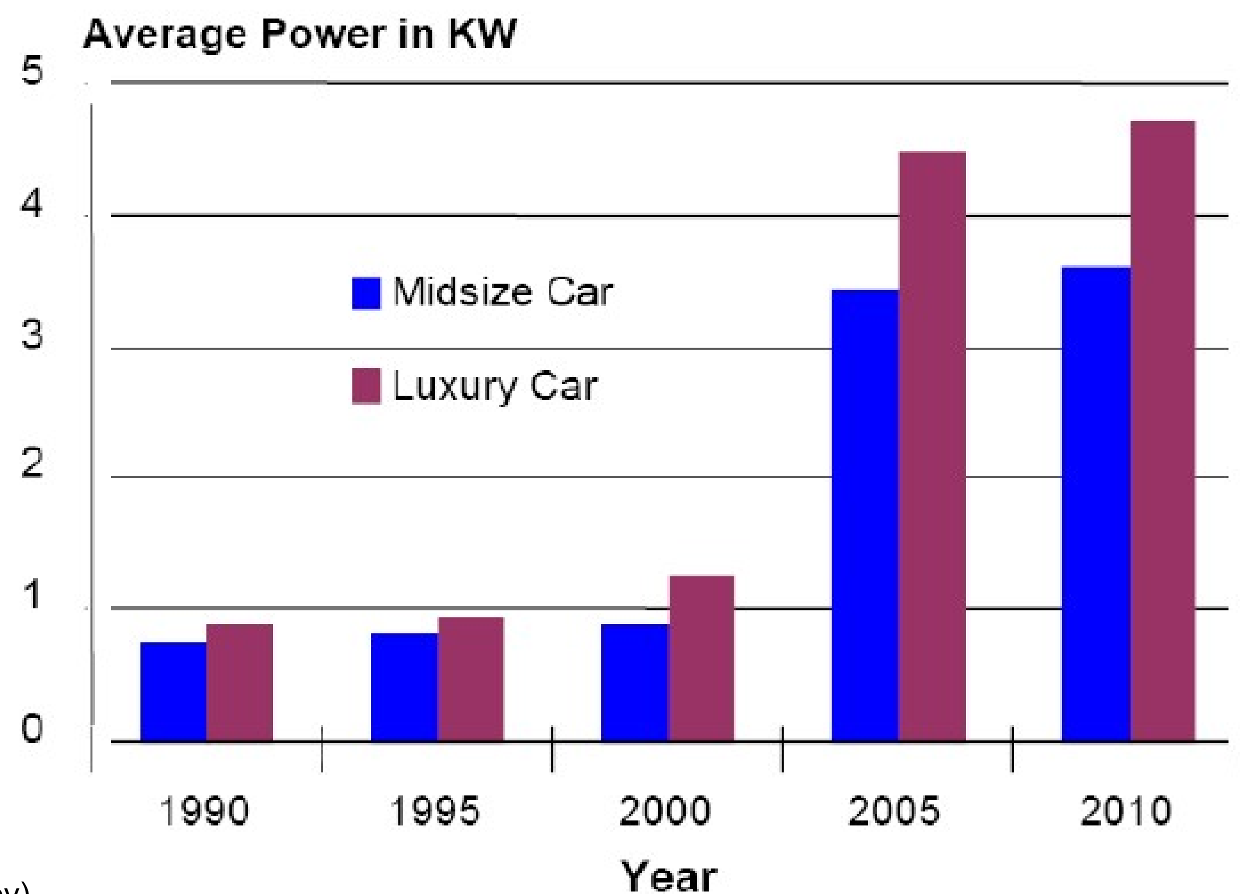
- Increase of communication systems

  → increased number of sensors and electronic devices in cars
  → Electrical generation by the alternator picks up mechanical energy from the engine → **detrimental to engine yield and fuel consumption**



APPLICATIONS

- **Automotive**
  - Increase of power needs for vehicles



(eere.energy.gov)

APPLICATIONS

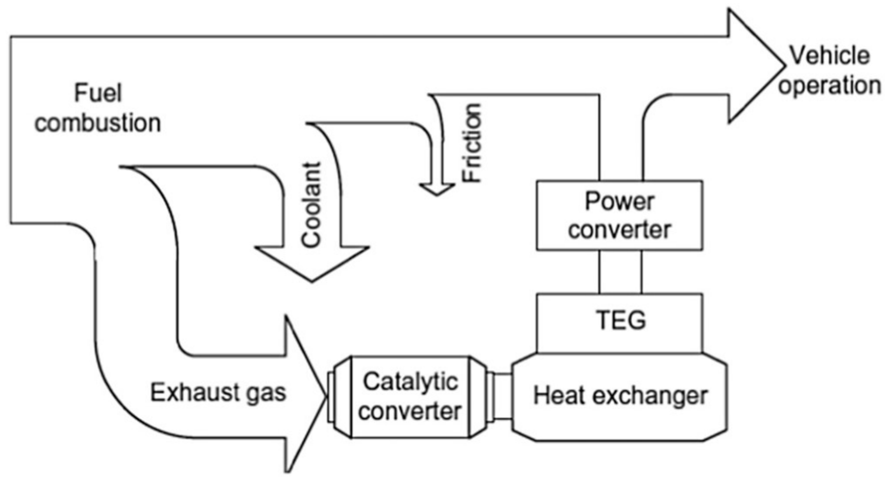
- **Automotive**
  - Use of TE systems for :

→ fuel saving (goal: 5 to 6%)

→ power used for auxiliary systems and accessories: lights, radar for parking aid, anti-collisions systems, navigational aid systems, sensors, etc.

→ size decrease of alternator (goal: 1/3 decrease)

→ decrease of gas emissions and greenhouse gas



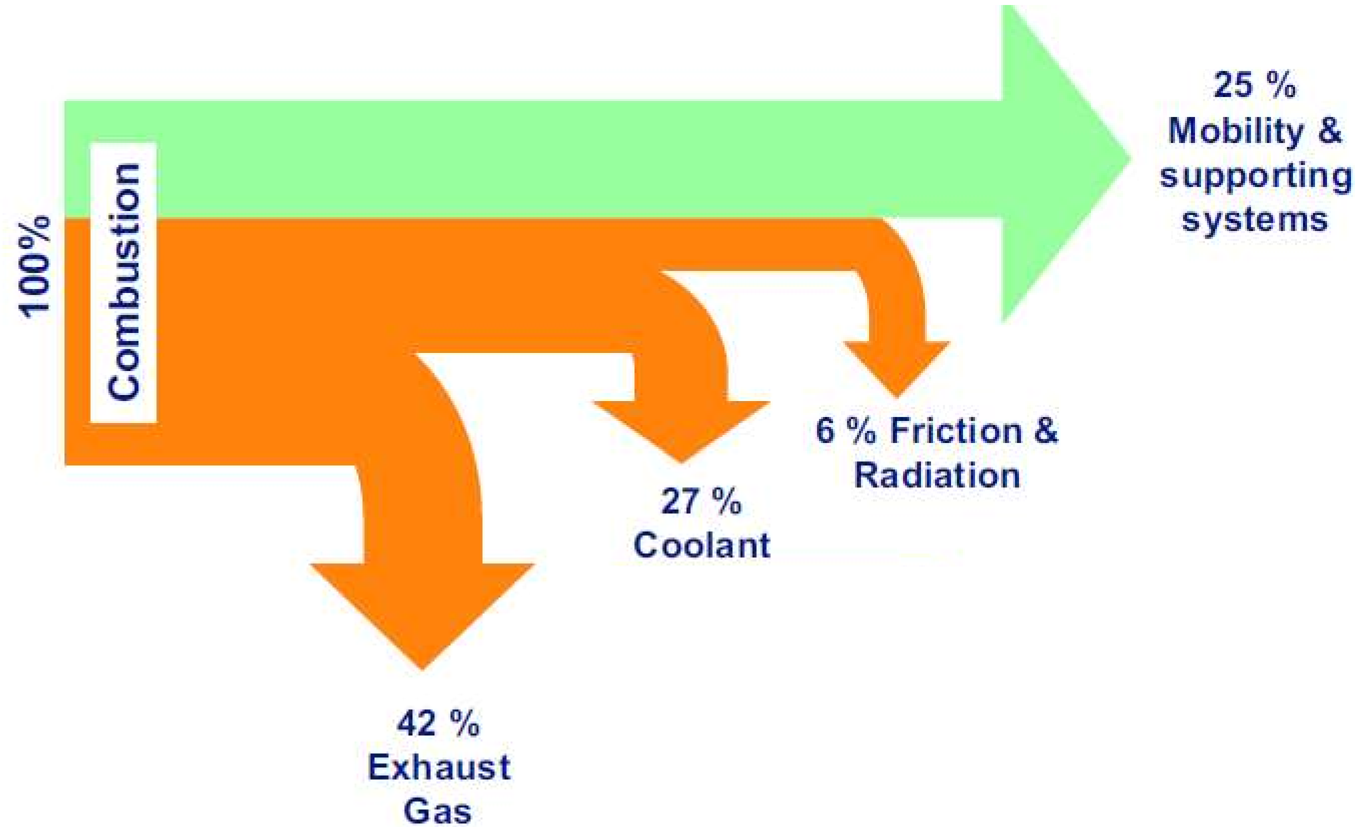
* W. He et al., Recent development and application of thermoelectric generator and cooler, Applied Energy 143 (2015) 1–25

- Involved manufacturers:

→ BMW, Chrysler, General Motors, Volvo, Fiat, Toyota, Honda, Renault Trucks, VW, Daimler, MAN…

- **Automotive**

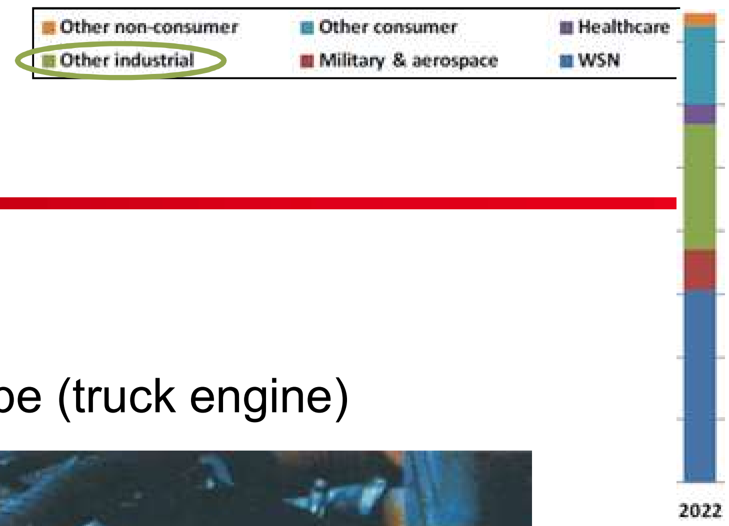
→ use of combustion energy:



A. Bodensohn, Daimler Chrysler, (2004)

Criteria for a car TEG

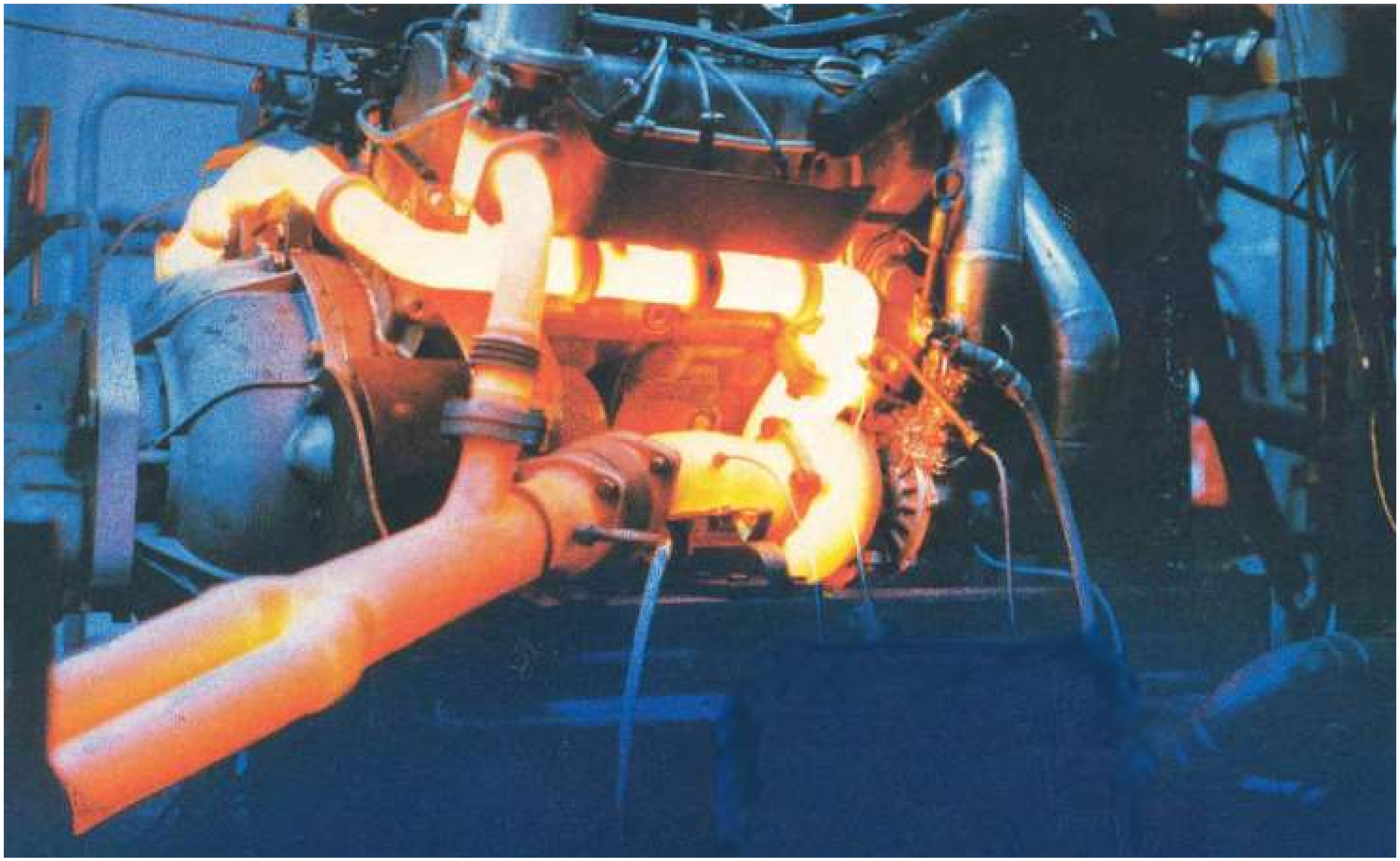
- Cost: < 1 €/W
- Volume
- Weight
- Performance: significant fuel savings
- Impact on engine performance: e.g. back pressure
- Reliability
- Sustainability, e.g. recyclability



APPLICATIONS

- **Automotive**

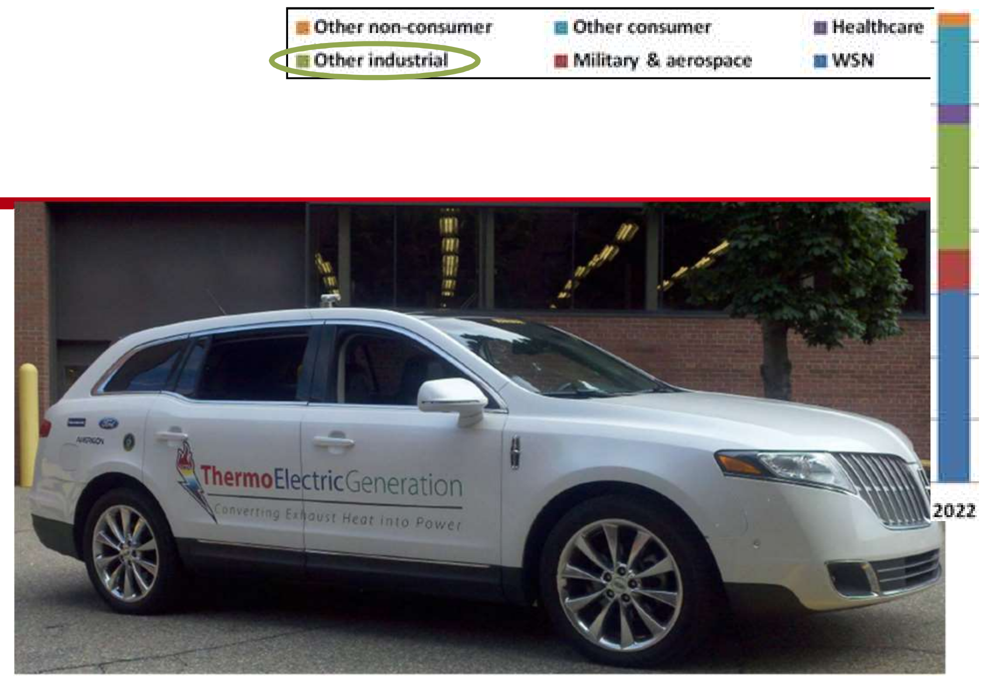
→ thermal energy available with exhaust pipe (truck engine)

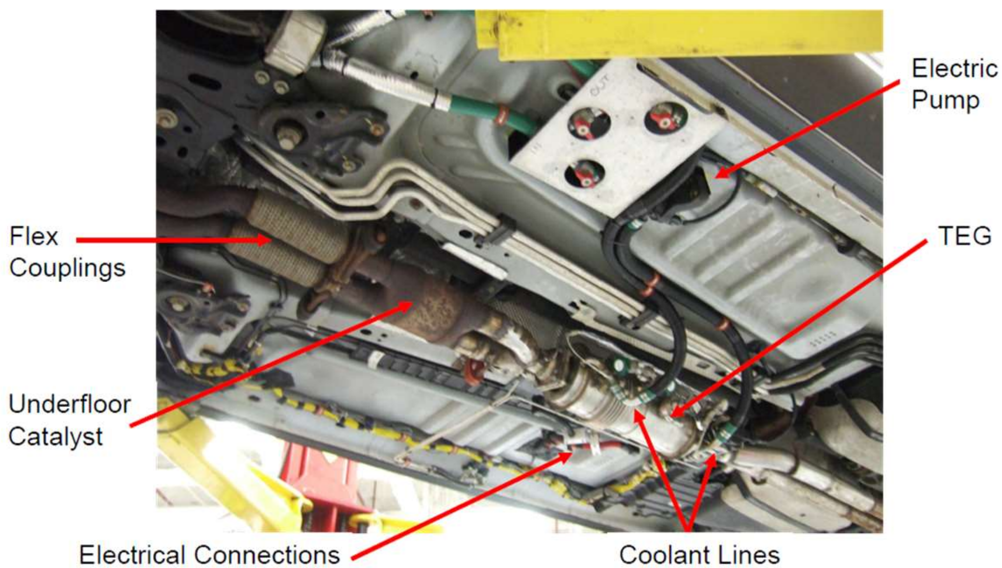


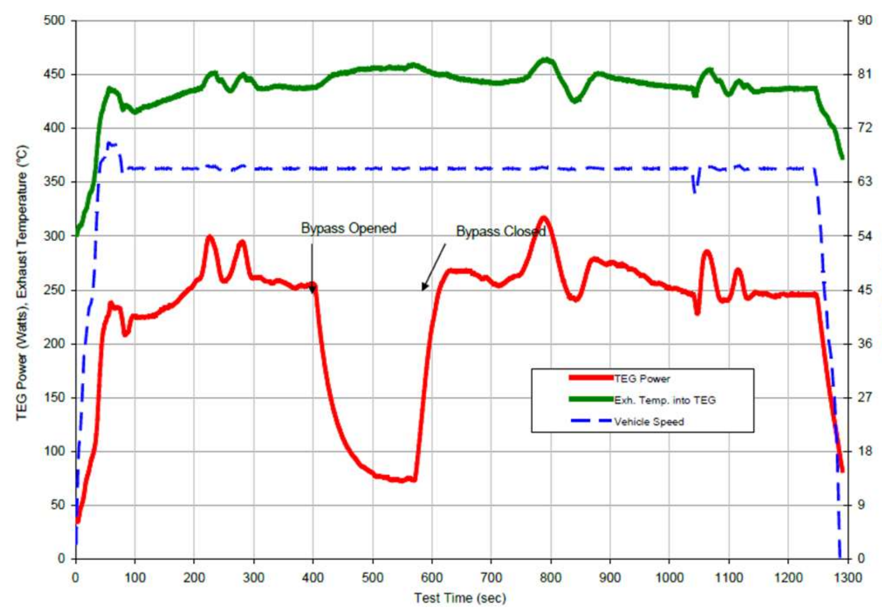
APPLICATIONS

- **Automotive**

  → Example 1:
  Lincoln MKT AWD 3.5L V6 GTDI







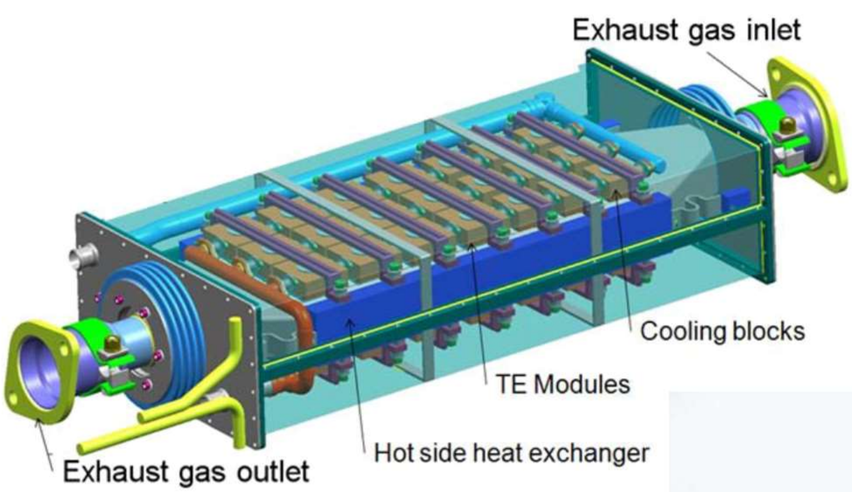
→ 250 W generated

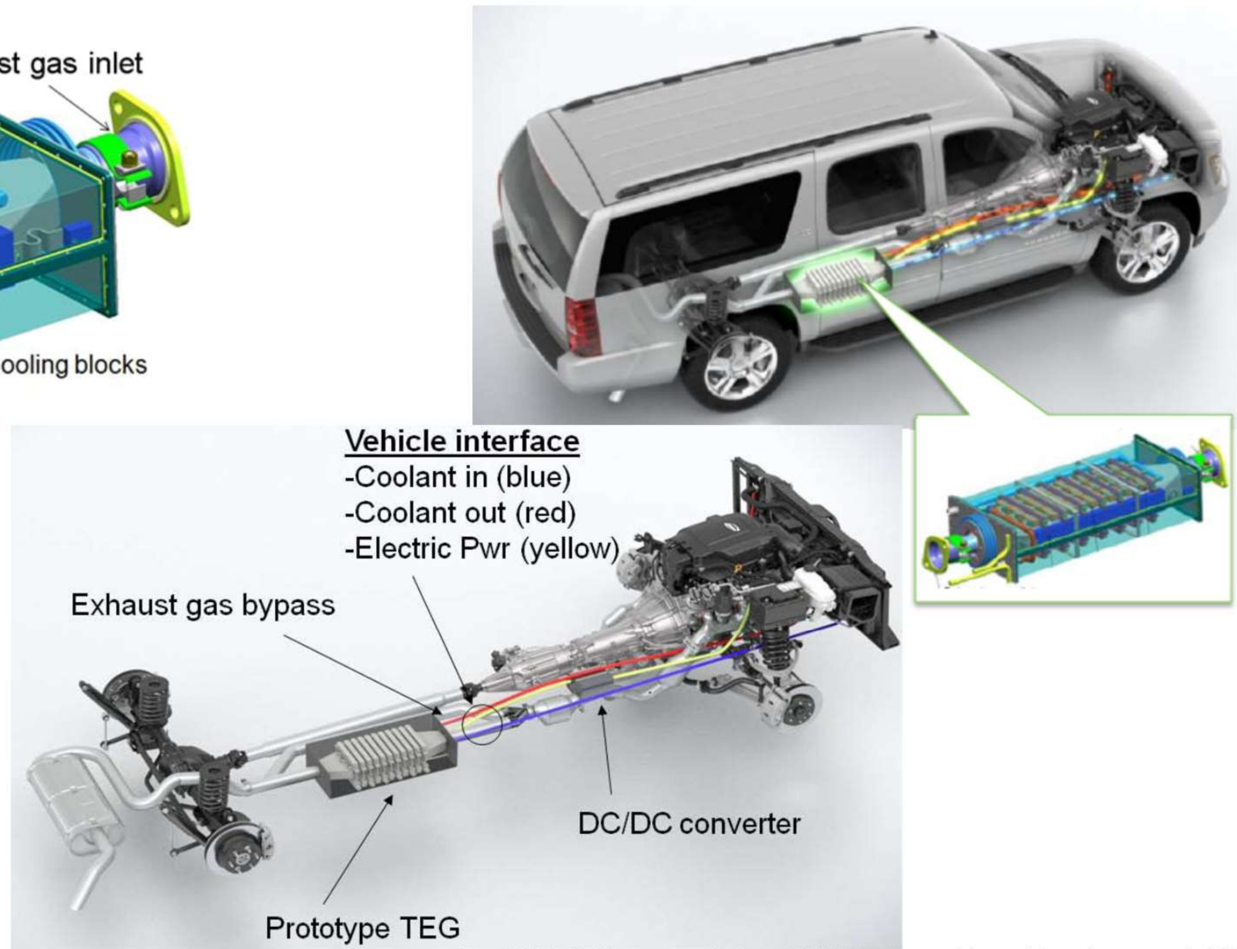
J. LaGrandeur, Amerigon, (2011)

APPLICATIONS

- **Automotive**

→ Example 2: GM prototype for Chevy Suburban



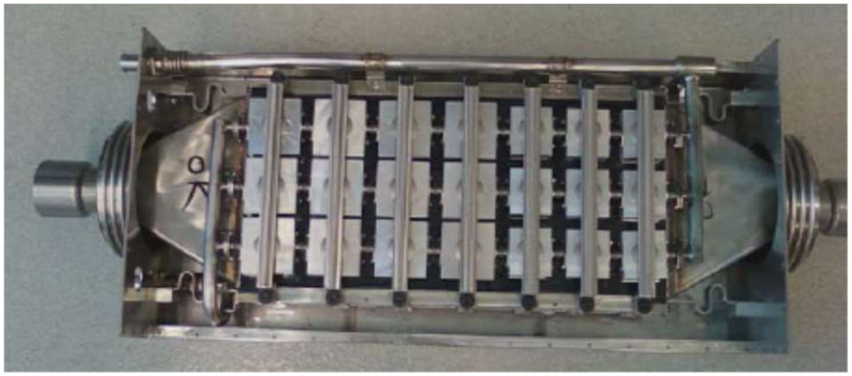


J. Fairbanks, DoE, (2011)

• **Automotive**

→ Example 2: GM prototype for Chevy Suburban

- generated power:
  . > 350 W in city
  . > 600 W in highway

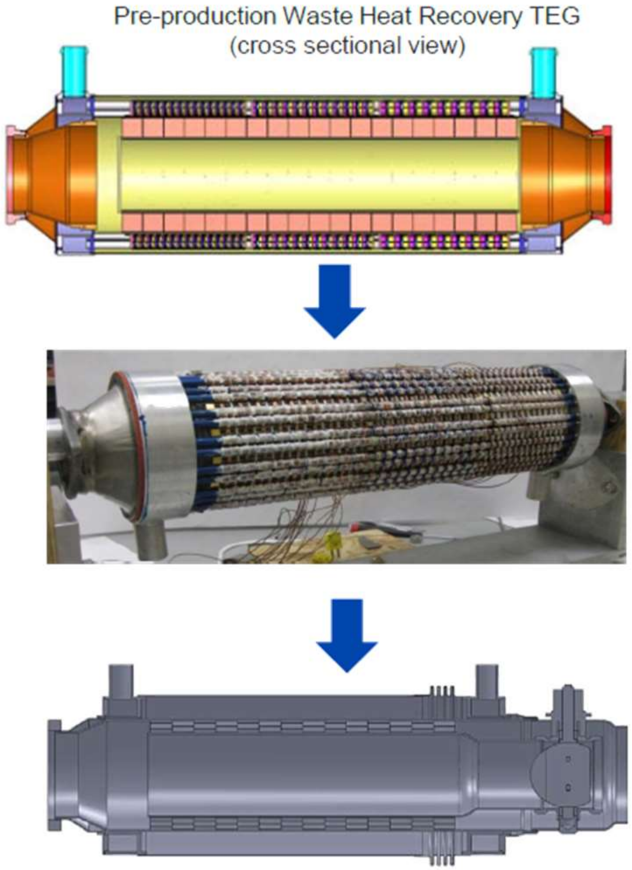


J. Fairbanks, DoE, (2011)

- **Automotive**

→ Example 3: BMW X6

- created to supply 500 W at 120 km/h (5% saving in fuel)



J. Fairbanks, DoE, (2011)

APPLICATIONS

- **Automotive**

  → Example 3: BMW X6

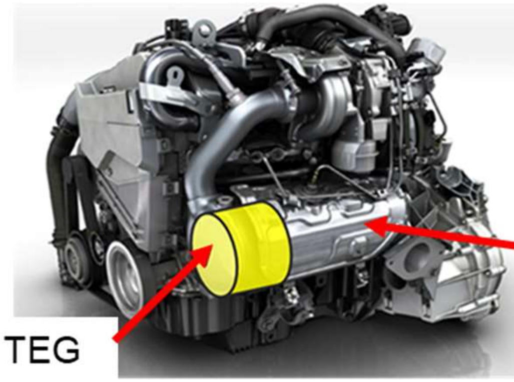
J. Fairbanks, DoE, (2011) & J. LaGrandeur, Amerigon, (2011) & www.caradisiac.com

APPLICATIONS

liten ceatech

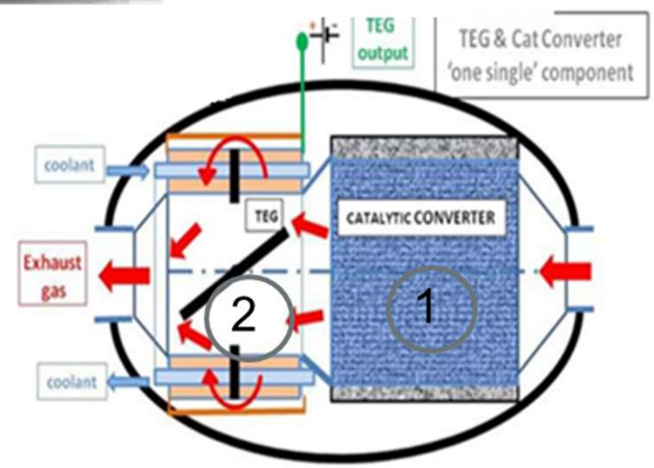
- **Automotive**

→ Example 4: Valeo



1 Existing Catalytic converter

2 TEG



2

TEG assembly

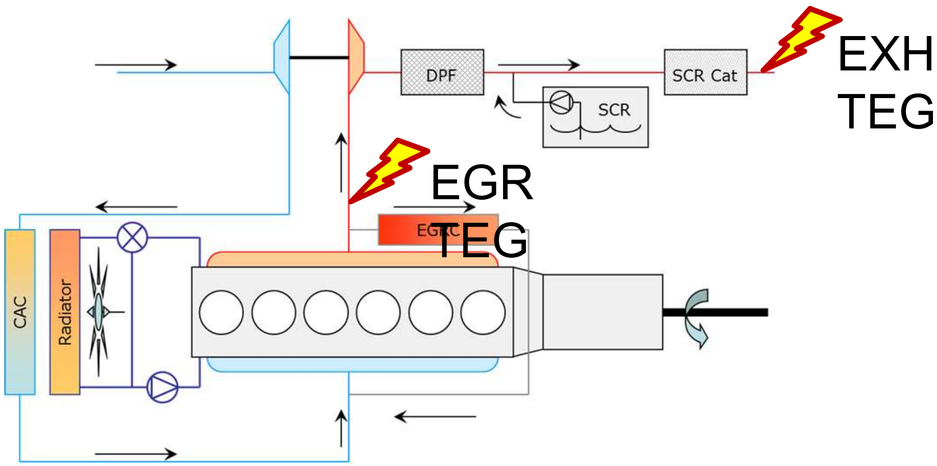
Bulk silicide 200 W/TEG
Cost < 1 €/W
$ZT_{[200\text{-}400°C]} > 0.5$

INTEGRAL
WASTE HEAT TO POWER

J.Y. Escabasse, (2019), ECT 2019, Limassol, Cyprus

http://www.integral-h2020.eu/

APPLICATIONS

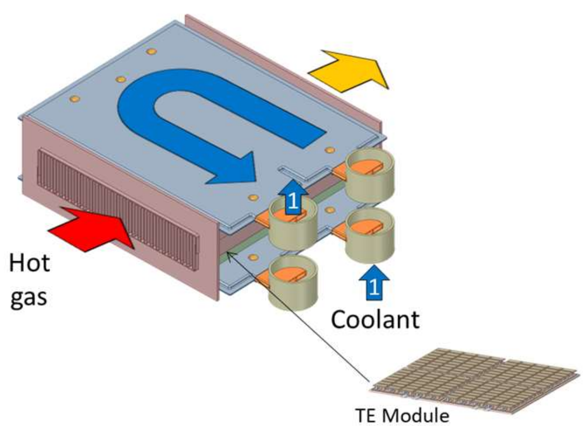


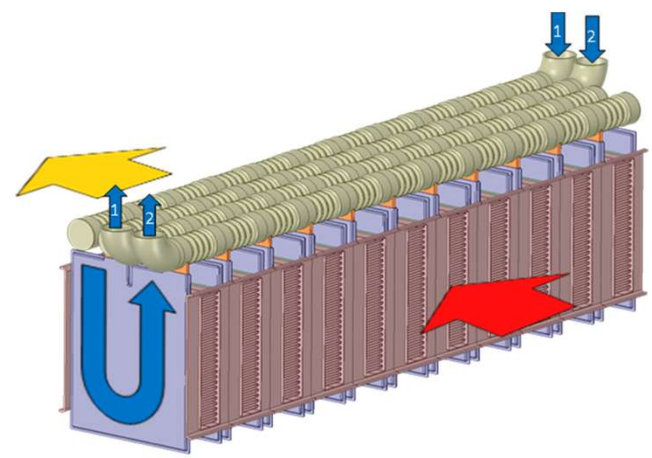
- **Automotive (Trucks)**

  → Example 5: TitanX

Half-Heusler
1000 W/TEG
Price 1.1 to 1.6 €/W
$ZT_{[100\text{-}500°C]} > 0.5$

INTEGRAL
WASTE HEAT TO POWER





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1 - Thermoelectrics : some definitions and effects

2 - Thermoelectric materials

3 - Nanostructuration : why and how ?

4 - Thermoelectric devices

5 - Applications

6 - Conclusions

CONCLUSIONS

→ conversion of thermal energy in electrical energy and reciprocally

→ a lot of studies on TE materials to increase devices performances, and so to make viable their industrialization

→ significant importance of nanostructuration which has led to major advances in materials performances

→ three main applications for TE devices: sensors, cooling and power generation

→ TE systems can be integrated in several and varied application fields (mobile, laptop, spatial, automotive, consumer goods…)

→ Introduction to mass markets must address sustainability issues + be price-competitive

Contacts

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THANKS FOR YOUR ATTENTION

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