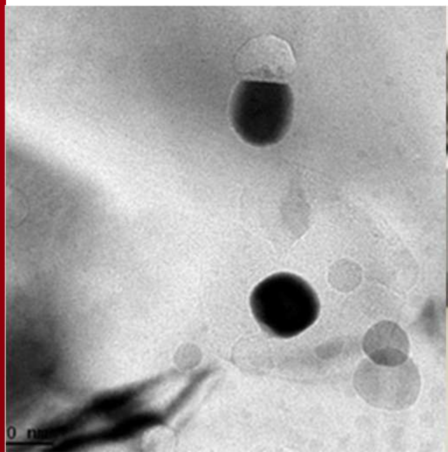
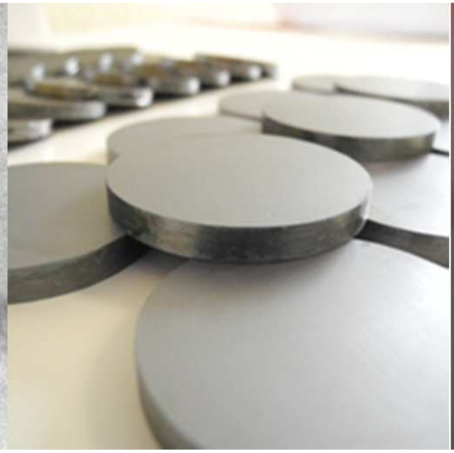
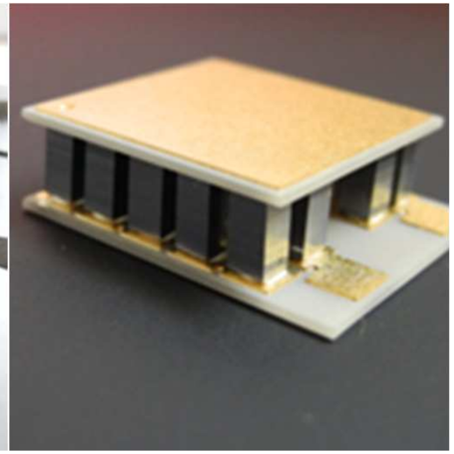
# HIGH PERFORMANCE RADIOISOTOPE & SOLAR THERMOELECTRIC GENERATORS INTEGRATING STATE-OF-THE-ART SI BASED NANOCOMPOSITES

9th ESA Round Table | **Simon Julia,** Caroff Tristan

# OUTLINE

- What are the benefits of nanotechnologies for Thermoelectrics ?
  - ➢ Major technological challenges for thermoelectrics
  - ➢ State-of-the-art approaches overview
  - ➢ Technology status at CEA-LITEN
    - ✓ Examples of « NEAT » nanocomposites
    - ✓ Current status on scalability and integration issues

- Application of state-of-the-art nanocomposites to the Radioisotope Thermoelectric Generator use case (RTG)
  - ➢ Expected performances in nanocomposites integrating GPHS-RTGs
  - ➢ Benefits of advanced heat sink

- Opportunities for Solar Thermoelectric Generators (STG)
  - ➢ Expected performances in nanocomposites integrating STG
  - ➢ Proof of concept of STG

- Conclusion

## OUTLINE

- **What are the benefits of nanotechnologies for Thermoelectrics ?**
  - ➢ Major technological challenges for thermoelectrics
  - ➢ State-of-the-art approaches overview
  - ➢ Technology status at CEA-LITEN
    - ✓ Examples of « NEAT » nanocomposites
    - ✓ Current status on scalability and integration issues

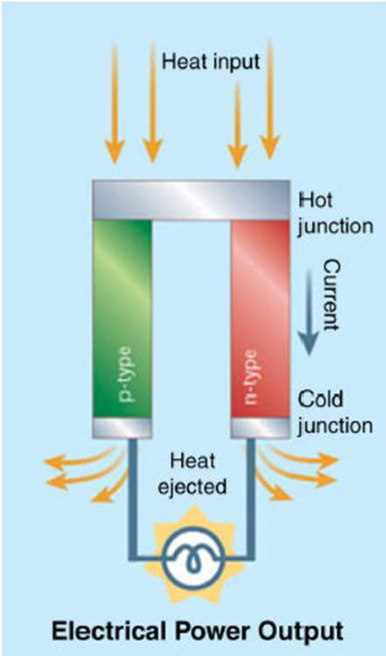
- Application of state-of-the-art nanocomposites to the Radioisotope Thermoelectric Generator use case (RTG)
  - ➢ Expected performances in nanocomposites integrating GPHS-RTGs
  - ➢ Benefits of advanced heat sink

- Opportunities for Solar Thermoelectric Generators (STG)
  - ➢ Expected performances in nanocomposites integrating STG
  - ➢ Proof of concept of STG

- Conclusion

# BASIC PRINCIPLE






## *Seebeck effect*

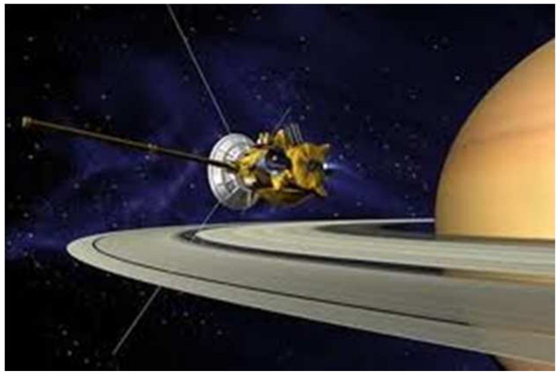
$$V = N \cdot S_{np} \cdot \Delta T$$

**Temperature gradient induces Seebeck voltage**

## *Power generation*

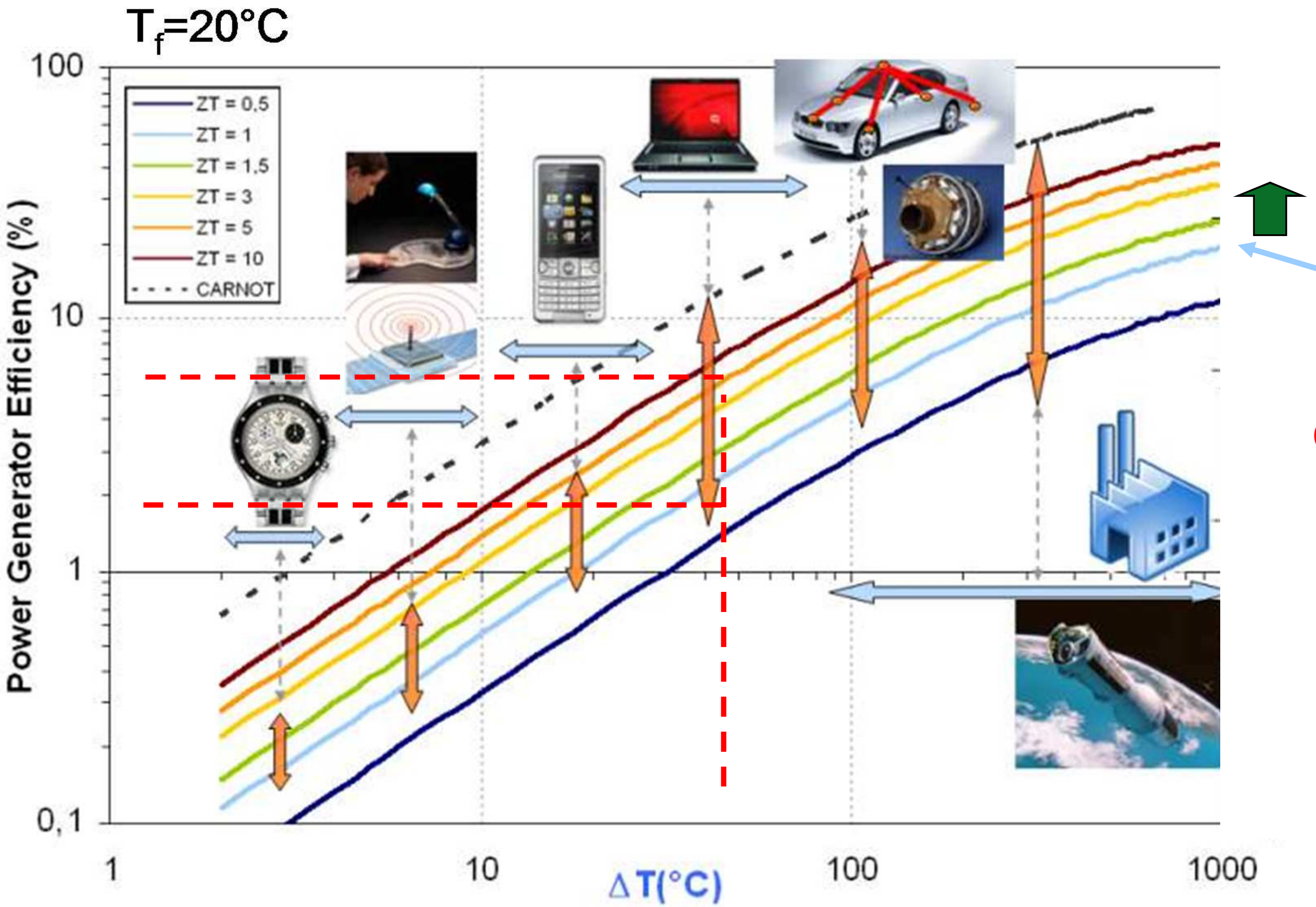
$$P = \frac{V^2}{4R_{int}}$$


SiGe MHW RTG (1970's)



*Source NASA*

# KEY CHALLENGE 1 : EFFICIENCY




**Nanostructured materials state-of-the-art**

**Standard materials state-of-the-art**

Conversion yield from 0,5 à 12% (depending on thermal gradient)

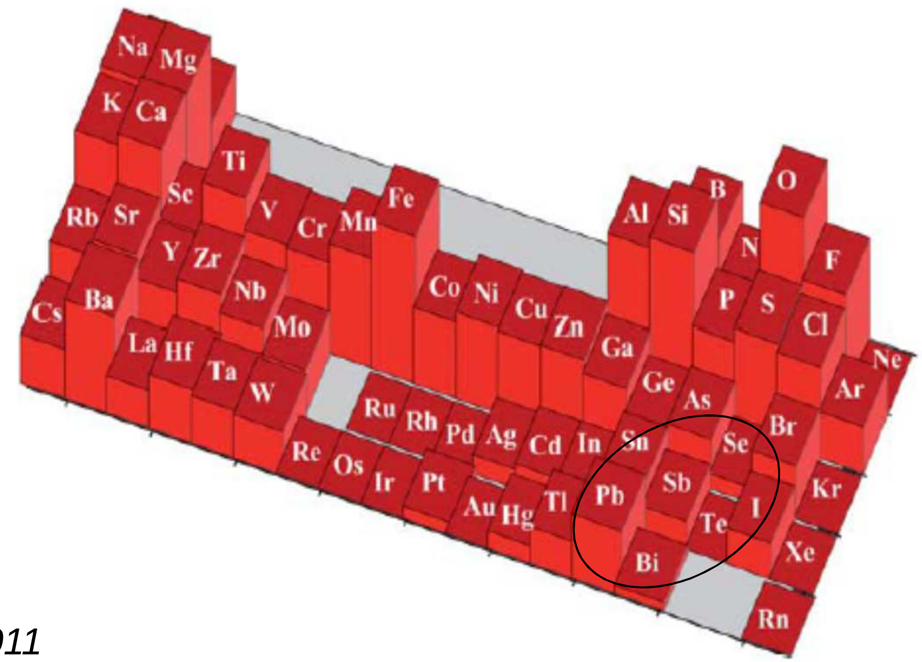
$$ZT = \frac{\sigma S^2 T}{\kappa}$$

**Material and system efficiencies are key challenges**

# KEY CHALLENGE 2 : SCALABILITY



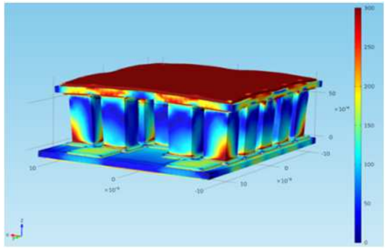
| TE Material State-of-art | N-type | P-Type | ZT 200°C | ZT 400°C | OK for 600°C Max Temperature | Est. € per dm³ |
|---|---|---|---|---|---|---|
| $Bi_2Te_3$ | ✓ | ✓ | 1 | - | NO (250°C) | 800-900 |
| PbTe | ✓ | ✓ | 0.75 | | | |
| LAST *(Ag-Pb-Sb-Te)* | ✓ | ✓ | 0.8 | | | |
| TAGS *(Te-Ag-Ge-Sb)* | - | ✓ | 0.7 | | | |
| $Zn_4Sb_3$ | - | ✓ | 0.7 | | | |
| $Mg_2Si$ | ✓ | ~ | 0.3 | | | |
| HMS | - | ✓ | 0.4 | | | |
| Skutterudites *(CoSb)* | ✓ | ✓ | 0.5 | | | |
| SiGe-nanostructured | ✓ | ✓ | 0.2 | | | |
| Clathrates (GaGe) | ✓ | ✓ | 0.2 | | | |

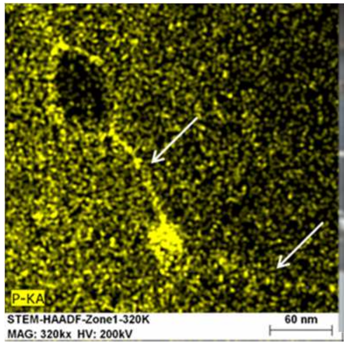


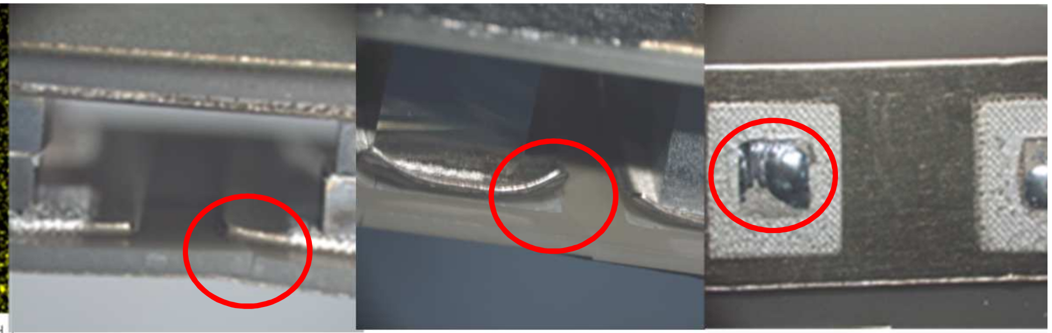

*Source Renault Trucks, DOE workshop 01/2011*

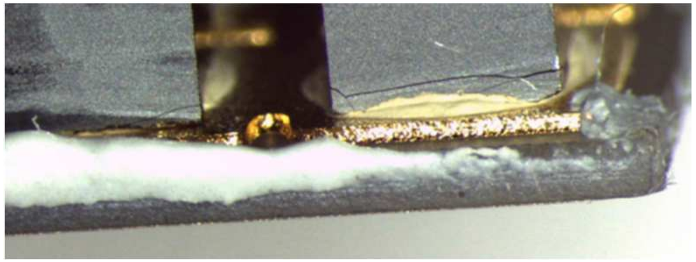
**Industrial process compatibility with mass market is the second major challenge (cost, abondance, eco-friendliness)**

# KEY CHALLENGE 3 : DURABILITY







Commercial modules operating under 250°C gradient maximum

Higher temperature operating range induces even larger level of stress on :

- ✓ Materials and interface stability (doping segregation, interdiffusion, oxydation, cracks)
- ✓ Substrates (thermo-mechanical reliability, contact oxydation)

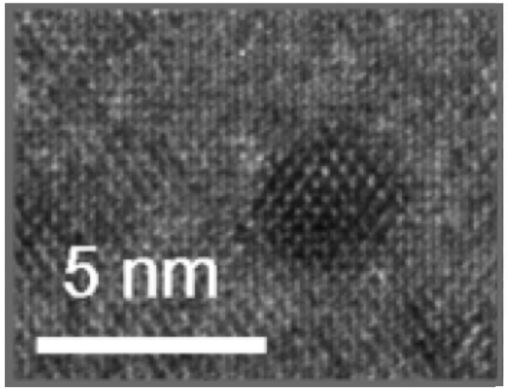
**Durability under large thermal gradient (steady-state, cycling, vibration..) is a pre-requisite for the cost efficiency of the technology in new application (automotive, energy efficiency…)**

# MAIN STATE-OF-THE-ART APPROACHES

**Controlled nanoparticles** (MBE, thin film):

SbTe:PbTe, ZT>2

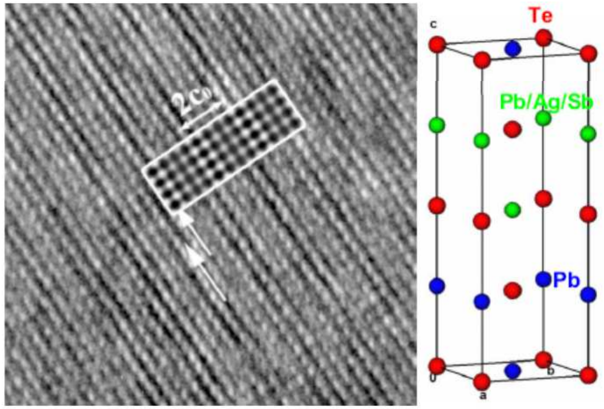
ErAs:InGaAs, ZT~1.6@800K



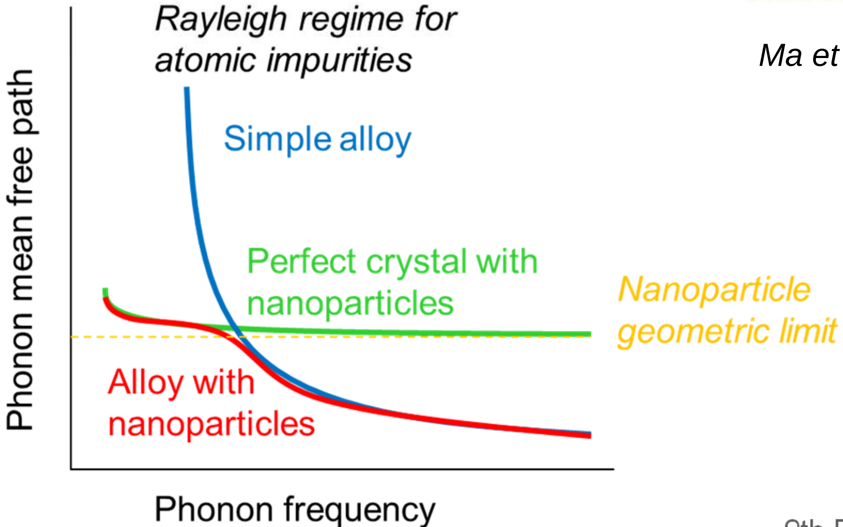

*Kim et al., J of Appl. Phys. 99 (2006)*

**Natural nanoinclusions**

LAST, ZT>2

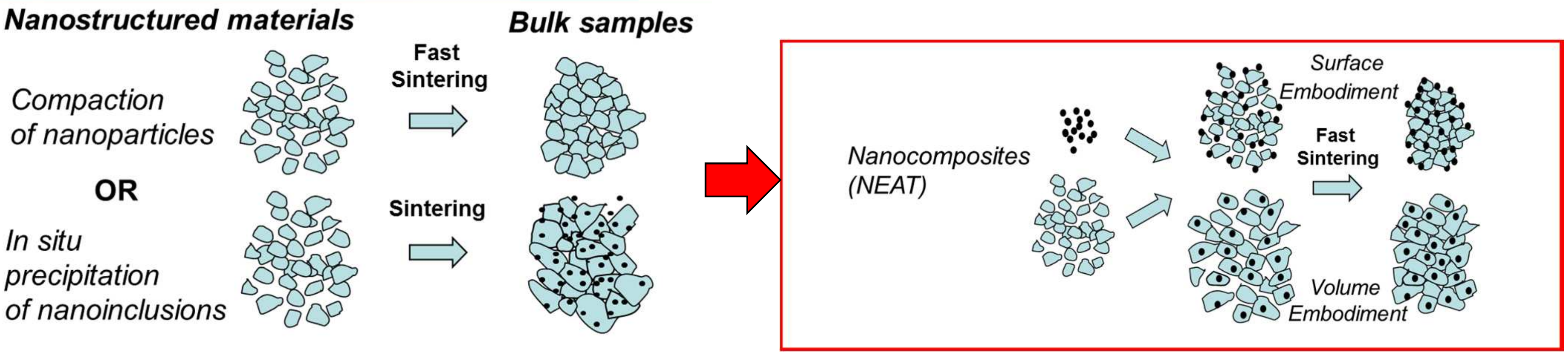



*Hsu et al., Science 303 (2004)*




A close relative: **sintered powder nanodomains**, ZT~1.2@300K


*Ma et al., Nano Lett. 8 (8) (2008)*




**Pros**

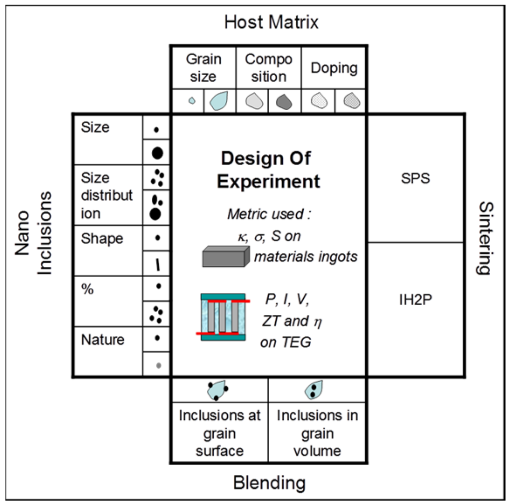
✓ Control of a large range of possible varying parameters *(NP size, size distribution, nature, concentration…)*

✓ Technology easier to scale up *(amount of nano, process control)*

**Cons**

✓ Keep nanostructuring during process *(dispersion, sintering)*

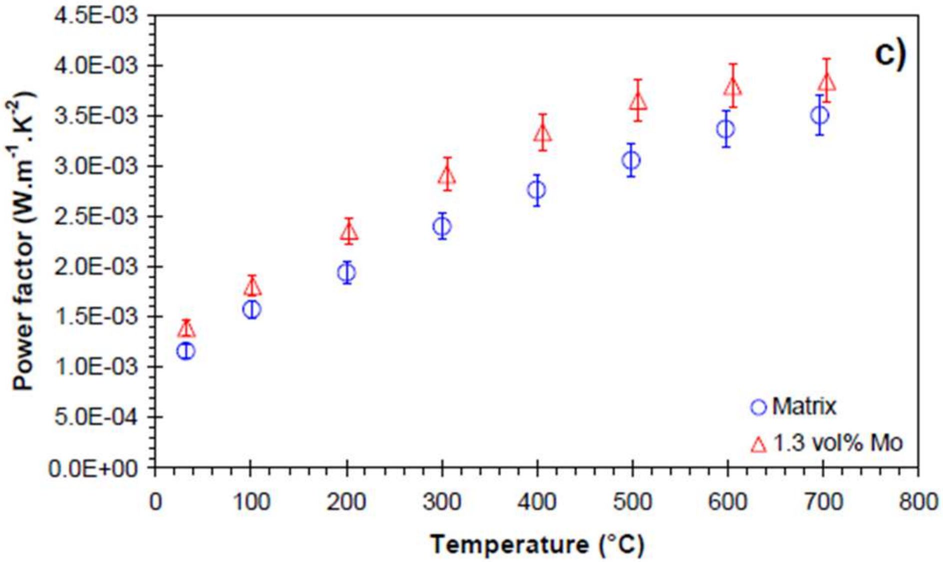
✓ Very large exploration domain

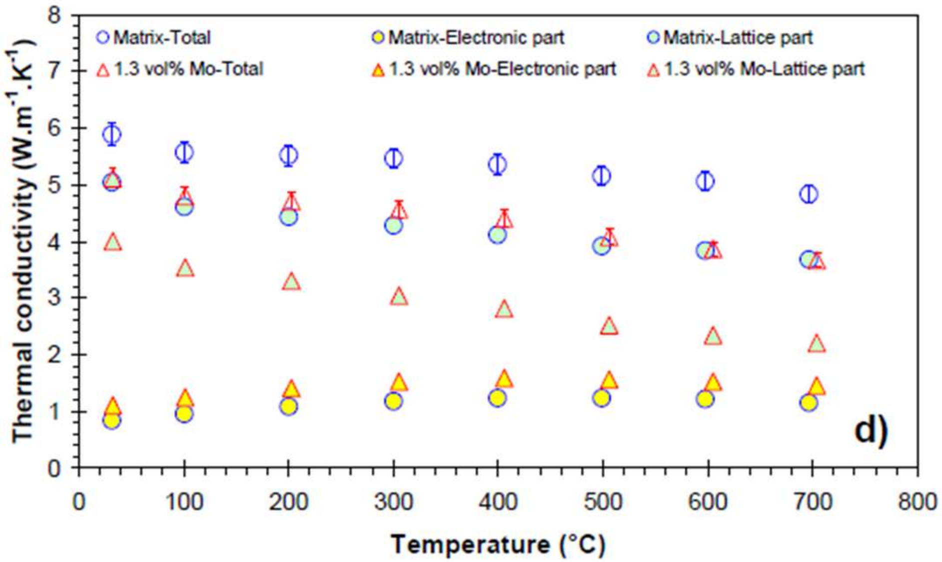


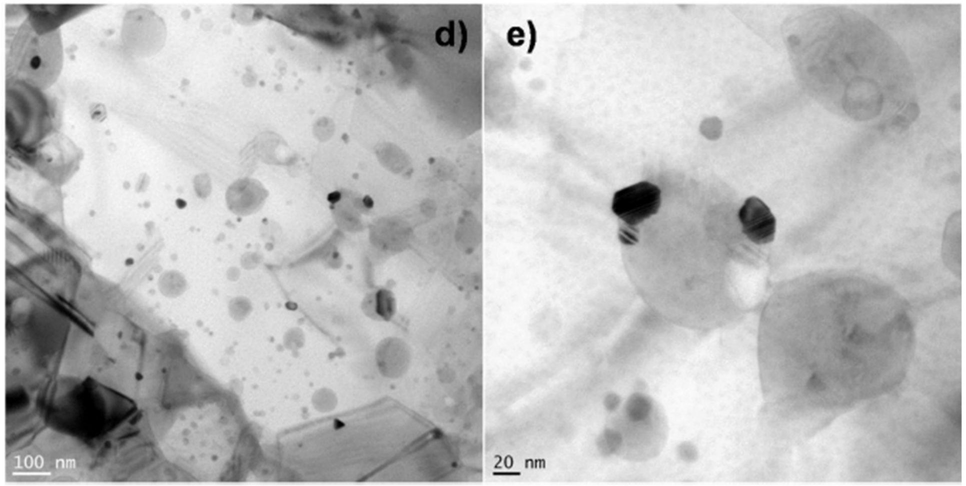

NEAT :

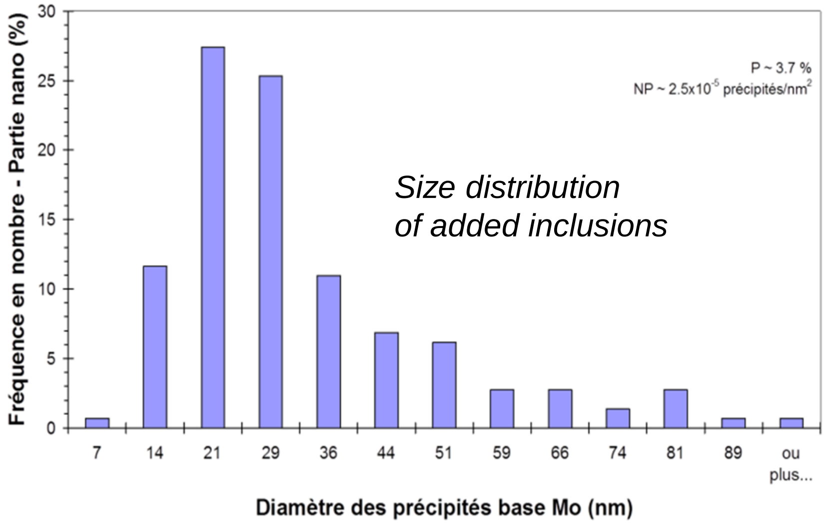
« Nanoparticle Embedded in an Alloy Thermoelectric »

# AN EXAMPLE OF HIGH TEMPERATURE NANOCOMPOSITE



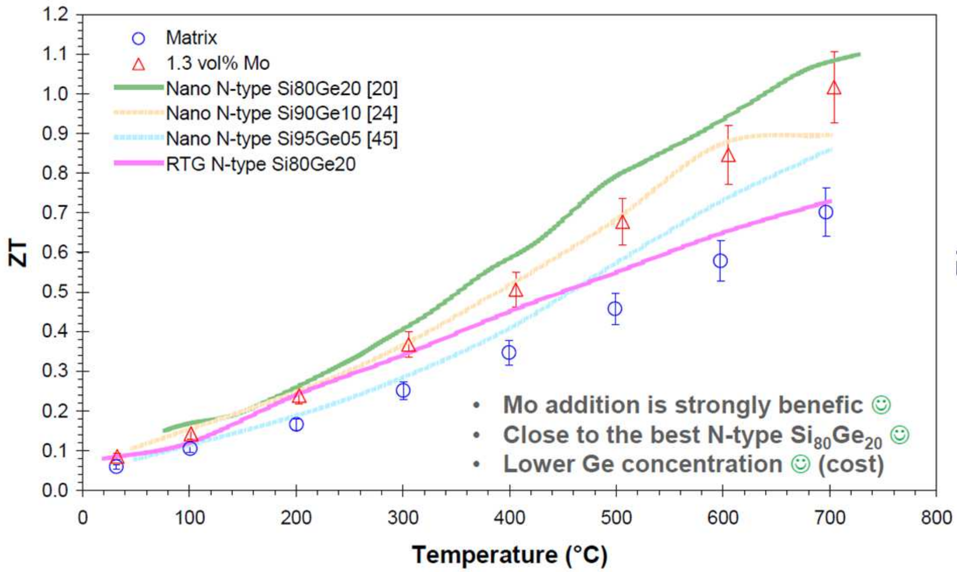



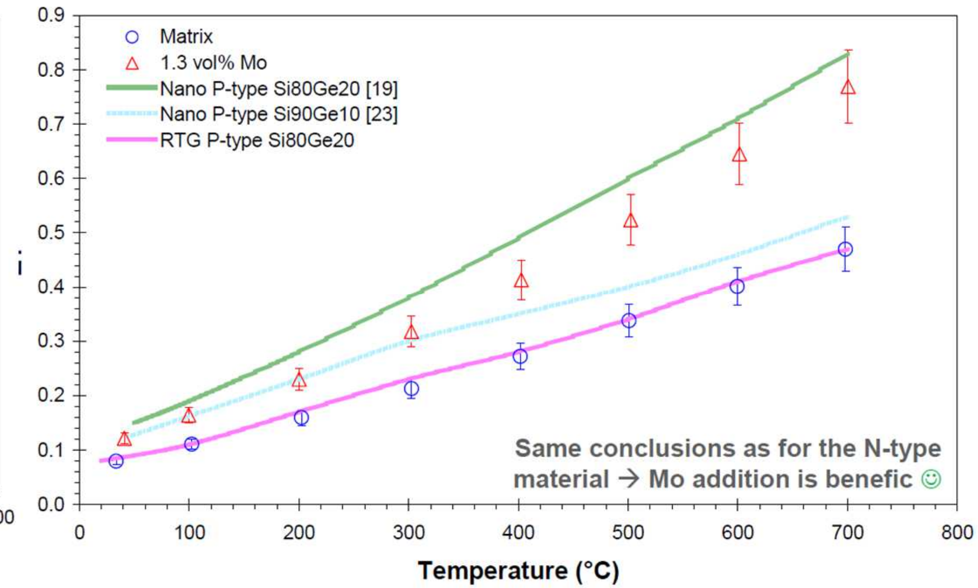




*Size distribution of added inclusions*

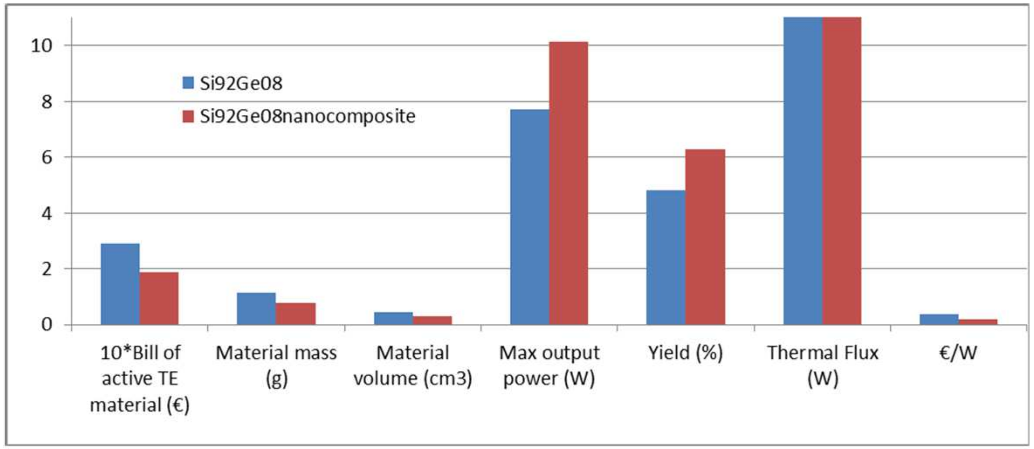
**The NEAT concept is working for the SiGe alloy investigated when $MoSi_2$ nano-inclusions are homogeneously dispersed in the sintered microstructure**

# AN EXAMPLE OF HIGH TEMPERATURE NANOCOMPOSITE



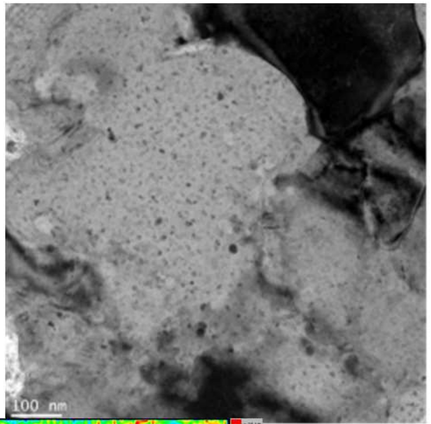

**The obtained N & P type nanocomposite reach the performance of best nano-grains samples of the state-of-the-art**

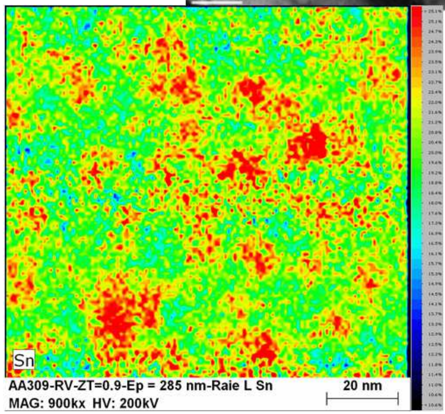


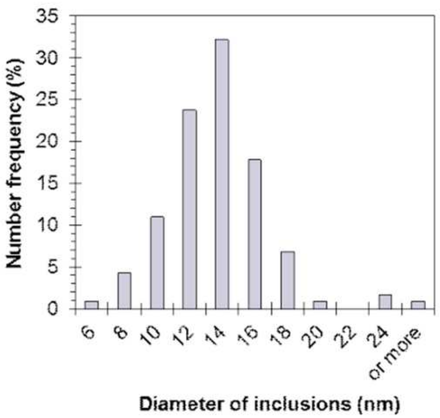

**In this case, at iso performance, a TEG integrating nanocomposites will present a reduced cost.**

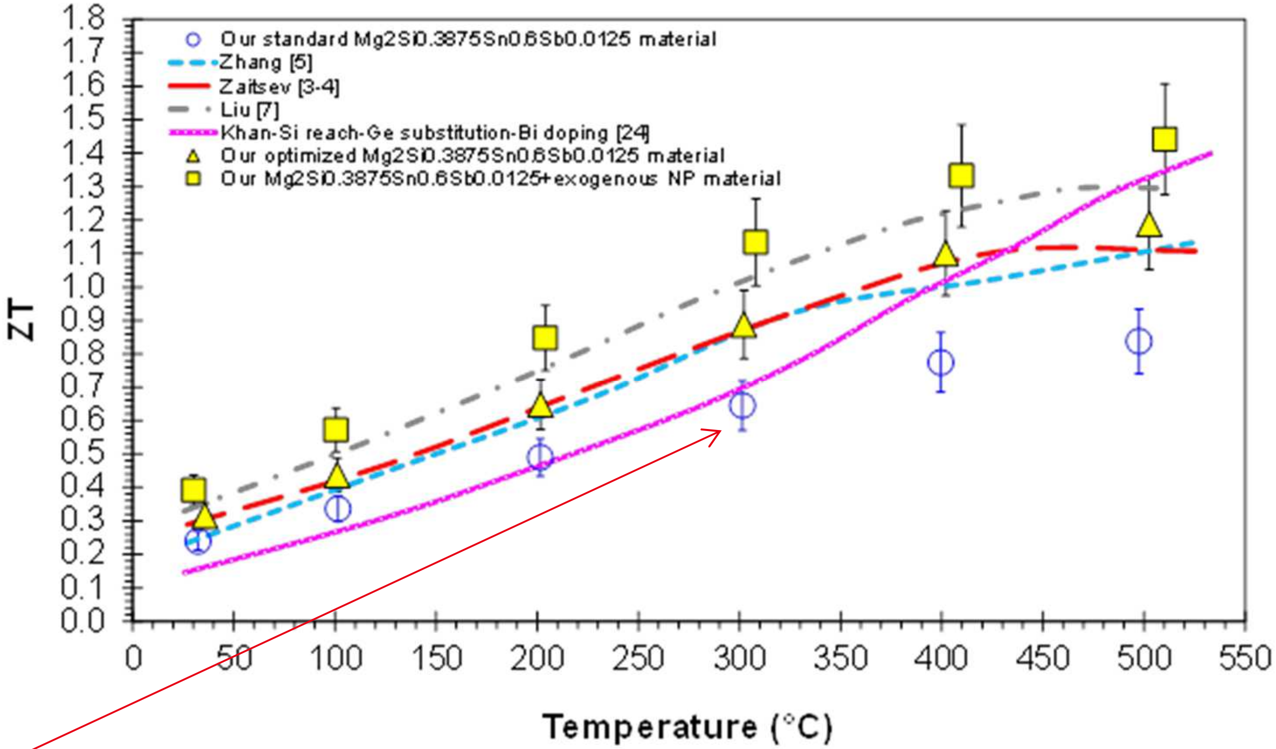
*K. Favier et al., Acta Materialia 64 (2014),* 10.1016/j.actamat.2013.10.062

# AN EXAMPLE OF MEDIUM TEMPERATURE NANOCOMPOSITE



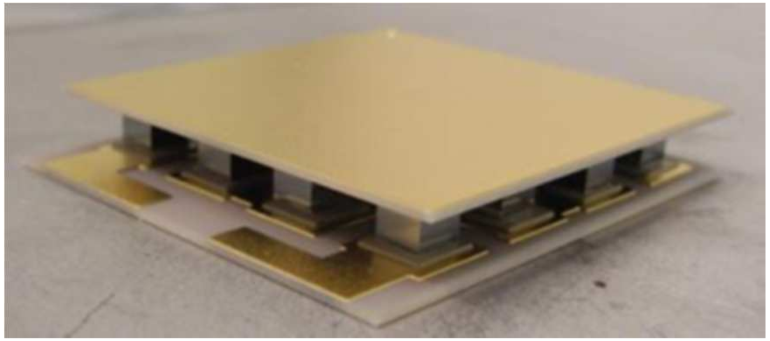
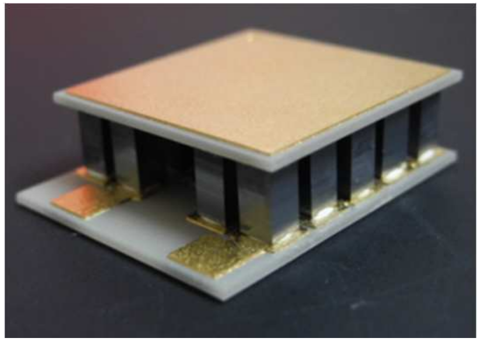
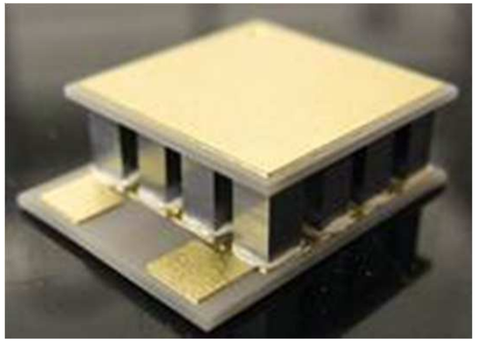



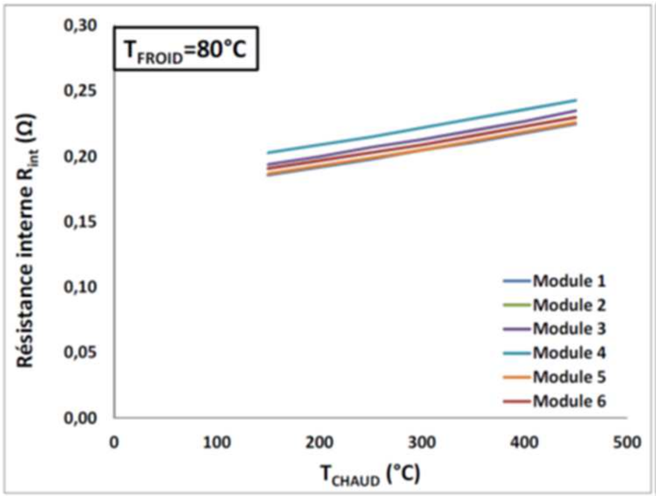

**The host $Mg_2SiSn$ alloy presents high amount of spontaneous precipitates, with ZT increasing with process optimization**

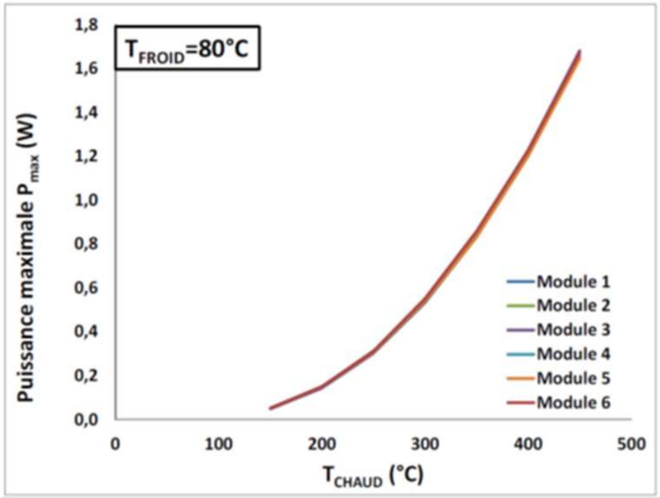
**The alloy incorporating exogenous nano-particles has the best ZT ever measured**

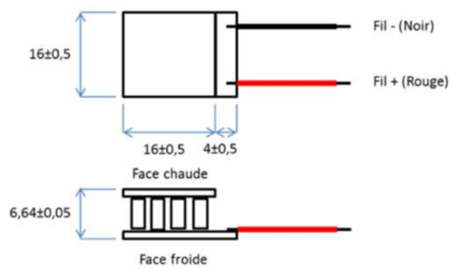
*R. Vracar et al., J of Alloys Comp. (2014)*
10.1016/j.jallcom.2014.02.040

**High temperature modules integrating SiGe host materials have been developped using a low stress, low contact resistance assembly process**
**Power density in the range 0,4-0,6W/cm$^2$ at $T_h$= 470°C**




**TEGs are commercialized via the company Hotblock on Board**

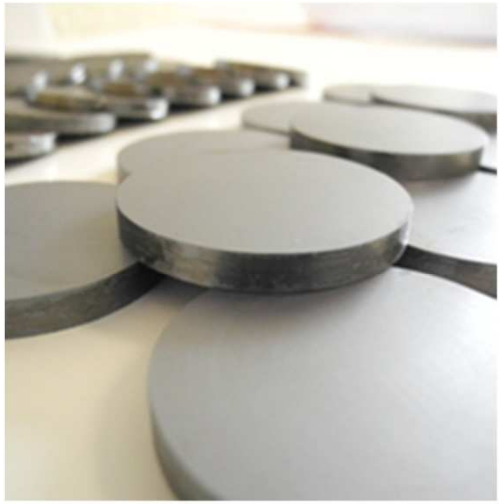
*http://www.hotblock.fr/*

# CURRENT STATUS ON SCALABILITY

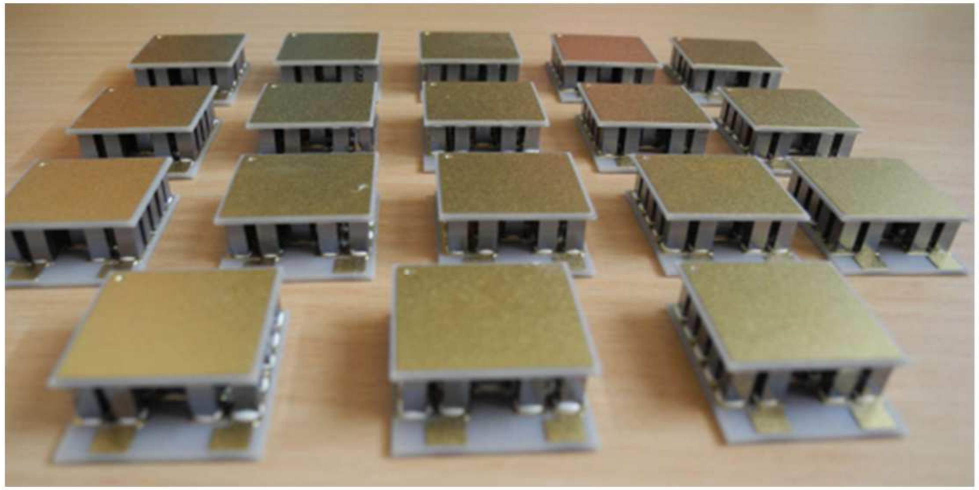


**Scale-up done at CEA on pilot line with up to 3kg/week capability on SiGe and $Mg_2SiSn$ alloys**

- ✓ Synthesis processes compatible high volume
- ✓ Industrial class machines
- ✓ Material to modules



*60mm ∅ thermoelectric Si-based materials pellets*



*High Termperature thermoelectric modules*

# OUTLINE

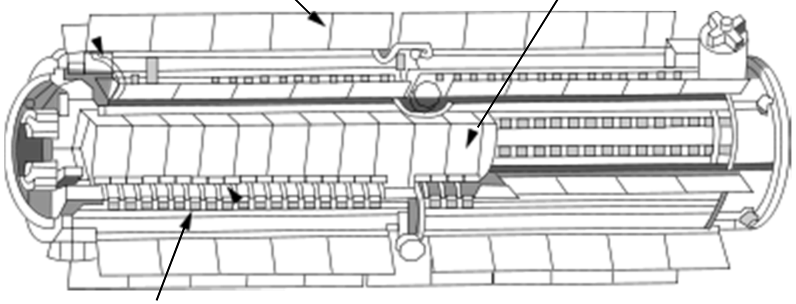
- What are the benefits of nanotechnologies for Thermoelectrics ?
  - Major technological challenges for thermoelectrics
  - State-of-the-art approaches overview
  - Technology status at CEA-LITEN
    - ✓ Examples of « NEAT » nanocomposites
    - ✓ Current status on scalability and integration issues

- **Application of state-of-the-art nanocomposites to the Radioisotope Thermoelectric Generator use case (RTG)**
  - Expected performances in nanocomposites integrating GPHS-RTGs
  - Benefits of advanced heat sink

- Opportunities for Solar Thermoelectric Generators (STG)
  - Expected performances in nanocomposites integrating STG
  - Proof of concept of STG

- Conclusion

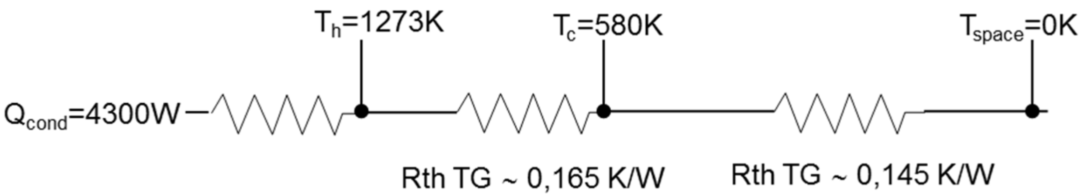
## Thermal and Electrical model used to simulate GPHS-RTG




$$P_{elec} = \frac{V_{seebeck}^{2}}{4 \times R_{\text{int}}}$$

*i.e.*

$$P_{elec} = \frac{S^2 \times Rth_{TG}^{2} \times Q_{cond}^{2}}{4 \times R_{\text{int}}} = \frac{Z_{mean} \times Rth_{TG} \times Q_{cond}^{2}}{4}$$




*with*

$$Z_{mean} = \frac{\int_{Tc}^{Th} Z(T)\,dT}{(T_h - T_c)}$$

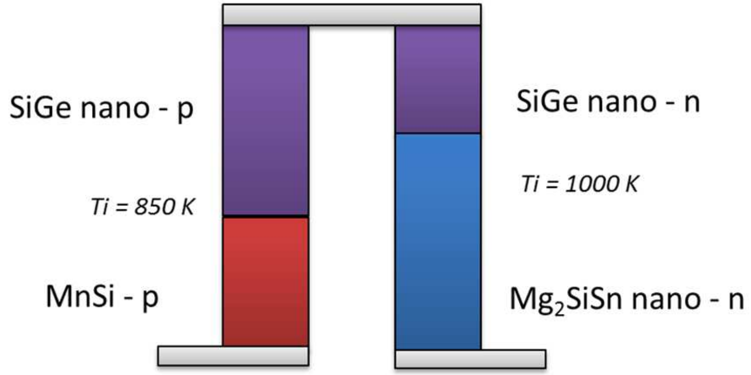
**Thermal and electrical data available in the litterature for GPHS-RTG** are :

Thermoelectric material = SiGe,

$T_h$ = 1273 K, $T_c$ = 580 K,

Pelec = 292 We (BOM), Ps = 5.1 We/kg et h = 6.8%, Qcond =  Pelec / h = 4300 W

**Integration of best nanocomposites in segmented legs architecture**

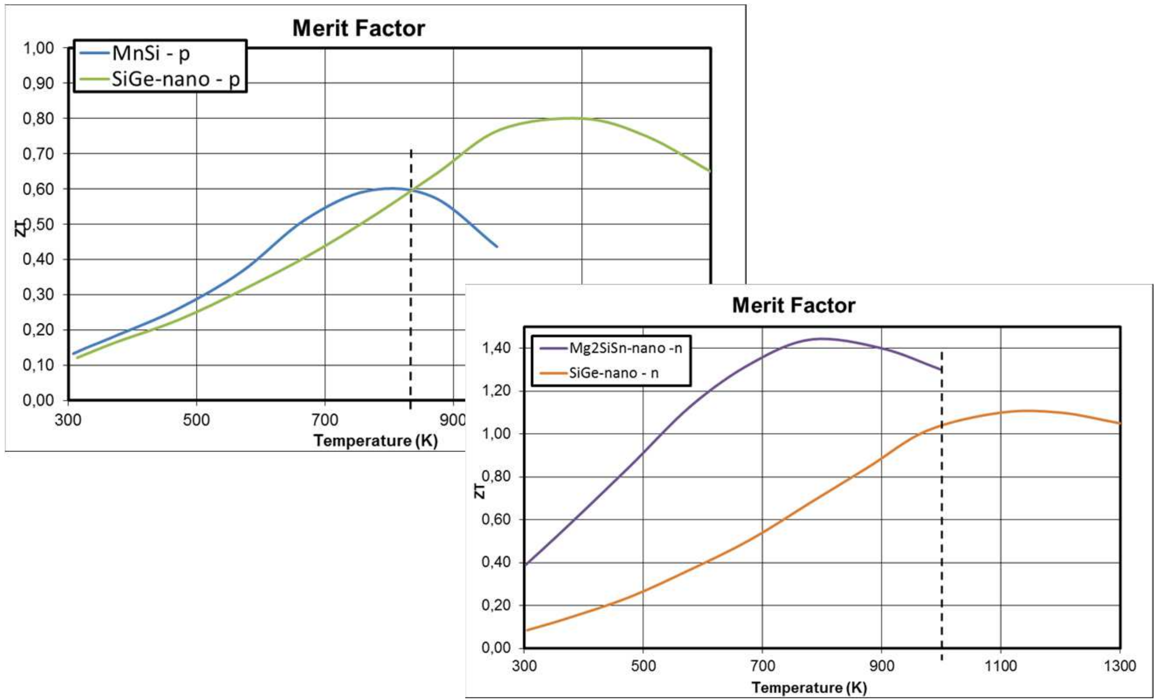



***With Ti, crossing temperature of ZT curves***

SiGe and $Mg_2SiSn$ have similar thermal and electrical properties, and are compatible at the targeted temperature.

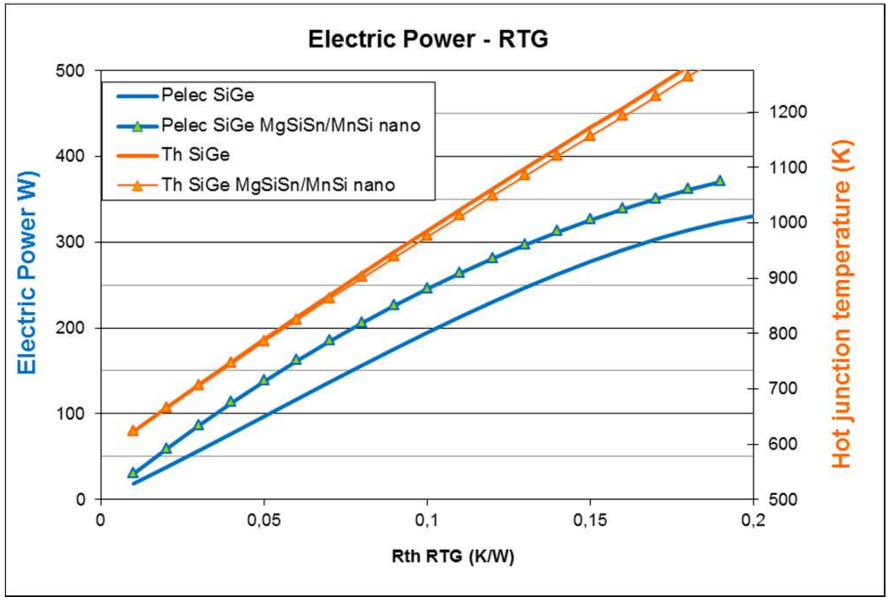
The resulting height ratio is the following :

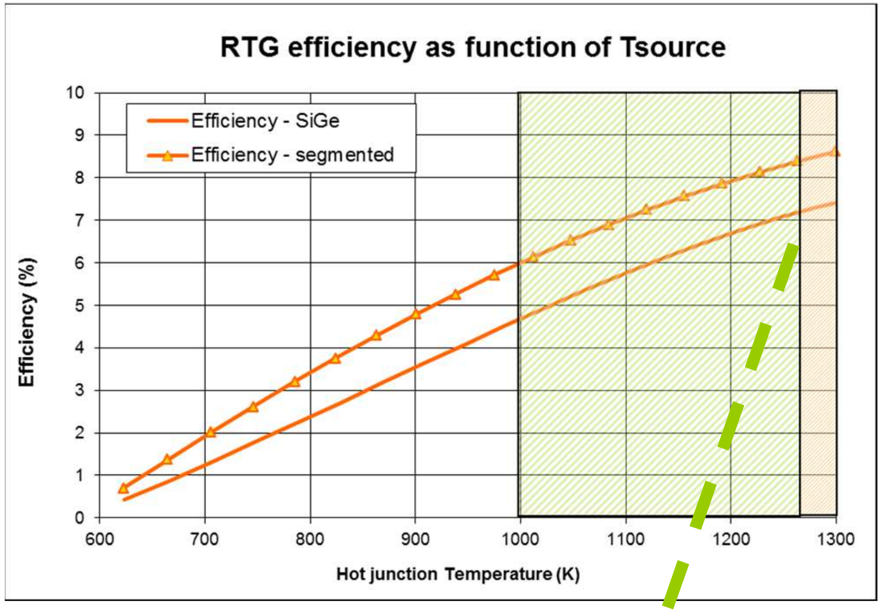
$$\frac{H_{SiGe}}{H_{Mg2SiSn}} = \frac{(T_h - T_i)}{(T_i - T_c)} \frac{\lambda_{SiGe}}{\lambda_{Mg_2SiSn}}$$

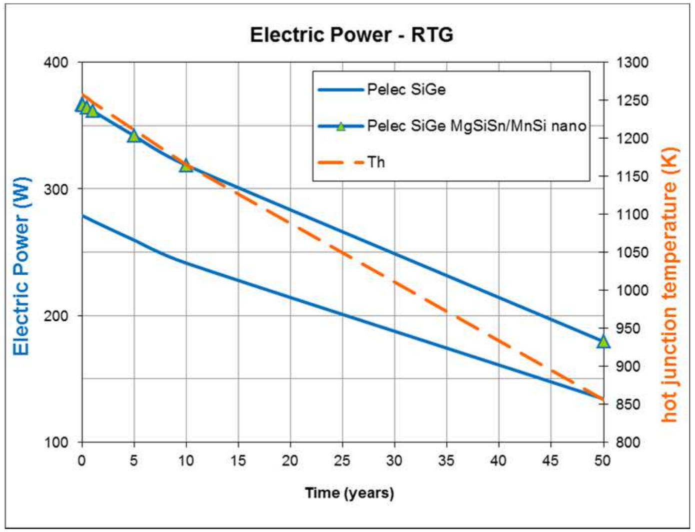


## NANOCOMPOSITE SiGe & $Mg_2SiSn$ in RTGs

### Simulated results of GPHS-RTG integrating best nanocomposites

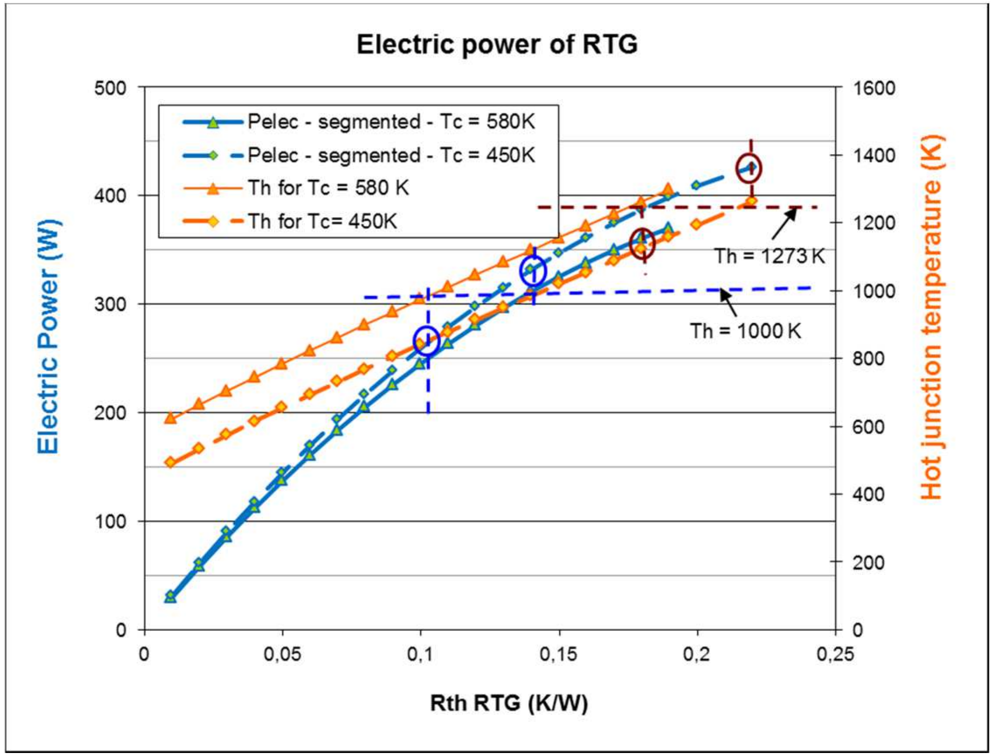


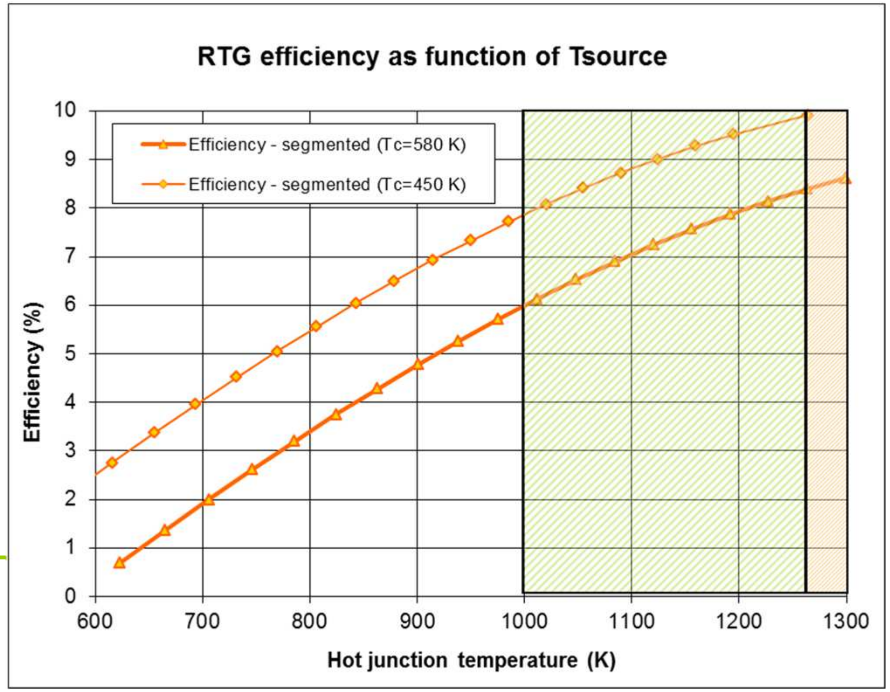

**Efficiency increase from 7 % to 8.5 %**
**For SiGe nanocomposites segmented with**
**$Mg_2SiSn$ nanocomposite and MnSi at 1273 K**

## Integration of an advanced heat sink (carbon based heat pipes)




Decrease of cold source temperature from $T_c$=580K to $T_c$ = 450 K

Offers the opportunity to work at lower hot junction temperature $T_h$=1000 K (Pelec = 350 W)




**SiGe nanocomposite segmented with $Mg_2SiSn$ nanocomposite and MnSi**
**Efficiency reaches :**
**10 % at $T_h$ = 1273 K**
**8 % at $T_h$ = 1000 K**

*A.J. Juhasz., NASA/TM-2008-215420*

# OUTLINE

- What are the benefits of nanotechnologies for Thermoelectrics ?
  - ➢ Major technological challenges for thermoelectrics
  - ➢ State-of-the-art approaches overview
  - ➢ Technology status at CEA-LITEN
    - ✓ Examples of « NEAT » nanocomposites
    - ✓ Current status on scalability and integration issues

- Application of state-of-the-art nanocomposites to the Radioisotope Thermoelectric Generator use case (RTG)
  - ➢ Expected performances in nanocomposites integrating GPHS-RTGs
  - ➢ Benefits of advanced heat sink

- **Opportunities for Solar Thermoelectric Generators (STG)**
  - ➢ Expected performances in nanocomposites integrating STG
  - ➢ Proof of concept of STG

- Conclusion

## Thermal and Electrical model used to simulate Solar Thermoelectric Generator

STG : Potential alternative solution to solar panel for near sun missions b.o.

- PV cells damaging due to ionizing radiation

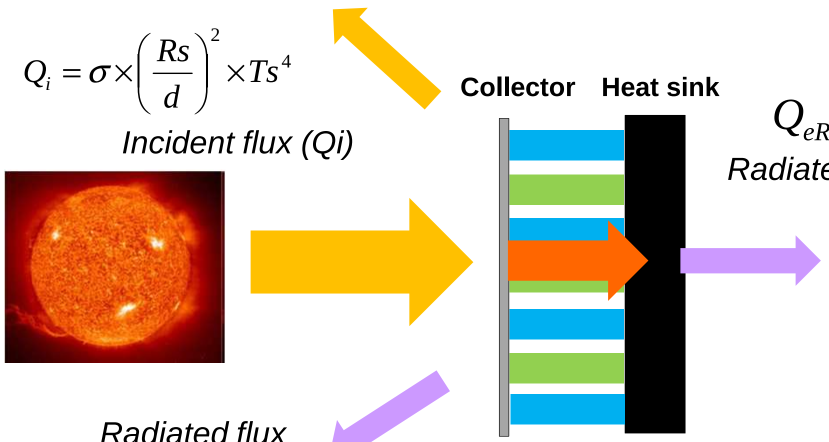
- Low PV yield at high temperature

STG : Converts thermal solar energy (black body radiation) into electrical energy

*Reflected flux (Qr)*

$$Q_i = \sigma \times \left(\frac{Rs}{d}\right)^2 \times Ts^4$$

*Incident flux (Qi)*




$$Q_{eRAD} = \varepsilon_r \times \sigma \times A_r T_f^4$$

*Radiated flux cold side (QeRAD)*

*Radiated flux hot side (Qe)*

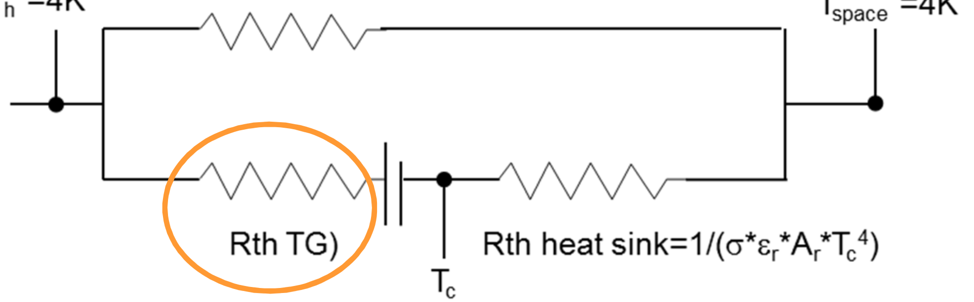
$$Q_e = \varepsilon_c \times \sigma \times A_c T_c^4$$

*Absorbed heat flux (Qa)*

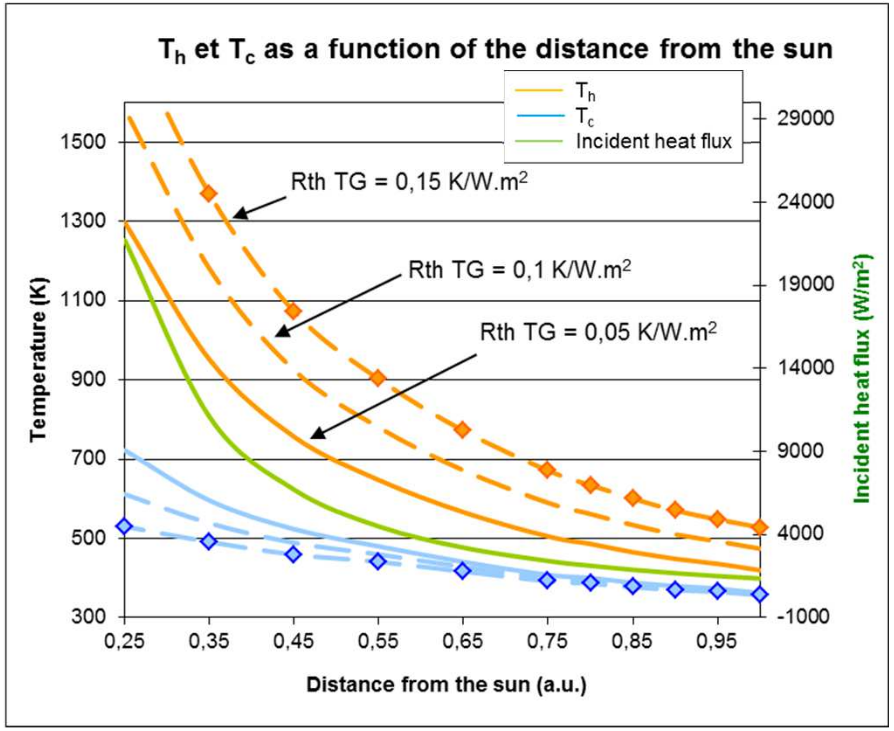
$$\boxed{Q_a = a \times A_c \times Q_i}$$

$$P_{elec} = \frac{V_{seebeck}^{\,2}}{4 \times R_{int}}$$

$$P_{elec} = \frac{S^2 \times Rth_{TG}^{\,2} \times Q_{cond}^{\,2}}{4 \times R_{int}} = \frac{Z_{mean} \times \boxed{Rth_{TG}} \times Q_{cond}^{\,2}}{4}$$



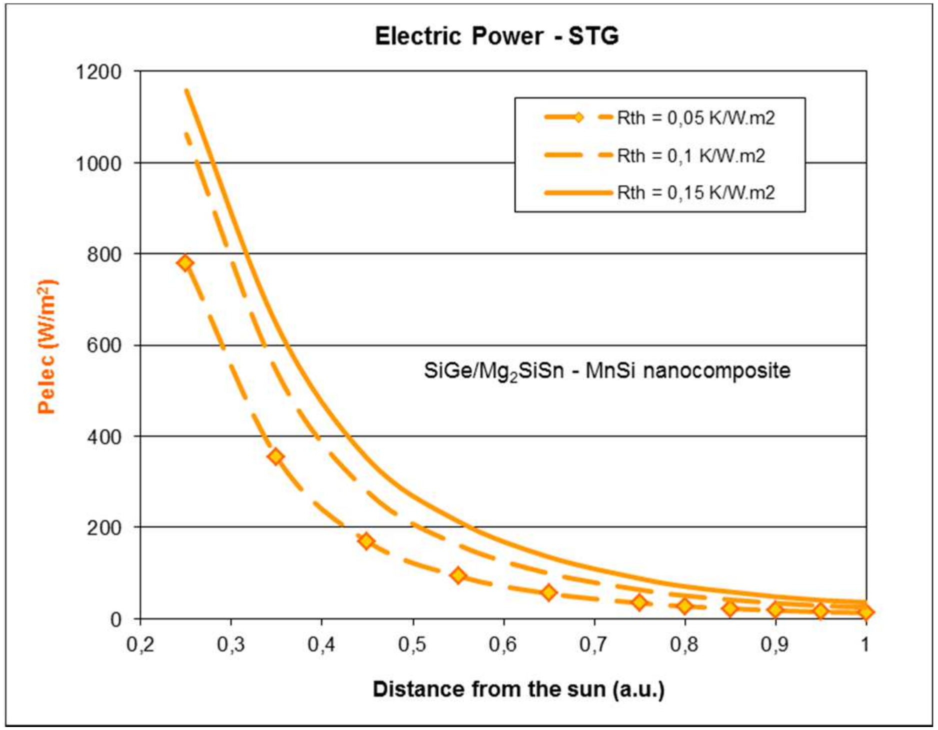
## Simulated results of STG integrating best nanocomposites




As opposed to the RTG use case, only part of the absorbed thermal flux conducts through the Thermoelectric Generator

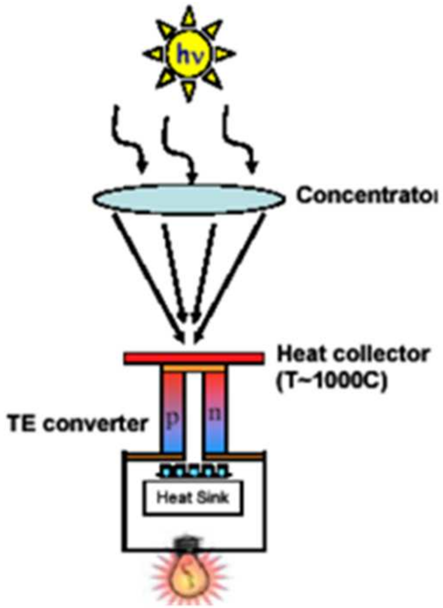
⇒ Rth TG should be minimized to maximize the heat flux going through

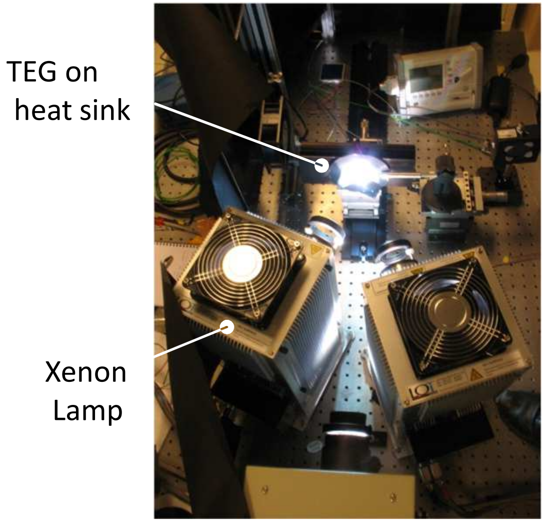
⇒ Maximize hot source temperature

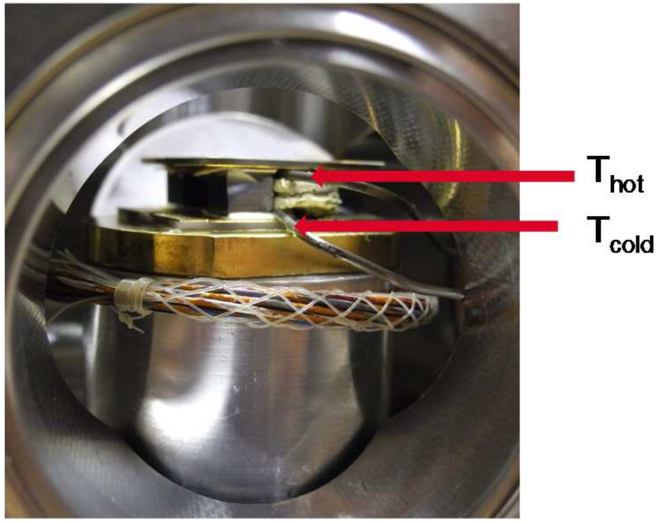



**Promising potential for STG use case : Simulated power in the order of 400 W/m² at 0,45 a.u.**

## High temperature Thermoelectric Generator in STG like configuration




**Energy harvesting from concentrated solar energy demonstrated with a power density of 2KW/m²**
**Yield around 4% at 550°C hot side in a SiGe TEG**

| TEG characteristics at ΔT=509°C under vaccuum | Performances |
|---|---|
| Maximum open circuit voltage | 429 mV |
| Internal resistance | 56mΩ |
| Pmax | 820 mW |

*A. Pereira et al., to be published*

# CONCLUSION

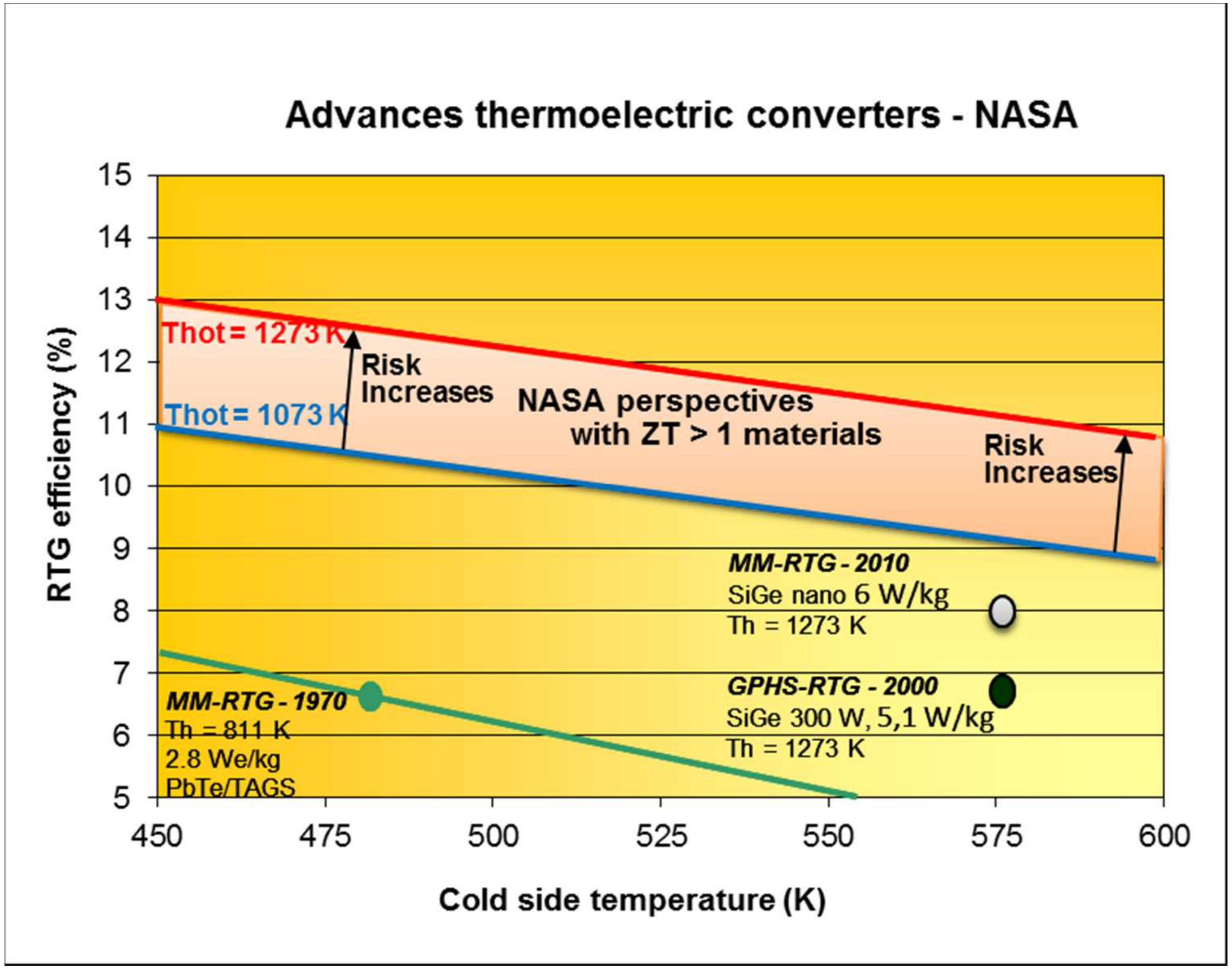
- **The proof of concept of the performance increase of Si-based thermoelectrics materials using the intentional incorporation of nanoparticles in the host matrix alloy has been demonstrated, using scalable techniques and eco-friendly materials**

- **The integration of these existing nanocomposites into GPHS - RTG technology could provide a performance equivalent to the currently used nanostructured materials**

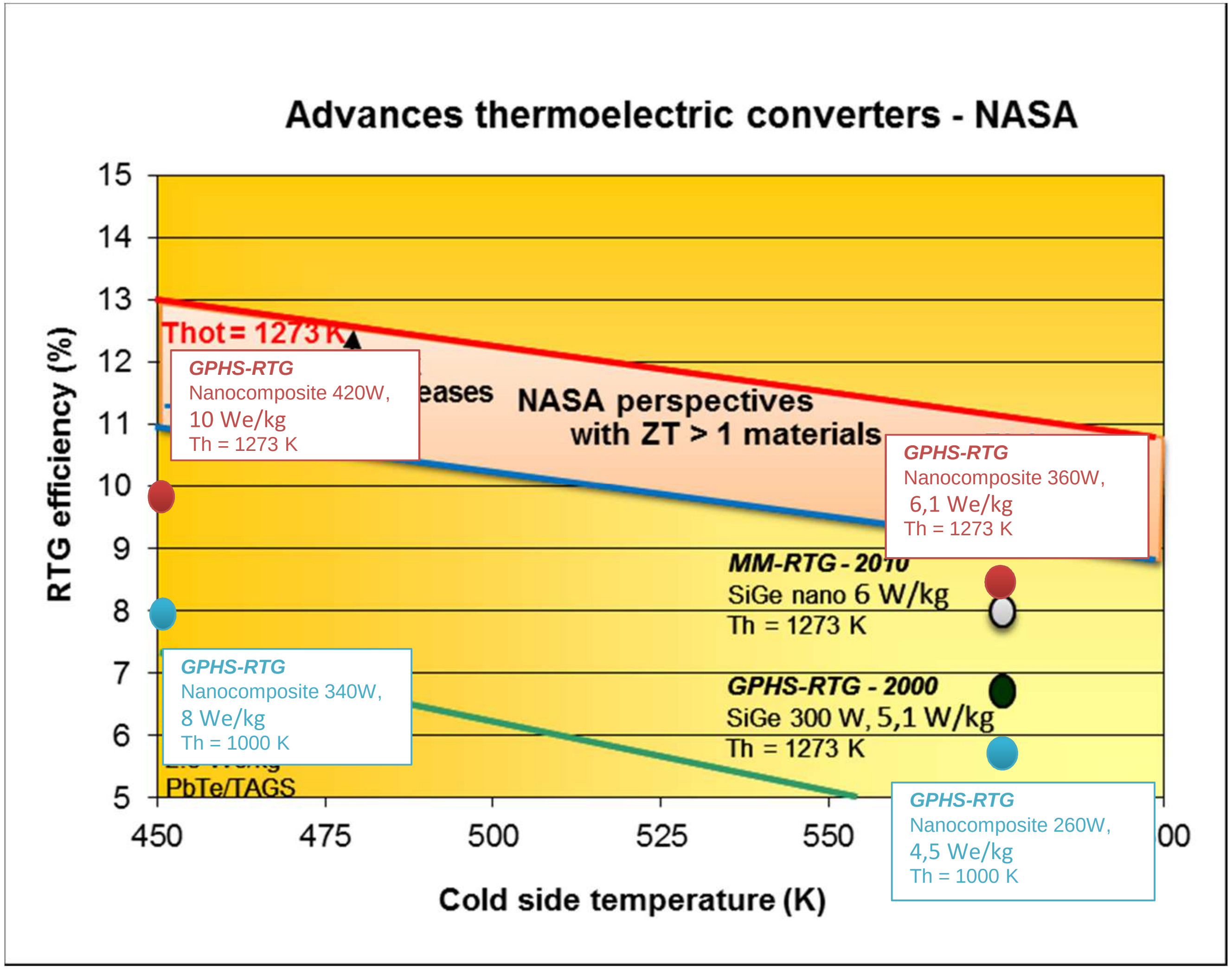
| Materials | Th max (K) | Heat sink type | P max (BOM) for 11 kg of $^{238}$Pu | Conversion Efficiency | Specific Power Density |
|---|---|---|---|---|---|
| SiGe | 1273 K | Standard | 290 W | 6,8 % | 5,1 W/kg |
| | 1000 K | Standard | 200 W | 4,8 % | 3,6 W/kg |
| SiGe + Zintl (MIT) | 1273 K | Standard | 340 W | 8 % | 6 W/kg |
| | 1000 K | Standard | 200 W | 5 % | 3,8 W/kg |
| SiGe-NEAT+ $Mg_2SiSn$-NEAT | 1273 K | Standard | 360 W | 8,3 % | 6,2 W/kg |
| | | Advanced | 420 W | 9,9 % | 10 W/kg |
| | 1000 K | Standard | 260 W | 6,1 % | 4,5 W/kg |
| | | Advanced | 340 W | 8 % | 8 W/kg |

- **STGs using the same materials could generate a power density in the order of 400 W/m² at a distance of 0,45 a.u. from the sun ($T_h$=1000K) or more than 600 W/m² at a shorter distance of 0,3 a.u. ($T_h$= 1273 K)**

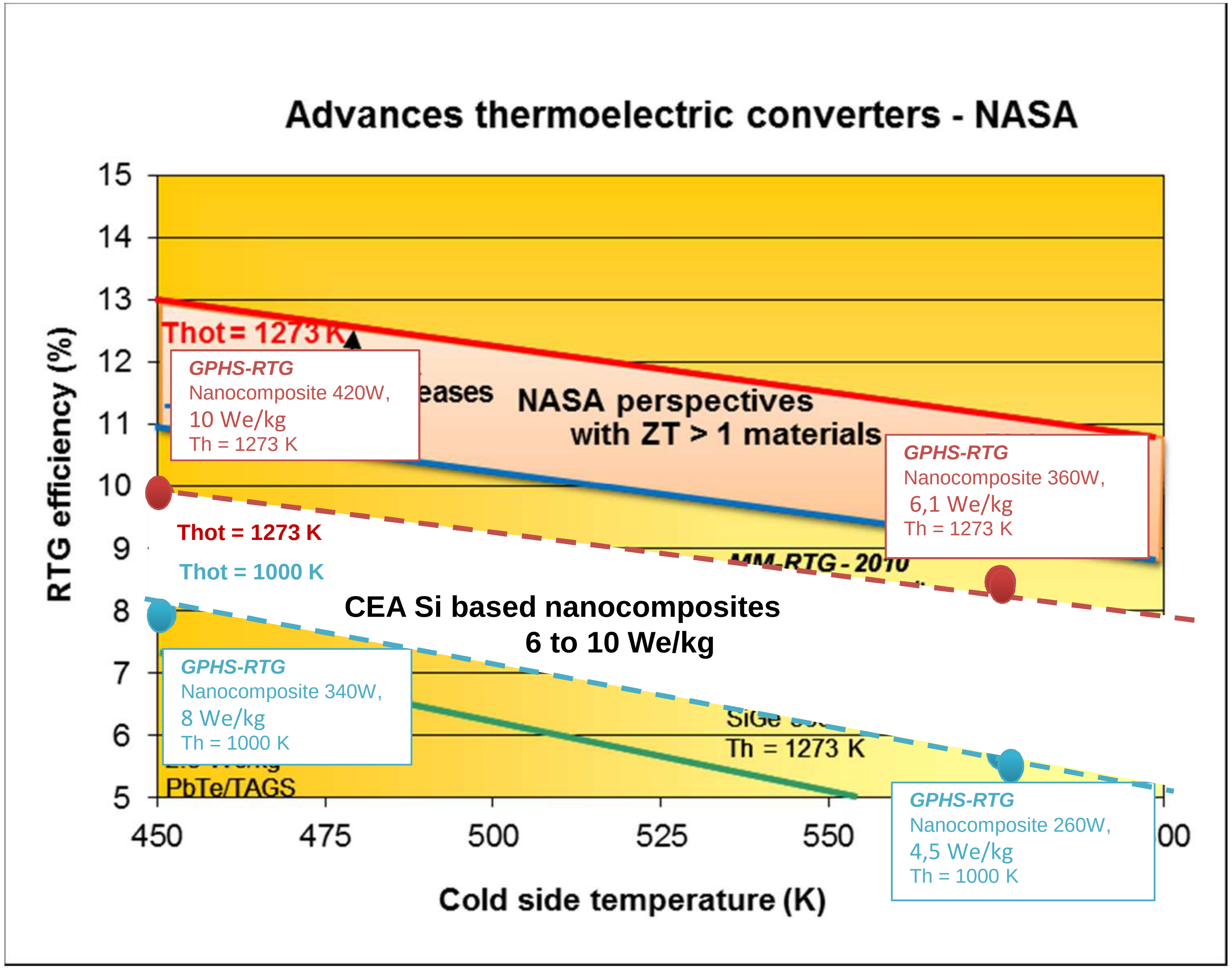
# CONCLUSION


Advances thermoelectric converters - NASA
RTG efficiency (%)
Cold side temperature (K)
15
14
13
12
11
10
9
8
7
6
5
450
475
500
525
550
575
600
Thot= 1273 K
Thot= 1073 K
Risk Increases
NASA perspectives with ZT > 1 materials
Risk Increases
MM-RTG - 2010
SiGe nano 6 W/kg
Th = 1273 K
GPHS-RTG - 2000
SiGe 300 W, 5,1 W/kg
Th = 1273 K
MM-RTG - 1970
Th = 811 K
2.8 We/kg
PbTe/TAGS

# CONCLUSION




*Source Nasa*



Advances thermoelectric converters - NASA
RTG efficiency (%)
Cold side temperature (K)
15
14
13
12
11
10
9
8
7
6
5
450
475
500
525
550
00
Thot= 1273 K
GPHS-RTG
Nanocomposite 420W,
10 We/kg
Th = 1273 K
eases
NASA perspectives
with ZT > 1 materials
GPHS-RTG
Nanocomposite 360W,
6,1 We/kg
Th = 1273 K
Thot = 1273 K
Thot = 1000 K
MM-RTG - 2010
CEA Si based nanocomposites
6 to 10 We/kg
GPHS-RTG
Nanocomposite 340W,
8 We/kg
Th = 1000 K
PbTe/TAGS
Th = 1273 K
GPHS-RTG
Nanocomposite 260W,
4,5 We/kg
Th = 1000 K


*Source Nasa*

## ACKNOWLEDGEMENT

The experimental results presented here are the fruit of research of CEA-LITEN thermoelectrics team : Thanks to G. Bernard-Granger, K. Favier, R. Vracar, C. Navone, M. Soulier, J. Leforestier, M. Boidot, B. Deniau, N. Mingo, N. Ayape-Katcho, V. Salvador, T. Baffie, K. Romanjek, A. Pereira, G. Lorin, C. Dubarry, N. Miloud-Ali, S. Vesin, N. Baud

The research leading to the nanocomposites results has received funding from the Seventh Framework Program [FP7/2007-2013] under grant agreement n° 263440 (**NEAT project** : 04/2011-03/2014) – http://www.neat-project.eu/

A preliminary study of the potential of nanocomposites thermoelectrics for spatial applications was funded by the CNES (**NEO project** : 10/2009-10/2010)

We also acknowledge the support of the Hotblock on Board company

THANK YOU
FOR YOUR ATTENTION