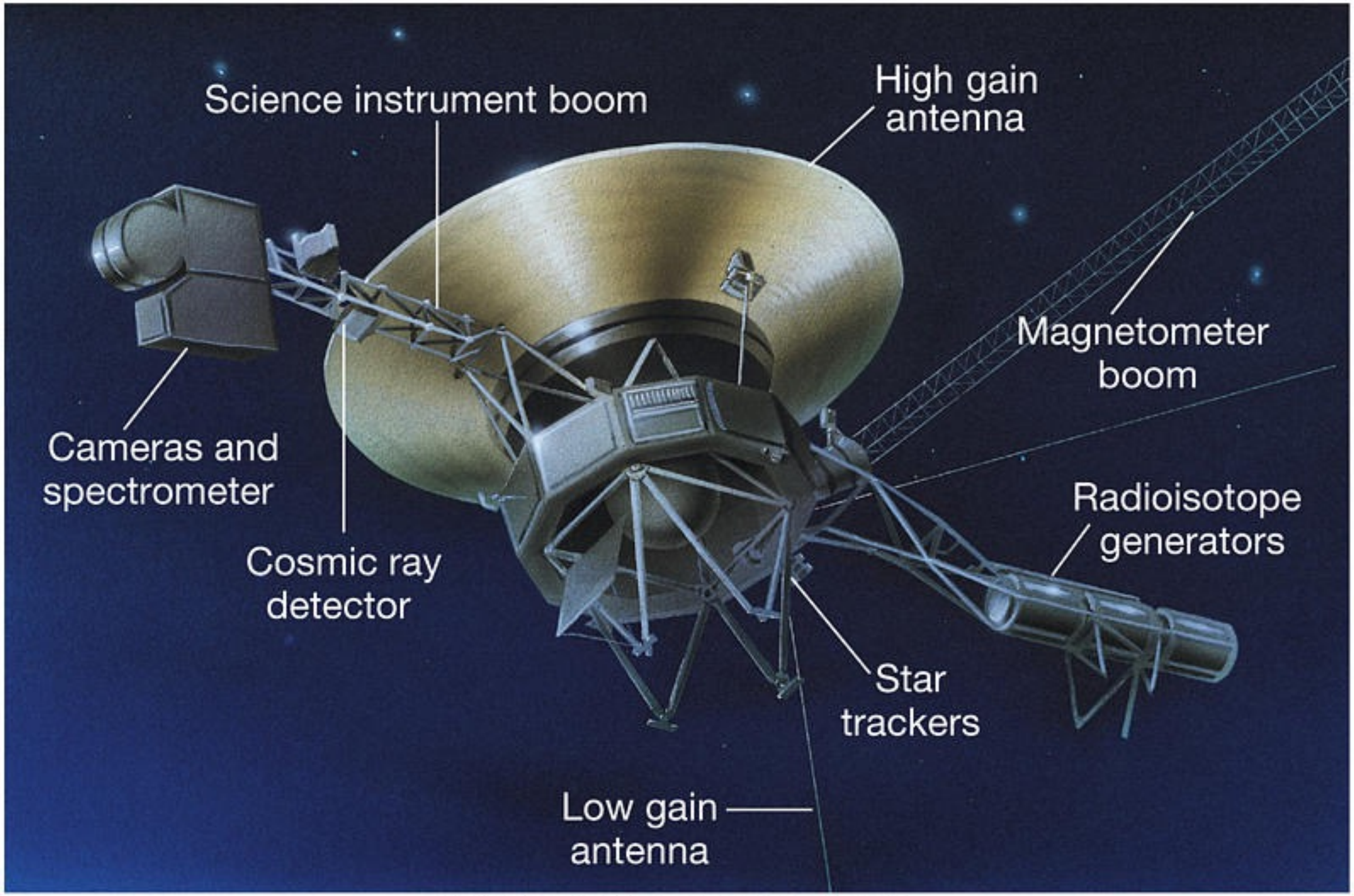
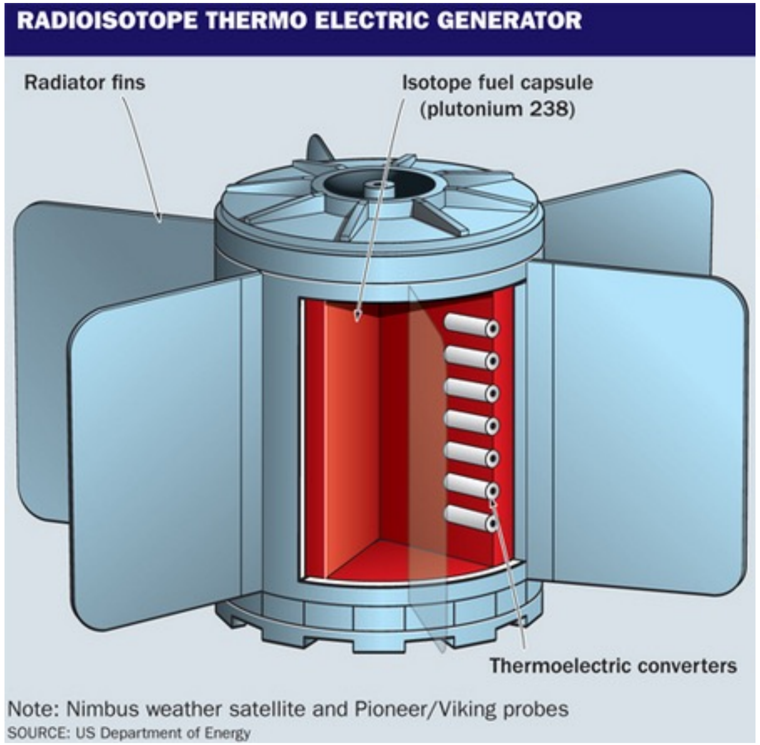
Thermo-electricity

Thermoelectric power for space vehicles

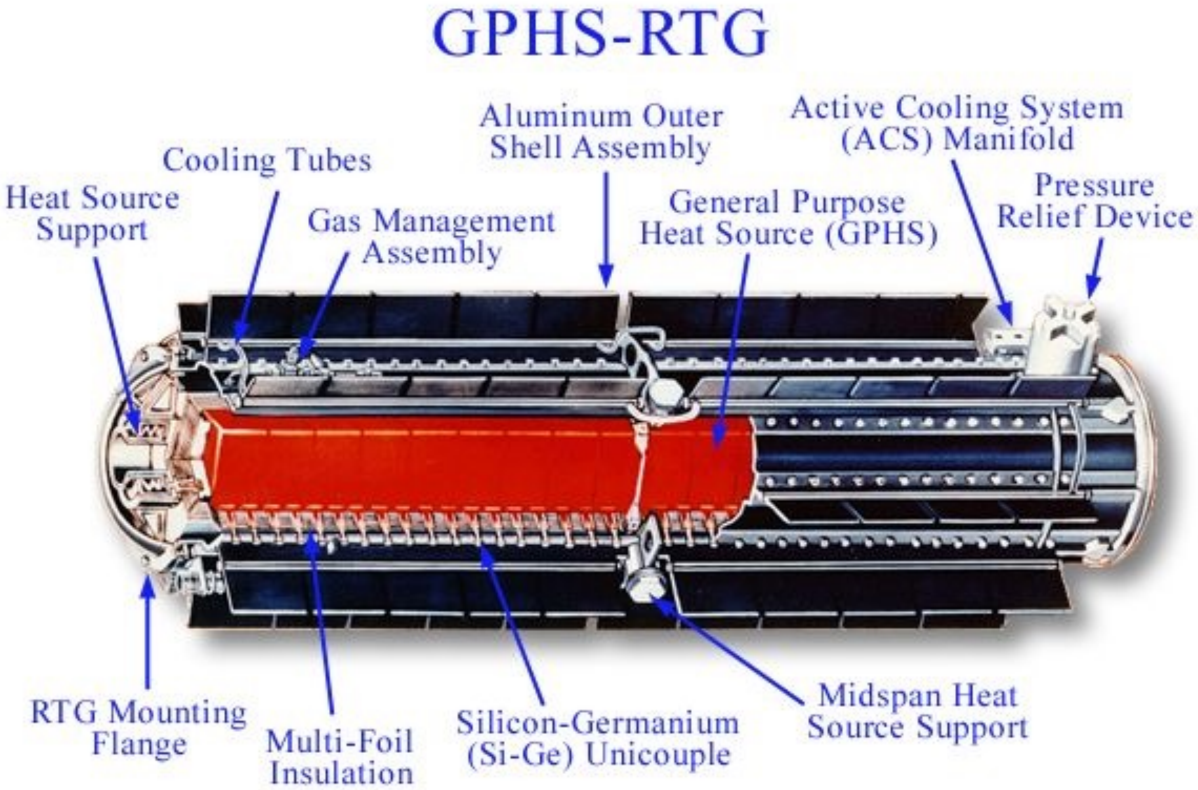
300 W of power for 40 years

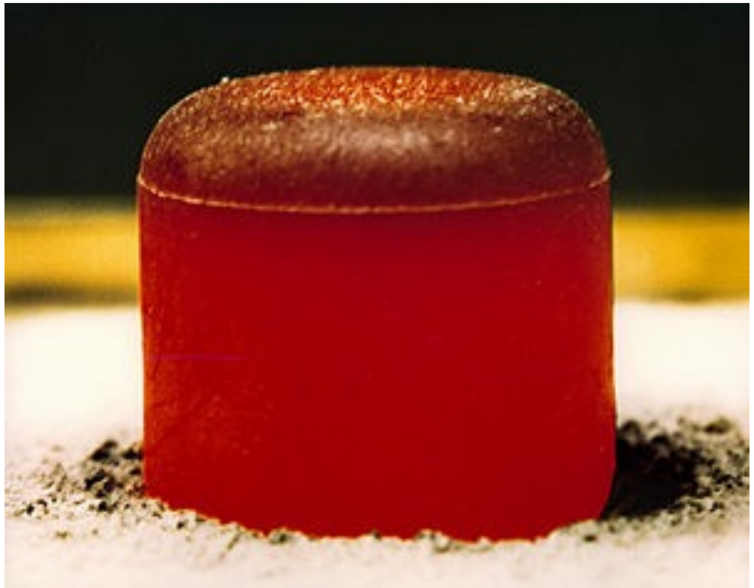




Note: Nimbus weather satellite and Pioneer/Viking probes

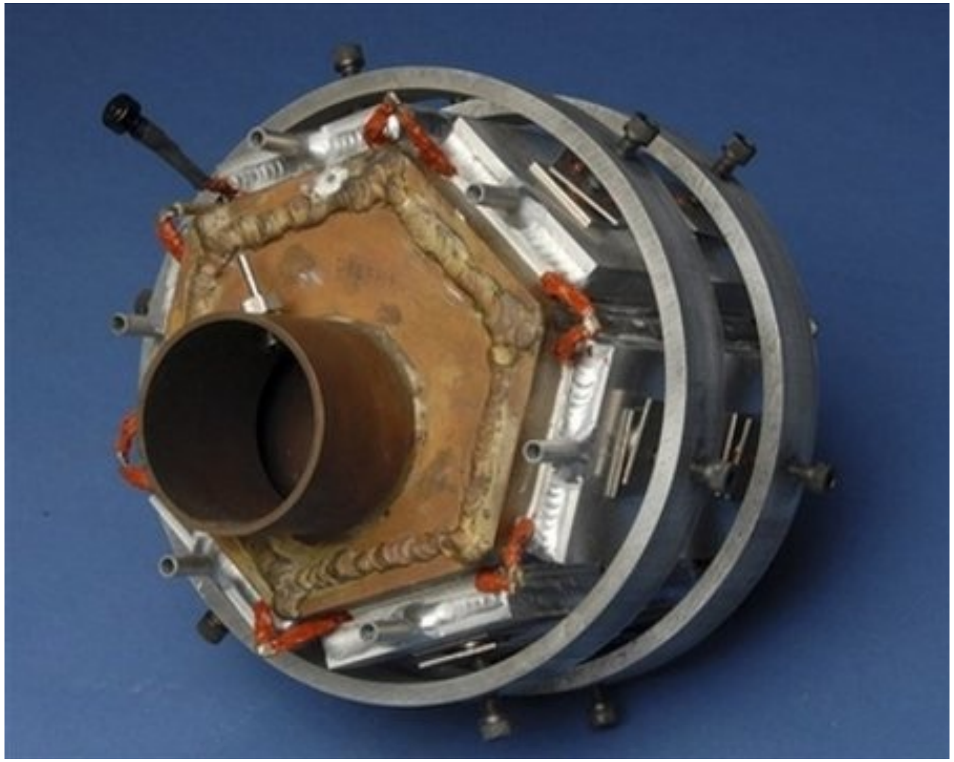
SOURCE: US Department of Energy





A pellet of 238-PuO_2 to be used in an RTG for either the Cassini or Galileo mission. The initial output is 62 watts. The pellet glows red hot because of the heat generated by the radioactive decay (primarily α).

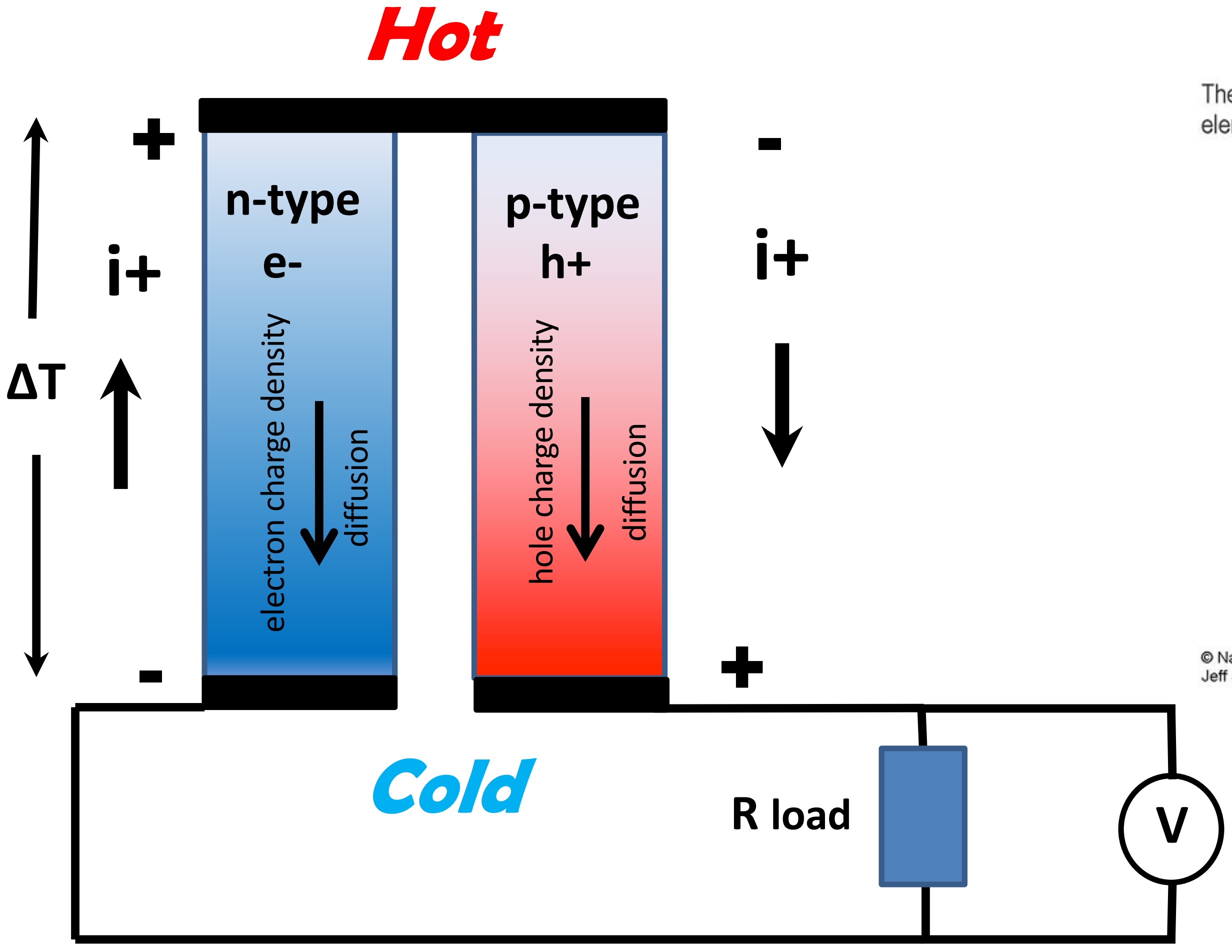
Thermoelectric waste heat recovery on vehicles

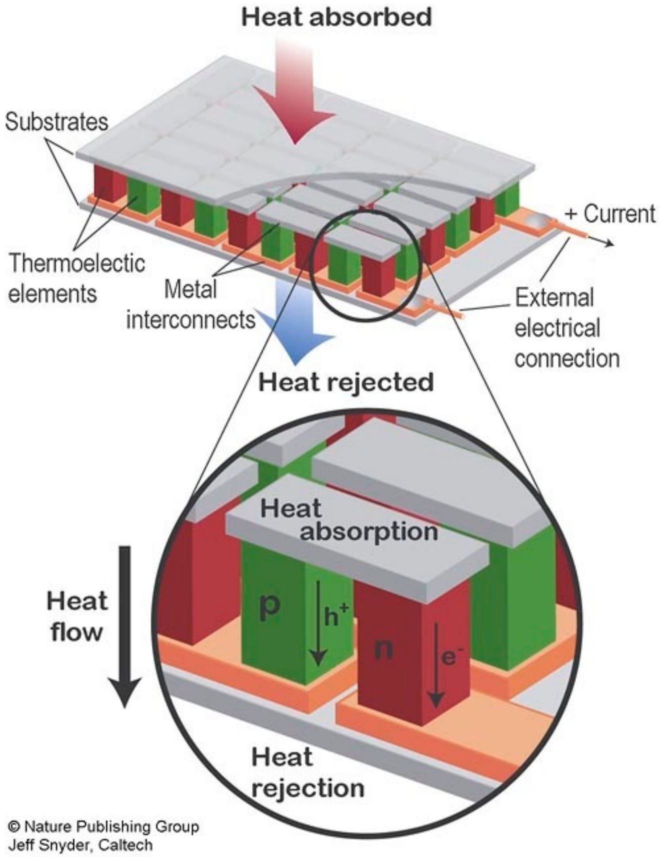


300 W (car)
1 kW (truck)

Thermoelectrics in the process industry to capture waste heat from industrial furnaces

Thermoelectric devices – basics





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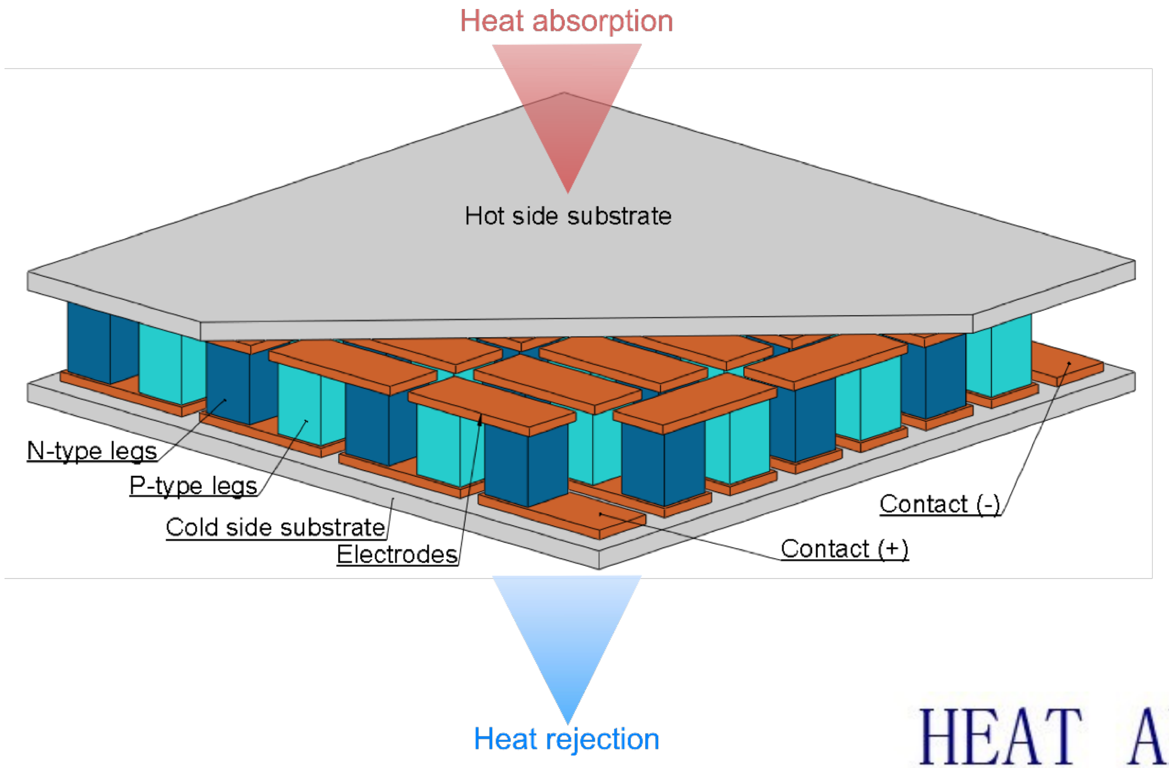
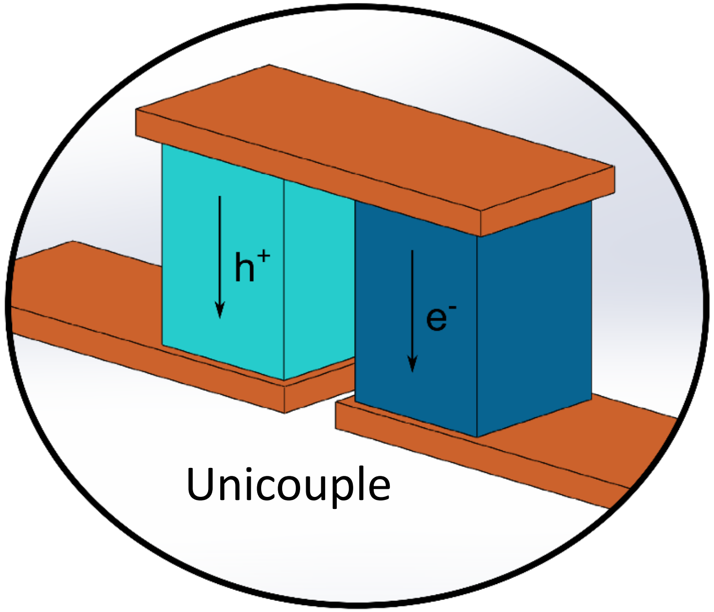
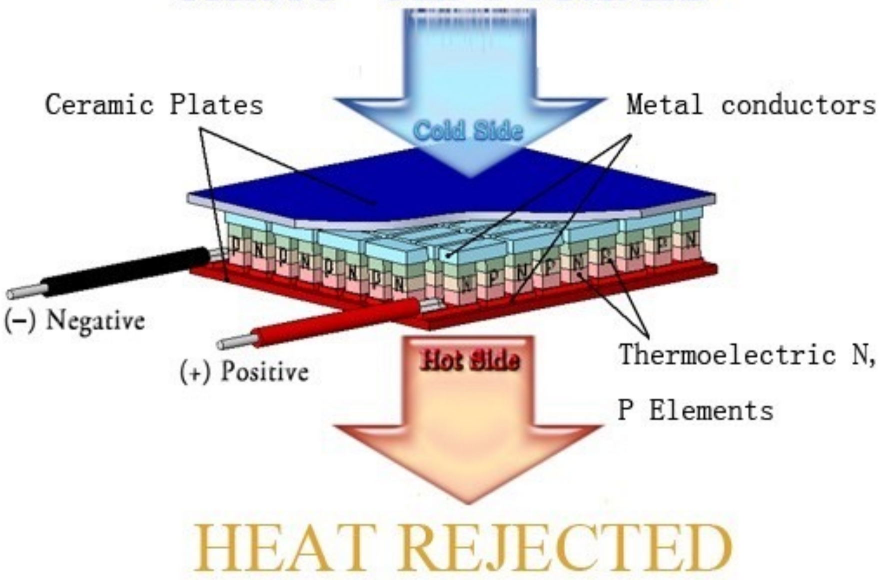
Jeff Snyder, Caltech

Thermoelectric module



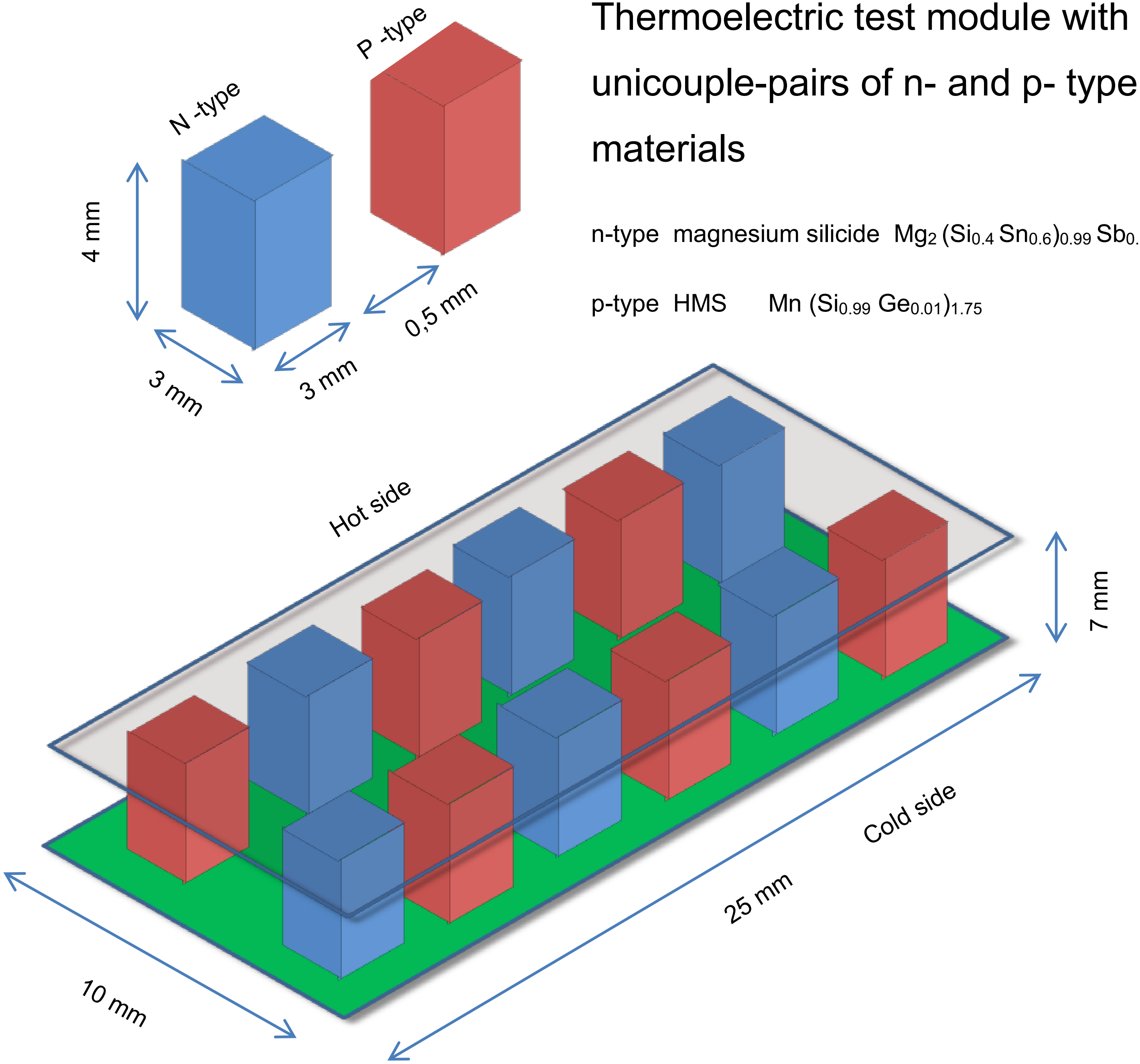




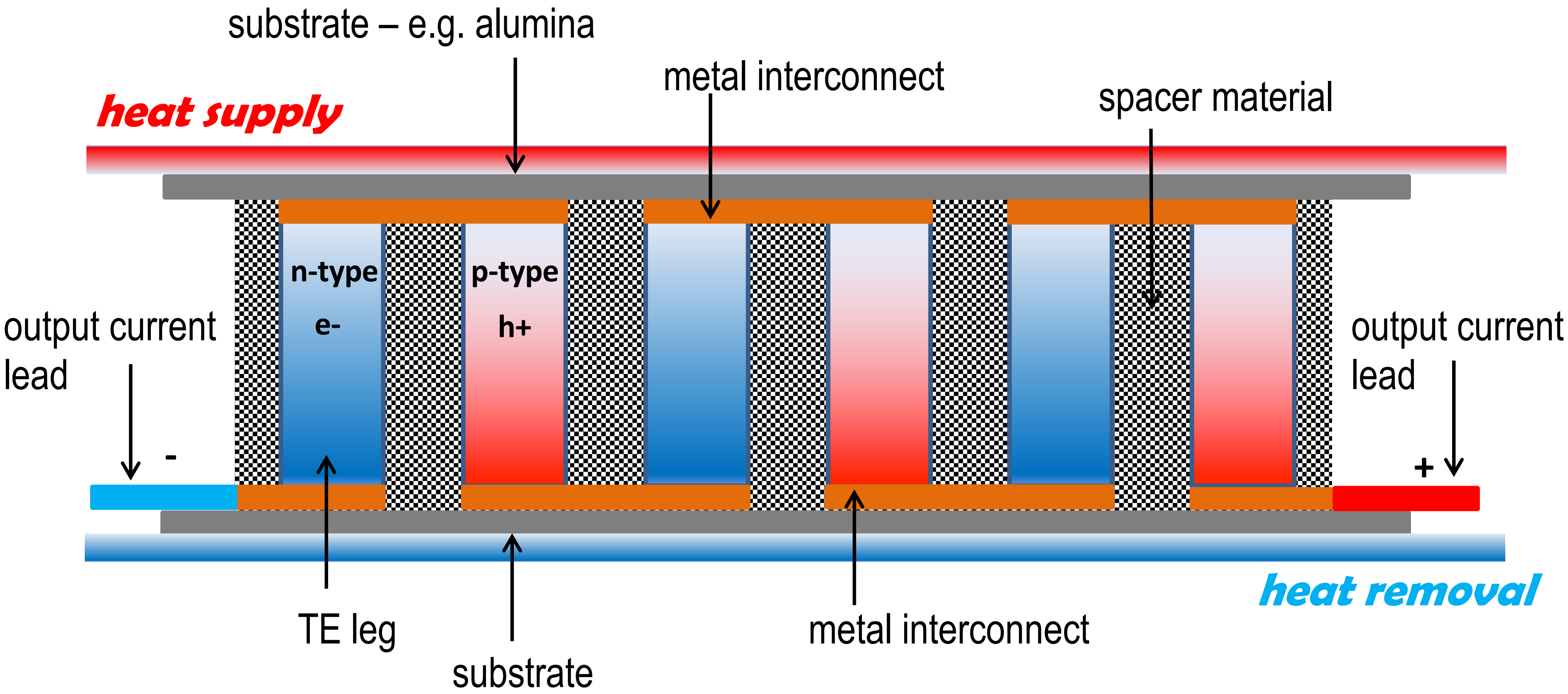
Thermoelectric test module with 6 unicouple-pairs of n- and p- type materials

n-type magnesium silicide $Mg_2(Si_{0.4}Sn_{0.6})_{0.99}Sb_{0.01}$

p-type HMS $Mn(Si_{0.99}Ge_{0.01})_{1.75}$



Thermoelectric module – assembly



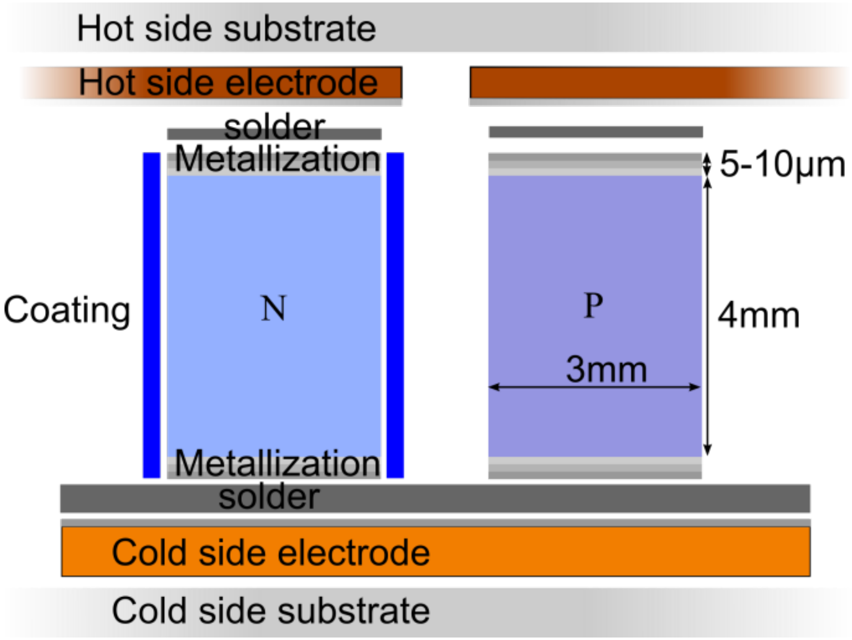
Voltage is built up by **series** arrays of TE legs (hence n-p legs in series; α has opposite sign)

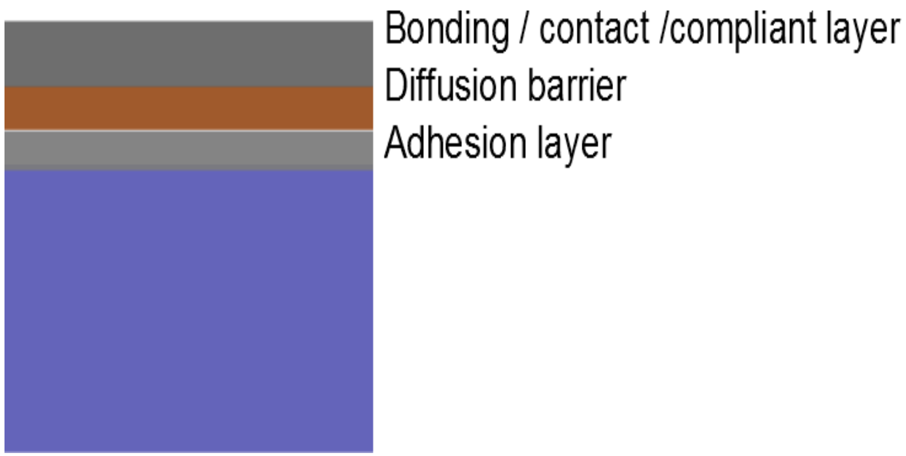
Current is built up by **parallel** arrays of TE legs

Power = voltage x current

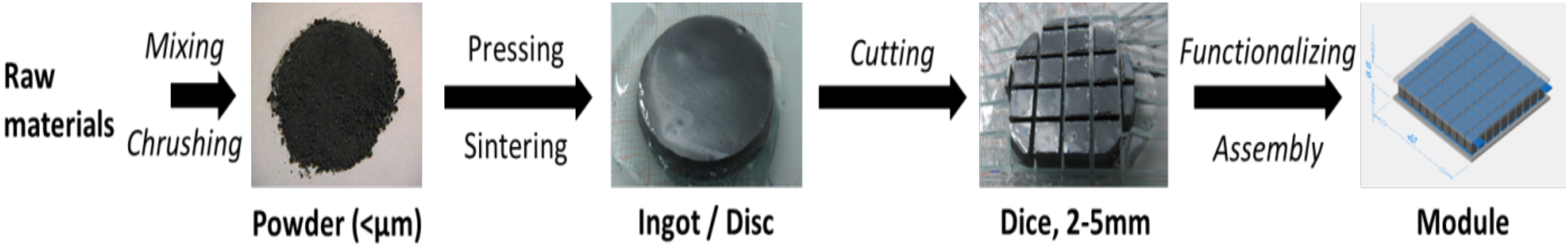
High power requires large temperature difference and low materials resistance

Layered assembly structures





From materials to module



Thermoelectricity – Seebeck effect

A metal or semiconductor generates a voltage when placed in a temperature gradient.

$V = \alpha \Delta T$ α = Seebeck coefficient / $\mu V K^{-1}$

α is small for a metal but larger for a semiconductor

Typical range: 0.1 to 1 mV per K

The charge density increases at the cold side due to a thermal diffusion gradient. At the hot side charge diffuses faster. This creates and maintains a voltage difference.

”Figure of merit”

Thermoelectric efficiency is described by the materials property Z.

Z is normally given as the dimensionless quantity “ZT”

$$ZT = \frac{\alpha^2 \ \boldsymbol{\sigma}\ T}{\mathbf{k}}$$

$\boldsymbol{\alpha}$ = Seebeck coefficient

$\boldsymbol{\sigma}$ = electrical conductivity

T = temperature in Kelvin

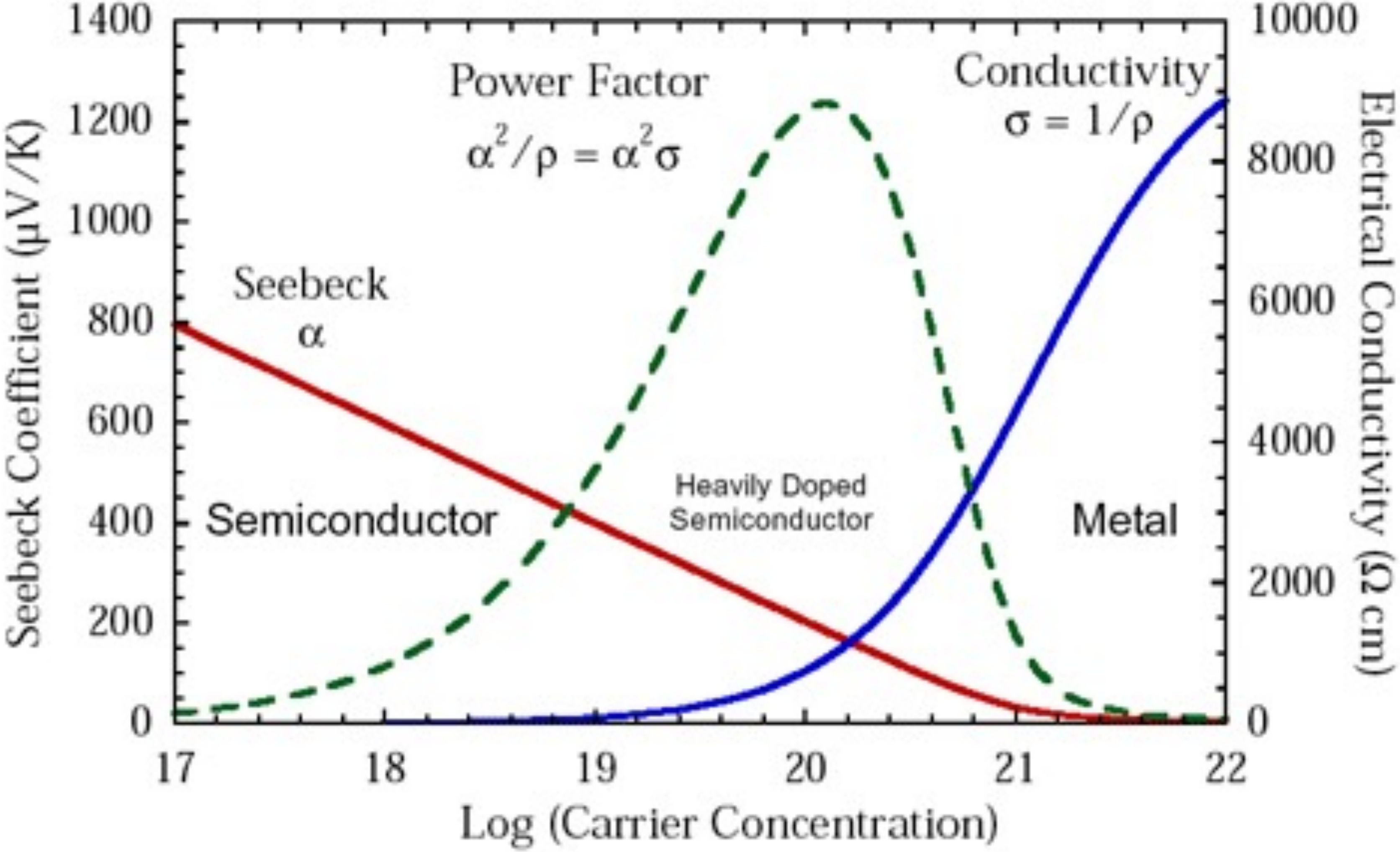
$\boldsymbol{\kappa}$ = thermal conductivity

ZT values are generally less than unity (ZT ≤ 1)

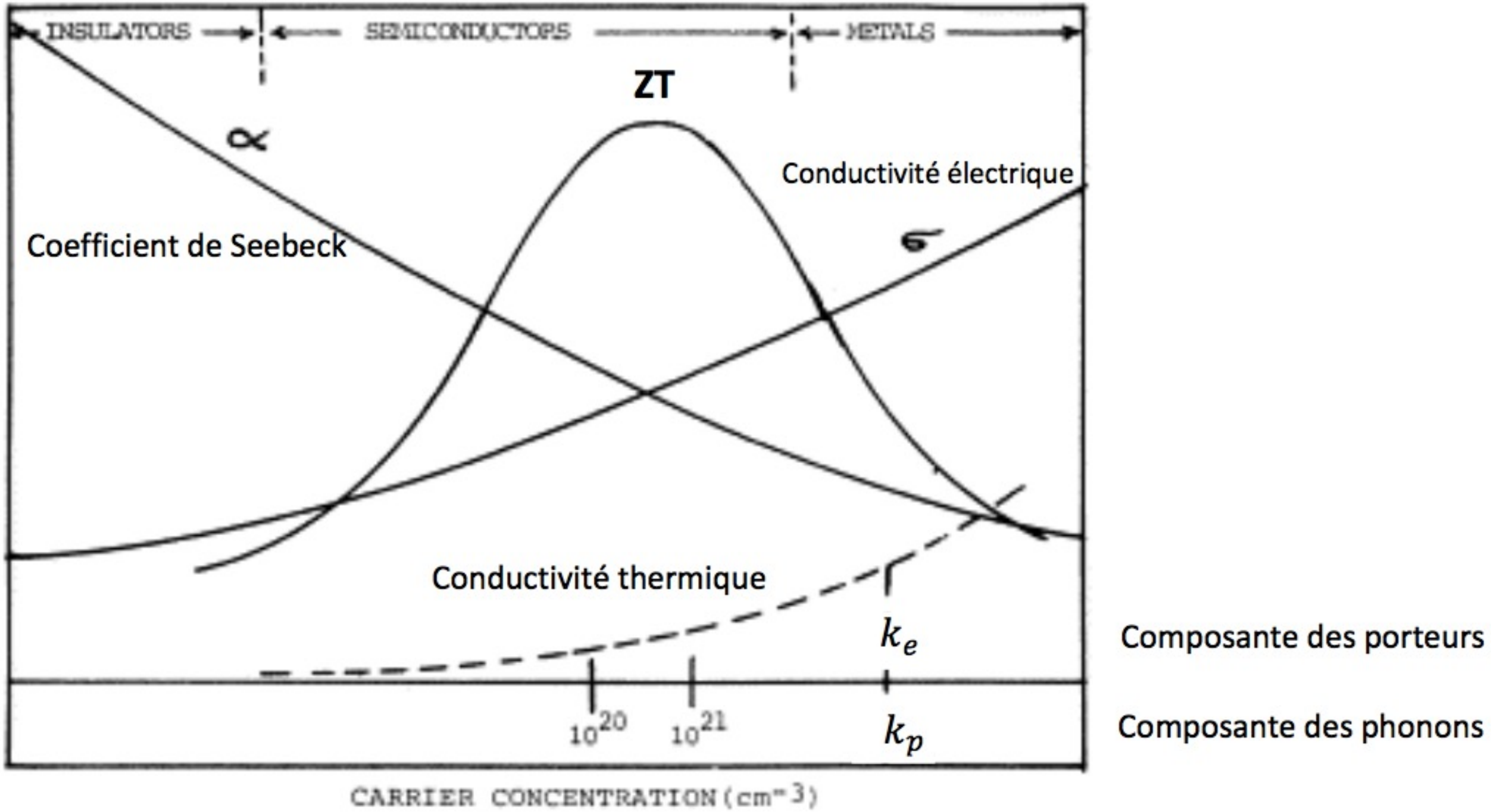
α, σ and κ are not independent of each other, making optimization difficult.

For thermoelectric power generation (heat recovery systems), ZT needs to be as high as possible - preferably greater than unity.

α and σ have opposite trends



Semiconductor = best compromise btw electrical conductivity and Seebeck coefficient



Phonon thermal conductivity is reduced by increasing their diffusion, i.e. by introducing heavy elements (reduce phonon vibration frequency), lattice misorganisation, cage structures, and small grain sizes (to reduce the mean free path of phonons).

Power Generation

Voltage: $V = \alpha \Delta T$

Power: $\mathrm{I}V = \frac{V^2}{R} = \alpha^2 \sigma \times \Delta T^2 \times \frac{A}{l}$

Power factor: $\alpha^2 \sigma$

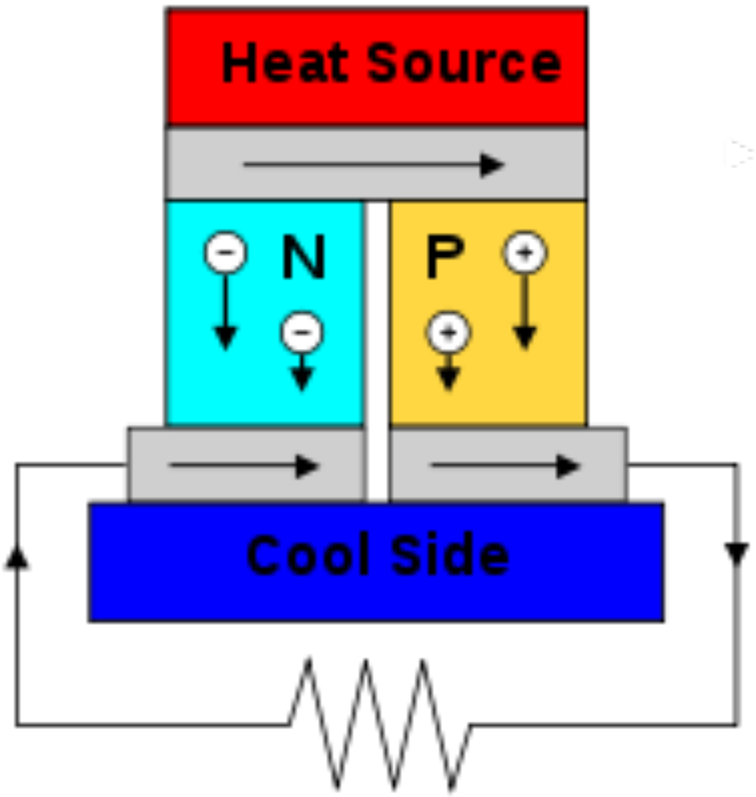
Max efficiency:

$$\frac{Electrical\ power}{\begin{matrix} Heat\ Removed \\ at\ hot\ source \end{matrix}} \approx \frac{\alpha^2 \sigma \times \Delta T^2}{\frac{I^2}{2\sigma} + \kappa \Delta T + \alpha T_H I}$$

Peltier

Joule effect

Fourier btw hot and cold sides

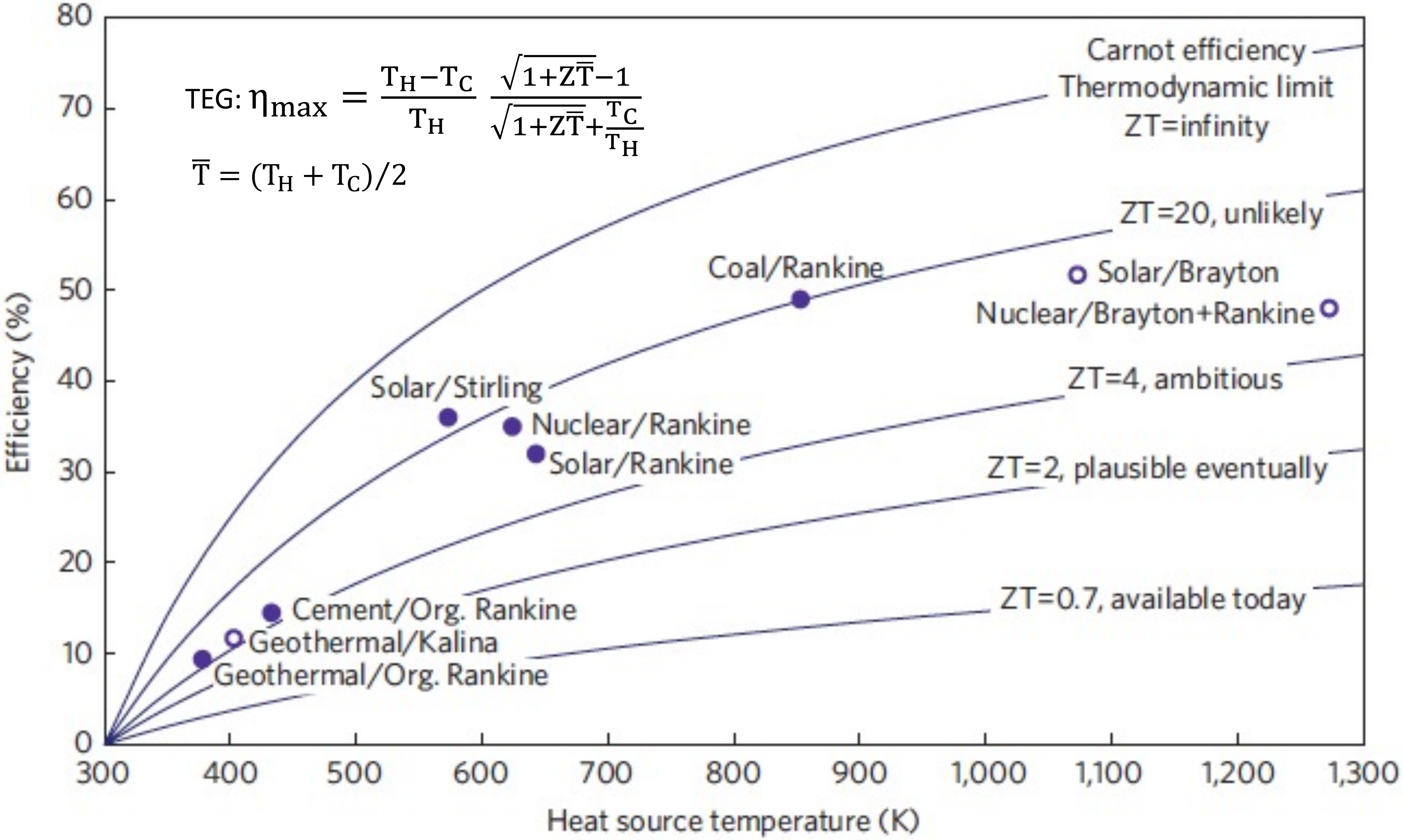


Thermoelectric properties

Material (one leg, n or p)	Module (multiple legs, n+p)
High Seebeck coefficient: α (>100 µV/K)	Open circuit voltage: $\boldsymbol{V_{OC}} = N_p \int_{T_C}^{T_H} \boldsymbol{\alpha_p}\, dT - N_n \int_{T_C}^{T_H} \boldsymbol{\alpha_n}\, dT$
High electrical conductivity: $\sigma = n\mu e$ (µ:mobility)	Inner resistance: $\boldsymbol{R_i} = N_p \int_0^l \frac{dx}{\sigma_p(T)A_p} + N_n \int_0^l \frac{dx}{\sigma_n(T)A_n} + R_{contacts}$
Low thermal conductivity: $\kappa = \kappa_{el} + \kappa_{ph}$ (el: charge carriers: ph: phonons)	Thermal conductance: $\boldsymbol{K} = \frac{N_p A_p \kappa_p}{l_p} + \frac{N_n A_n \kappa_n}{l_n}$
Figure of merit (material): $\mathbf{z} = \frac{\alpha^2\, \sigma}{\kappa}$	Figure of merit (module): $\boldsymbol{Z} = \frac{\alpha_{np}^2}{R_i K}$

(κ_{el} increases like σ; the only way to limit κ is via κ_{ph})

Efficiency = Carnot * f(ZT)

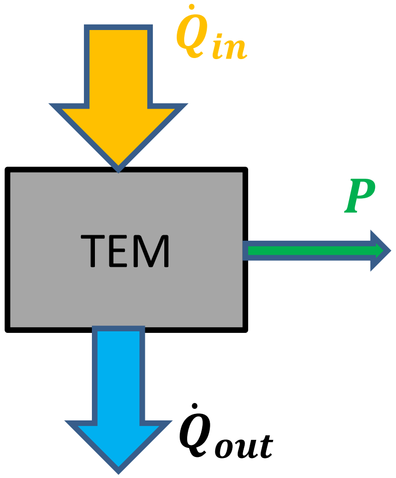


$$\text{TEG: } \eta_{max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+Z\overline{T}}-1}{\sqrt{1+Z\overline{T}}+\frac{T_C}{T_H}}$$

$$\overline{T} = (T_H + T_C)/2$$

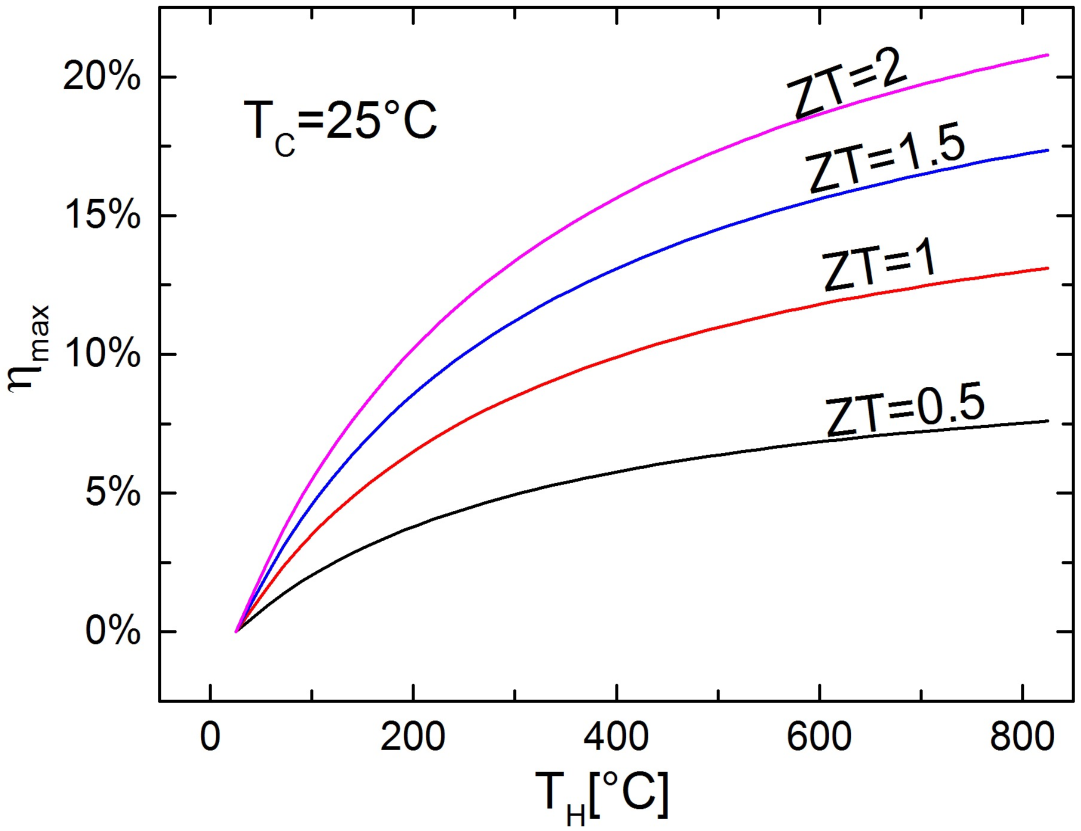
Thermoelectric conversion **efficiency**

$$Efficiency = \frac{Electric\ power}{Heat\ input}$$



$$\eta_{max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + Z\overline{T}} - 1}{\sqrt{1 + Z\overline{T}} + \frac{T_C}{T_H}}$$

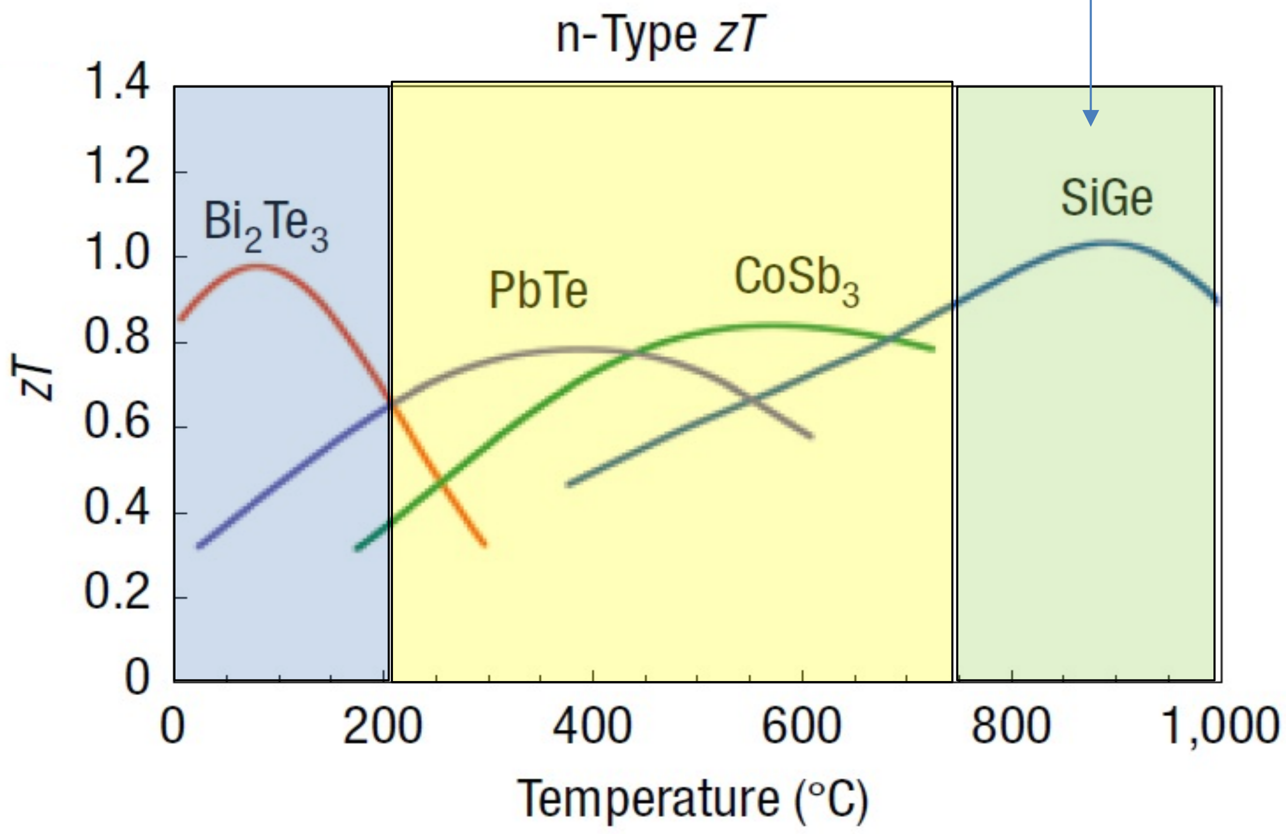
Carnot limit * thermoelectric properties



zT vs temperature

$$zT = \frac{\alpha^2 \sigma T}{\kappa}$$

Radio-isotope TEG

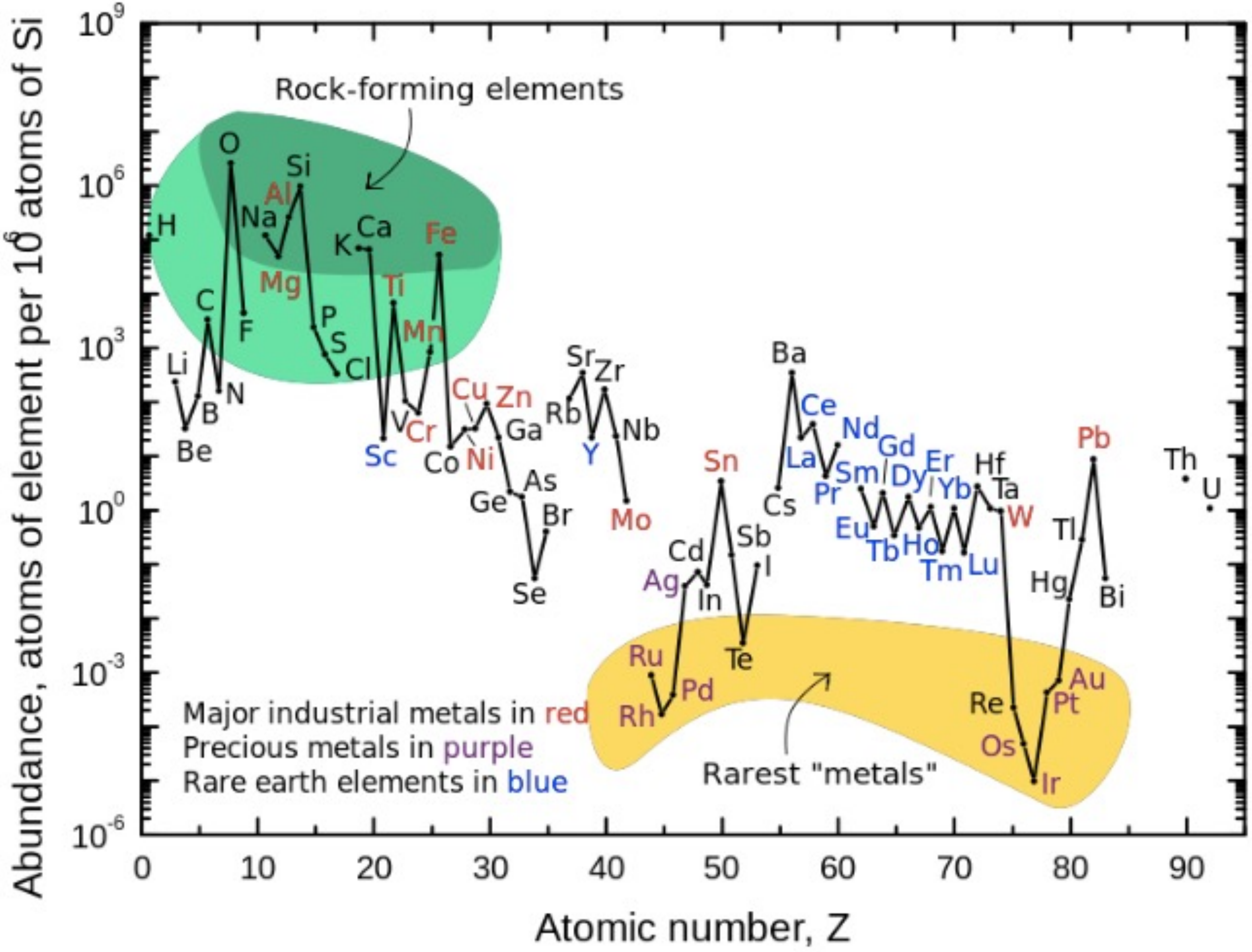


Low

Medium

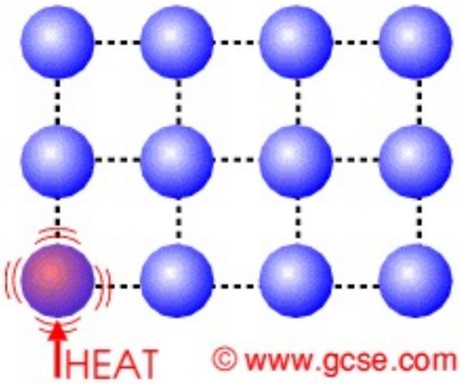
High

Snyder, G.J. and E.S. Toberer, *Complex thermoelectric materials.* Nature Materials, 2008. 7(2): p. 105

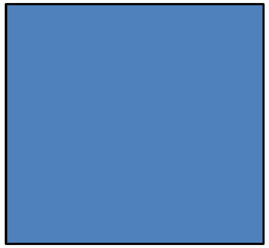

Abundance, atoms of element per 10^6 atoms of Si
Atomic number, Z
10^9
10^6
10^3
10^0
10^-3
10^-6
0
10
20
30
40
50
60
70
80
90
Rock-forming elements
Rarest "metals"
Major industrial metals in red
Precious metals in purple
Rare earth elements in blue
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Thermally activated degradation processes

Atoms vibrate …



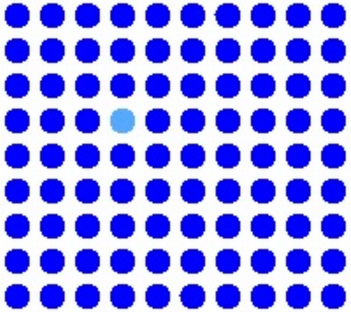
… expand…



Coefficient of Thermal Expansion (linear)

$$CTE = \frac{1}{x}\frac{dx}{dT}$$

… and move



Diffusion coefficient

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right)$$

TE Materials

Skutterudites $CoSb_3$

promising high temperature low cost materials

example of PGEC *Phonon Glass Electron Crystal*

Binary intermetallic family of minerals of the general structure MX_3

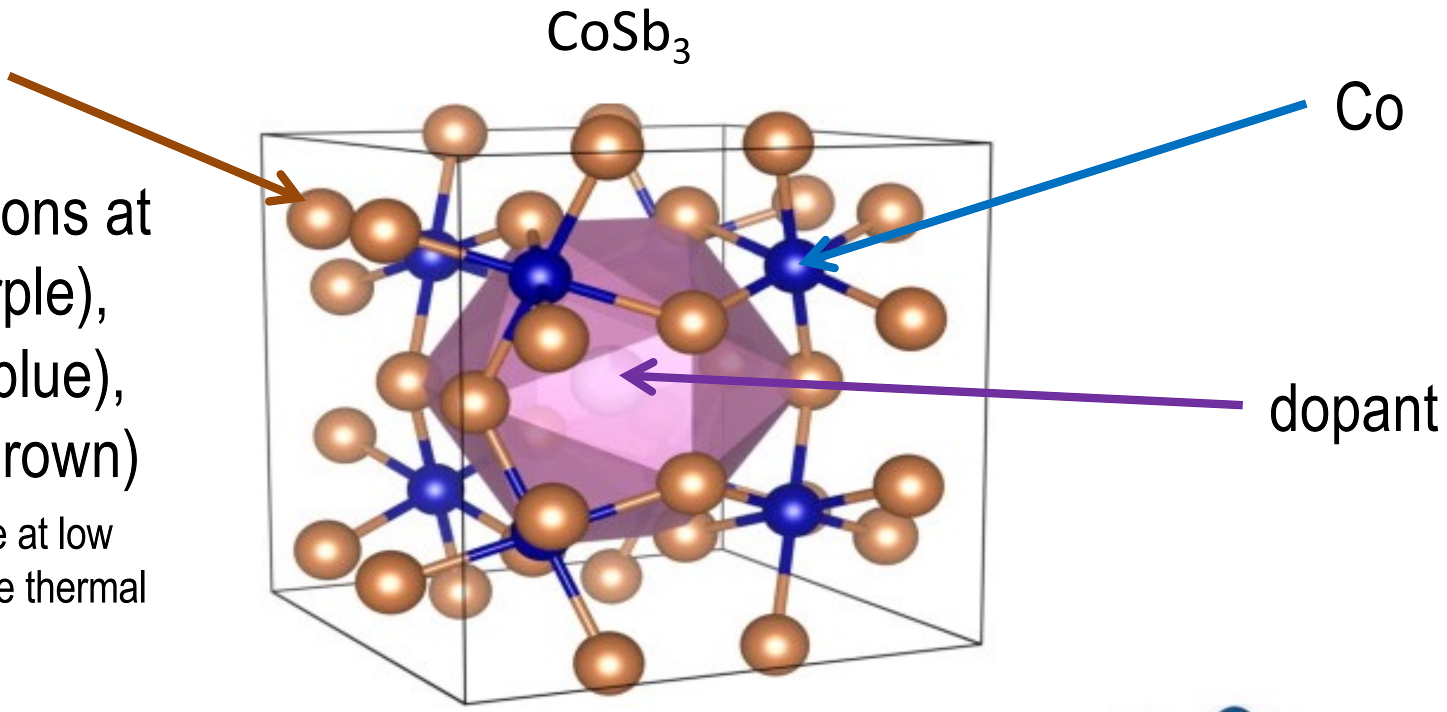
Crystal structure : cubic with Co atoms at the vertices and Sb atoms forming cage clusters or voids

n or p- types obtained by doping – with Ce, In, Fe, Ni

Skutterudite: cage structure, to trap heat carrying phonons

Rattler positions at centre (purple), Co atoms (blue), Sb atoms (brown)

(rattlers = vibrate at low frequency, disperse thermal energy)

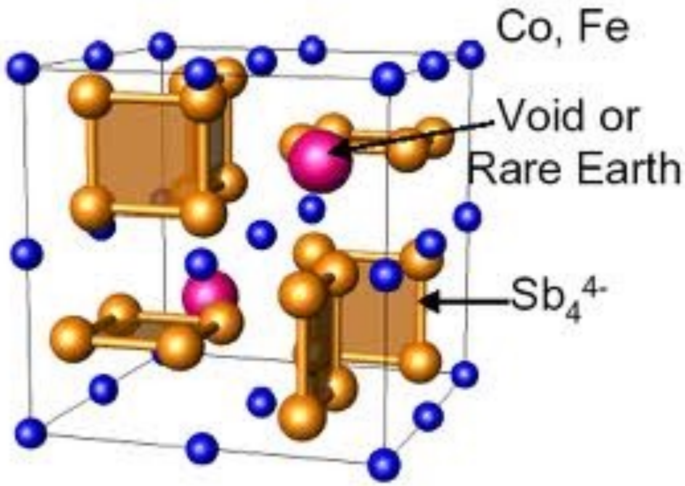


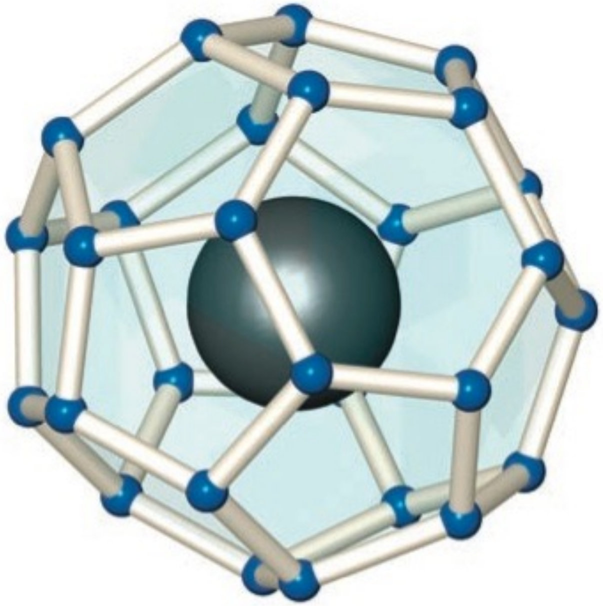
$CoSb_3$

Sb

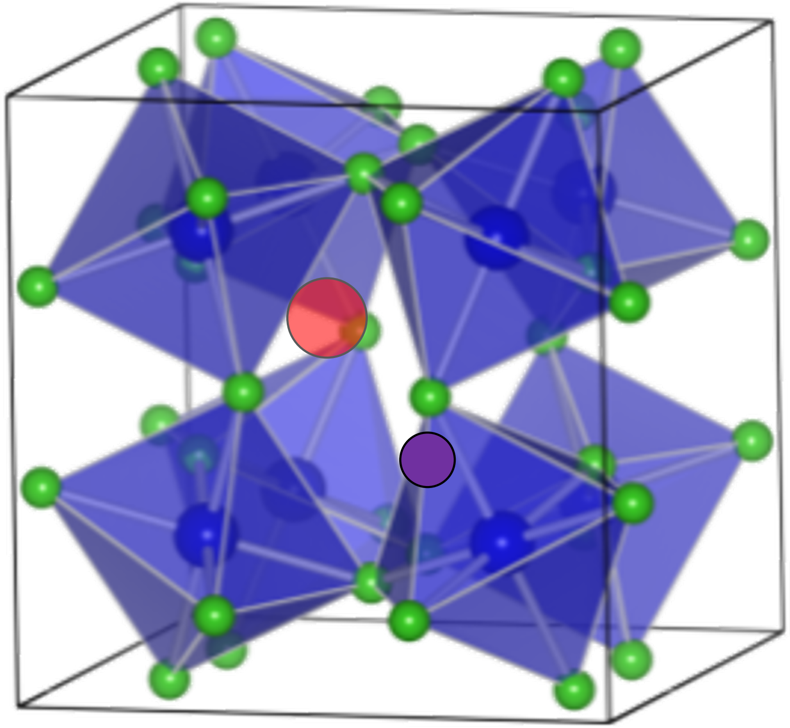
Co

dopant





Skutterudites



Unfilled: Co_4Sb_{12}

Filled n-type: $Fi_yCo_4Sb_{12}$

0…1

Fe^{2+} replaces Co^{3+} → holes

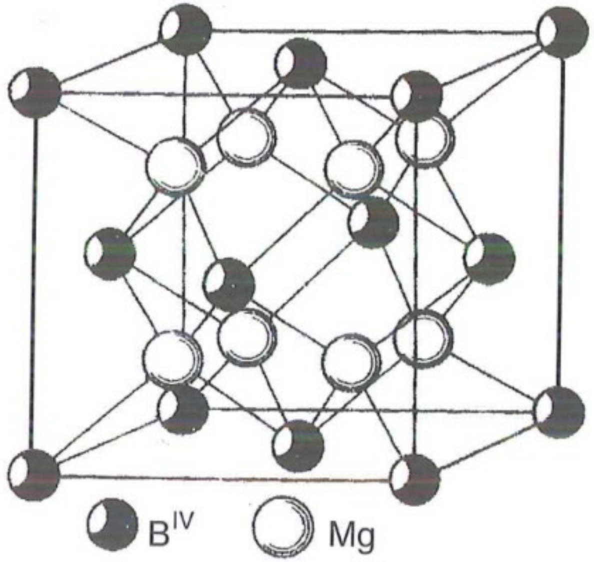
Filled p-type: $Fi_yCo_{4-x}Fe_xSb_{12}$ → κ decreases

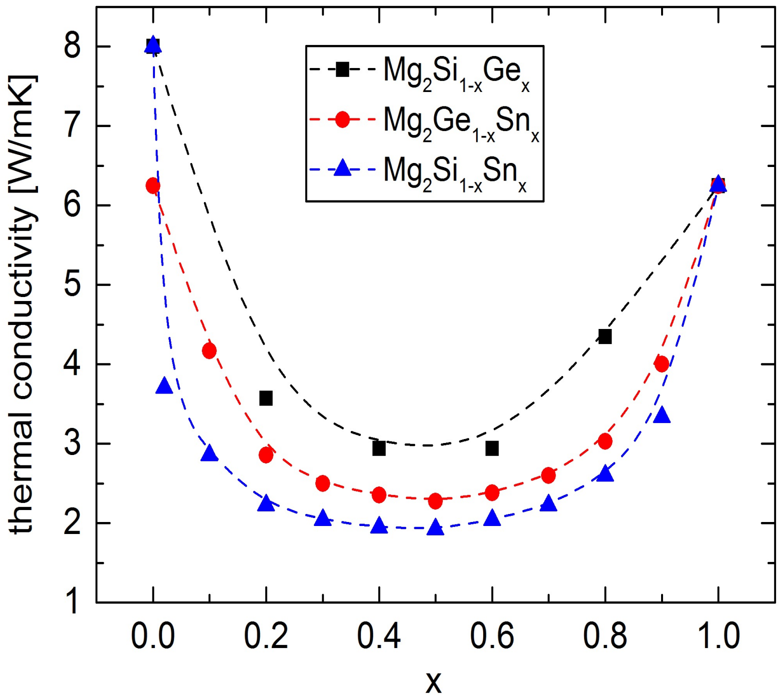
0…4

Fi = In, Ce, Yb, …

Silicides

- Silicides – compounds formed between (almost) any other element and silicon
- Many of these are (like silicon) semiconductors → potential good TE materials
- Mg_2Si best n-type silicide, zT up to 1
- $MnSi_{1.75}$ best p-type silicide, zT up to 0.8
- By replacing Si with Sn or Ge, point defects (scattering centers for phonons) are introduced, drastically reducing thermal conductivity → zT up to 1.5

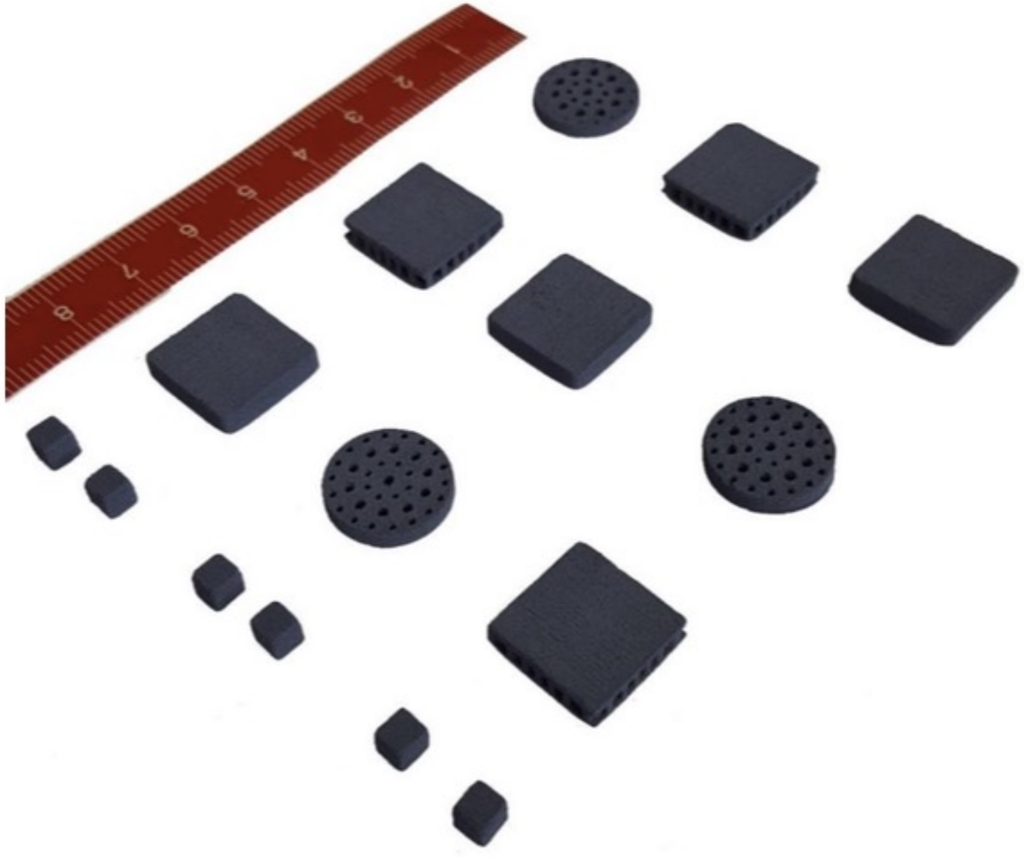




Mg_2Si synthesized at EPFL-GEM

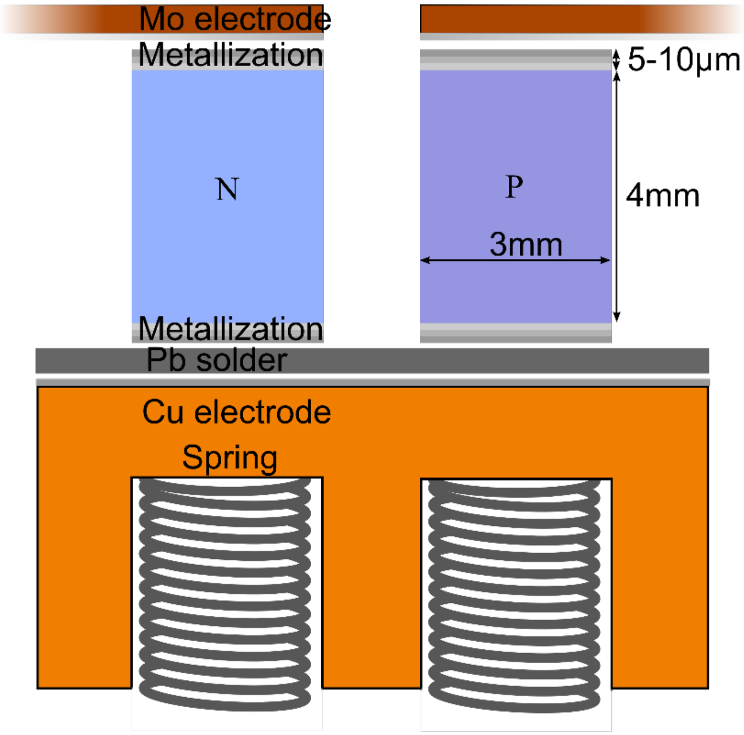
Pellets

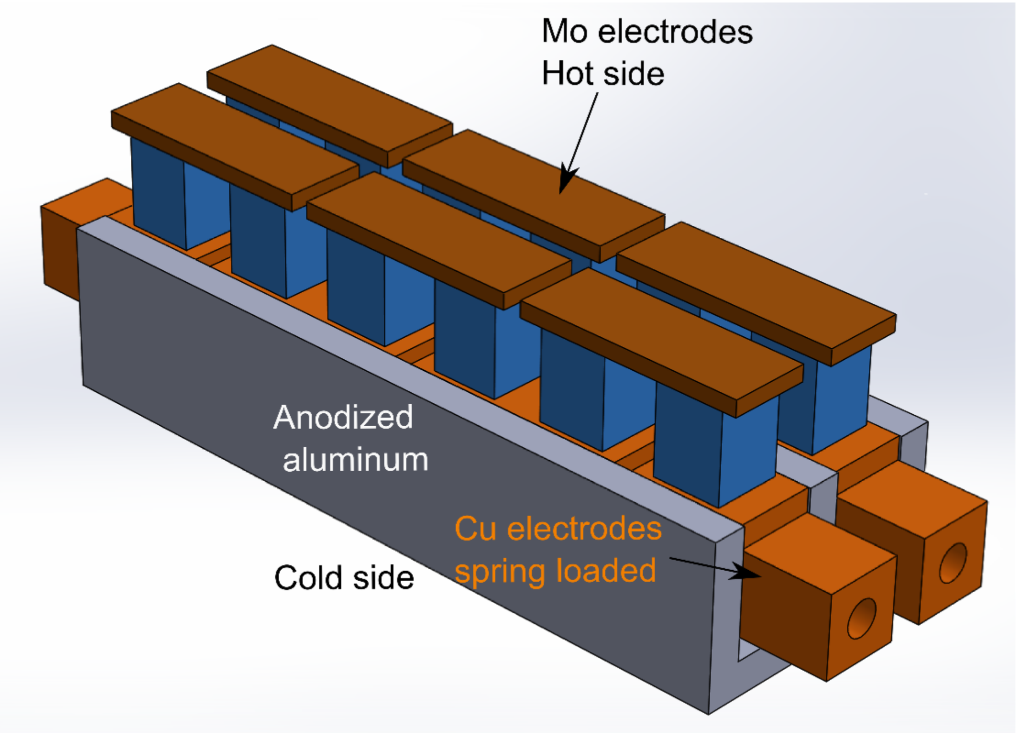
3D-printed shapes



Silicide modules, prototype design

$Mg_2Si_{0.4}Sn_{0.6}$ $MnSi_{1.75}$





Performance

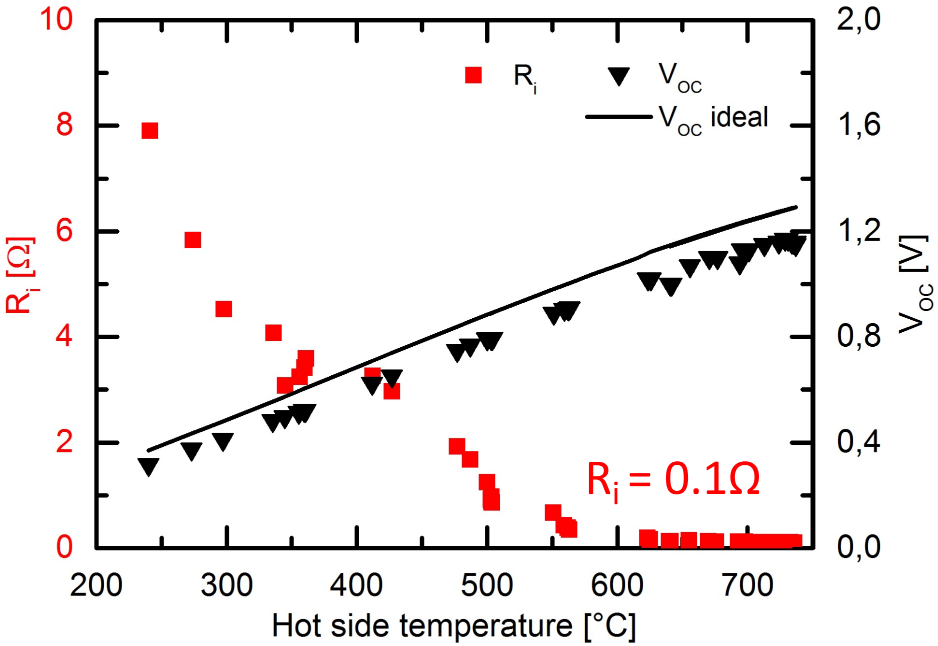
$$V_{OC} \sim \alpha \Delta T$$

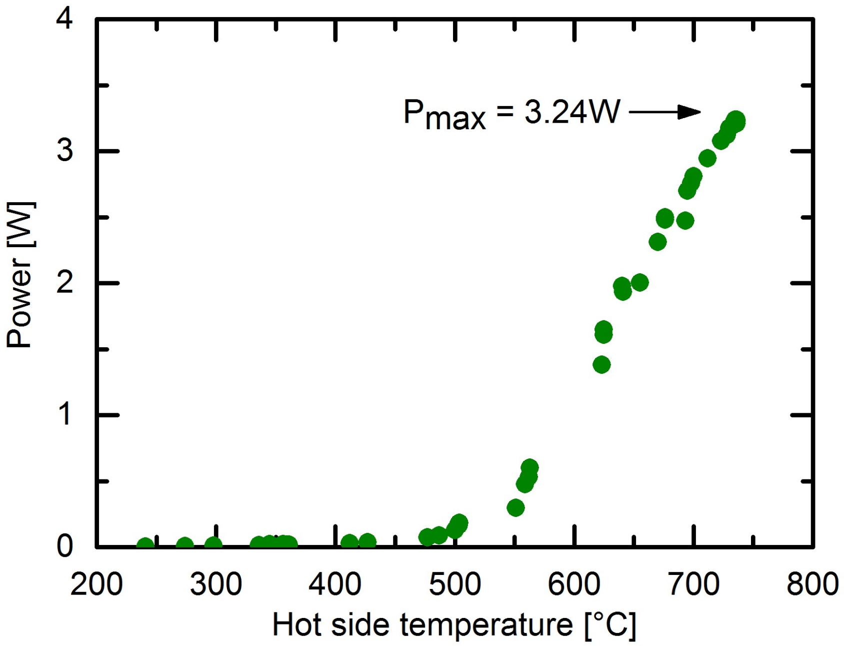
$$P_{max} = \frac{V_{OC}^2}{4R_i}$$

P_{max} @ dT ~700°C: **3.24 W**

per TE area: **3 W/cm^2**

efficiency: **5.3%**

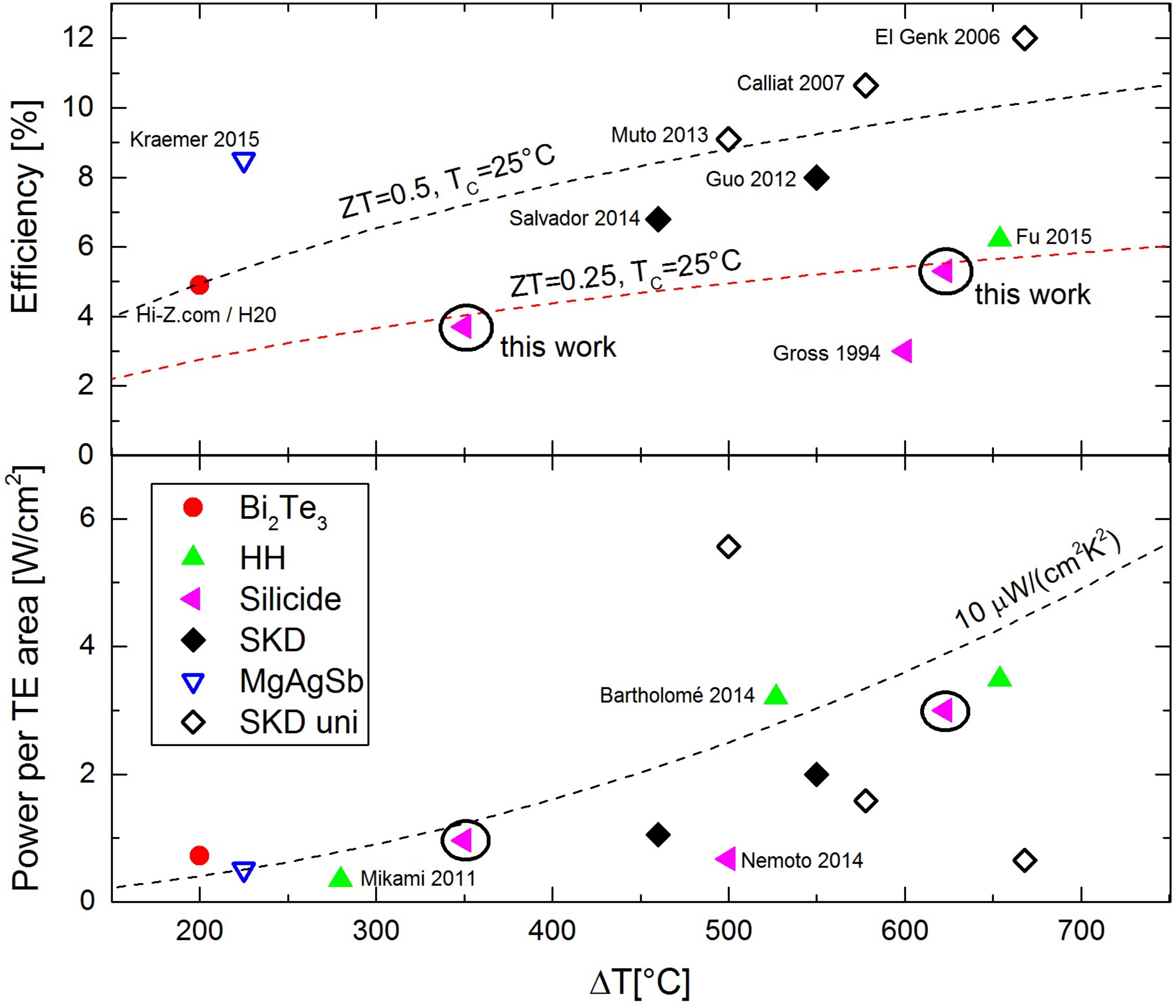


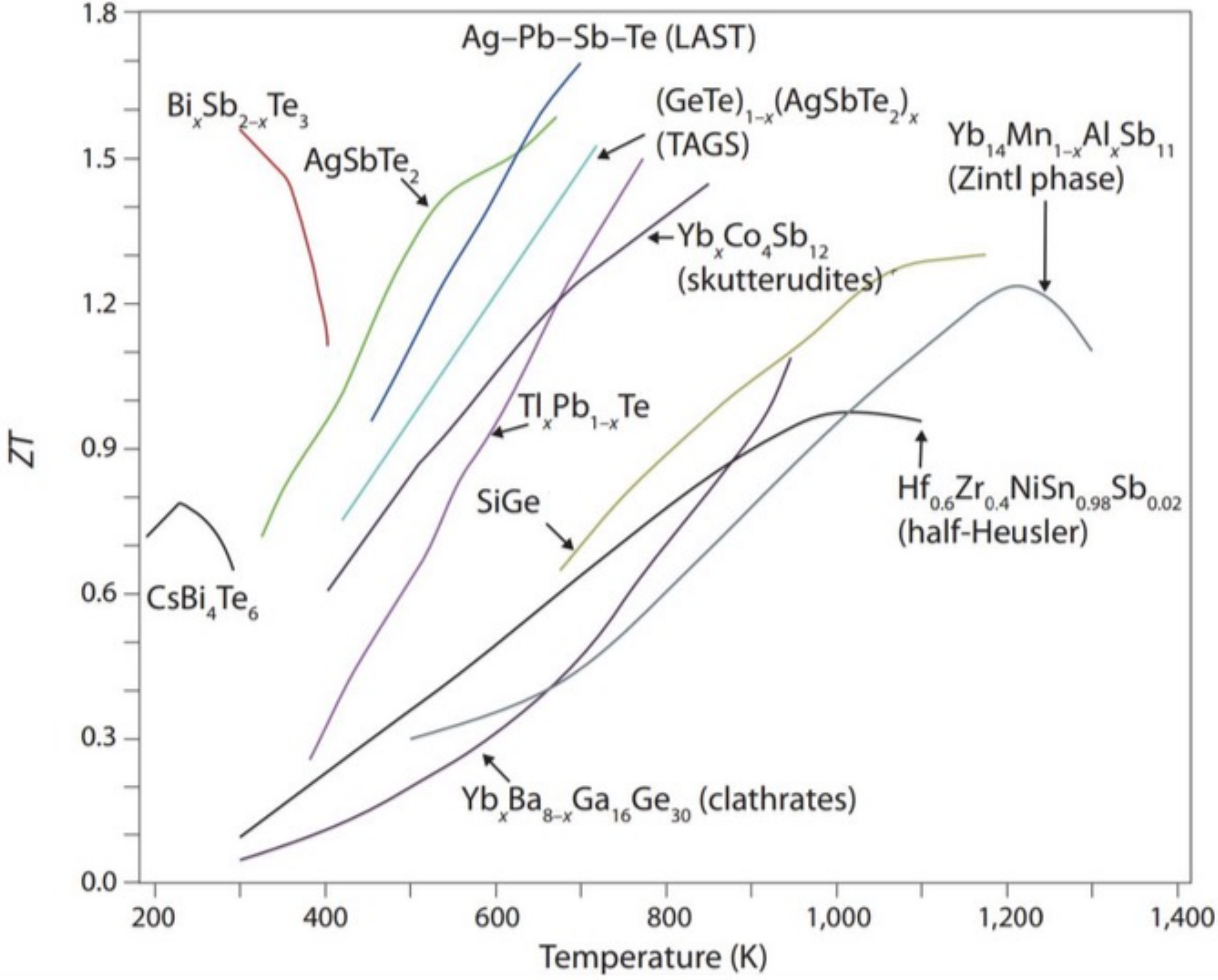


→ ~1mΩ contact resistance per leg

→ ~10-15% of total R_i

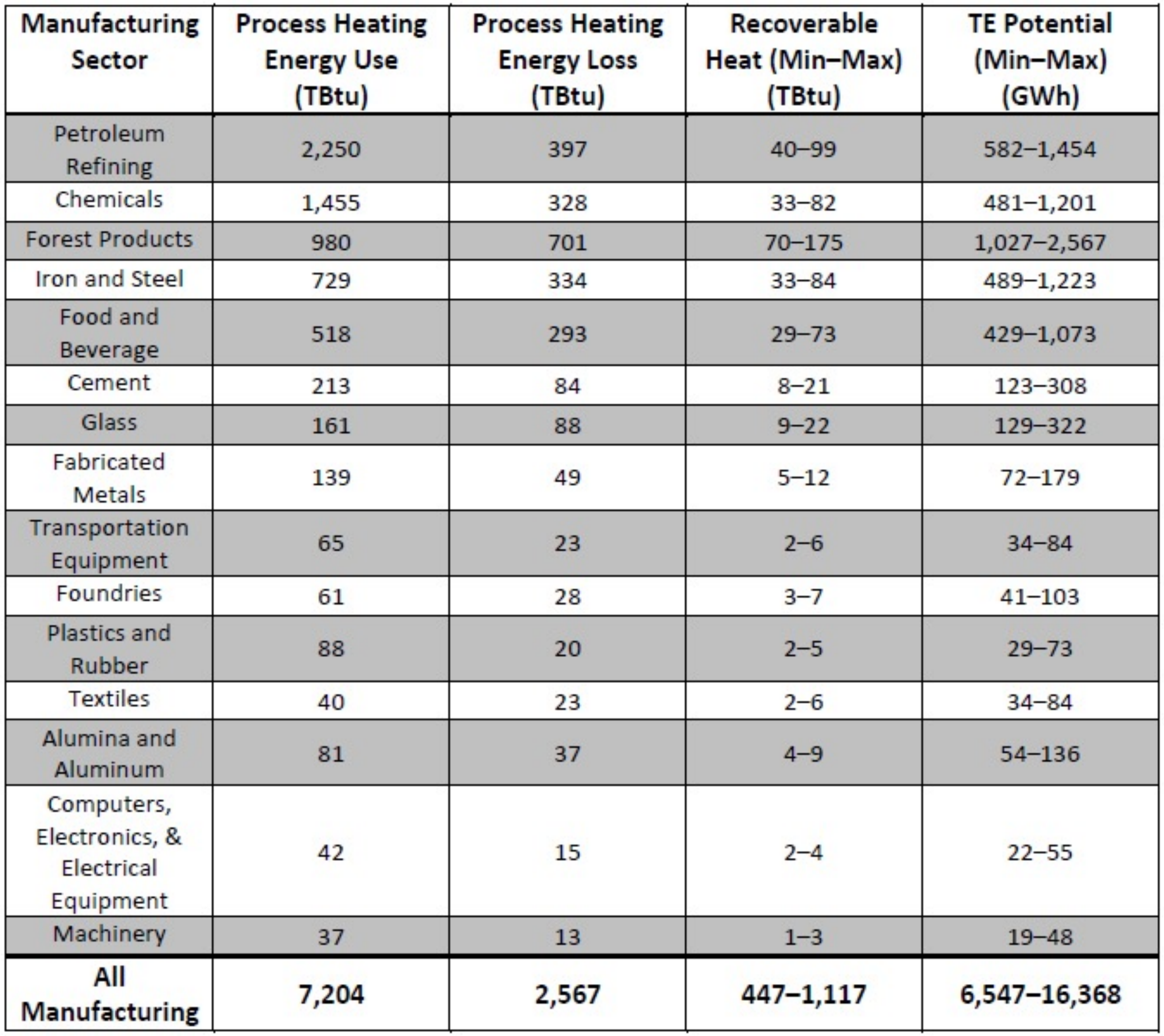
Comparison among TE materials





1.8
1.5
1.2
0.9
0.6
0.3
0.0
ZT
200
400
600
800
1,000
1,200
1,400
Temperature (K)
Ag–Pb–Sb–Te (LAST)
$Bi_xSb_{2-x}Te_3$
$AgSbTe_2$
$(GeTe)_{1-x}(AgSbTe_2)_x$
(TAGS)
$Yb_{14}Mn_{1-x}Al_xSb_{11}$
(Zintl phase)
$Yb_xCo_4Sb_{12}$
(skutterudites)
$Tl_xPb_{1-x}Te$
SiGe
$Hf_{0.6}Zr_{0.4}NiSn_{0.98}Sb_{0.02}$
(half-Heusler)
$CsBi_4Te_6$
$Yb_xBa_{8-x}Ga_{16}Ge_{30}$ (clathrates)

Industrial waste heat recovery

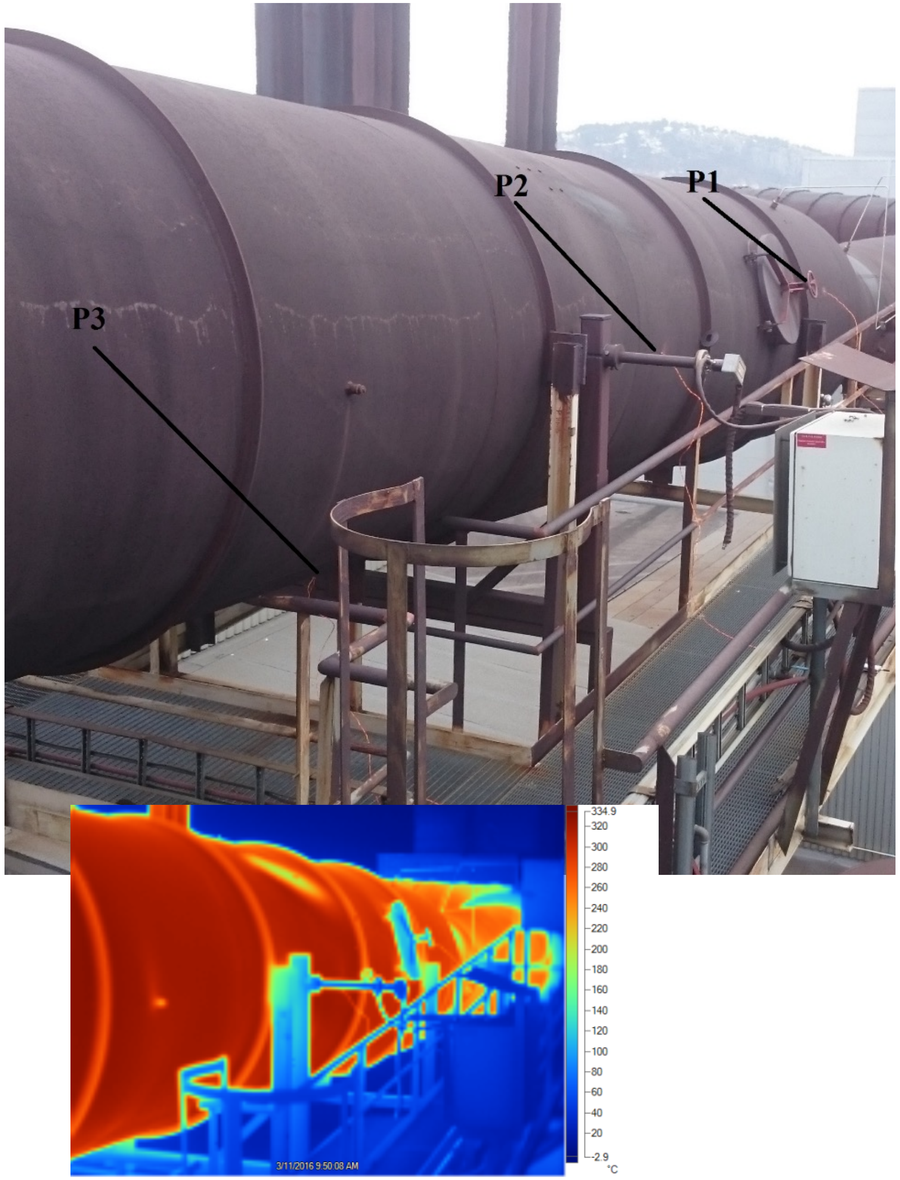


Manufacturing Sector	Process Heating Energy Use (TBtu)	Process Heating Energy Loss (TBtu)	Recoverable Heat (Min–Max) (TBtu)	TE Potential (Min–Max) (GWh)
Petroleum Refining	2,250	397	40–99	582–1,454
Chemicals	1,455	328	33–82	481–1,201
Forest Products	980	701	70–175	1,027–2,567
Iron and Steel	729	334	33–84	489–1,223
Food and Beverage	518	293	29–73	429–1,073
Cement	213	84	8–21	123–308
Glass	161	88	9–22	129–322
Fabricated Metals	139	49	5–12	72–179
Transportation Equipment	65	23	2–6	34–84
Foundries	61	28	3–7	41–103
Plastics and Rubber	88	20	2–5	29–73
Textiles	40	23	2–6	34–84
Alumina and Aluminum	81	37	4–9	54–136
Computers, Electronics, & Electrical Equipment	42	15	2–4	22–55
Machinery	37	13	1–3	19–48
All Manufacturing	**7,204**	**2,567**	**447–1,117**	**6,547–16,368**

Thermoelectric Materials, Devices and Systems: 1 -Technology Assessment (US potential)

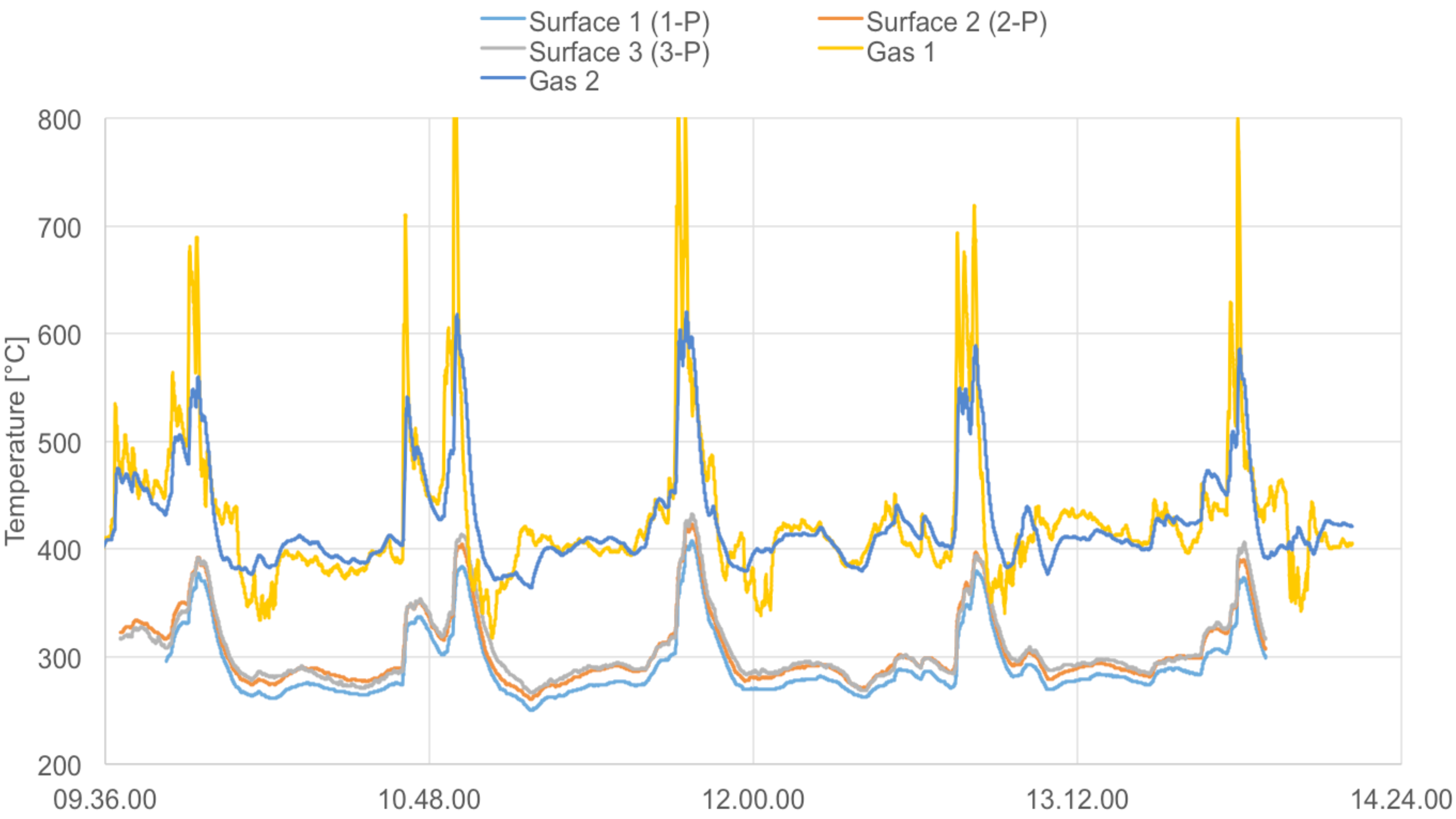
Exhaust pipe site

Location 1



Location 2

Location 1

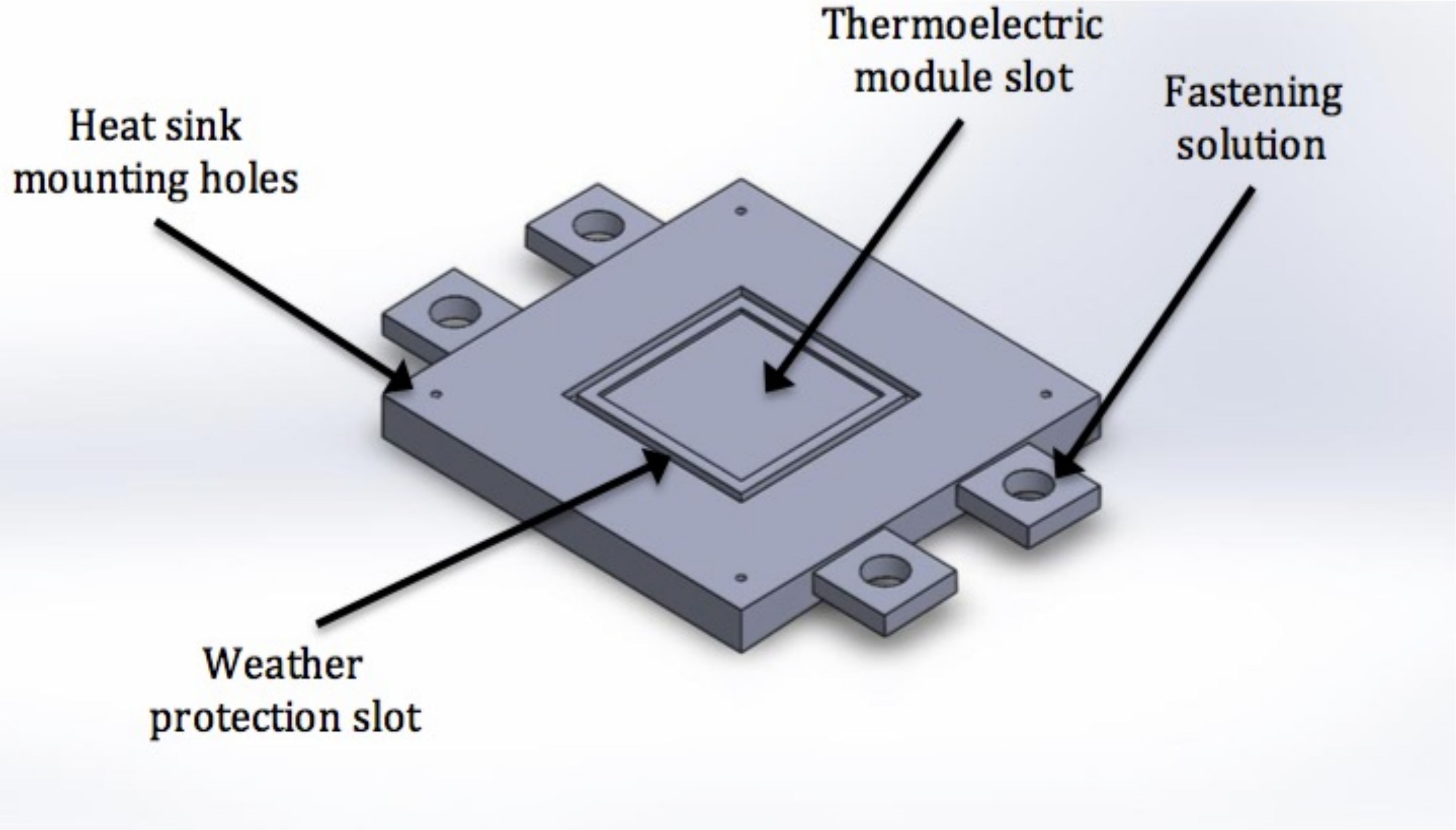

Surface 1 (1-P)
Surface 2 (2-P)
Surface 3 (3-P)
Gas 1
Gas 2
Temperature [°C]
800
700
600
500
400
300
200
09.36.00
10.48.00
12.00.00
13.12.00
14.24.00

Design conditions

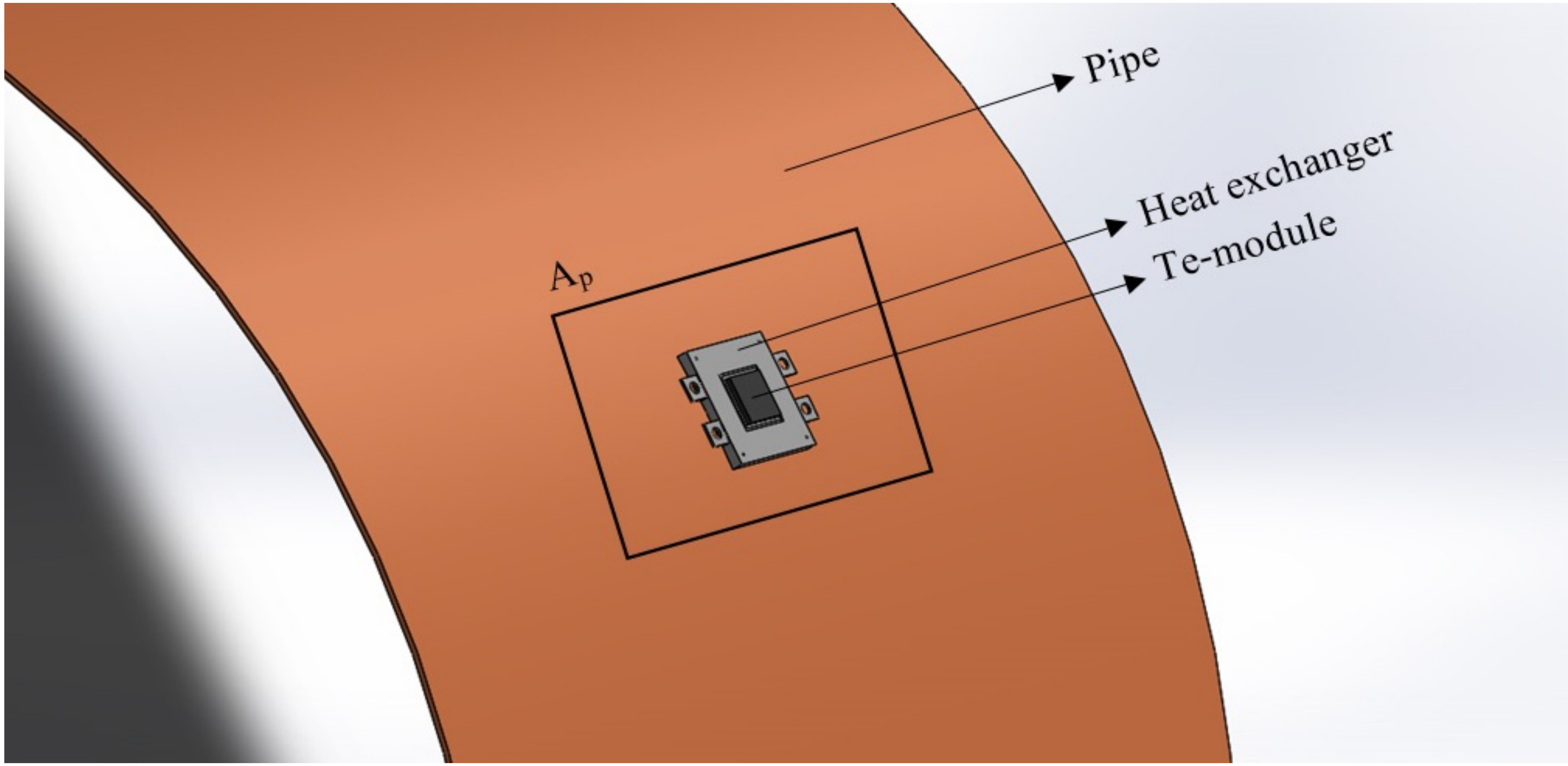
Location 1	
Parameter	Value
T_{hot}	301.6°C
$T_{amb,pipe}$	29.97°C
T_{amb}	10°C
Q	12.1 kW/m^2
u	Windless
Q_{TE}	120 W
$T_{cold,TE}$	50°C
ΔT	251.6°C
$T_{hot,silicide}$	550°C
L_{leg}	2 mm

Location 2	
Parameter	Value
T_{hot}	223.24°C
$T_{amb,pipe}$	27.18°C
T_{amb}	10°C
Q	7 kW/m^2
u	Windless
Q_{TE}	70 W
$T_{cold,TE}$	50°C
ΔT	173.24°C
$T_{hot,silicide}$	550°C
L_{leg}	2 mm

Heat exchanger

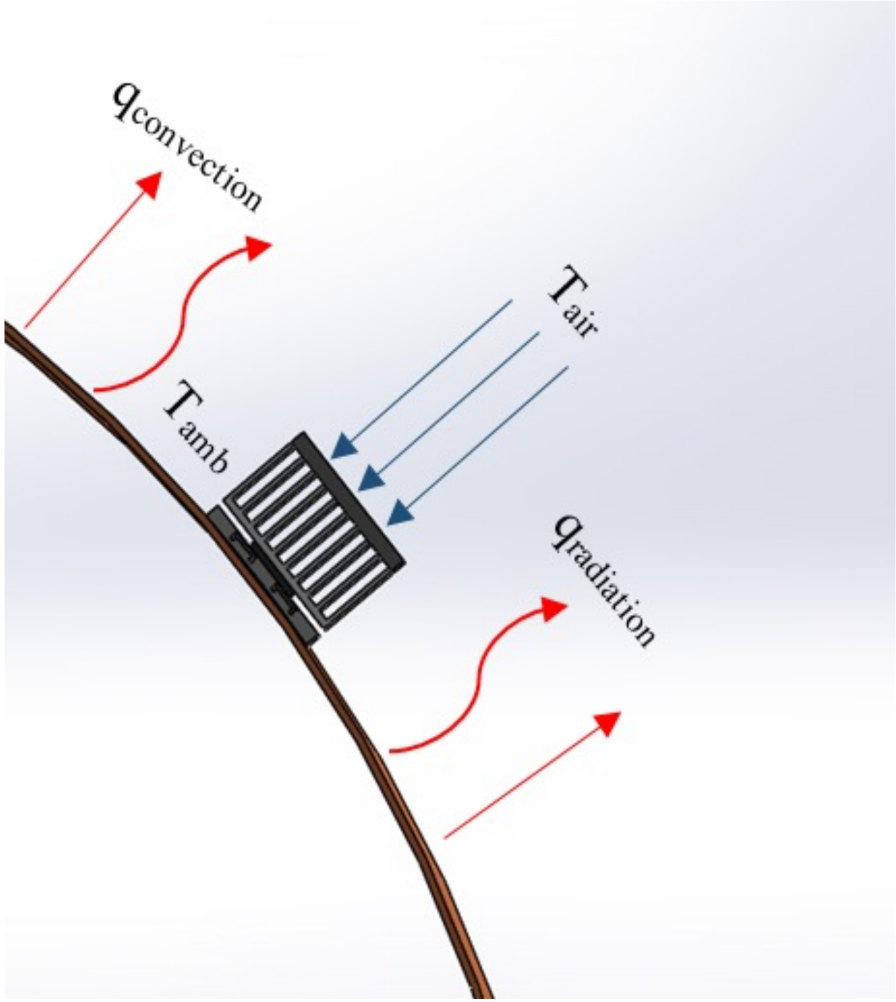


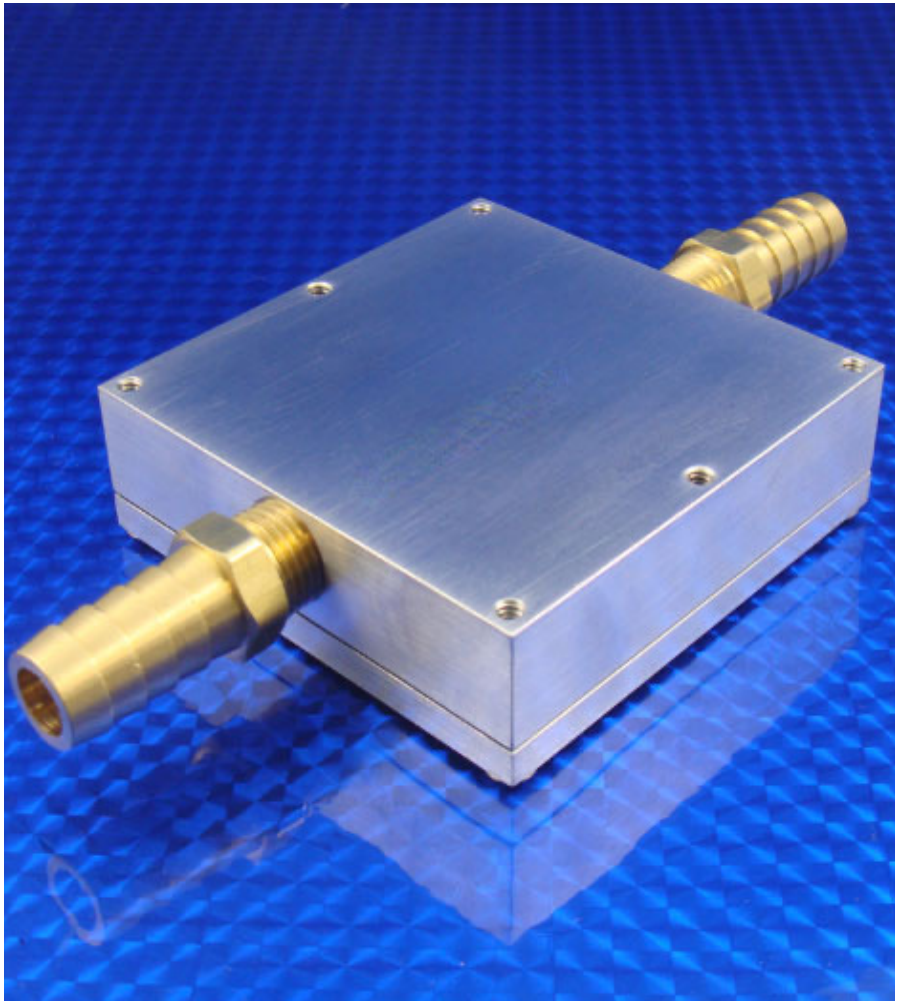
Heat transfer area



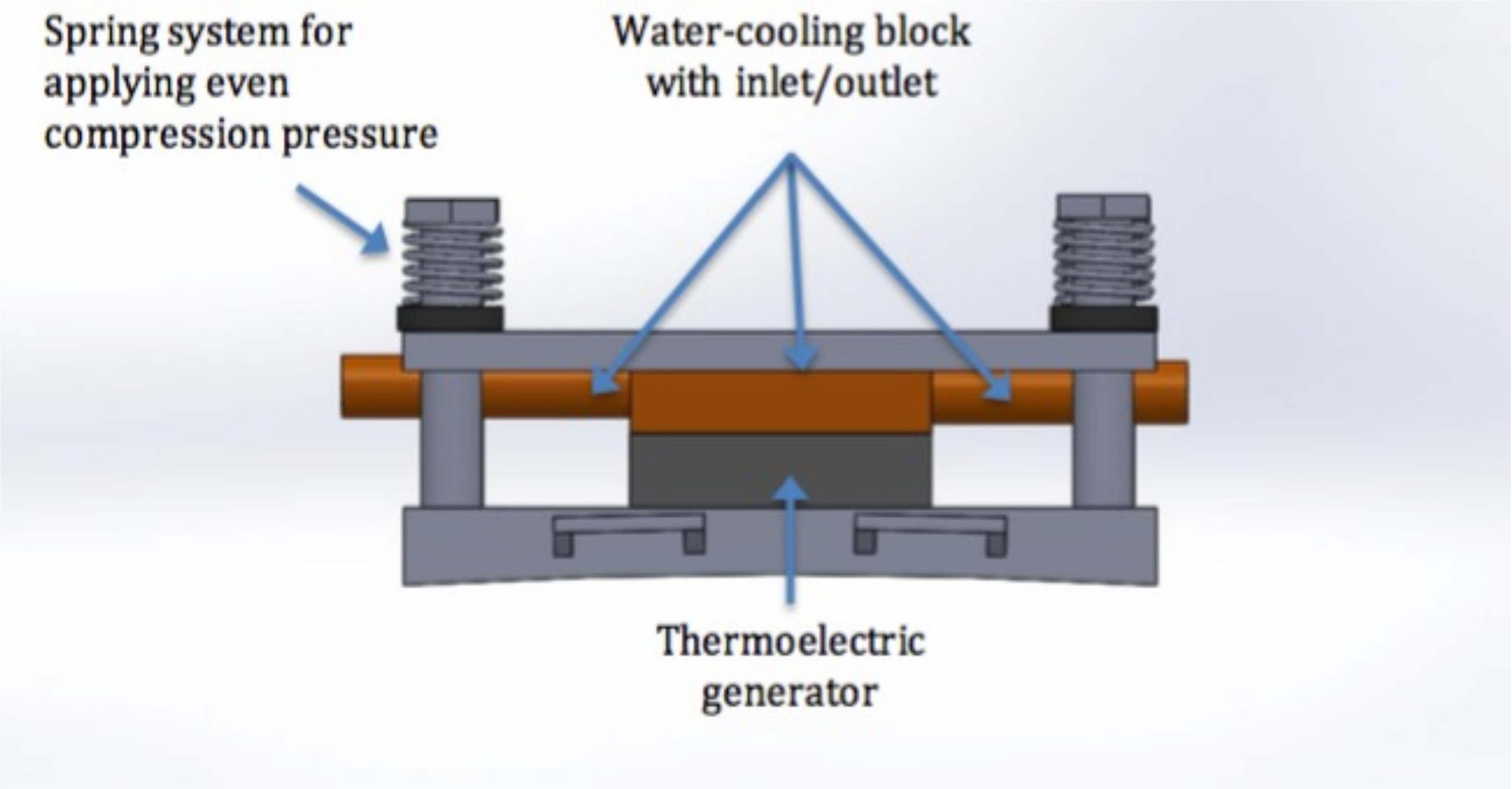
$$A_p = \frac{Q_{TE} + q_{hex} + q_{hex,rad} - h_{pipe}A_{hex}\Delta T - \varepsilon\sigma A_{hex}{T_h}^4 + \varepsilon\sigma A_{hex}{T_{amb}}^4}{Q - h_{pipe}\Delta T - \varepsilon\sigma {T_h}^4 + \varepsilon\sigma {T_{amb}}^4}$$

Heat sink



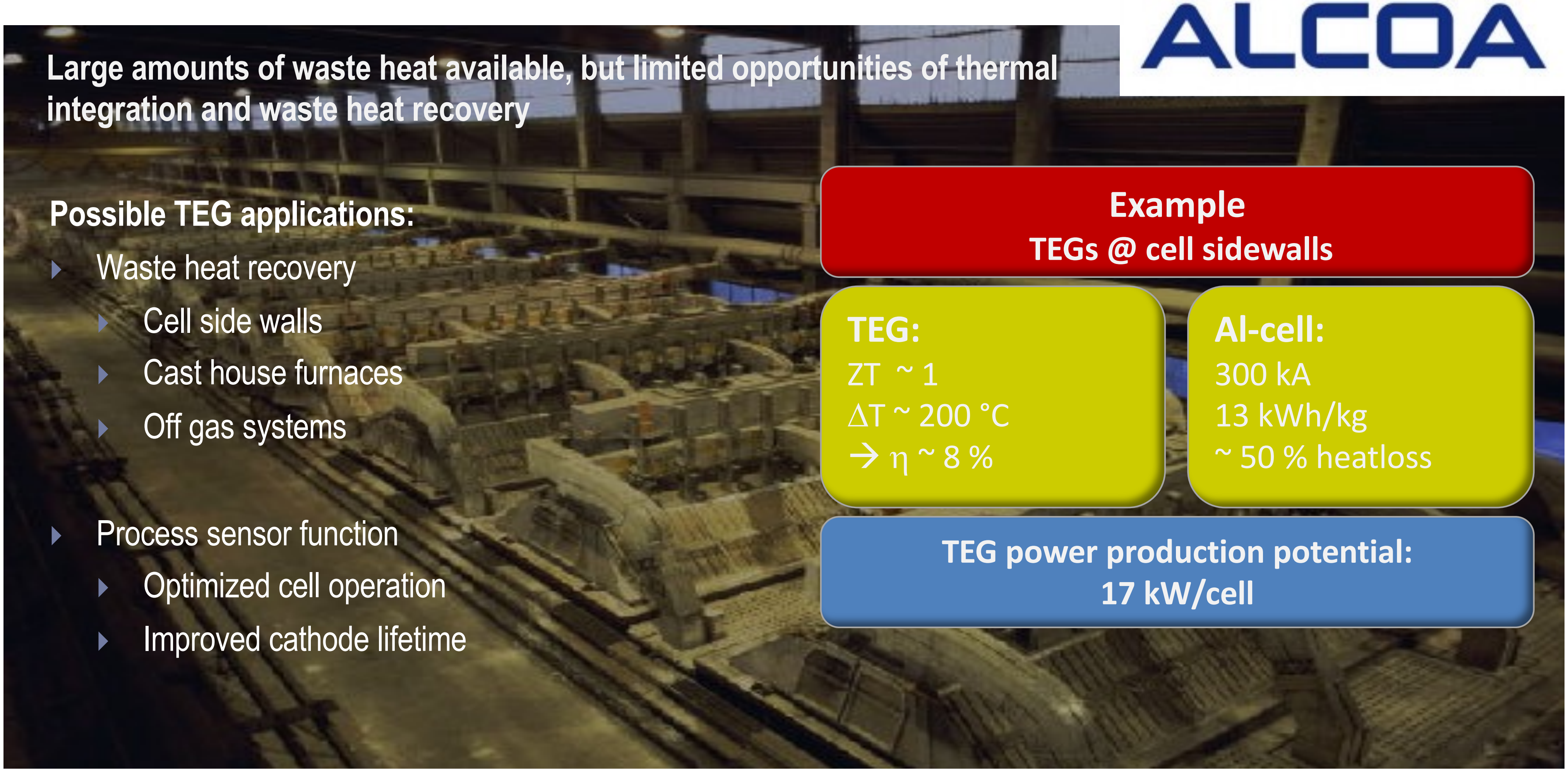


Heat sink


Spring system for applying even compression pressure
Water-cooling block with inlet/outlet
Thermoelectric generator

Example - TEG in primary Al industry

ALCOA



Large amounts of waste heat available, but limited opportunities of thermal integration and waste heat recovery

Possible TEG applications:

- Waste heat recovery
  - Cell side walls
  - Cast house furnaces
  - Off gas systems

- Process sensor function
  - Optimized cell operation
  - Improved cathode lifetime

Example
TEGs @ cell sidewalls

TEG:
ZT ~ 1
ΔT ~ 200 °C
→ η ~ 8 %

Al-cell:
300 kA
13 kWh/kg
~ 50 % heatloss

TEG power production potential:
17 kW/cell

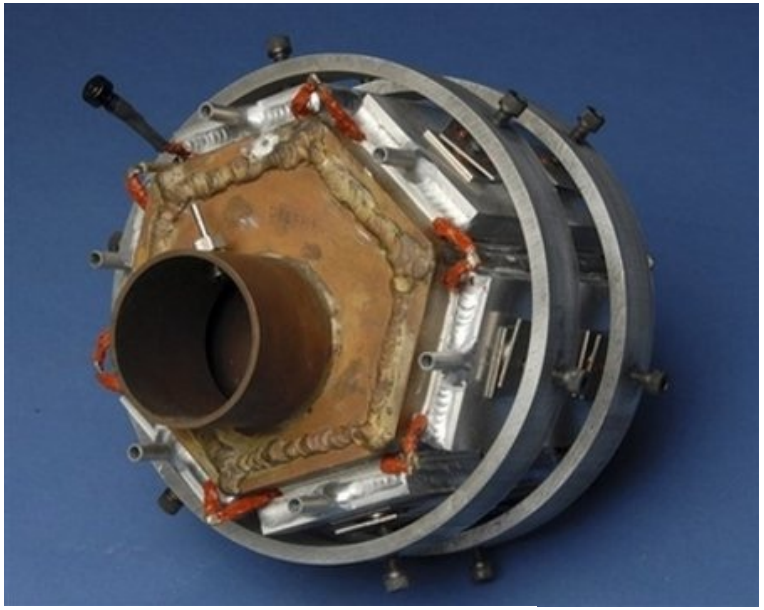
TEGs at aluminum cell sidewalls

Concept

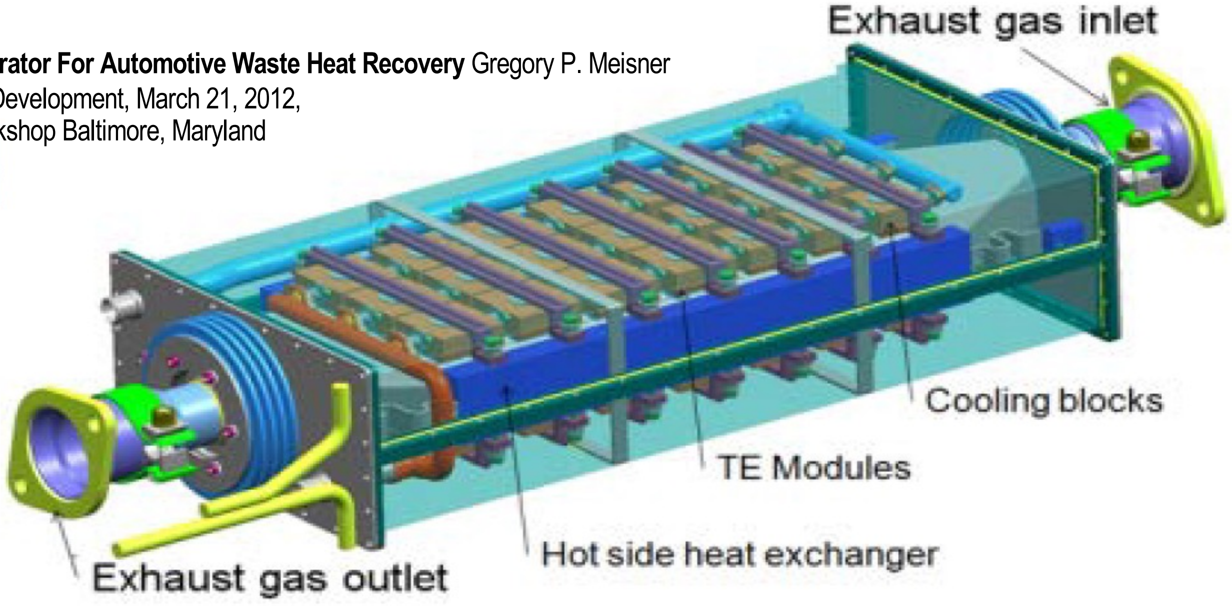
- **TEG panels**
  - Passive (no fluids/moving parts)
  - Modular (size and location flexible)

- **TEG panels on cell sidewalls**
  - Size adapted to cell design
  - Location adapted to cell design
  - Energy recovery
  - Pot status control
- **Development scenario**
  - Short term: ad-on TEG-panels on side walls of existing cell design
  - Medium term: integrate TEG-panels in side walls of test cell design
  - Long term: integrate TEG-panels in side walls of standard cell design

Thermoelectric waste heat recovery on vehicles



Skutterudite Thermoelectric Generator For Automotive Waste Heat Recovery Gregory P. Meisner
General Motors Global Research & Development, March 21, 2012,
3rd Thermoelectric Applications Workshop Baltimore, Maryland



Thermoelectric properties – closer look

Material (one leg, n or p)	Module (multiple legs, n+p)
High Seebeck coefficient: $$\alpha = \frac{dV}{dT}$$	1. Open circuit voltage: $$\boldsymbol{V_{OC}} = N_p \int_{T_C}^{T_H} \boldsymbol{\alpha_p} dT - N_n \int_{T_C}^{T_H} \boldsymbol{\alpha_n} dT$$
High Electrical conductivity: $$\sigma = n\mu e$$	2. Inner resistance: $$\boldsymbol{R_i} = N_p \int_0^l \frac{dx}{\sigma_p(T) A_p} + N_n \int_0^l \frac{dx}{\sigma_n(T) A_n} + R_{contacts}$$
Low Thermal conductivty: $$\kappa = \kappa_{el} + \kappa_{ph}$$	3. Thermal conductance: $$\boldsymbol{K} = \frac{N_p A_p \kappa_p}{l_p} + \frac{N_n A_n \kappa_n}{l_n}$$
Figure of merit (material): $$\mathbf{z} = \frac{\alpha^2\ \sigma}{\kappa}$$	4. Figure of merit (module): $$\boldsymbol{Z} = \frac{\alpha_{np}^2}{R_i K}$$

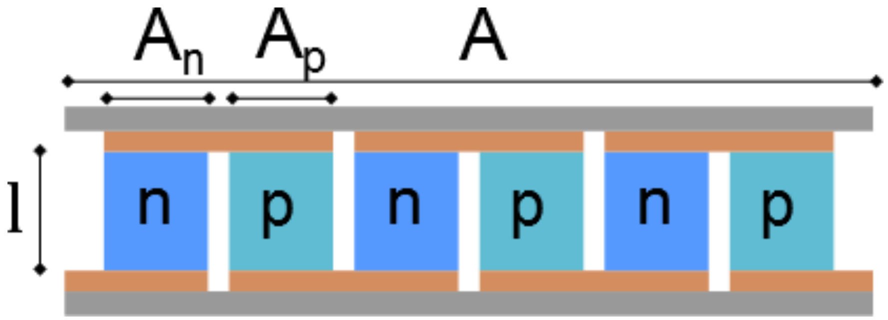
Module geometry

Heat *concentrated*: substrate area / TE area = concentration factor

cf Concentrated Solar Power (CSP)

Inverse = fill fraction (FF) = TE area / substrate area

$$FF = \frac{N(A_n + A_p)}{A}$$



Thermoelectric downsizing – height over cross sectional area important, not absolute size!

BUT: limited due to contact resistance losses and parasitic heat losses

→ **Typical leg size: 2-5 mm**

1 x 1 x 1 mm^3

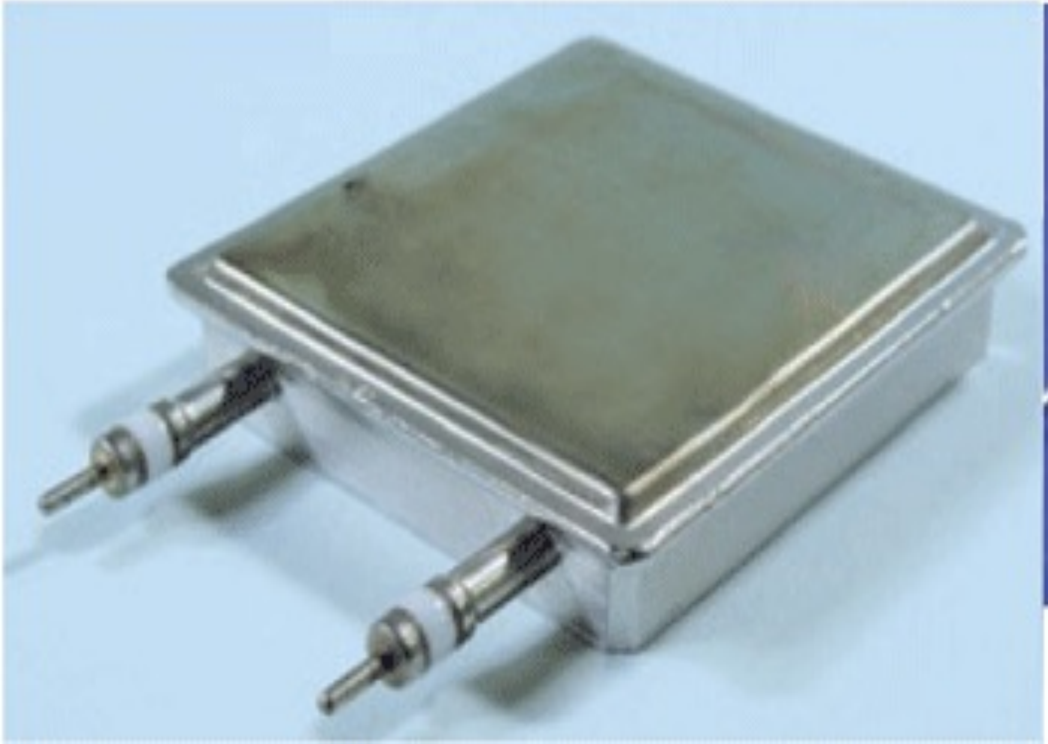
10 x 3.16 x 3.16 mm^3

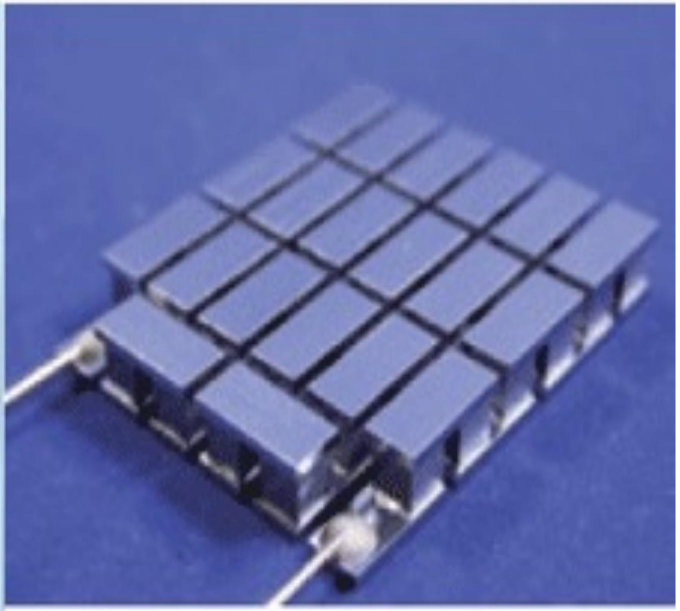
Electrical resistance (as low as possible) $\boldsymbol{R} = \rho \frac{\boldsymbol{l}}{\boldsymbol{A}}$

Thermal conductance (as low as possible) $\boldsymbol{K} = \kappa \frac{\boldsymbol{A}}{\boldsymbol{l}}$

Encapsulation

- protect TE material from corrosive atmosphere
- e.g. oxidation of SiGe above ~600°C





SiGe module
(Internal appearance)

Summary TE-module assembly

- Electrically in series:
  - N number of legs, alternating n- and p-type TE material
  - Open circuit voltage, V_{OC}, adds up seebeck voltage over each leg
  - Inner resistance, R_i, adds up resistance of each leg + contact resistance
- Thermally in parallel:
  - Each of N legs experience same ΔT
- I-V curves:
  - Power scales with ΔT^2
  - Max power at **load matching conditions, i.e. $R_{load} = R_i$**
- Geometry (length, area, fill fraction) used to optimize module for given heat source (W/m^2 and temp)
  - Compromise between low R_i and high K
  - Ex: low $\dot{Q}$ → low K → large l/A → high R_i → low P
  - Ex: high $\dot{Q}$ → high K → small l/A → low R_i → high P
- Electrical and thermal contact resistance
  - Too high electrical contact resistance → high Ri → low P
  - Too high thermal contact resistance → low K → lower ΔT → low V_{OC} → low P

$$\boxed{V_{OC} \approx N\alpha_{np}(T_H - T_C)}$$

$$\boxed{R_i \approx N\frac{l}{\sigma_{np}A_{np}}}$$

$$\boxed{K \approx \kappa_{np}\frac{NA_{np}}{l}}$$

$$\boxed{P_{max} = \frac{{V_{OC}}^2}{4R_i}}$$

$$\boxed{\eta = \frac{P}{\dot{Q}}}$$

Pro’s / Con’s of thermoelectricity

- Direct conversion; no intermediate fluid
- Reliable, durable

- Low efficiency
- Complicated assembly (cost, abundance, toxicity, shaping, CET, mec. properties of elements/compounds)