EPSRC Thermoelectric Network Workshop
26Feb., 2014 @ Manchester, UK

Exploiting Oxide Thermoelectrics

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Ikeda, Osaka, Japan

The 32nd International Conference on Thermoelectrics

30th June – 4th July in Kobe

Participant: 745

Oral: 207

Poster: 350

Country	Number
Japan	303
China	65
United States of America	54
Republic Korea	51
Germany	41
Taiwan	26
France	21
United Kingdom of Great Britain and Northern Irelar	19
Sweden	14
Thailand	13

Oil deposit

Loch Ness

How many “cups of Loch Ness ?

a) 2.8 b) 28 c) 280 d) More

Water volume: **7.5×10^9 m^3**

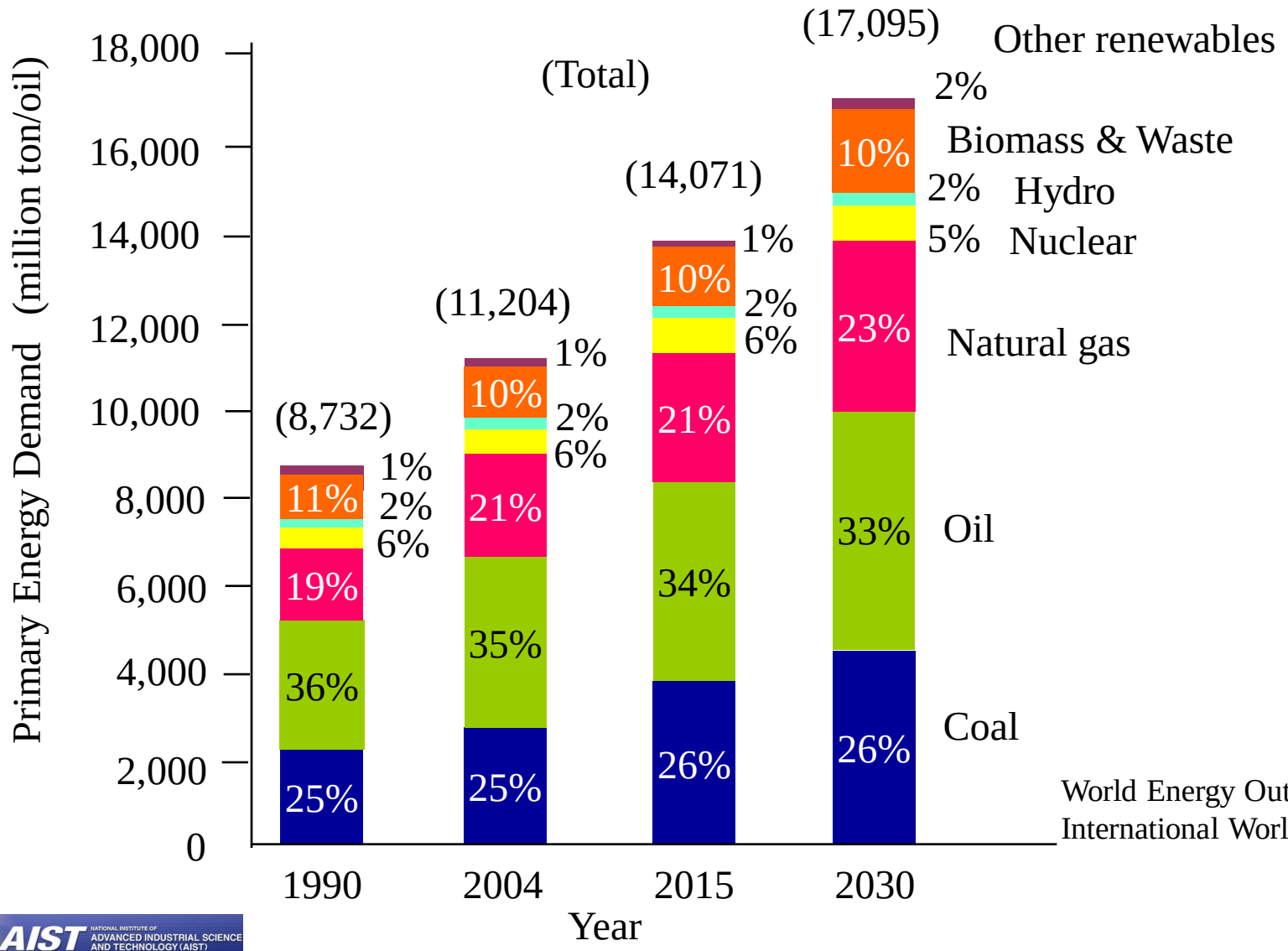
$2.07 \times 10^{11} / 7.5 \times 10^9$ = **27.6** cups of Loch Ness

Consumption : 3.0×10^{10} barrel/year = 4.77×10^9 m^3/year

Depletion: ~43 years

Energy Consumption

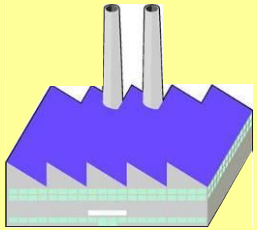
World Primary Energy Demand



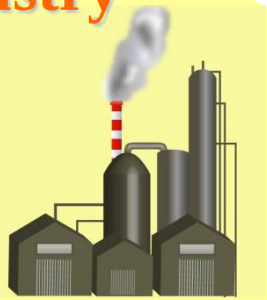
World Energy Outlook 2006 Edition, International World Energy, 2006

Waste heat

Industry



Factory



Incinerator

Transport

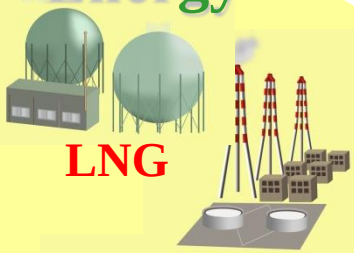
Ship

Diesel train

Automobile

Energy

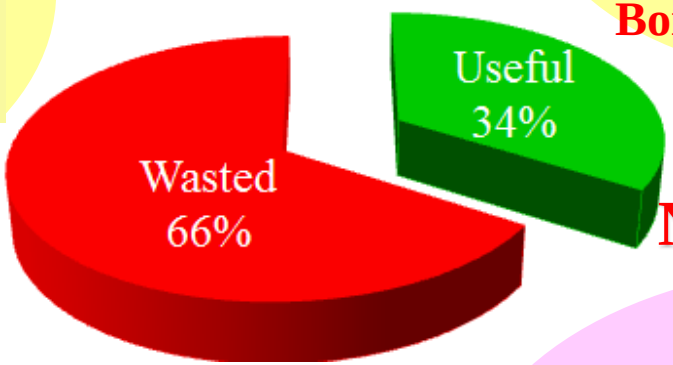
Boiler



LNG

Thermal power plant

Waste heat



New Energy

Geothermal

Solar

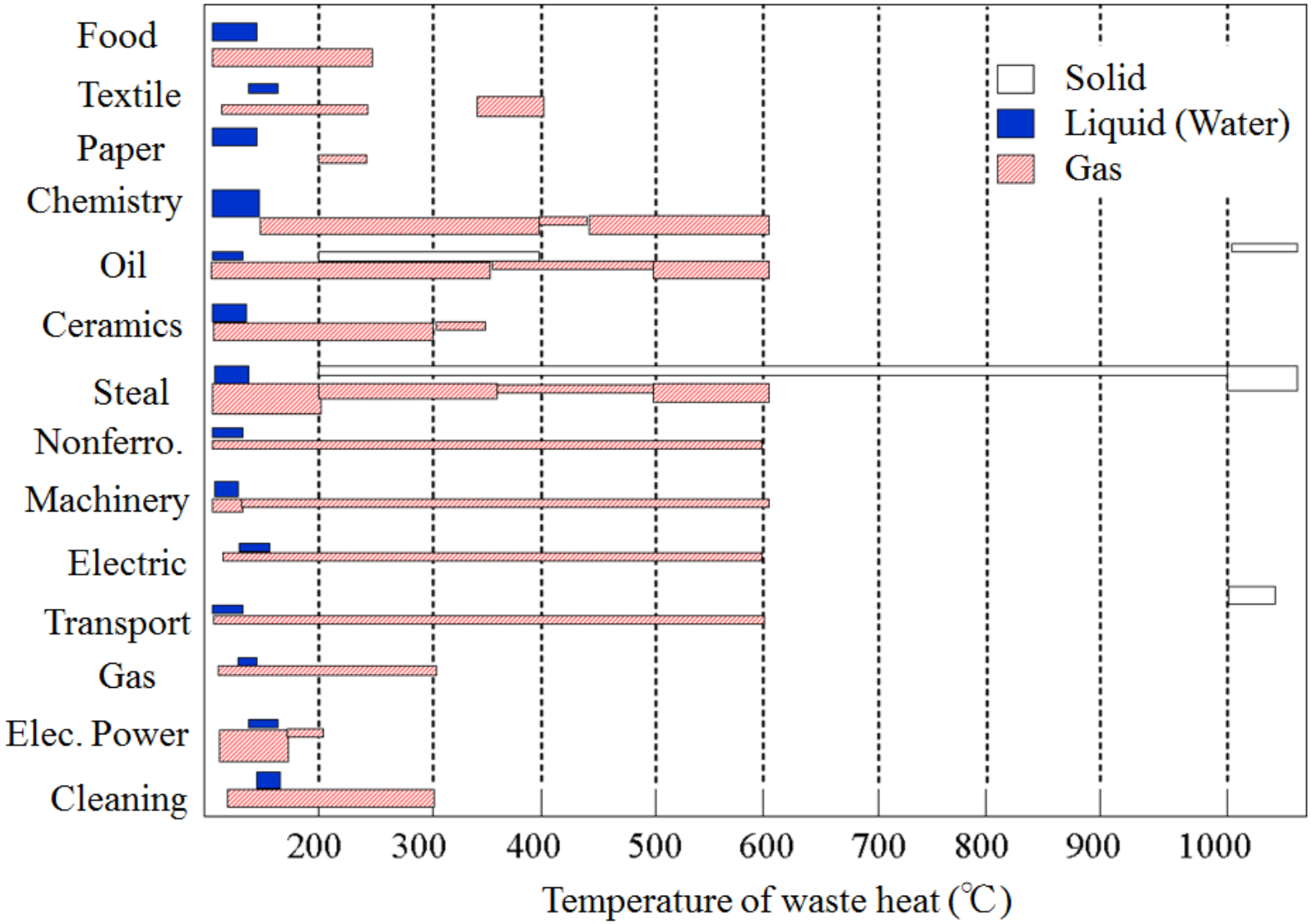
Biomass

Thermoelectric conversion

Electrical energy

M. Hirata, *Syou Enerugi Ron* (Ohmu Sha), p. 37, 1994.

Waste heat from industry

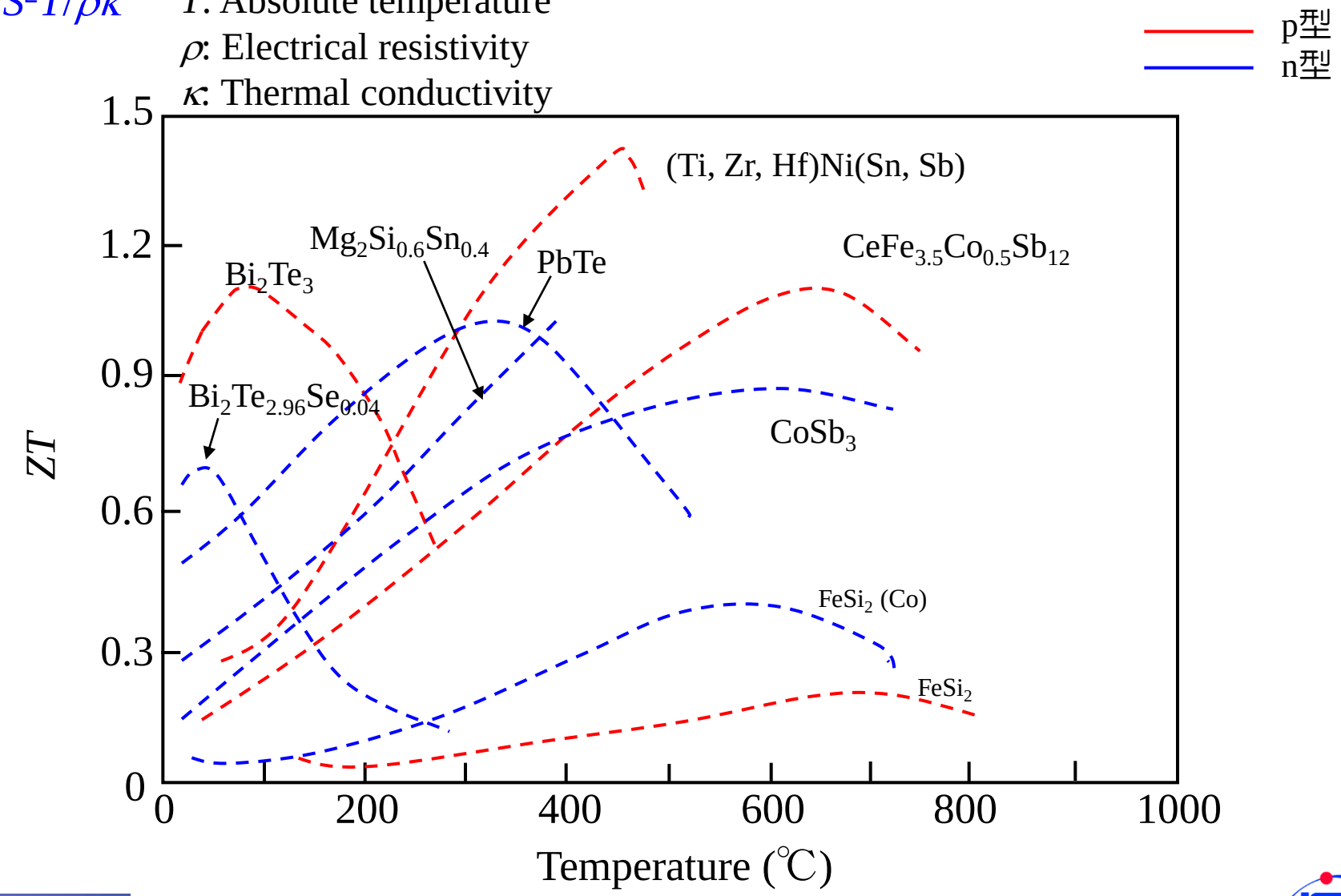


http://www.eccj.or.jp/diffusion/04/diffusion.pdf.

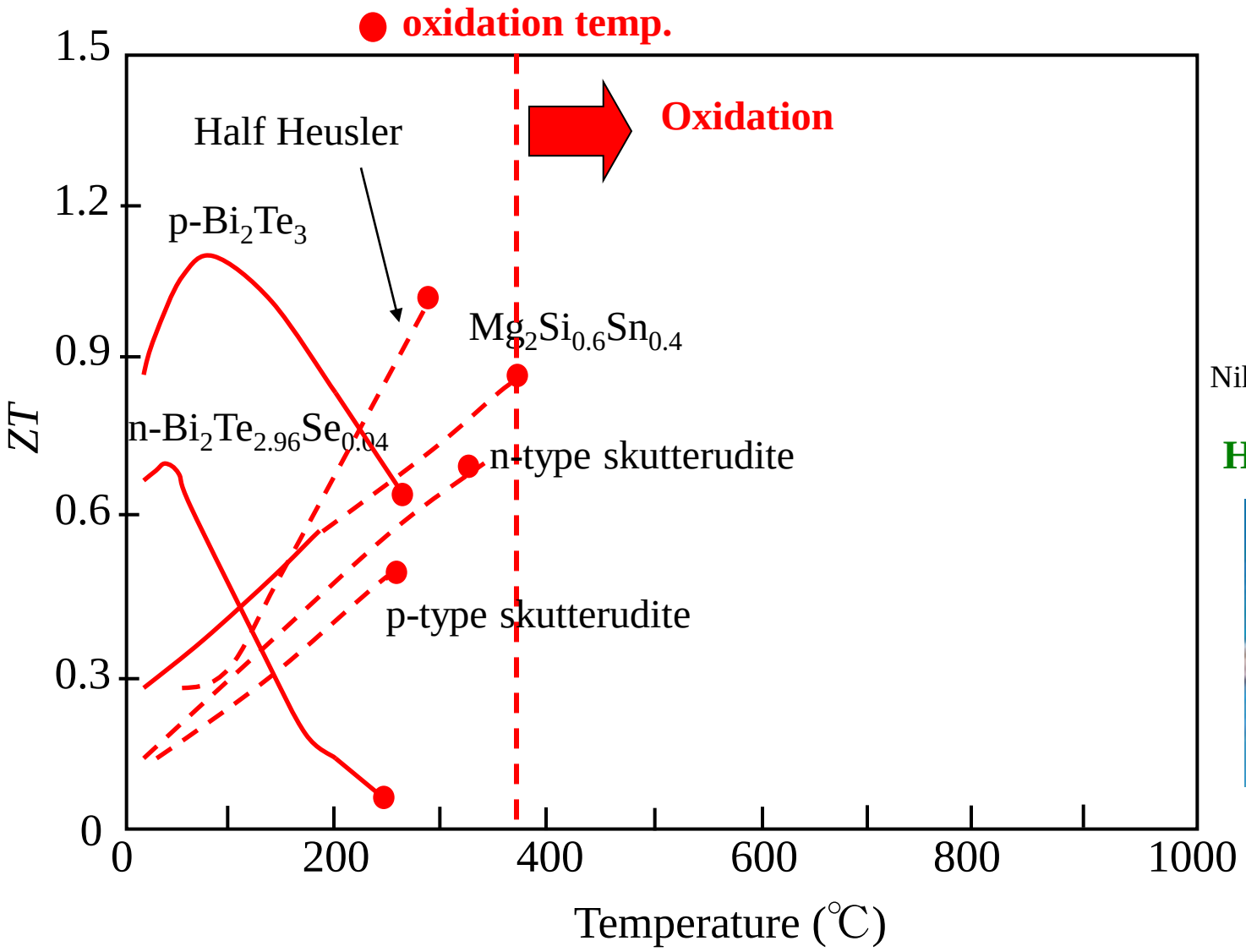
Thermoelectric materials

$ZT = S^2T/\rho\kappa$

S: Seebeck coefficient
T: Absolute temperature
ρ: Electrical resistivity
κ: Thermal conductivity



TE materials in air



Skutterudite module

SHOWA DENKO

Nikkei Electronics 2010. 3. 8

Half Heusler module

TOSHIBA

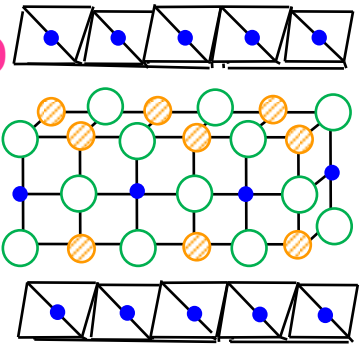
Seal in inert gas

CoO_2 layered compounds

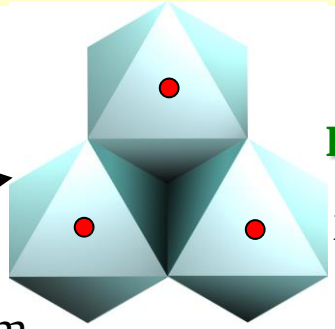
$Ca_3Co_4O_9$ (Co-349)
$(Ca_2CoO_3)_xCoO_2$

CoO_2 layer (Conducting)

Rock-salt layer (Insulating)



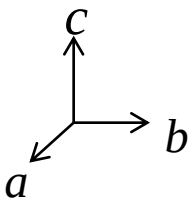
~1.1 nm



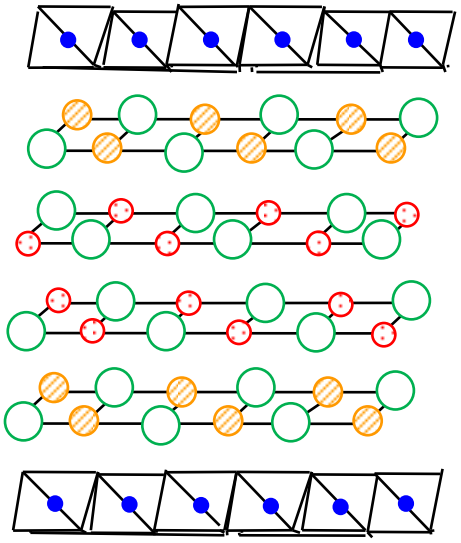
misfit structure

x: irrational number

A. C. Masset, et al., Phys. Rev. B, **62**, 166 (2000).
Y. Miyazaki, et al., Jpn. J. Appl. Phys. **39**, L531 (2000).
H. Leligny, et al., Acta Cryst., **B 56**, 173 (2000).

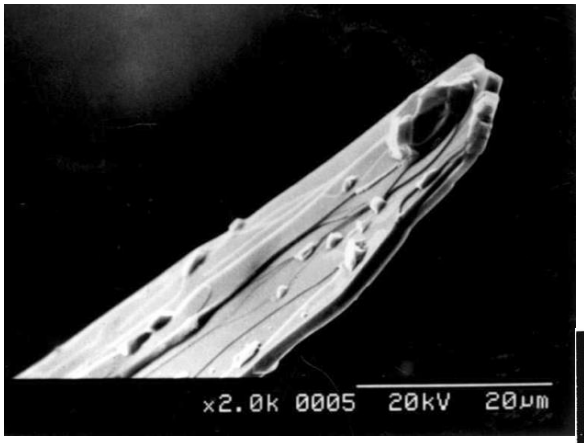


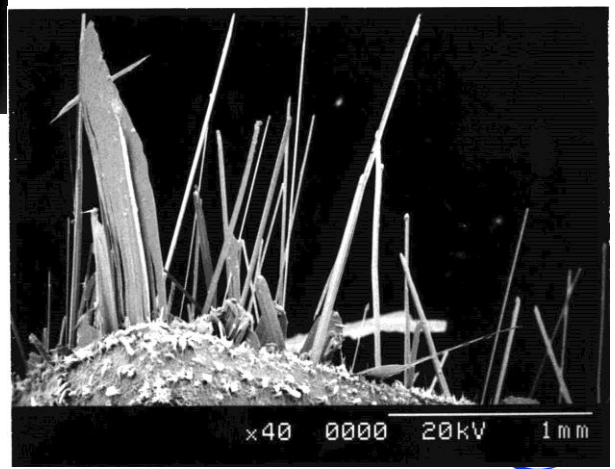
$Bi_2Sr_2Co_2O_9$ (BC-222)
$(Bi_2Sr_sO_4)_xCoO_2$



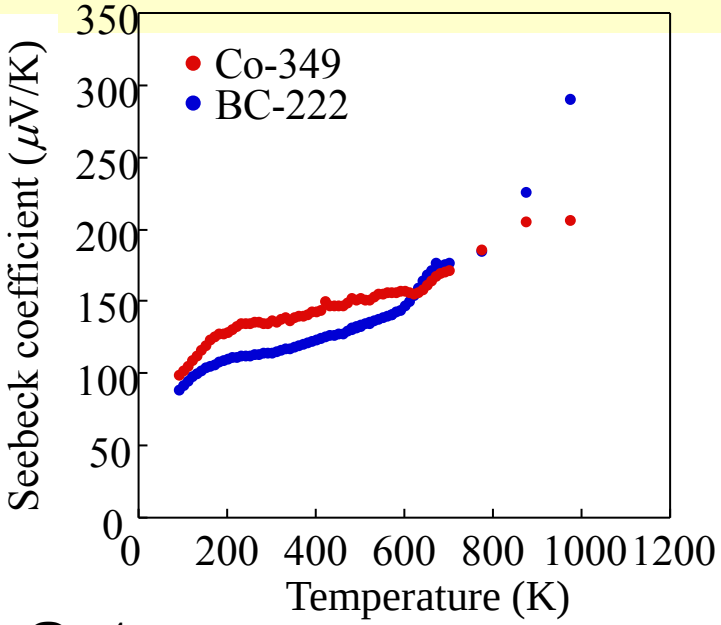
~1.5 nm

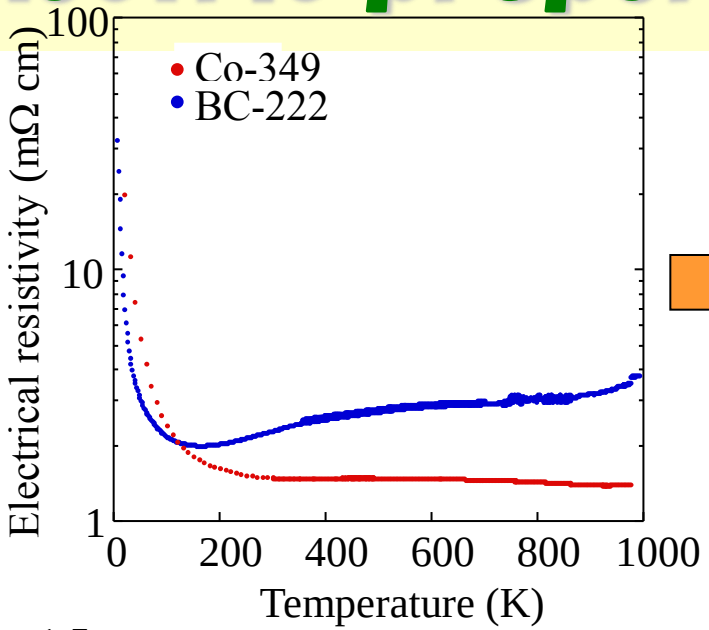
● Co
Ca, Sr
Bi
○ O



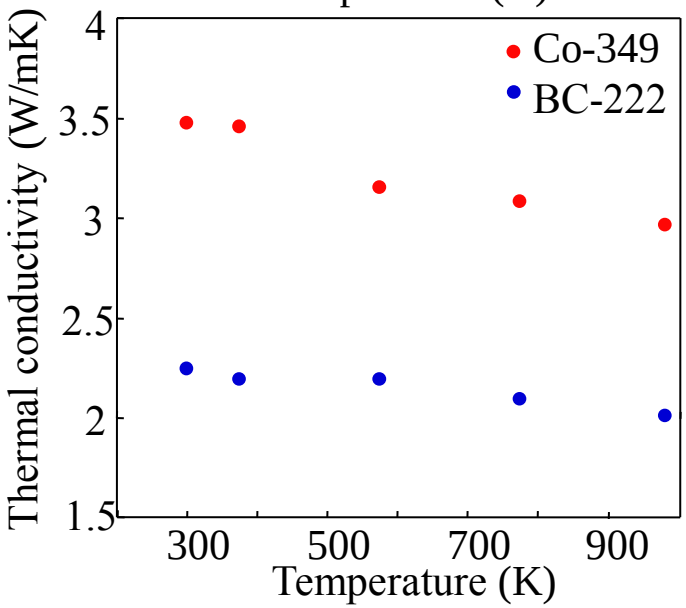


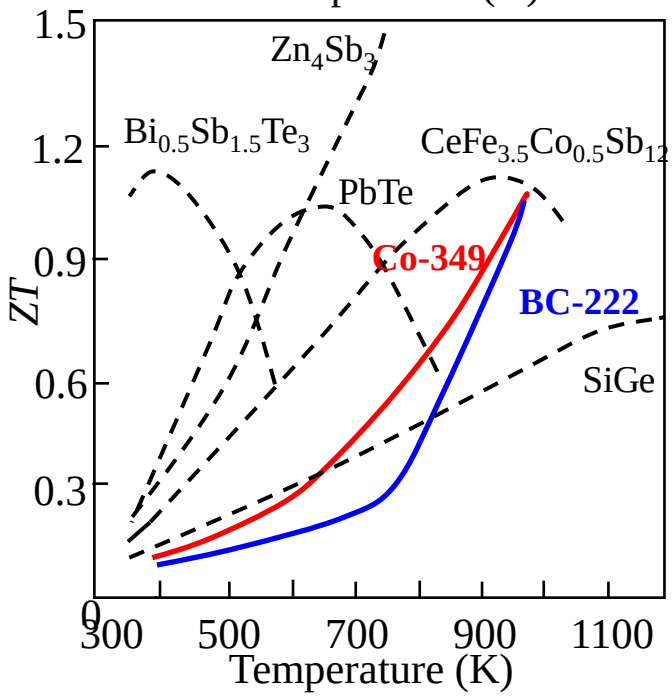
Thermoelectric property





Strongly correlated electron system





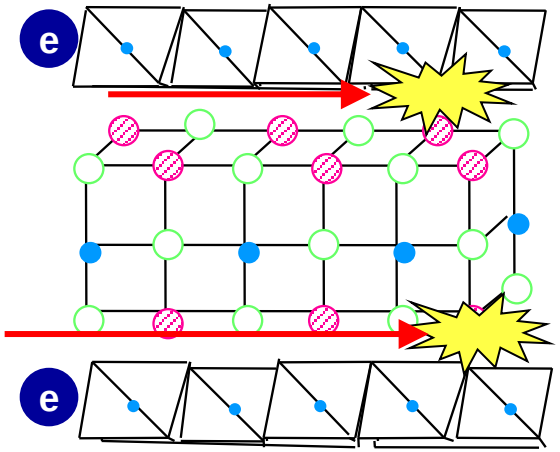
Nanoblock integlation

Thermoelectrics ・・・

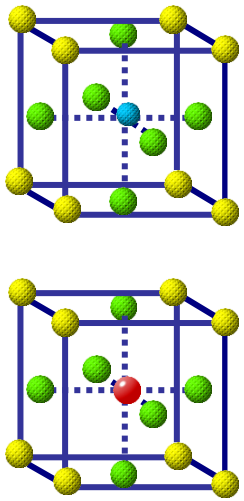
Combined function of heat and electrics

“Division of functions”

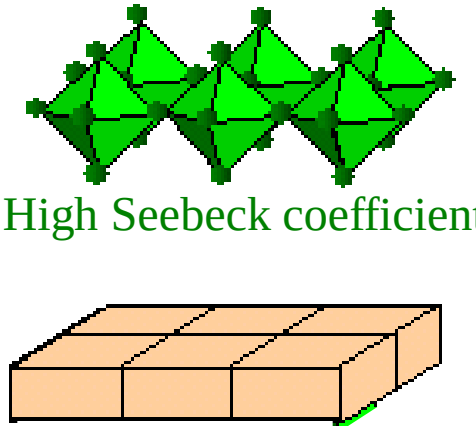
Lattice = smallest unit for functions



“Lattice”



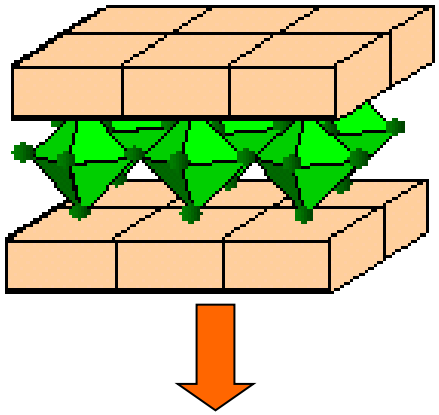
“Nanoblock”



High Seebeck coefficient

Low thermal conductivity

“Hybrid-crystal”

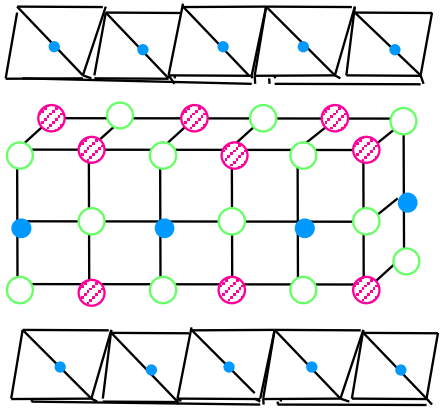


Good TE material

Thermoelectric oxides

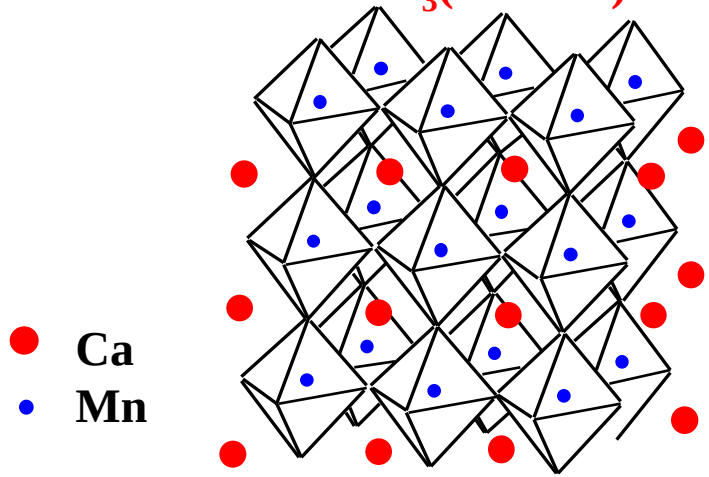
p-type

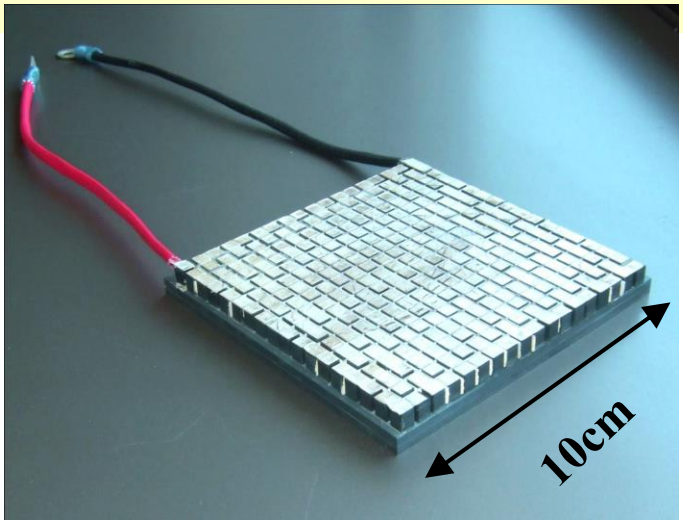
$Ca_3Co_4O_9$ (Co-349)

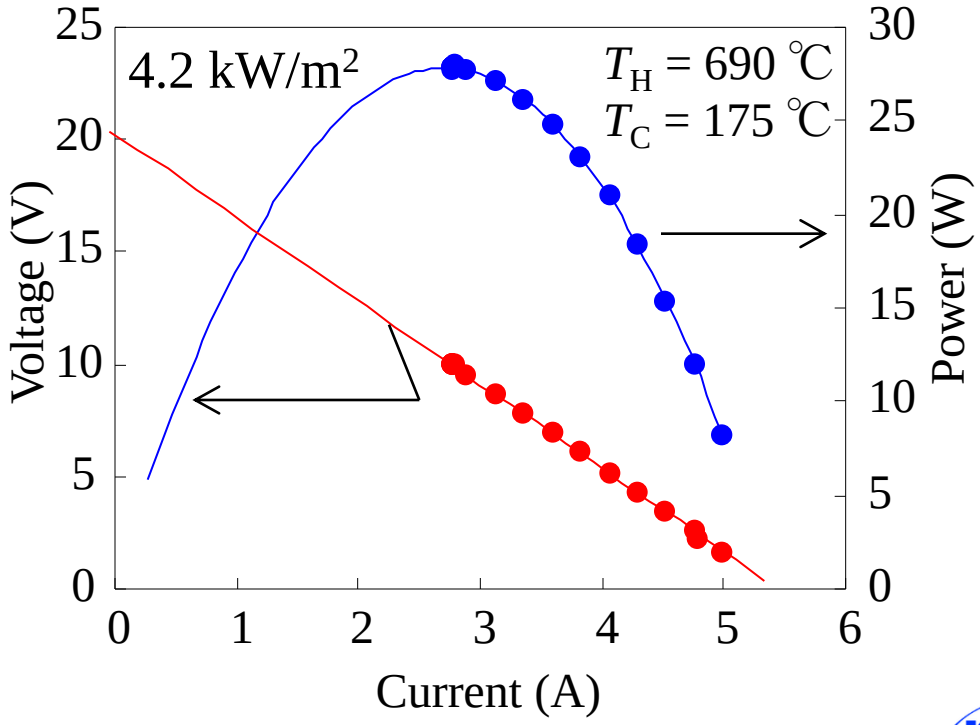


n-type

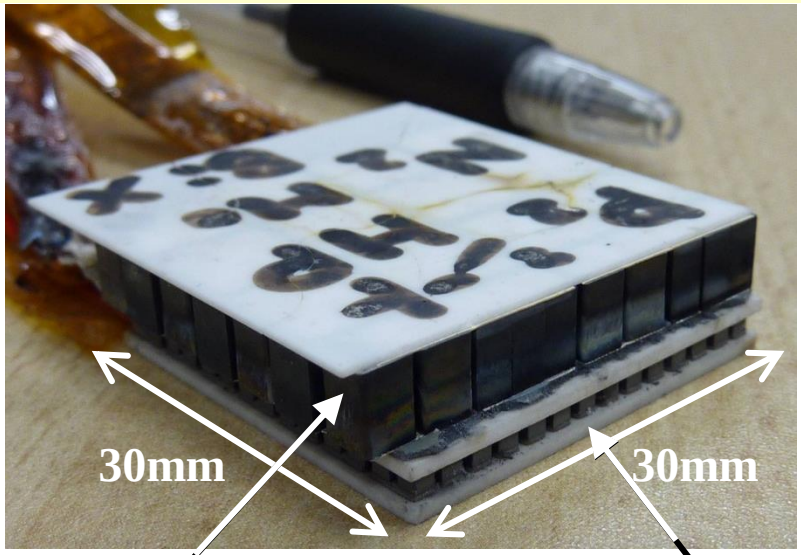
$CaMnO_3$(Mn-113)

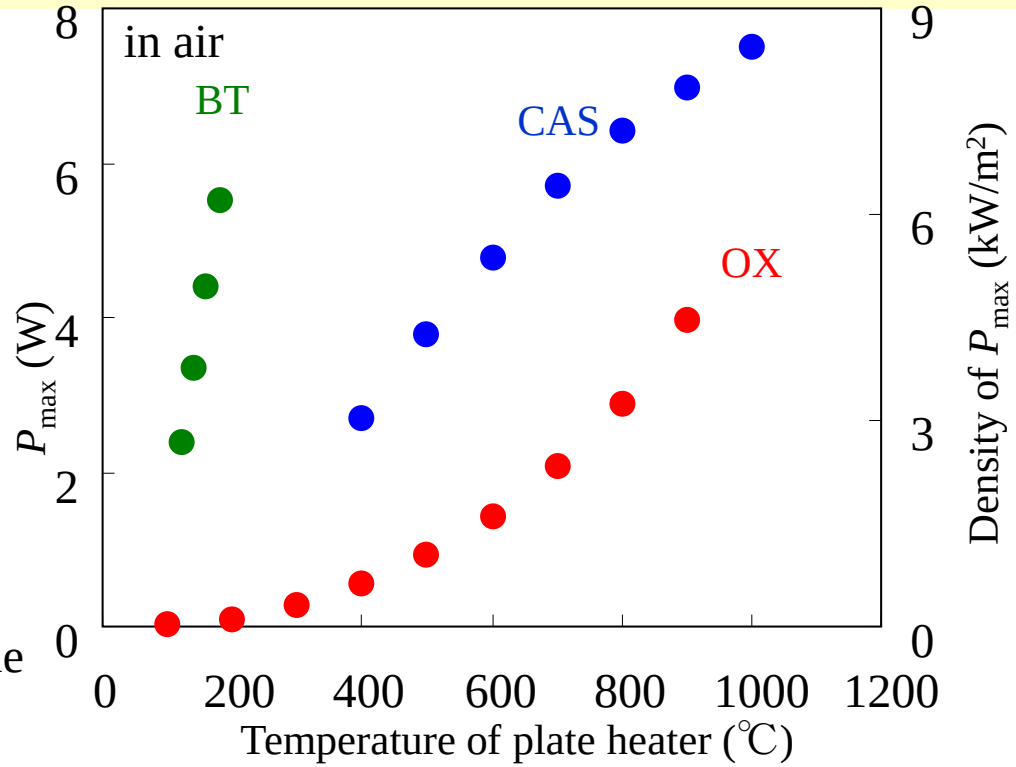


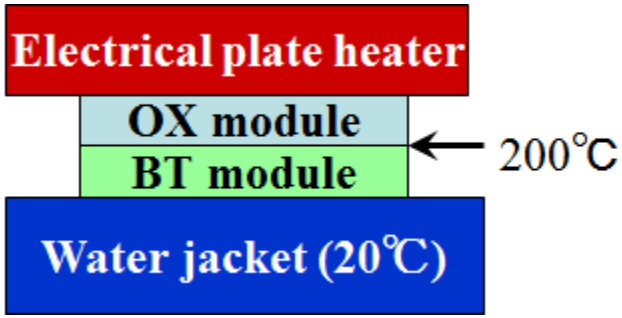




Cascade module





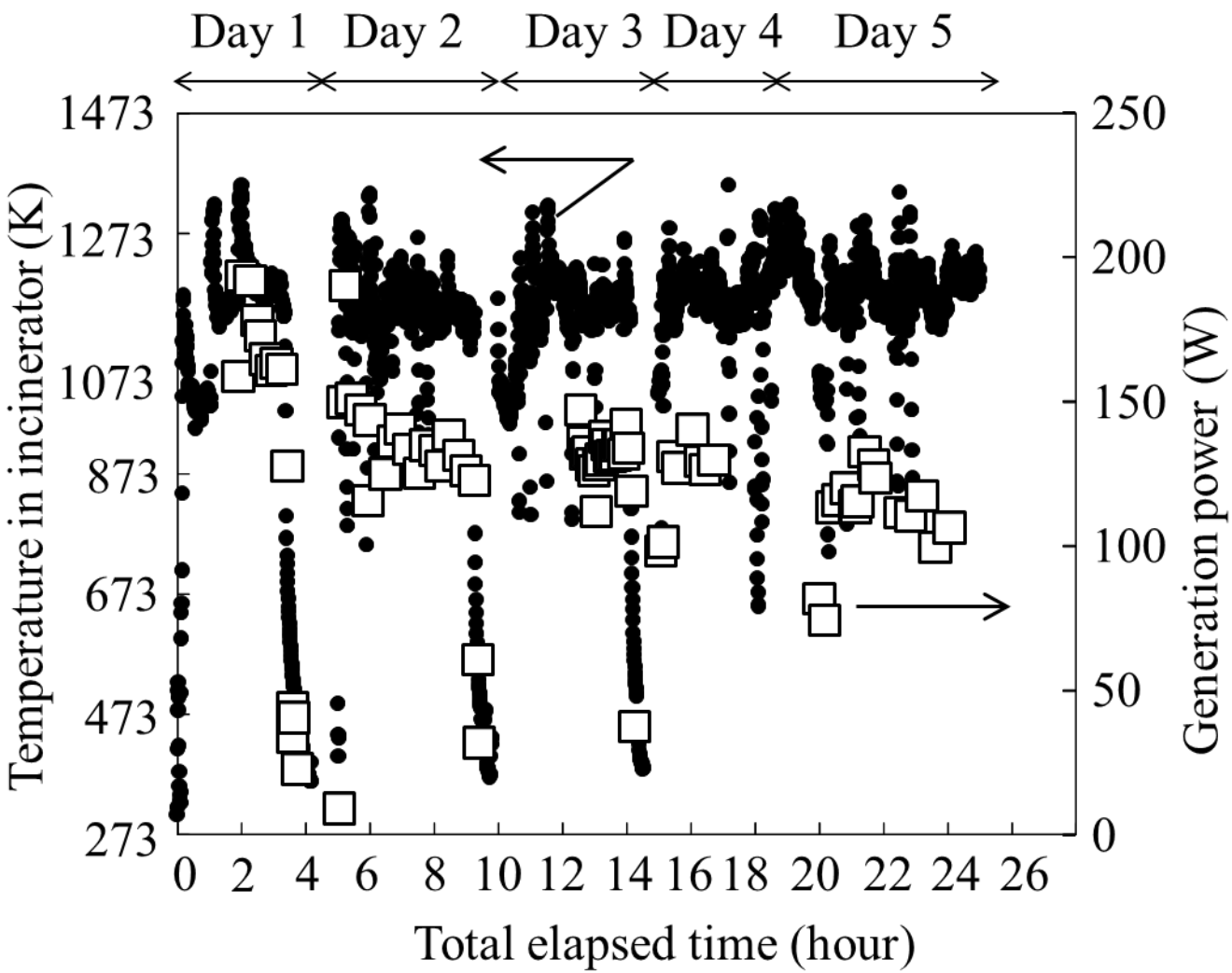


BT module: 20-200℃ 6.1kW/m^2

OX module: 20-900℃ 4.2kW/m^2

Cascade module: 20-900℃ 7.8kW/m^2

TE generation property



TE generation property

	Incinerator A (Pilot)	Incinerator B (Lumbers)
I. Fuel	Natural gas	Lumber
II. Numbers of units to measure	1	4
III. Temperature around heat collection (K)	1370	1273
IV. Temperature of coolant water at inlet (K)	285	298
V. Temperature of coolant water at inlet (K)	287	317
VI. Flow rate of coolant water (L/min)	8.0	6.0
VII. Heat flux into coolant water (W)	1004	3567
VIII. Generation power (W)	49.3	200
IX. Conversion efficiency (%) VIII/(VII+VIII) x 100	4.7	5.3
X. Density of power (kW/m^2)	2.5	2.6

Present TE

Efficincy： less than 10%

Bi_2Te_3： ~ 7%

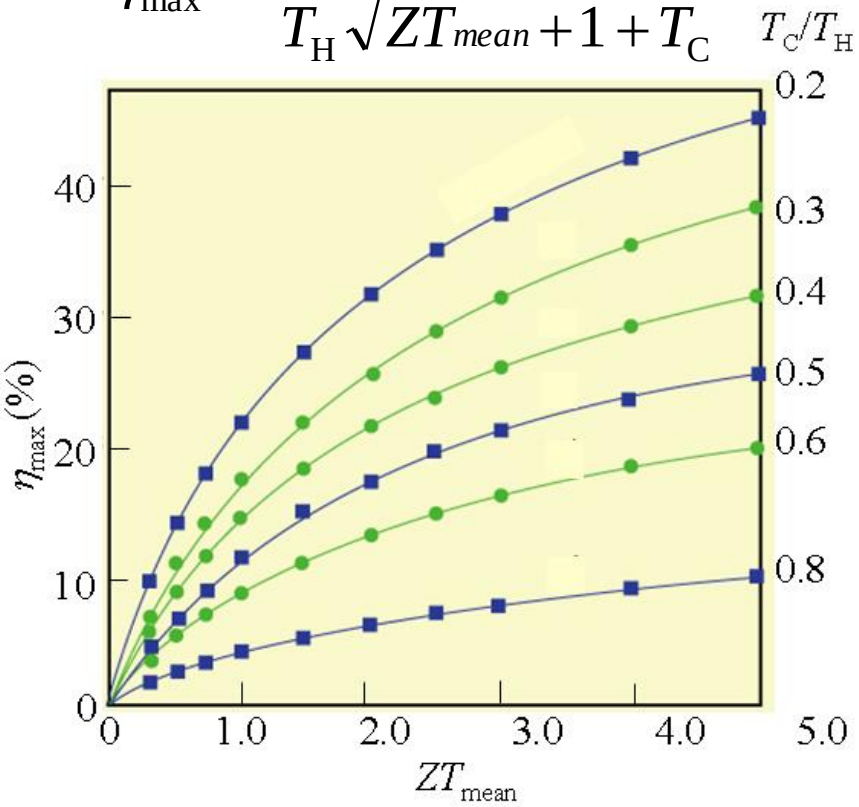
(ZT~1 T_H = 200℃、 T_C = 30℃)

Oxide： ~ 3-5 %

(ZT~0.3 T_H = 800℃、 T_C = 30℃)

cascade (Bi_2Te_3/Oxide)：~10%

$$\eta_{max} = \frac{\Delta T(\sqrt{ZT_{mean}+1}-1)}{T_H\sqrt{ZT_{mean}+1}+T_C}$$



TE < Turbine or PV

Strong points：Maintenance, Long-life, Small & light-weight Silence, Safety

Ideas：Emergency, Sensor, Mobile, Continuous operation

TE in near future

TE materials benefited by nano-technology

- Quantum effect by low dimensionality: Giant Seebeck coefficient
- Scattering of carriers based on PGEC: Low κ and ρ

ZT = 3 at the highest?

Efficiency： 18% (T_H = 300℃, T_C = 30℃)

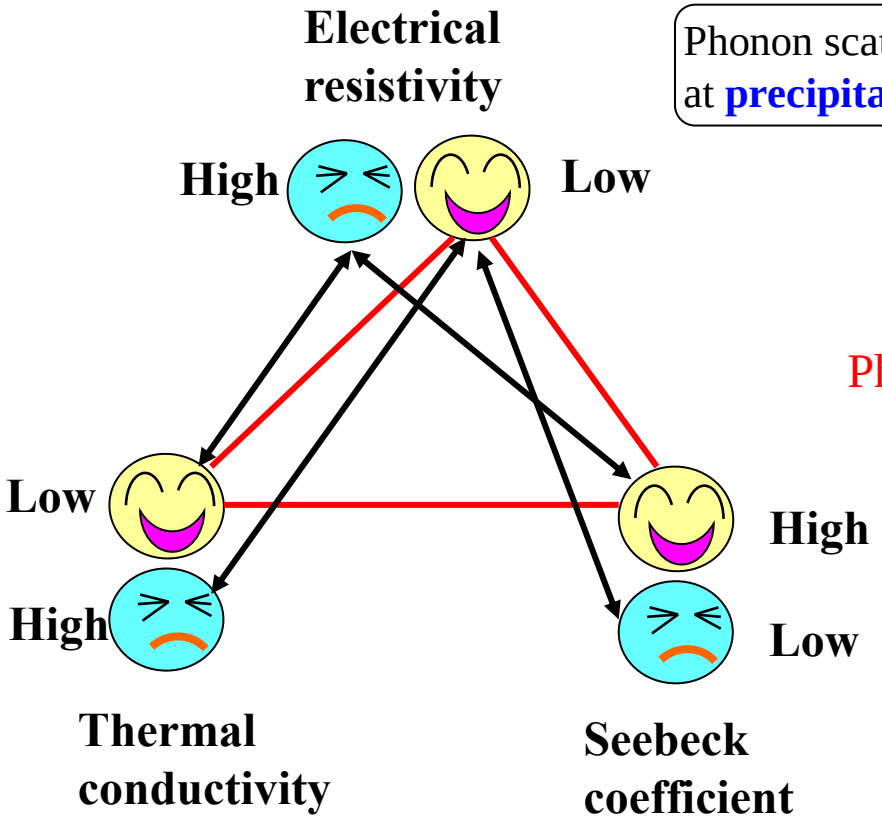
Efficiency： 31% (T_H = 800℃, T_C = 30℃)

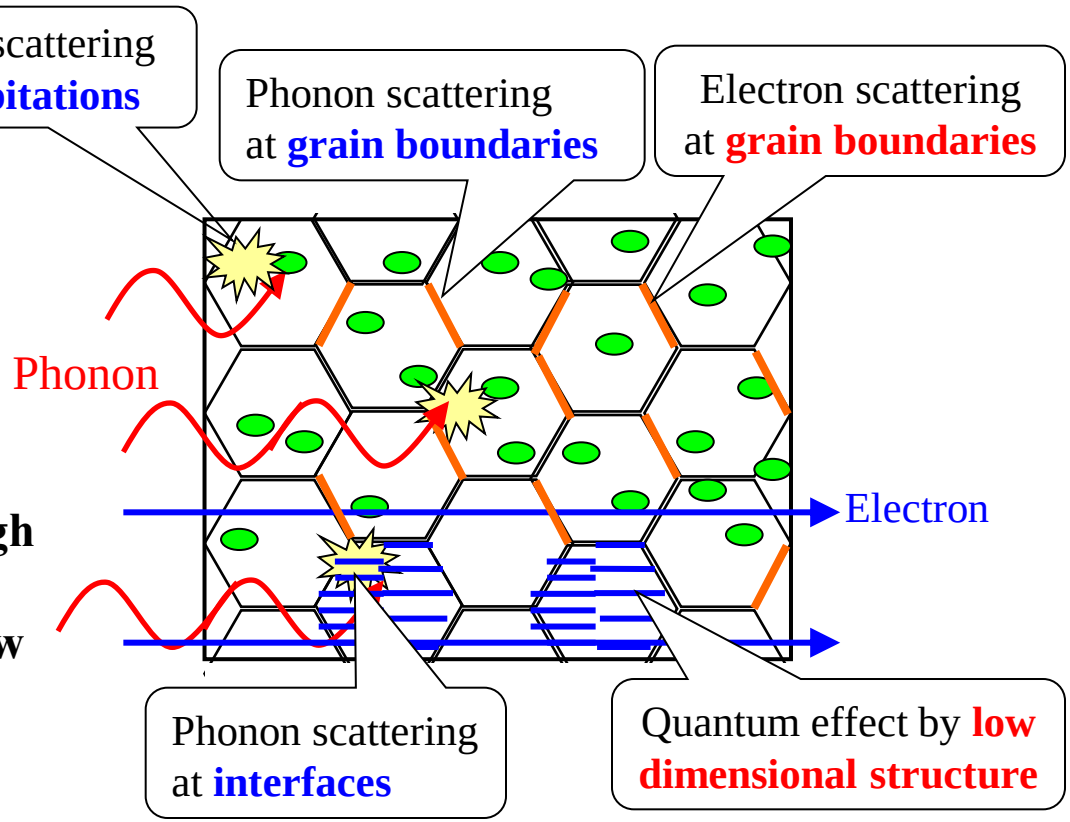
Higher than PV, comparable to Turbine

Strong points：Maintenance, Long-life, Small & light-weight
Silence, Safety

Exchanging present systems：Industrial furnace, Incinerator,
Automobile, Solar heat

Enhancement of TE property





Nanostructured bulk material

High *ZT* → **Nano technology** **indispensable**

Quantum effect

PGEC

↓

Bulk application

~ 10^3 kg/month → **Processing**

Nanostructured materials using "common technology"

Separation

Phase separation, Decomposition, Precipitation, etc…

Composite

Intercalation, Nanoblock integration, etc…

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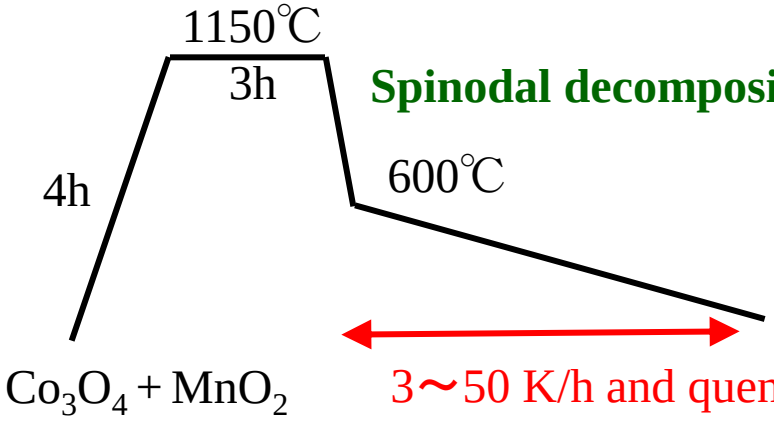
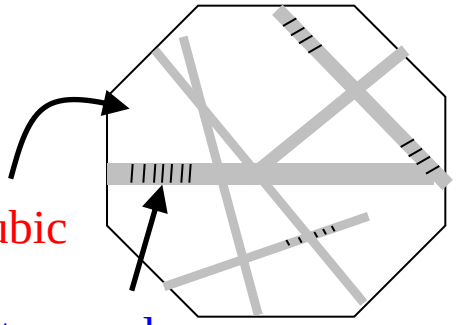
Phase separation

$Co_{1.5}Mn_{1.5}O_4$



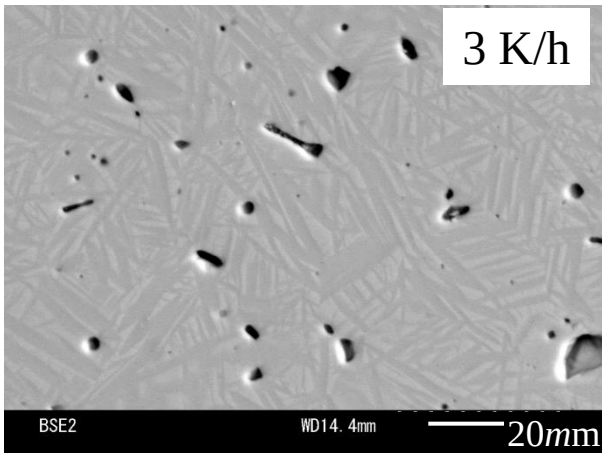
Spinodal decomposition + Twin

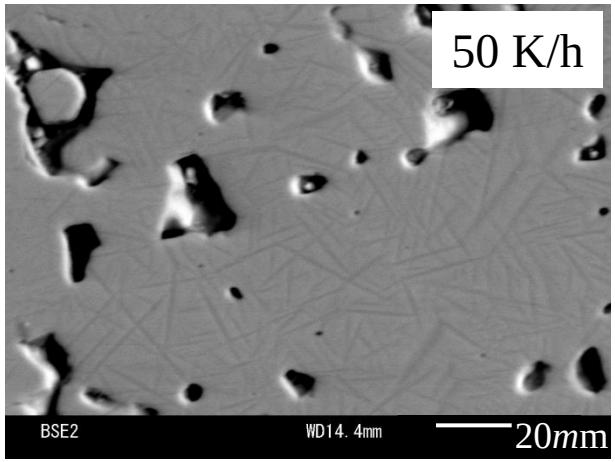


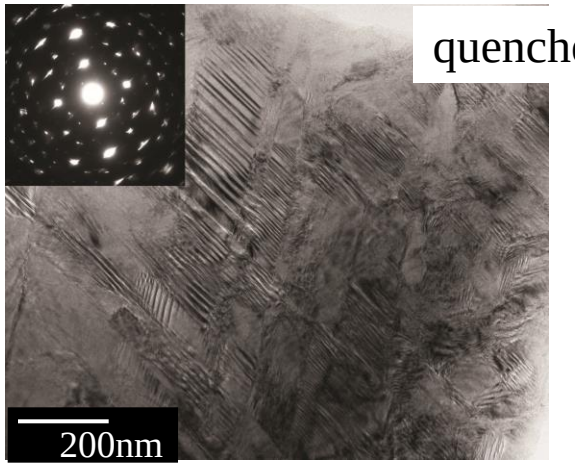
Co-rich : Cubic

Mn-rich : Tetragonal
Twin

3～50 K/h and quenching



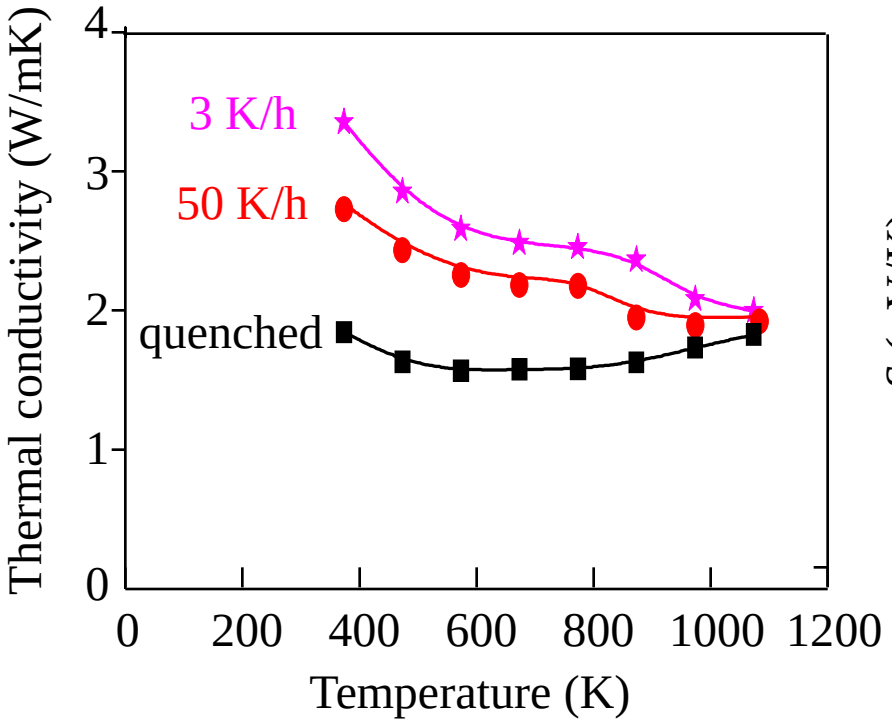


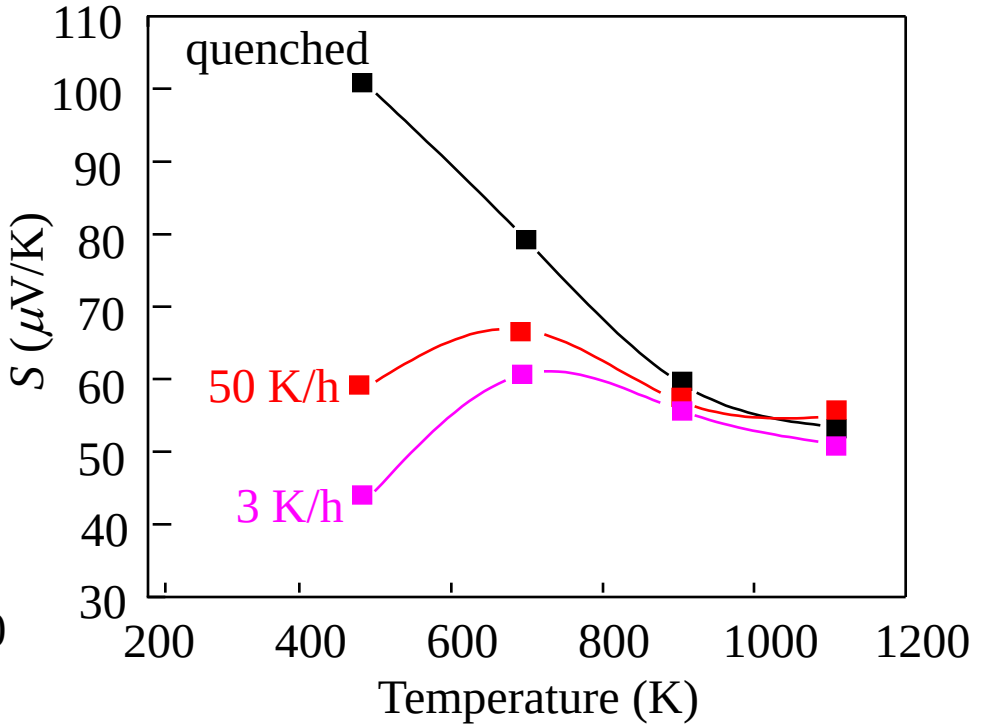


Slow **Cooling speed** **Fast**

Dendrite: fine
Twin: many

Thermoelectric properties





Partial melting process

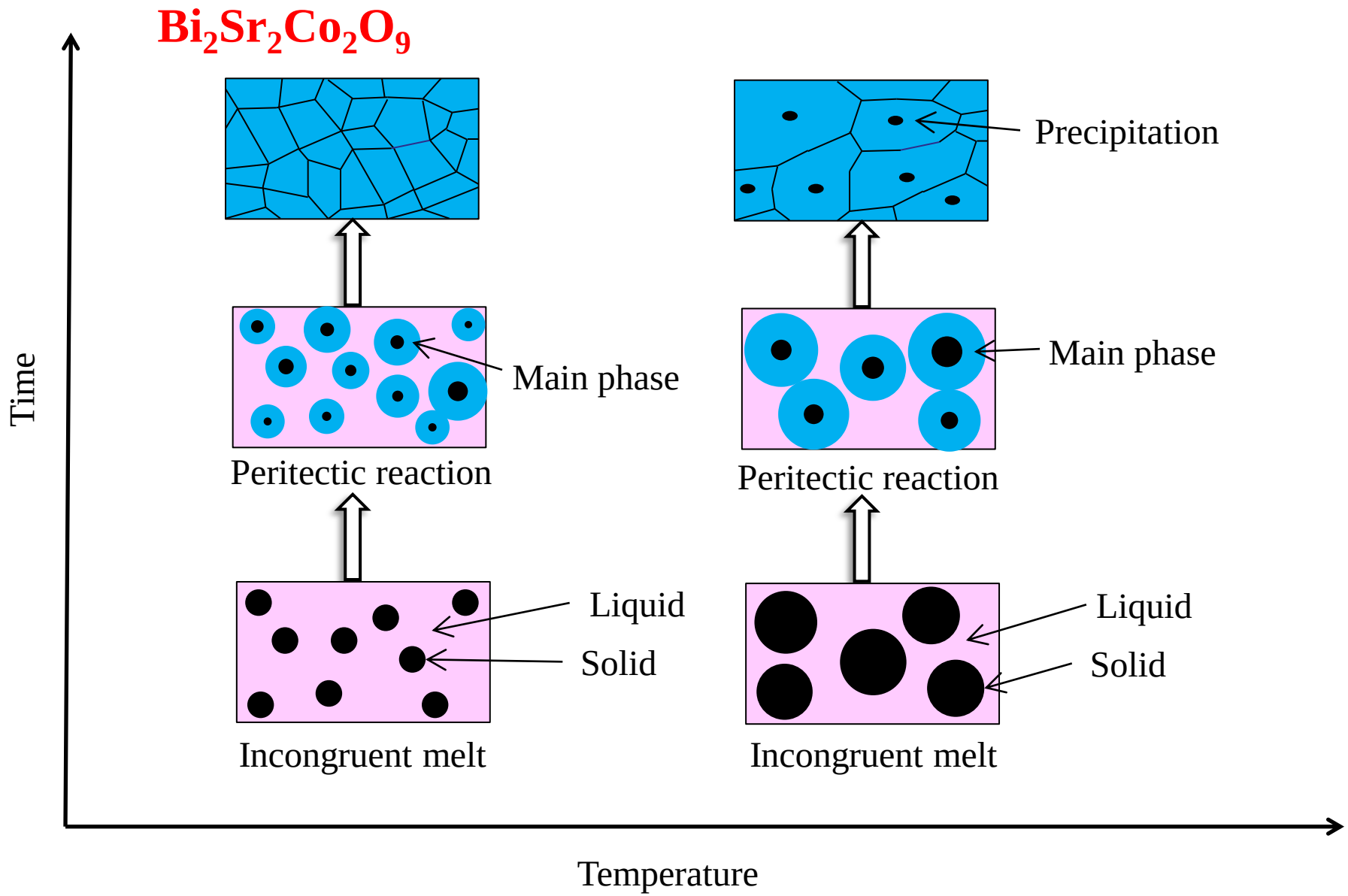
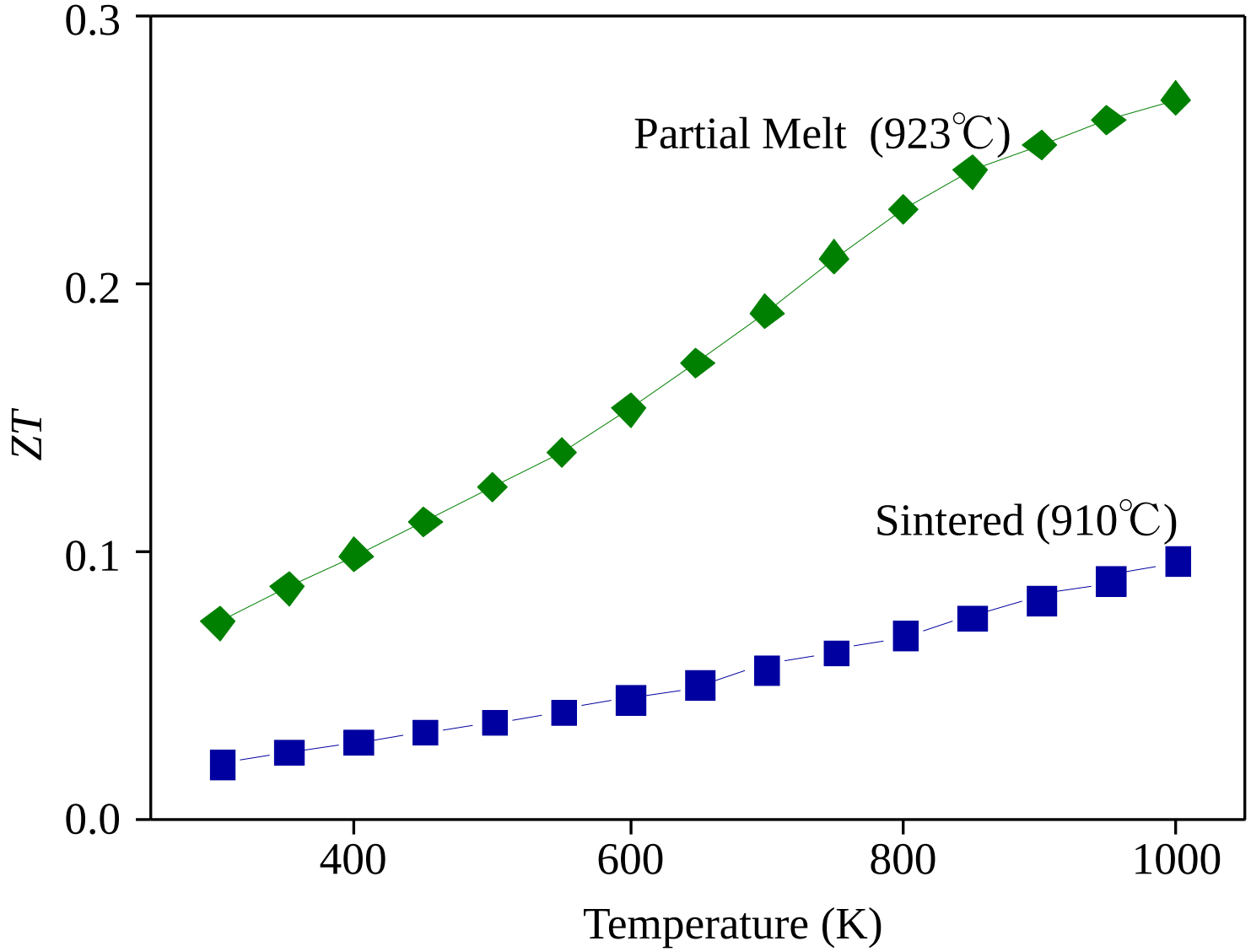
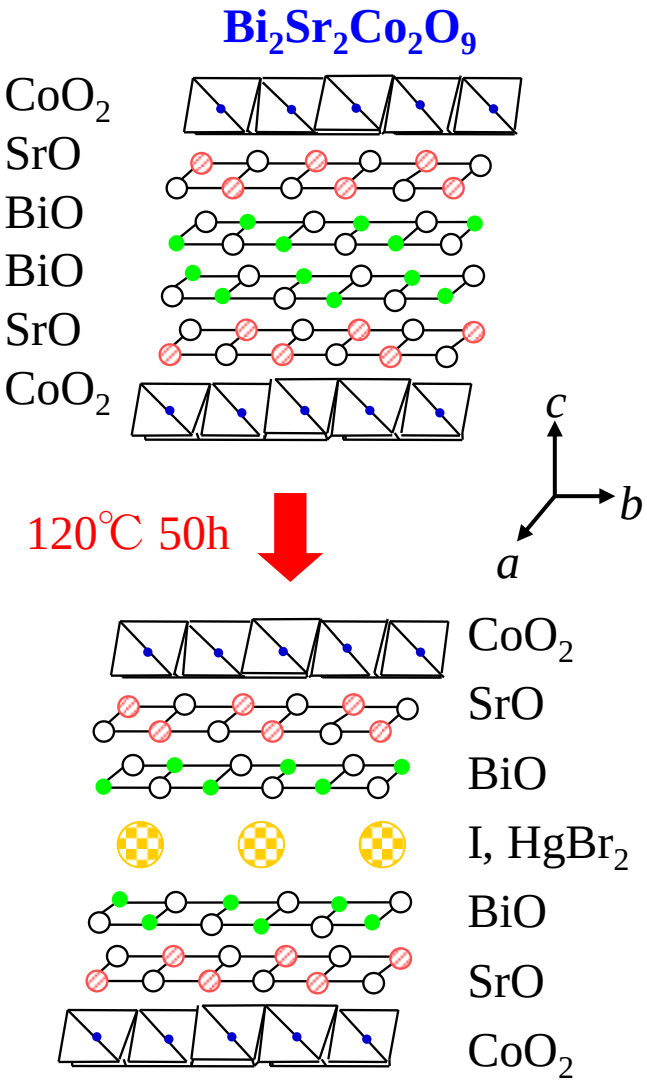
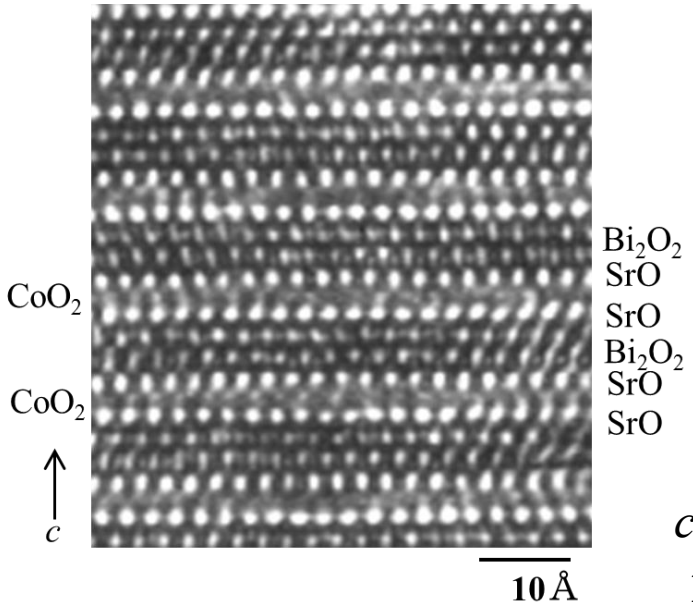


Figure of merit



Intercalation

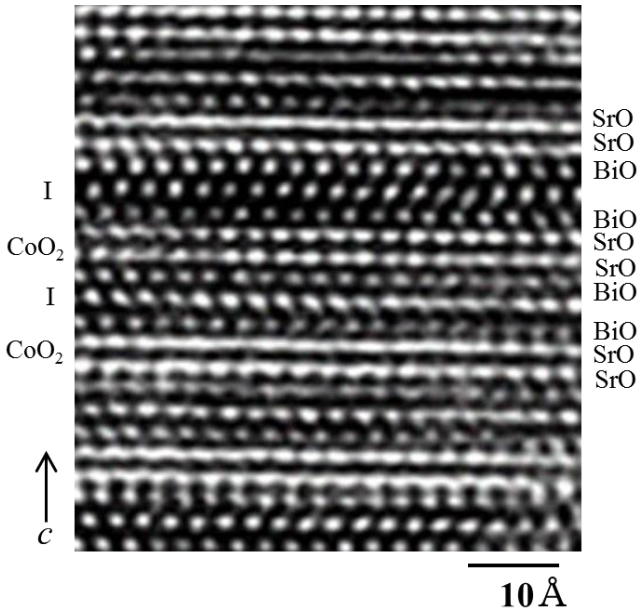




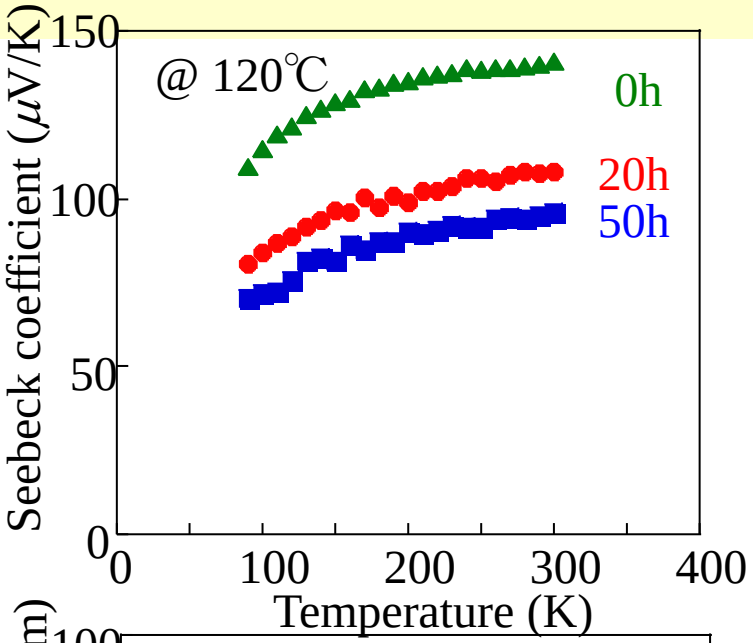
c-cell parameter

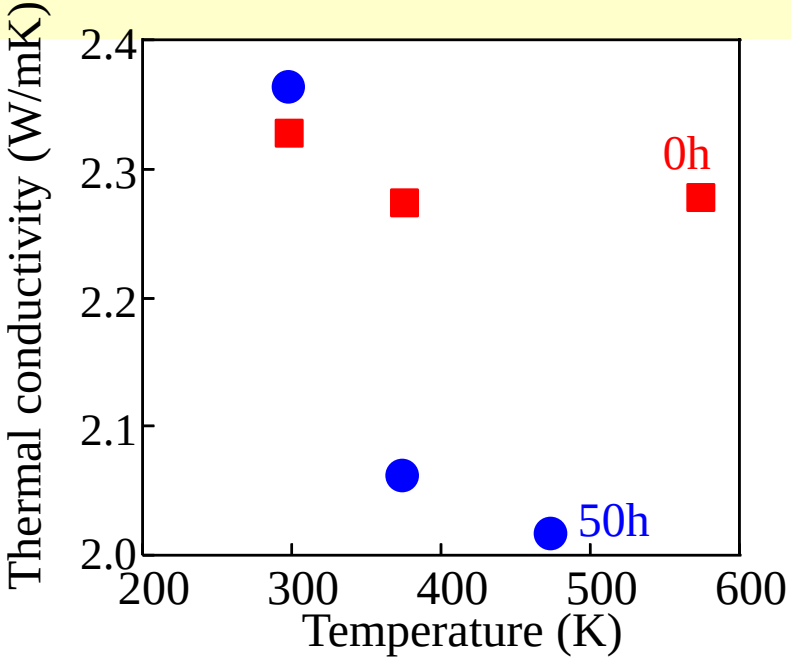
14.8 Å ⟶ 18.4 Å

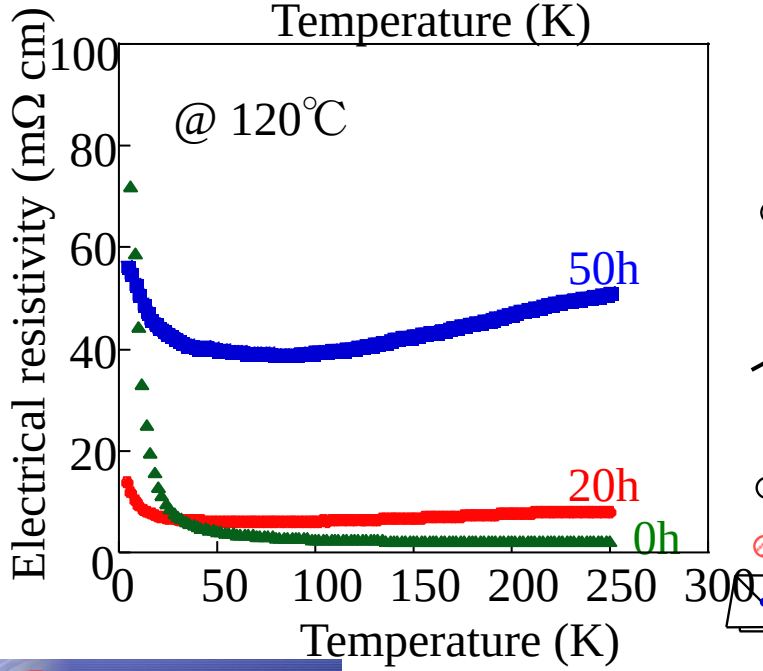
Ionic radius: 2.0 Å

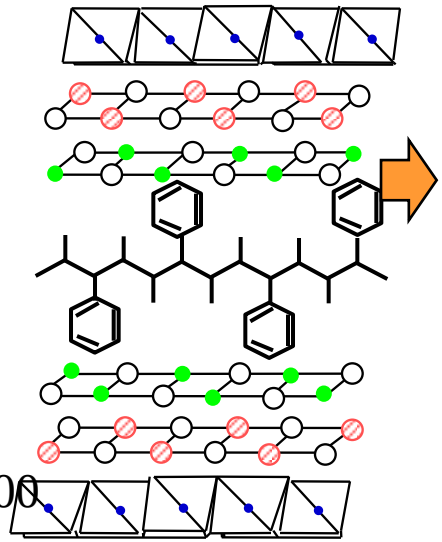


Thermoelectric property







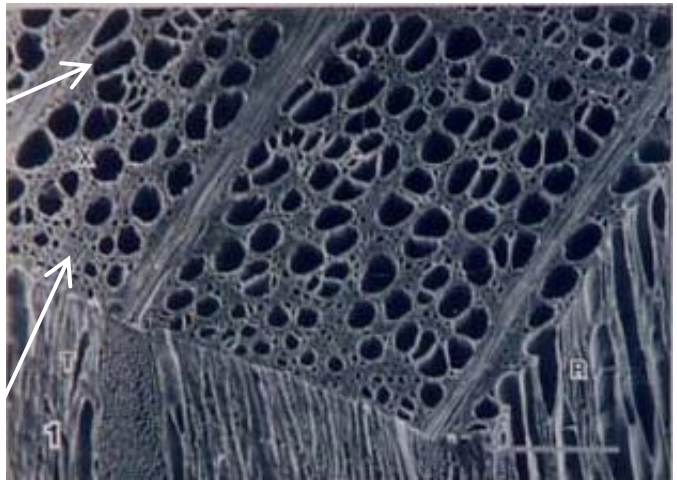


High *ZT*

Multi functional Material
(Self-contained power source, etc…)

Tree structured material

Tree structure (ex. Beech)



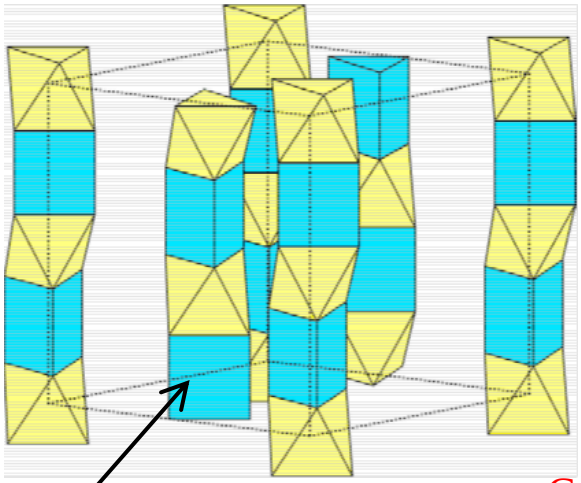
Vessel (water supply)

Xylem (matrix) (Low κ)

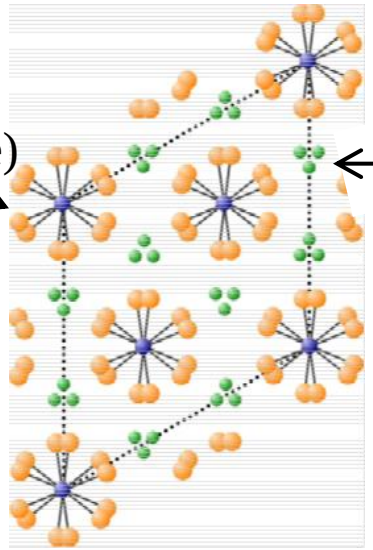
Good transportation

Low thermal conductivity

1D material (ex. $Ca_3Co_2O_6$)



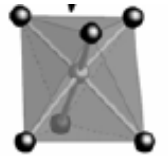
1D chain (conductive)



Matrix Ca (Low κ)

CoO_6: Triangular prism

Face sharing



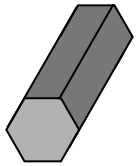
CoO_6: Octahedron

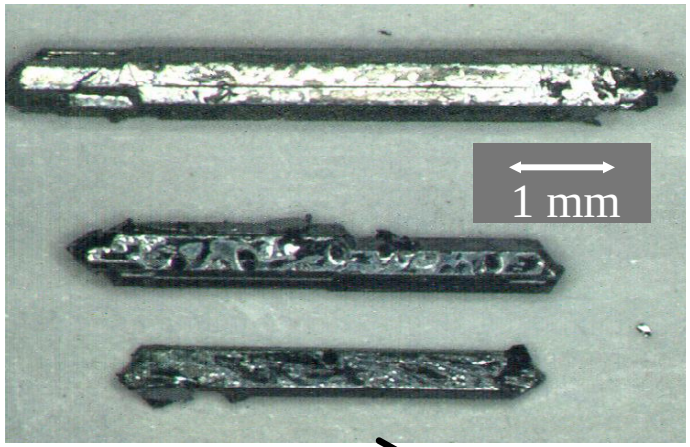
Thermoelectric property

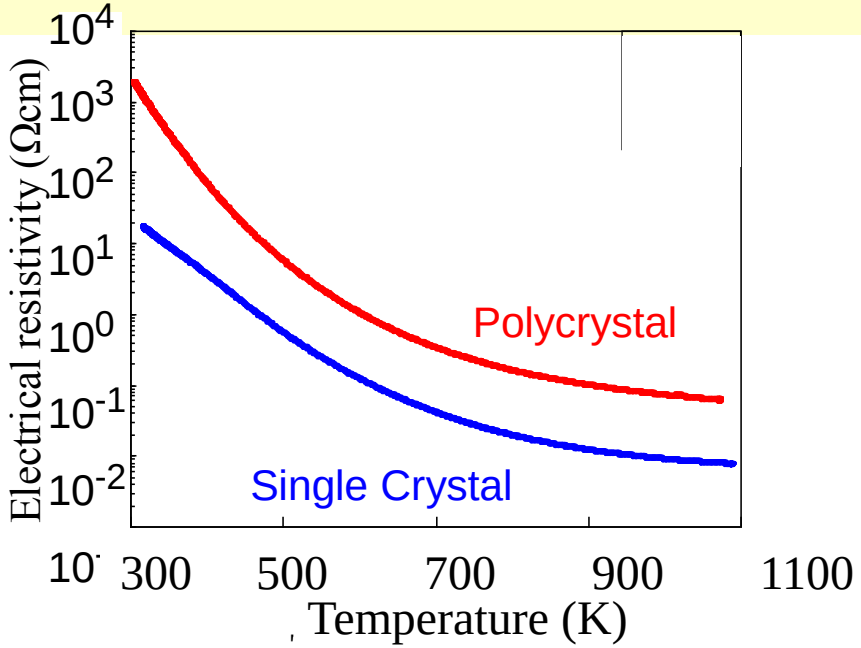
$Ca_3Co_2O_6$

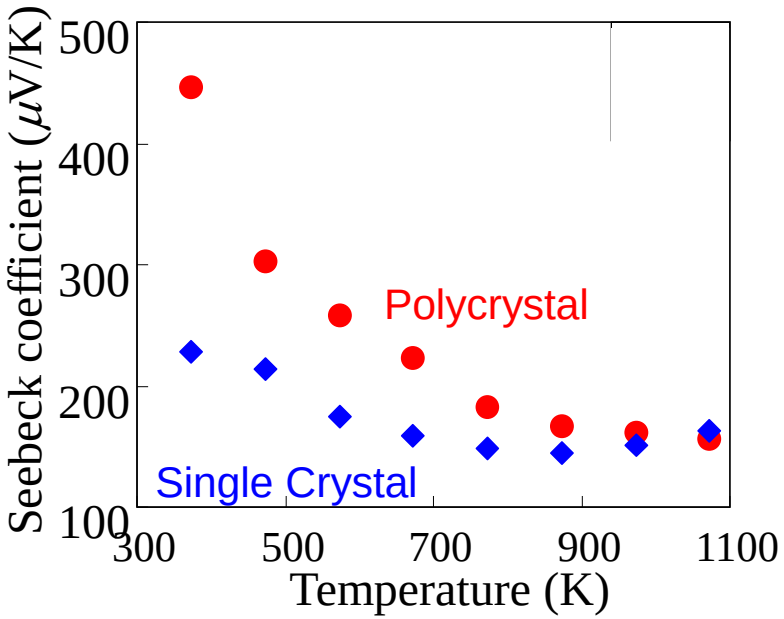
- size: $1 \times 1 \times 5$ mm^3.
- well grown *c*-axis

Hexagonal rods



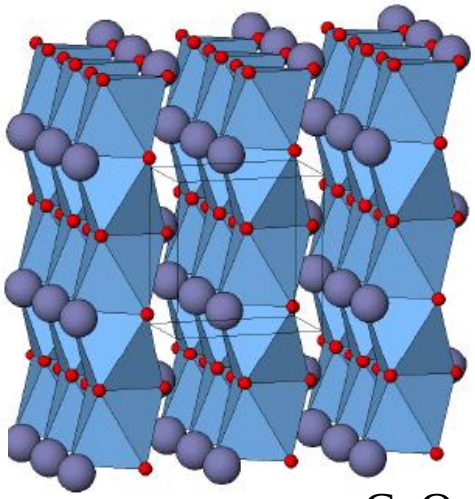




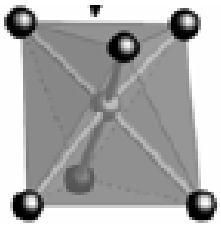


1D material

$BaCoO_3$

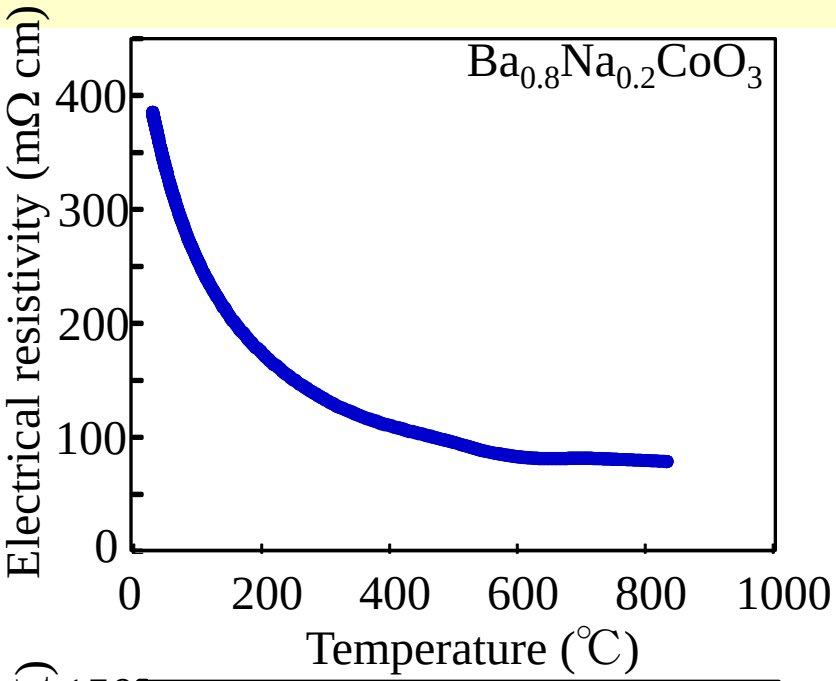


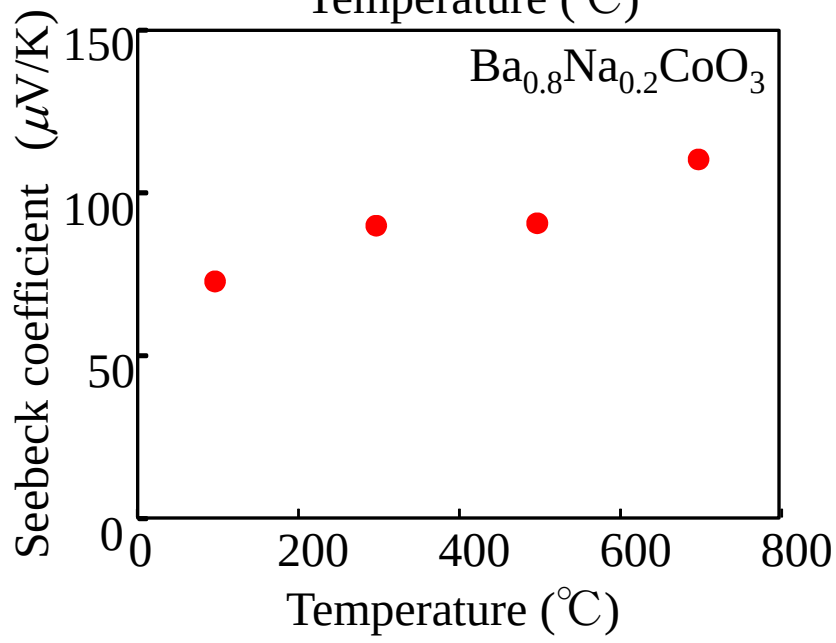
Ba CoO_6



CoO_6: Octahedron

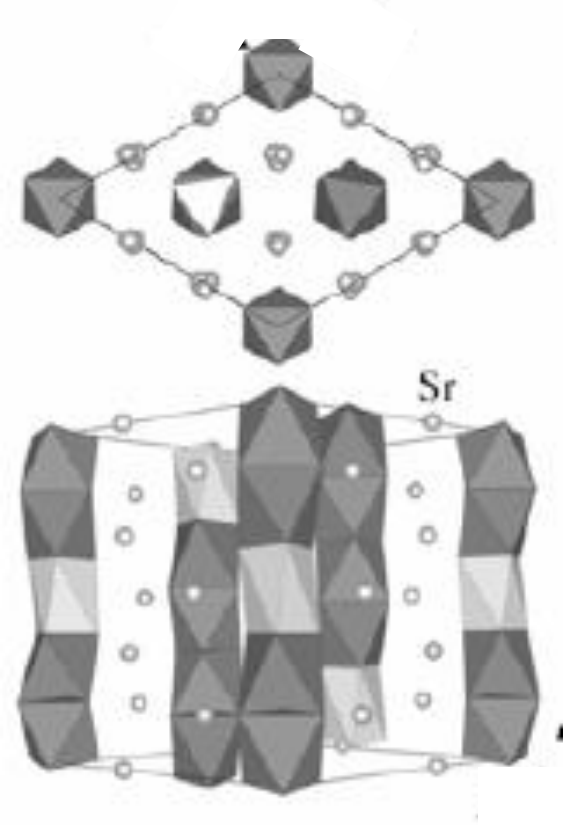
Edge sharing





Reconstruction

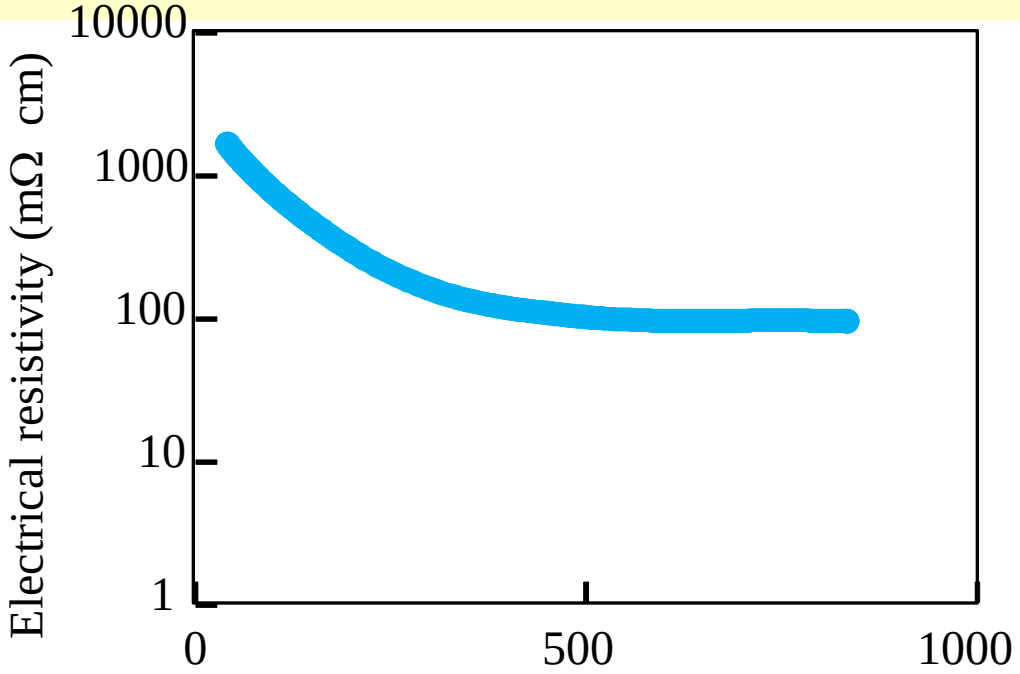
$Sr_6Co_5O_{15}$



Homologous series

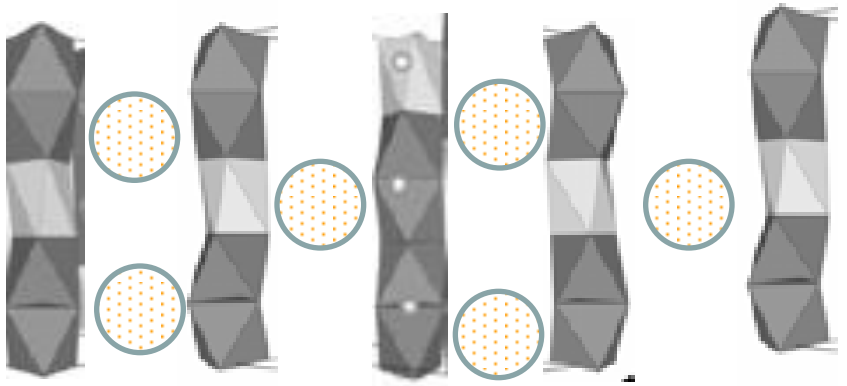
$(Ca_3Co_2O_6)_m\,(BaCoO_3)_{3n}$

m = 1, n = 1



Optimization of m and n
Separation of nano-rods
Binding nano-rods

Weak bonding (ex. Van der Waals)



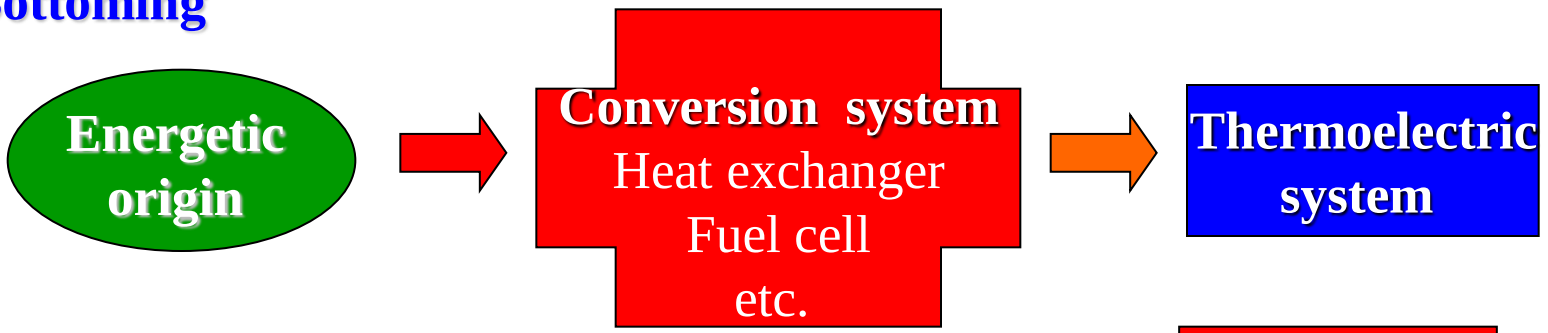
Topping heat recover

Oxides

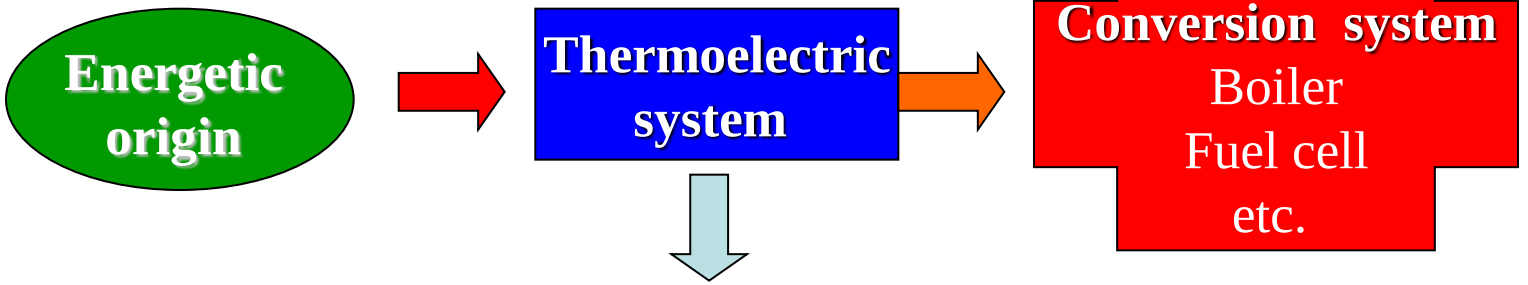
High Temperature Use (Topping)
No toxic & Low price

Overcoming Recovery of Waste Heat Only (Bottoming)

Bottoming

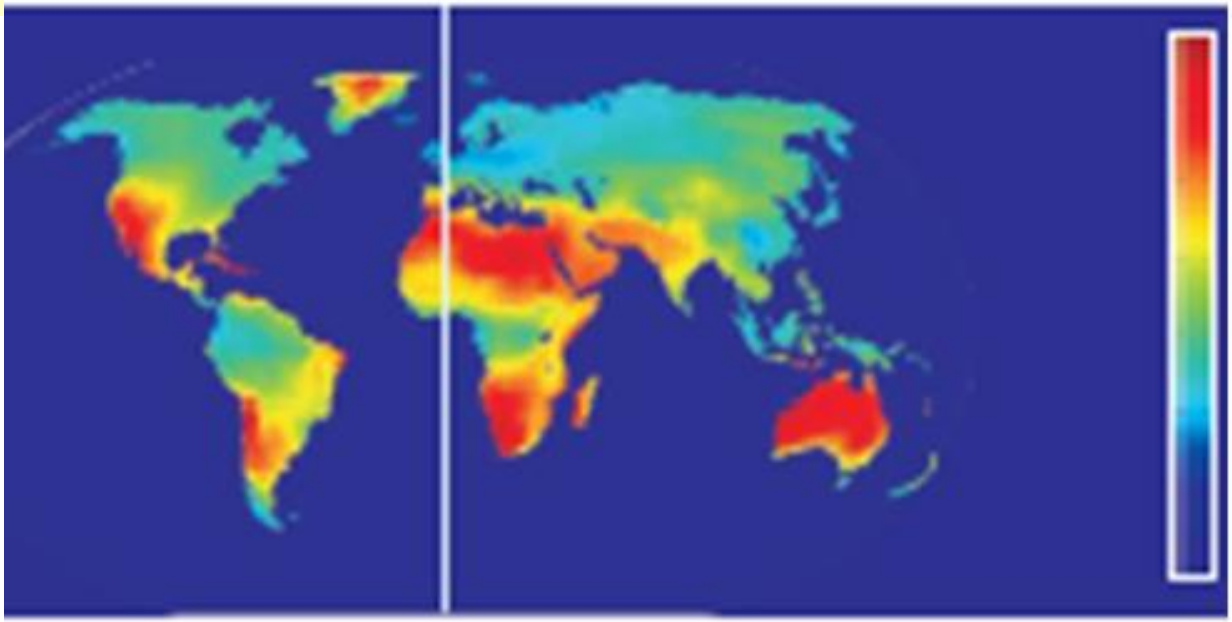


Topping



Establish New Conversion Systems with High efficiency

Solar heat power generation

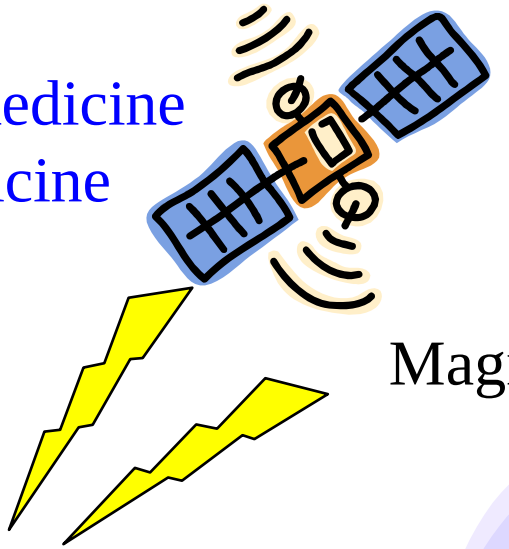


Mojave Desert, CA USA

664MW
(0.5mil. households)

Medical application

Preventive medicine
Remote medicine



LifeTouch Patient Surveillance System

Heart rate monitor

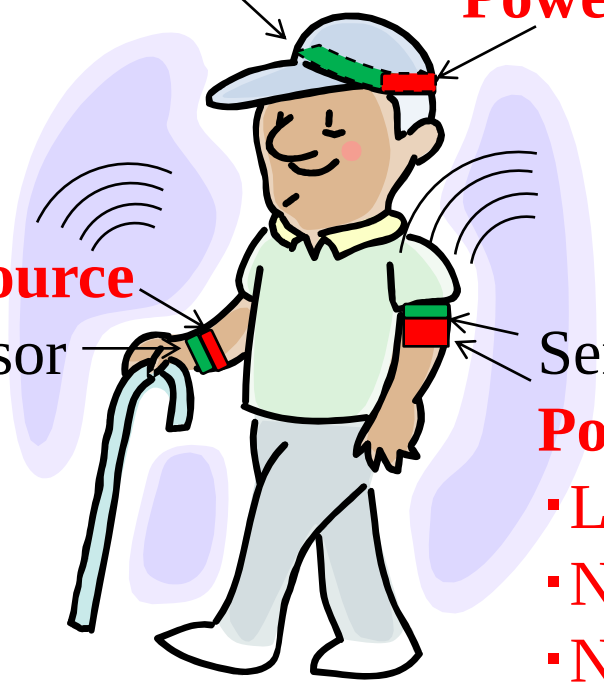
Isansys

Magnetic sensor

Power source

Power source

GPS sensor



Sensor

Power source

- Light weight
- No charging
- No exchanging
- Body heat generation

For security

Flight recording

Watching atomic power station

Sensors for automobiles

F1: MGU-H

Waste heat recovery by Rankine cycle

Strong points of oxides

Durability

Mass and reliable processing

Nanoblock integration

Light weight

Topping recovery

Noninvasive

etc…