Overview of Japanese Activities in Thermoelectrics

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Shonan Institute of Technology

Outline

- Introduction
- Overview of R and D Projects on Thermoelectric Power Generation Technology
- Several Topics and Future Prospects
- Conclusions

Principal Recognition:

Thermoelectric technology can contribute to the realization of environment-friendly society all over the world in the future.

3-Key Viable Missions of Thermoelectric Power Generation Technology

Energy Security

Creation of energy resources from waste heat

Energy conservation

Environmental Conservation

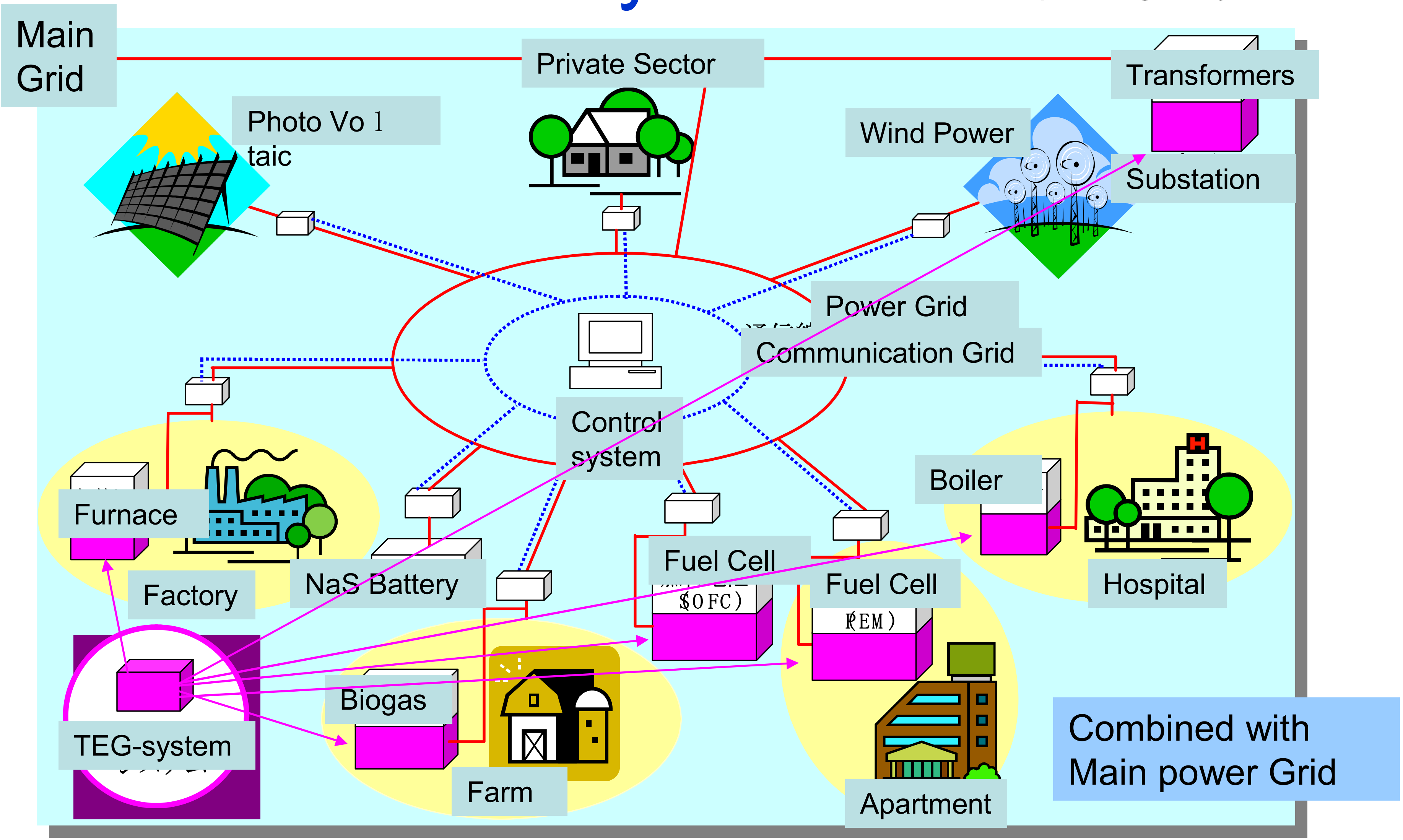
Reduction of Carbon emission

Thermoelectric Power Generation Technology

Economy

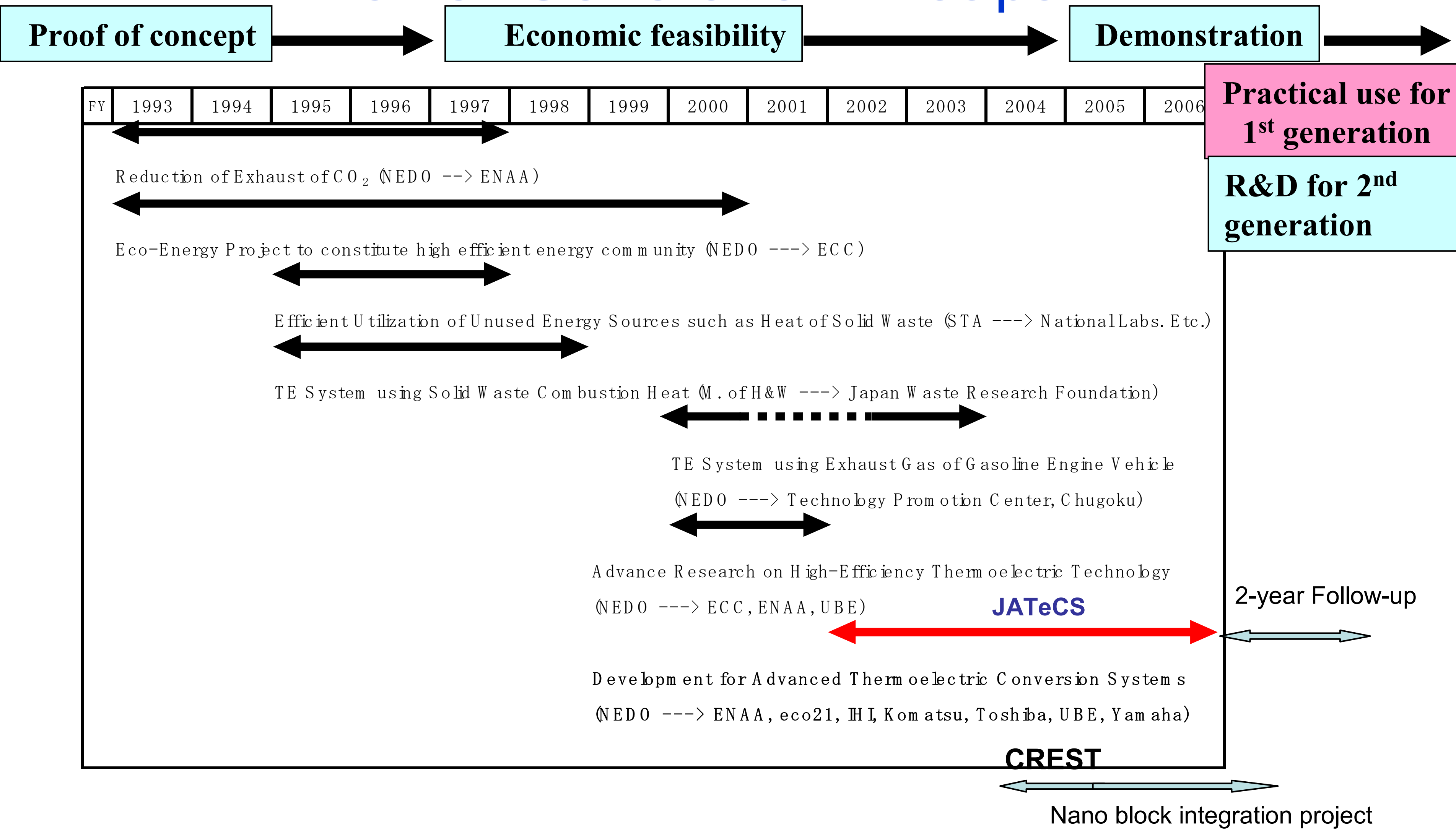
Activation of new industry

Micro-Grid System in the future power grid system



Thermoelectric power generation systems can be applied to all kinds of waste heat sources in the micro grid systems, which are expected to play an important role in the efficient energy system in the future.

Former R&D Projects on Thermoelectric Power Generation in Japan



Ongoing and Initiated Thermoelectric R&D Projects in Japan

Description: Title/ Sponsor/ Term/ Organization/ Budget/ Goal

Development of High-Performance Thermoelectric Materials by Controlling Nano-Structure of Caged Compounds

NEDO/METI, 2009.6-2017.3, Hiroshima Univ. ,Denso Co.Ltd, and 3 Institutes, \210M for 1^{st} stage / \600M for 2^{nd} stage, **ZT～1.3,12**%@DeltaT of 300K by advanced cage-structured materials

Development of High-Efficiency Thermoelectric Materials and Systems

CREST/MEXT,2008.10-2014.3,Nagoya Univ., and 3 Institutes,\227M,High-efficient materials such as layered oxides、Si-based Clathrates and nanostructured **,ZT>1.5,** η **sys～10%**

- Development of Thermoelectric Materials

JST/MEXT,2008.9-2013.3, Nagoya Univ.,\40M,Basic research on high performance layered oxides combined low-dimension-structured materials

- Development for High Temperature Thermoelectric Materials to recover unused waste heat sources

NIMS/MEXT,2009.4-2014.3,NIMS,\22M,Complex structured materials such as $RB_{17}CN$ and $RB_{22}C_2N$,and Higher Borides

- Research on Spin-Seebeck Effect for Innovative Thermoelectric Materials

NEDO/METI,2009.6-2011.3,Tohoku Univ.,\25M,Basic research on technology assimilation between thermal insulation material technology and spin electronics

- Development of Novel Thermoelectric Modules by Ink-jet Technique

MEXT,2009.4-2013.3,JAIST and KELK,\26M, High performance and low cost thermoelectric modules based on nanoball ink-jet technique

CREST (Core Research for Evolutional Science and Technology), **JST** (Japan Science and Technology Agency) , **METI** (Ministry of Economy, Trade and Industry) , **MEXT** (Ministry of Education, Culture, Sports, Science & Technology) , **NEDO** (New Energy and Industrial Technology Development Organization) ,**NIMS** (National Institute for Materials Science), **JAIST** (Japan Advanced Institute of Science and Technology)

Development of High-Performance Thermoelectric Materials by Controlling Nano-Structure of Caged Compounds

P.L.: Professor T. Takabatake, *Hiroshima University*
T. Koyanagi, K. Akai, *Yamaguchi University*
K. Ueno, *National Inst. of Advanced Industrial Science and Technology*
T. Taguchi, *DENSO Co., Ltd.*
K. Fukuda, *KELK Co., Ltd.*

Materials
Modules
Systems

NEDO PROJECT for Novel Practical Materials by Nano-Structuring, FY 2009-2011 (1st stage)

Development of High-performance TEG Systems for Practical Use

FY2012-2014 (2nd Stage)

29/09/2009

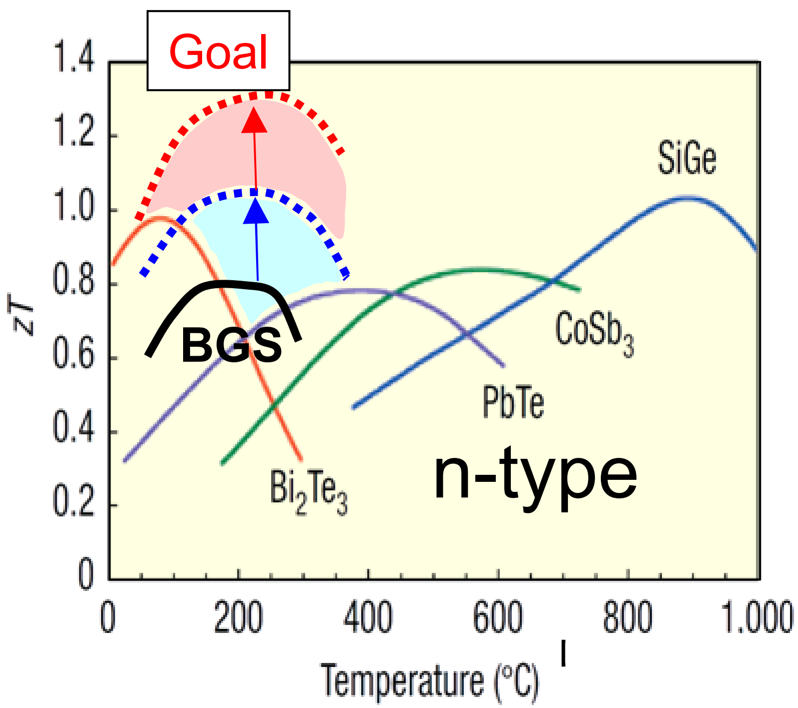
Project Goal; *ZT*=1.3 at 200-300 ºC

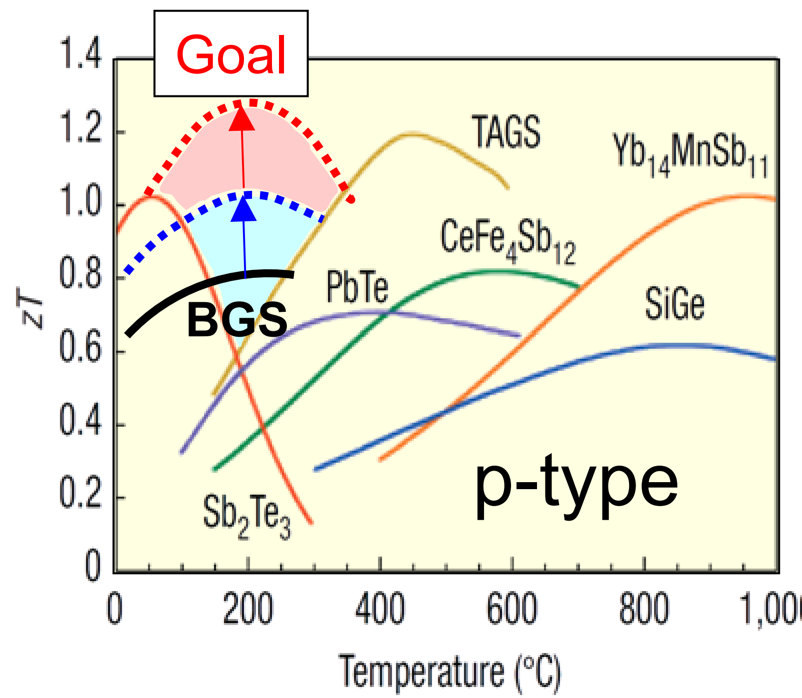
- Temperature range： T_h= 400 ºC, T_c= 100 ºC, Δ*T* = 300 ºC
- *ZT* for previous materials has a valley at 200-300 ºC
- nano-scale caged material **$Ba_8Ga_{16}Sn_{30}$**： ***ZT*** ＝ 0.8 for both n- and p-types

ZT（200-300 ºC）＝0.6～0.7 **double** → *ZT* ＝1.3

Bi_2Te_3, PbTe toxic → Safe, nano-scale caged material

Snyder, Nat. Mater. 7, 105 (2008).



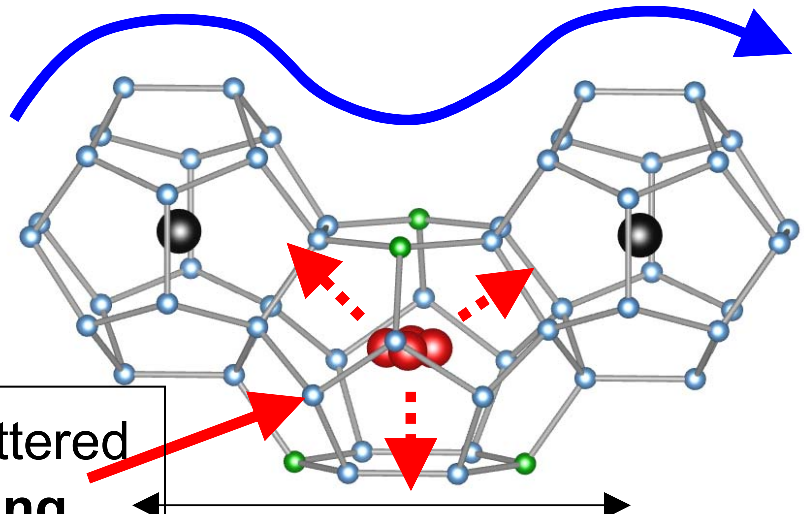


Key Ideas and Methods: Nano-Structure Control of Caged Compounds

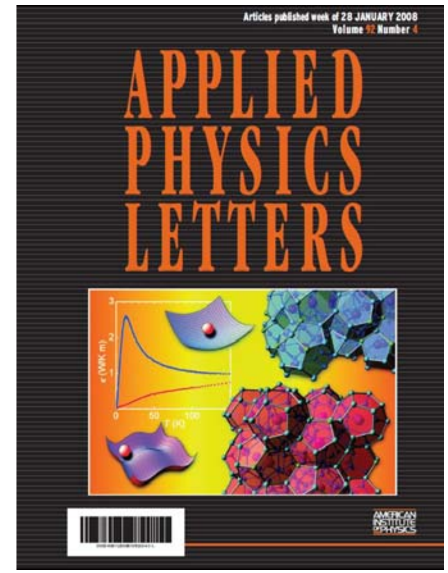
Following the concept of "Phonon Glass and Electron Crystal" proposed by Slack, project teams of Hiroshima & Yamaguchi Universities have succeeded in reducing κ to 0.4 W/Km at 300 K by controlling the structure of intermetallic clathrates.

Electrons flow the network of the cage

Heat flow is scattered by **off-center rattling** of the guest



$Ba_8Ga_{16}Sn_{30}$



Issue of Jan. 2008

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

Important step: Introduction of different guest ions in the two type of cages should lead to the coexistence of higher σ and the sufficiently low κ.

Japan Science and Technology Agency - CREST Project

<2008.10.1 ~ 2014.3.31>

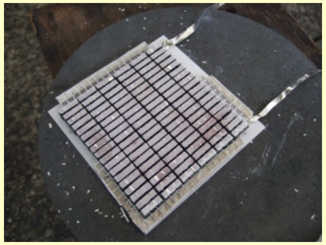
"Exploration of Innovative Technology to Reduce Carbon Dioxide Emission"

Nontoxic, Nonhazardous, Nat. Abundant Elements !

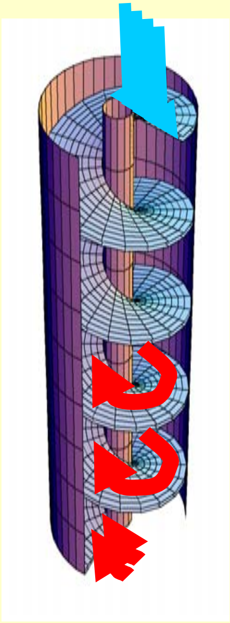
Development of High-Efficiency Thermoelectric Materials and Systems

K. Koumoto (Nagoya University)

TE module



TE system

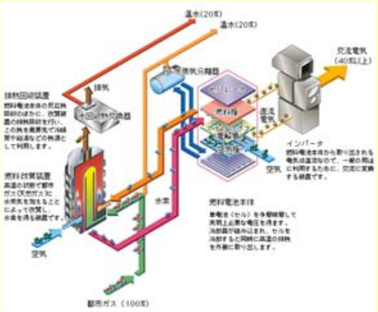


Cars

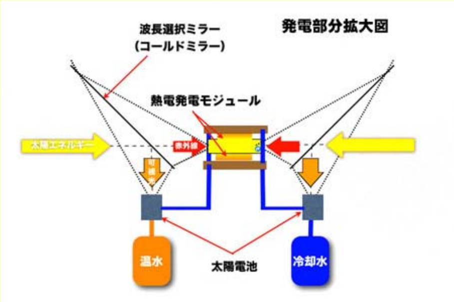
Incinerators

Ind. furnaces

Fuel cells

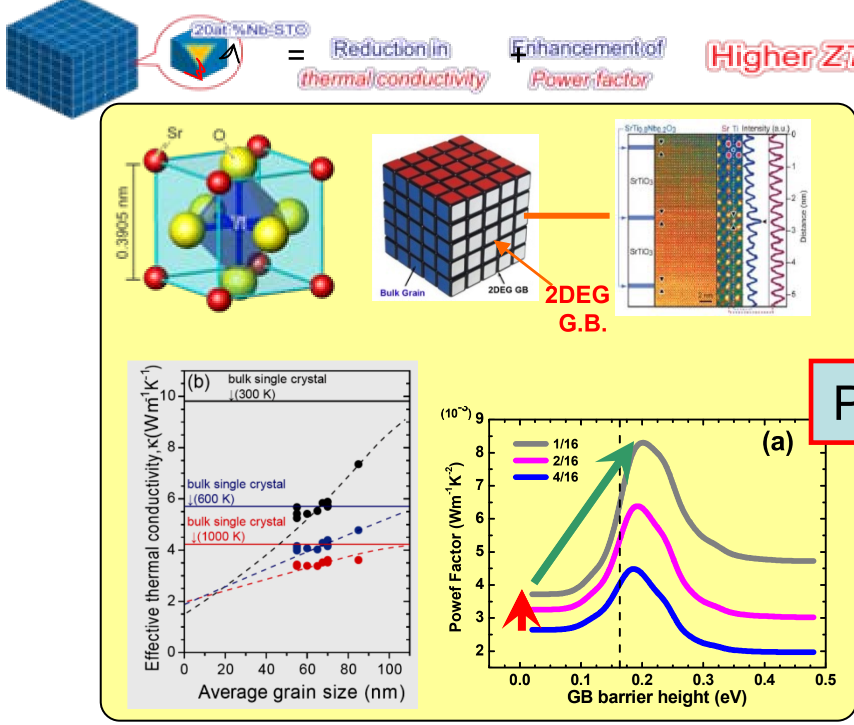


Solar heat

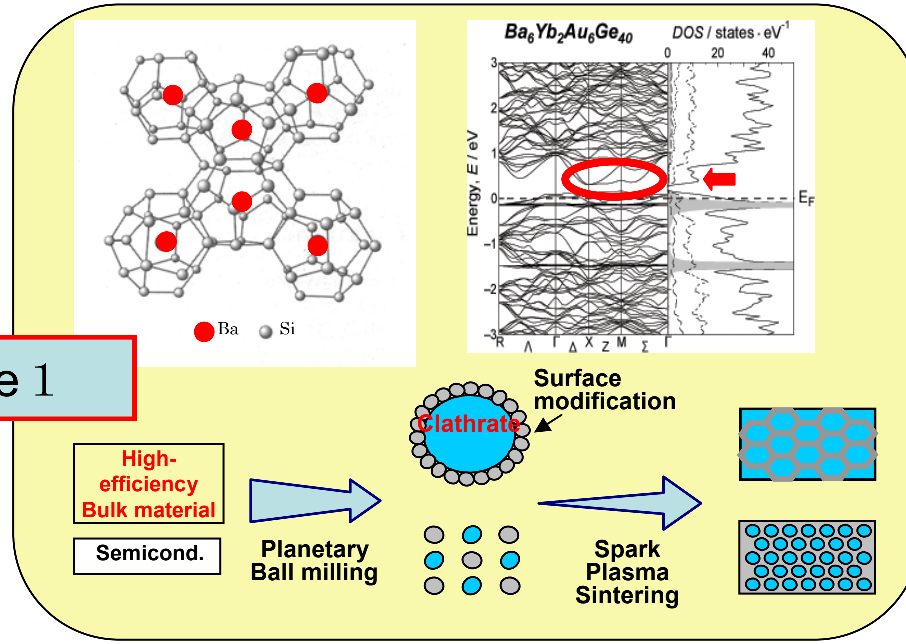


Collaborating Group Leaders:
R. Funahashi（AIST)
H. Anno（Tokyo Univ. of Sci.）
R. Suzuki（Hokkaido Univ.）
M. Kusunoki (Nagoya Univ.)

(1) Quantum Nanostructured Bulk Materials



(2) Si Clathrate Nanocomposite

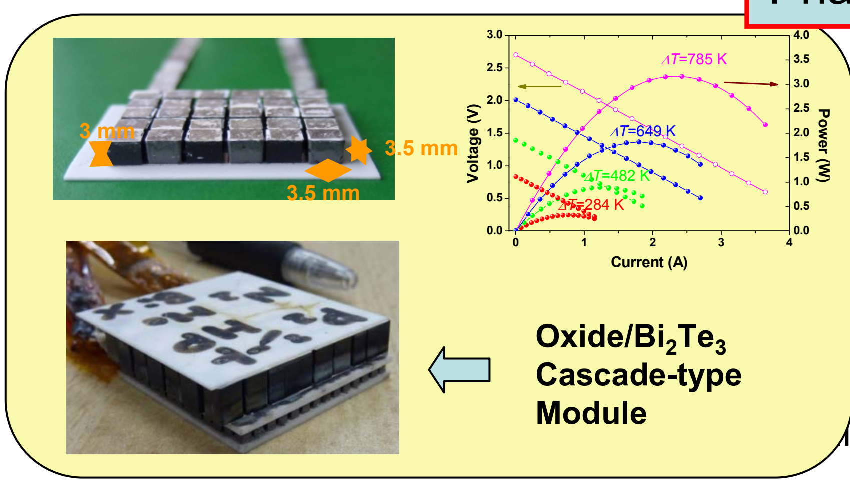


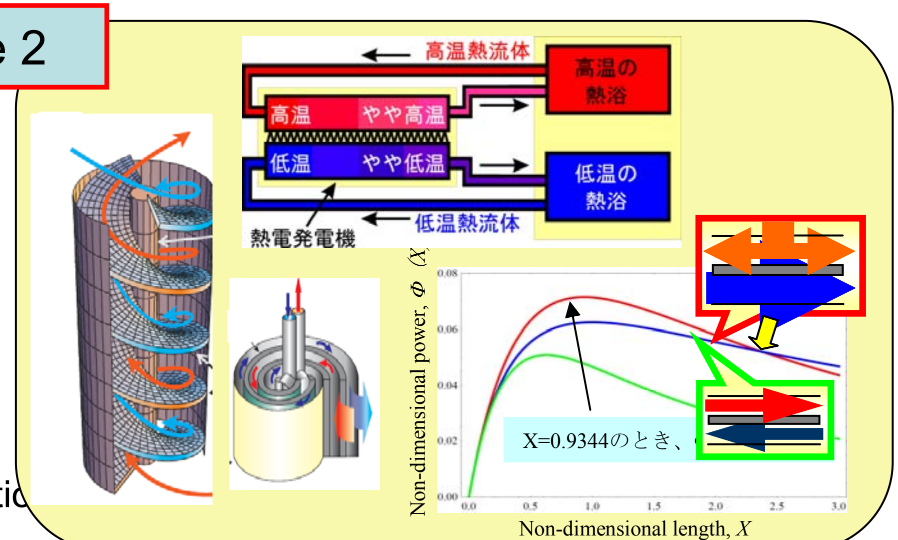
Phase 1

(4) System Design

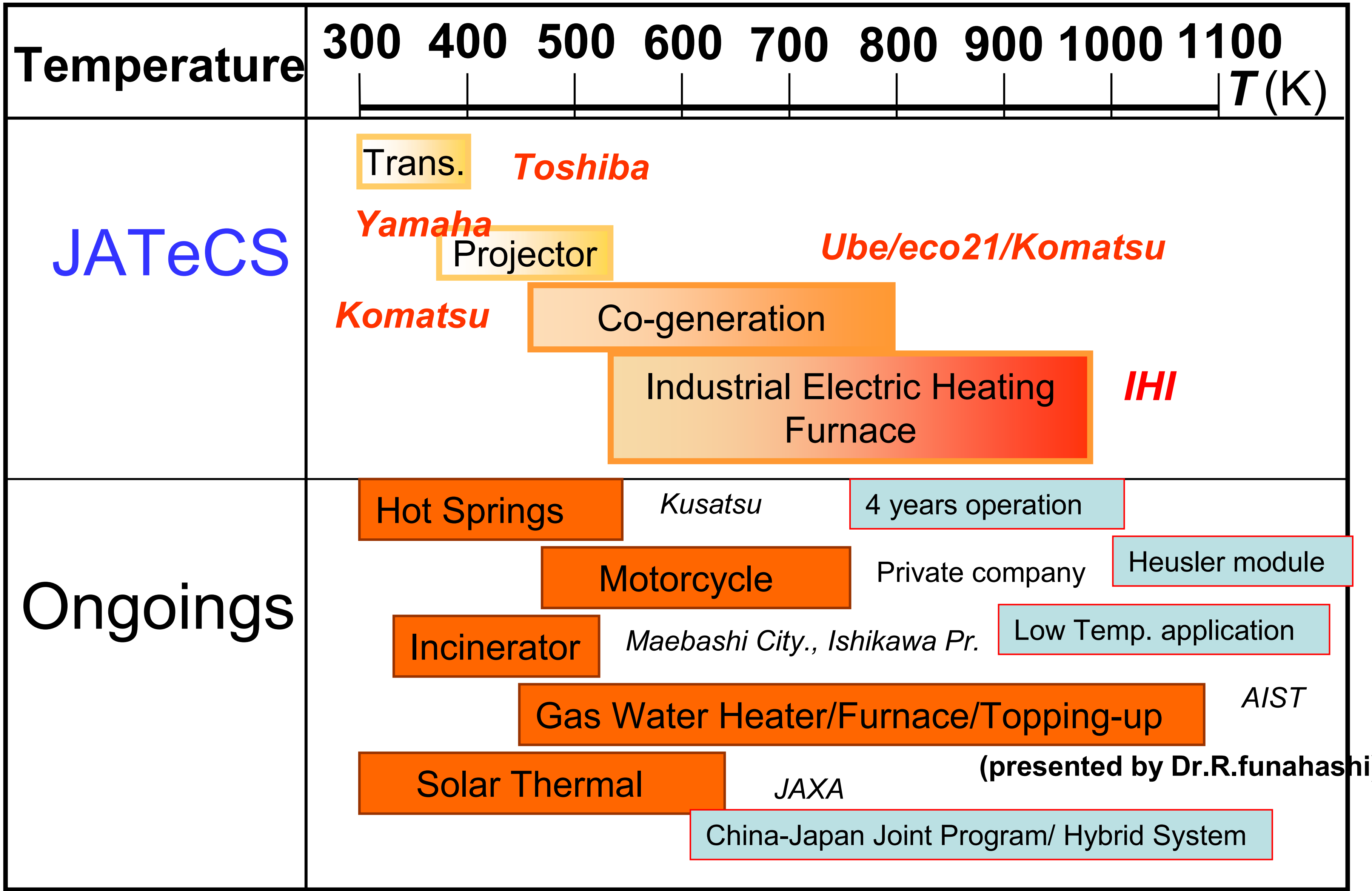
(3) TE Module Development

Phase 2

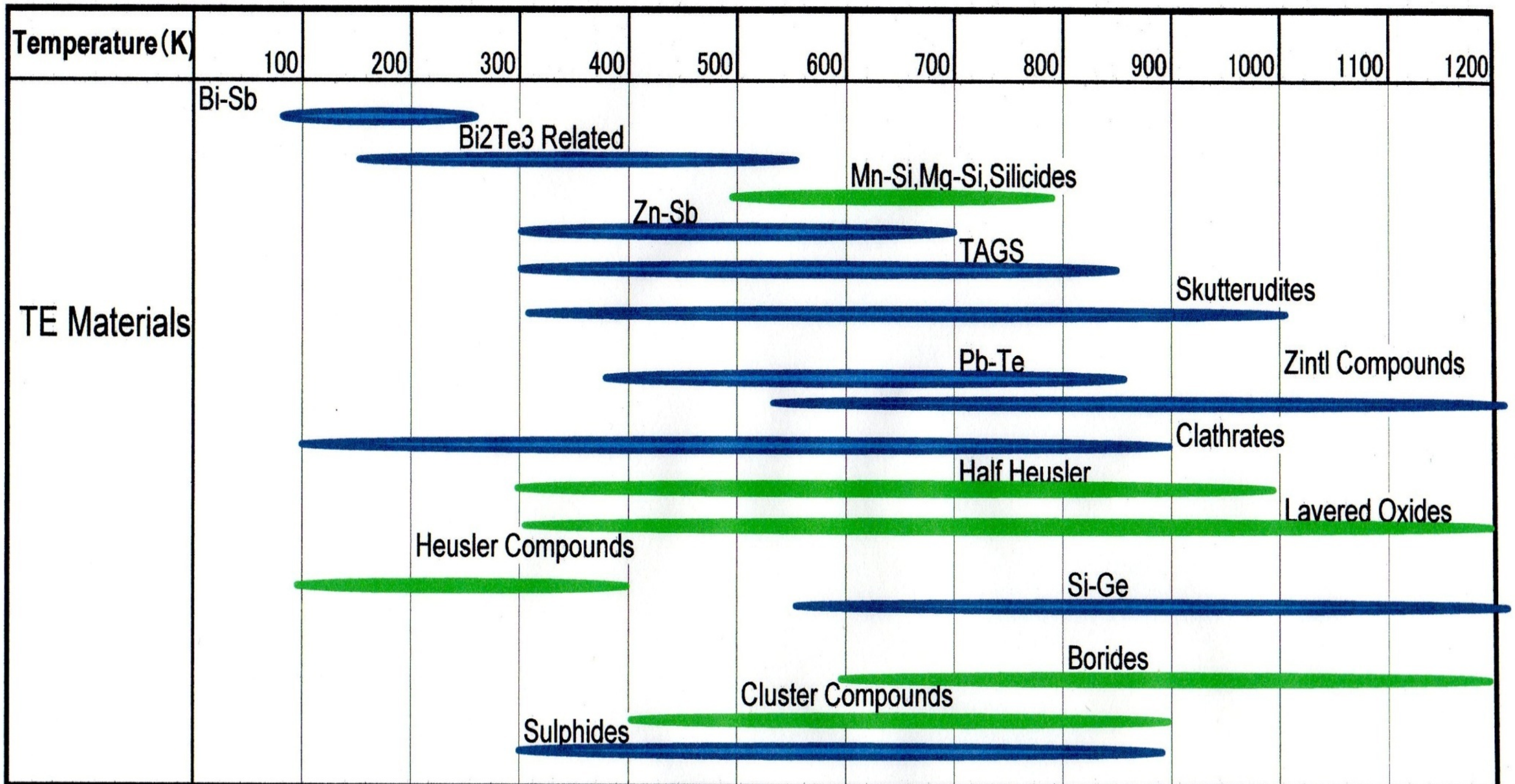




Application Systems



Over view of TE Materials



Topics on TE Materials Research-1

- Environment-Friendly Materials

Half Heusler

MNiSn (M=Zr,Nb) ,ZT 0.66 (n),0.45 (p), at1000K

Heavy Fermion Intermetallic

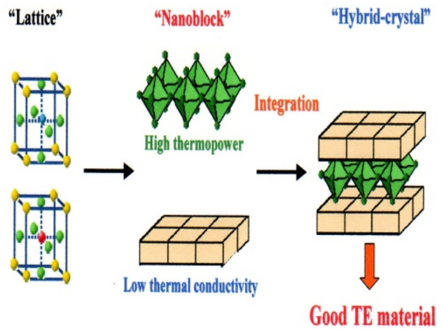
YbAl3Mx system, ZT was obtained 0.32 at 323K for Yb1.05Al3B0.1.

Higher Borides

Alkaline-Earth Hexaborides (Ca,Sr)B6 ZT=0.35 was obtained at 1073K.

Layered Oxides (presented by Dr.R.Funahashi)

Some Topics on the Enhancement Approaches due to Nanostructure Tech.



- Nanoblock integration

The ZT was obtained **2.4** at 300K for one cell layer of Nb doped $SrTiO_3$ system.・・・Nagoya Univ.,Waseda Univ., AIST

- Nanovoid forming

Thermal conductivity reduced by **30-35%** with forming nanovoid in ZnAlO system. The ZT was **0.54-0.59** at 1273K: nearly two times more than that of no nanovoid dispersion.・・・Kyusyu Univ.

- Nanophase separation

Nanophase separation effect for n-type half-Heusler (MA0.5,MB0.5)NiSn System (MA,MB=Hf,Zr,Ti) :The ZT increased from **0.55** for ZrNiSnto 0.9 at 873K.・・・Tokyo Inst. of Technology、AIST

- Nanoparticle inclusion

The ZT increased from 1.1 to **1.22** at 773K for filled skutterudite $CeFe_3CoSb_{12}$-MoO_2 composite .・・・Osaka Univ.

Future Prospects

Approach to Commercialization of TE Power Generation

1st Step : Public Relations ; TE technology can contribute to the solutions of environmental issues, energy security and industry.

Commercial TEG modules by KELK & Komatsu , and Yamaha as the outcome with JATeCS-project

2nd Step : Users ' Acceptance of Full-grown TE Power Generation Technology ; Establishment of the commercial production line

3rd Step : Establishment of TE Power Generation Industry and Market

Future Prospects

Near-term applications to be commercialized:

Small-scale, low-temperature, and dispersed waste heat recovery systems from all energy-utility fields using high-ZT- Bi-Te based modules, or low-cost, environment-friendly, moderate-ZT- materials based modules, and micro-scale, multi-purpose TEG systems

Long-term applications:

Large-scale (kW order) and wide-temperature range waste heat recovery systems, and topping-up TEG systems

Innovative thermoelectric material systems:

The Key is best-mix nano and robust nanotechnology.

Conclusions

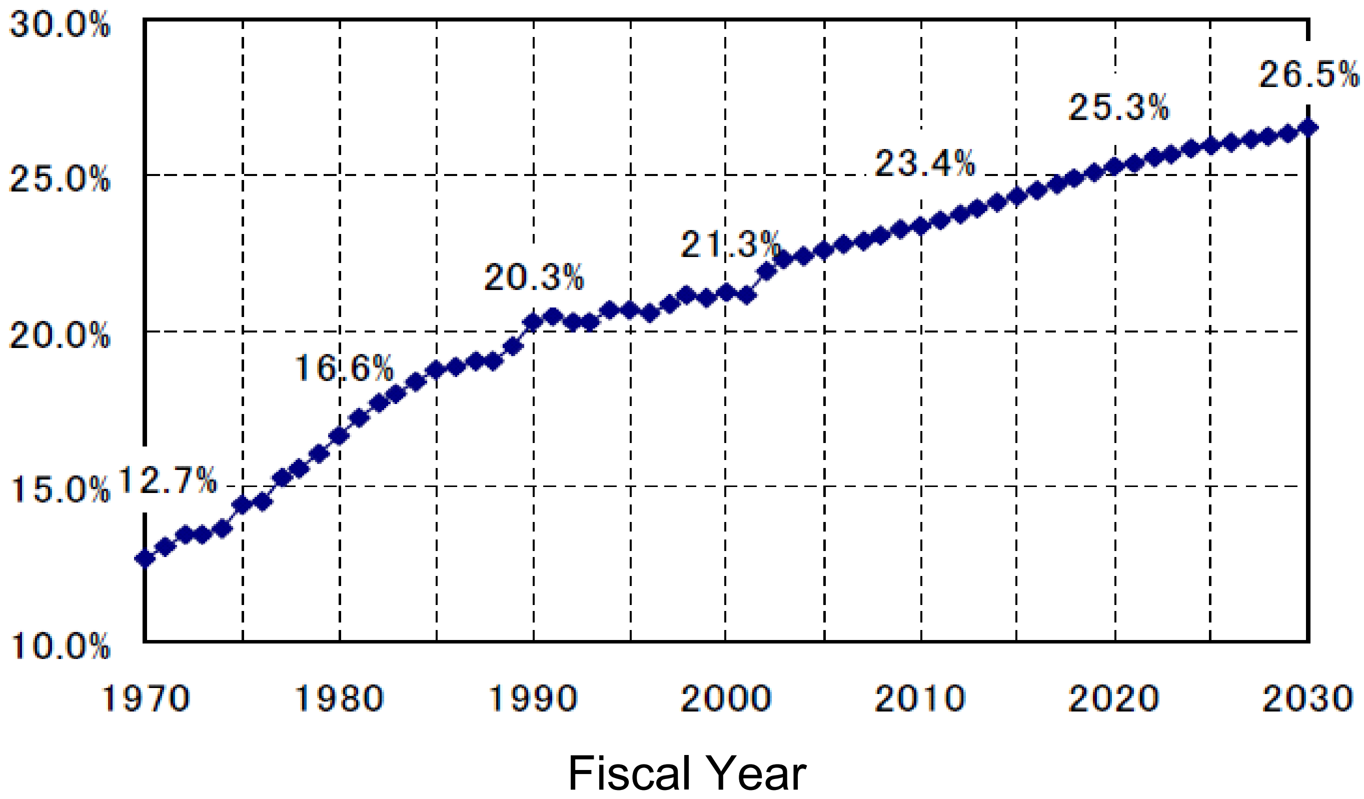
- Several ongoing projects on TEG technology in Japan are summarized, in which the goals in ZT are 1.3~1.5.
- The effort to proceed the TEG technology has been intensively achieved for the small-scale applications and advanced materials.
- Near-term applications to be commercialized are prospected to be small-scale, low-temperature, and dispersed waste heat recovery systems from all energy-utility fields using high-ZT- Bi-Te based modules, or low-cost, environment-friendly, moderate-ZT- materials based modules

Thank you for your attention !!

Where there is heat, there is Thermoelectrics !!

Electrification Ratio in Japan

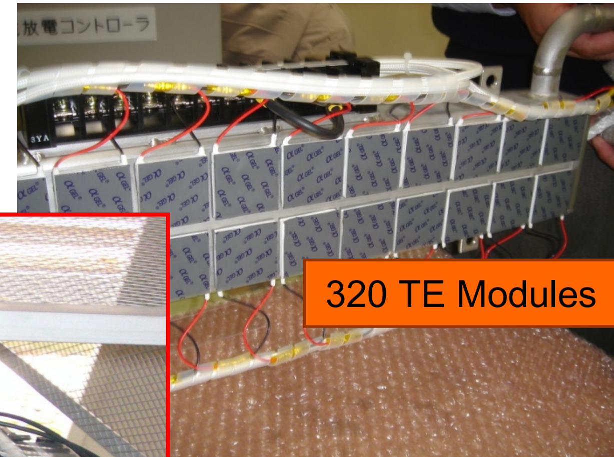
＊＊＊Progress and Prospects＊＊＊



The role of the electricity has been increasing year and year in Japan. The high performance of power generation and the efficient use of energy resources are inevitable and urgent to sustain the electrified society.

Kusatsu Hot Springs TE Power Generation System:
Continuous operation for **nearly 4 years** since Dec. 26th,2005

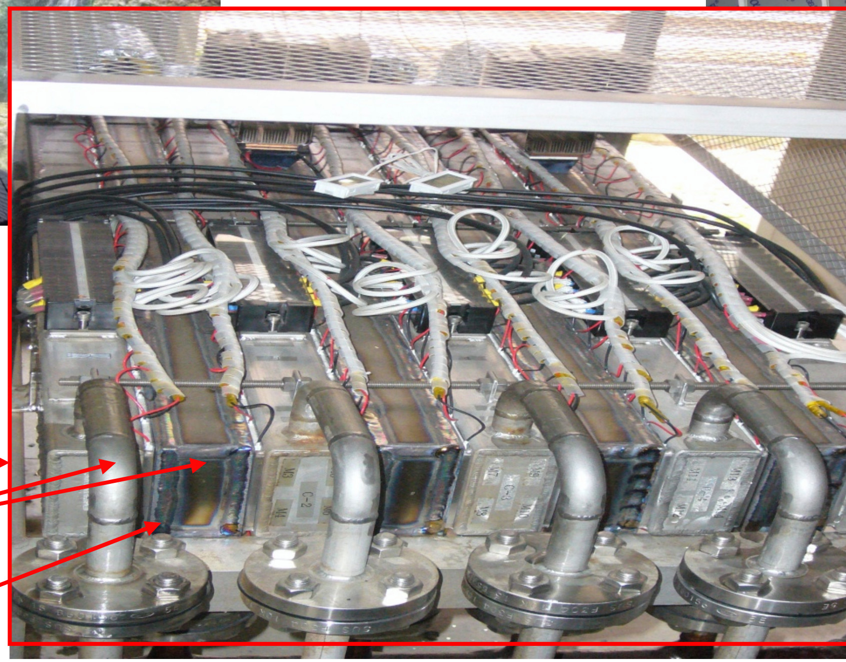
Temperature of the hot spring is 369K constant, and pH is1.46.

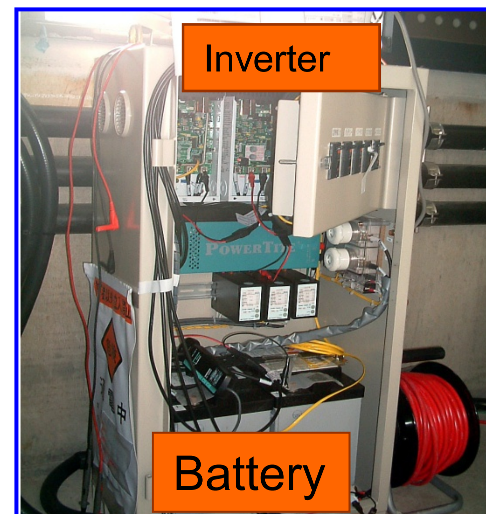


Cold channels

TE modules

Hot spring channels

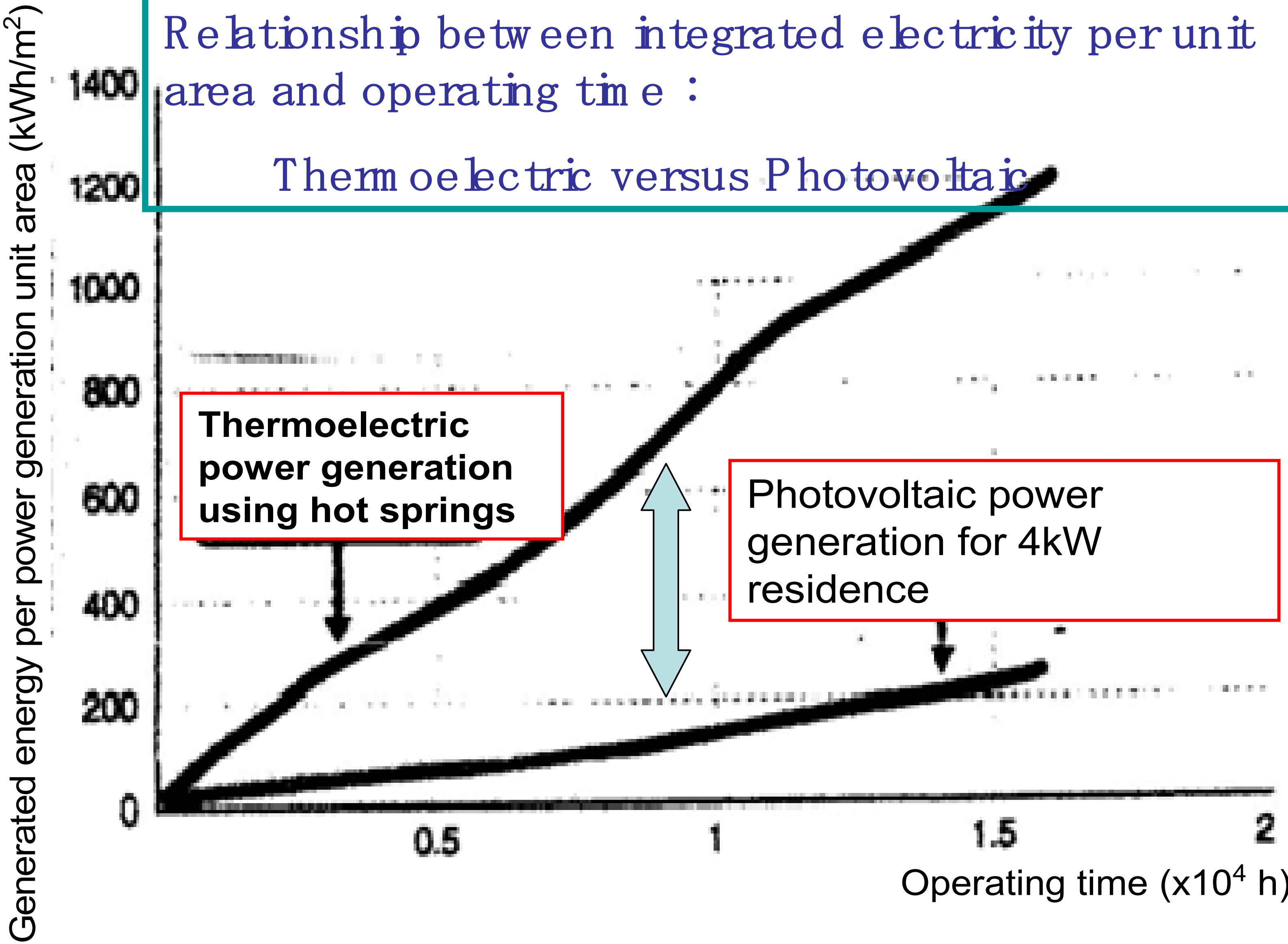




The generated electricity has been consumed in TV ,illumination and display during the daytime, and for the charge to the battery in the nighttime. The cumulative electric energy had been 1360kWh by August 22,2009.

Relationship between integrated electricity per unit area and operating time :

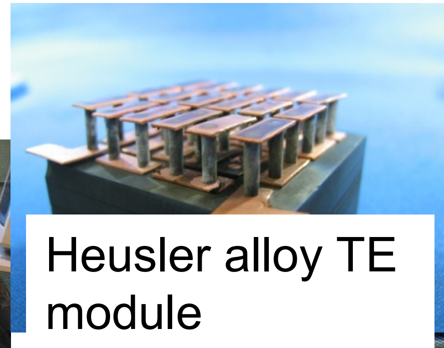
Thermoelectric versus Photovoltaic



Waste heat recovery from Motorcycle

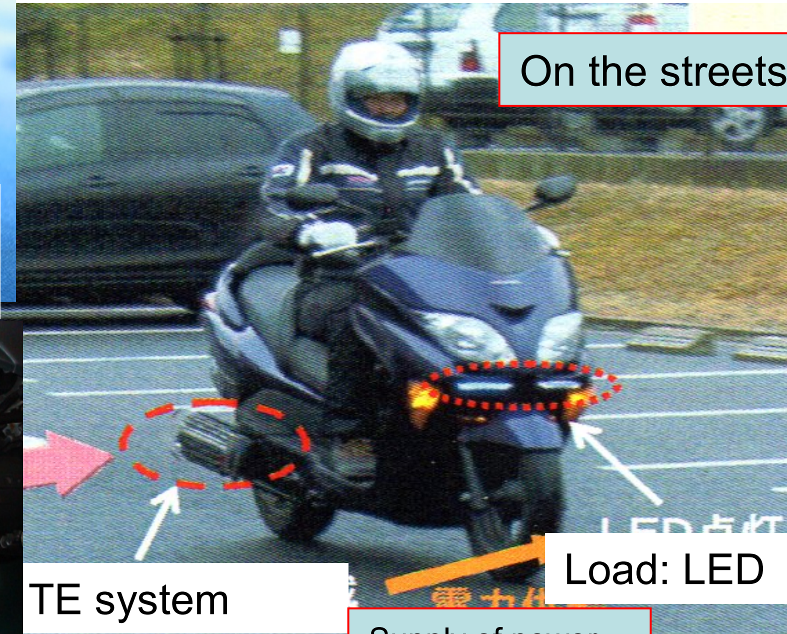
On the test bench

Annual production of motorcycles: 40M/y



Heusler alloy TE module

On the streets

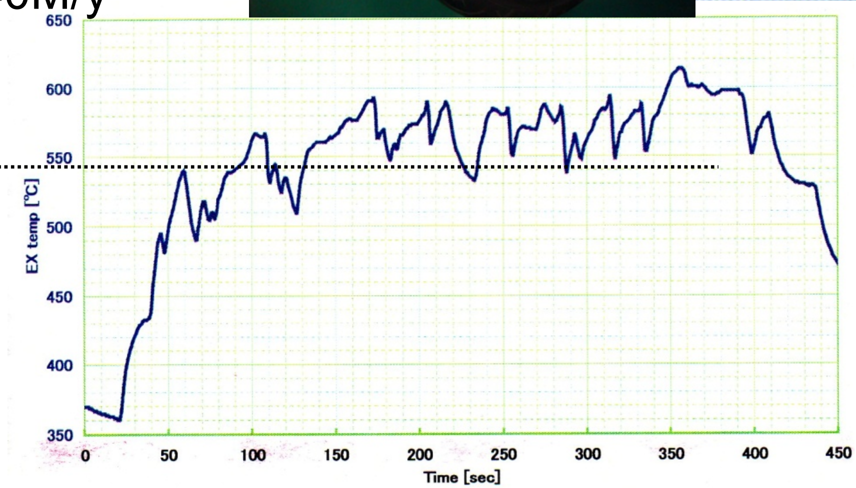


TE system

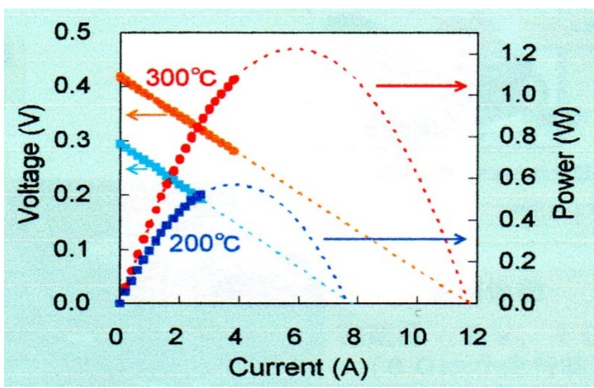
Load: LED

Supply of power

823K



Time variation of exhaust gas temperature



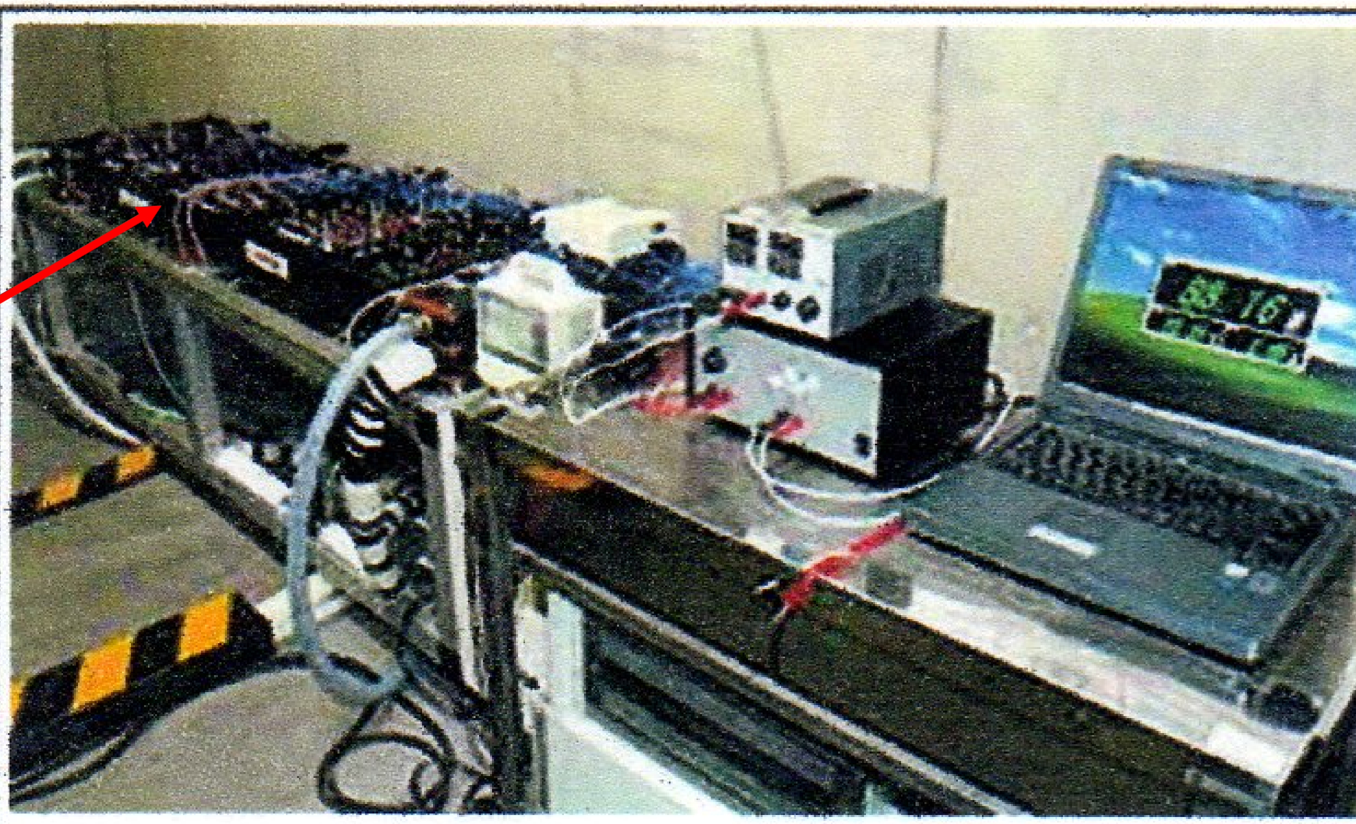
Power Characteristics

TEG demonstration systems to low temperature waste heat (<373K) from incinerator

in Maebashi City, Gunma Pref. ,and Ishikawa Pref.

Press release on September 16th,2009

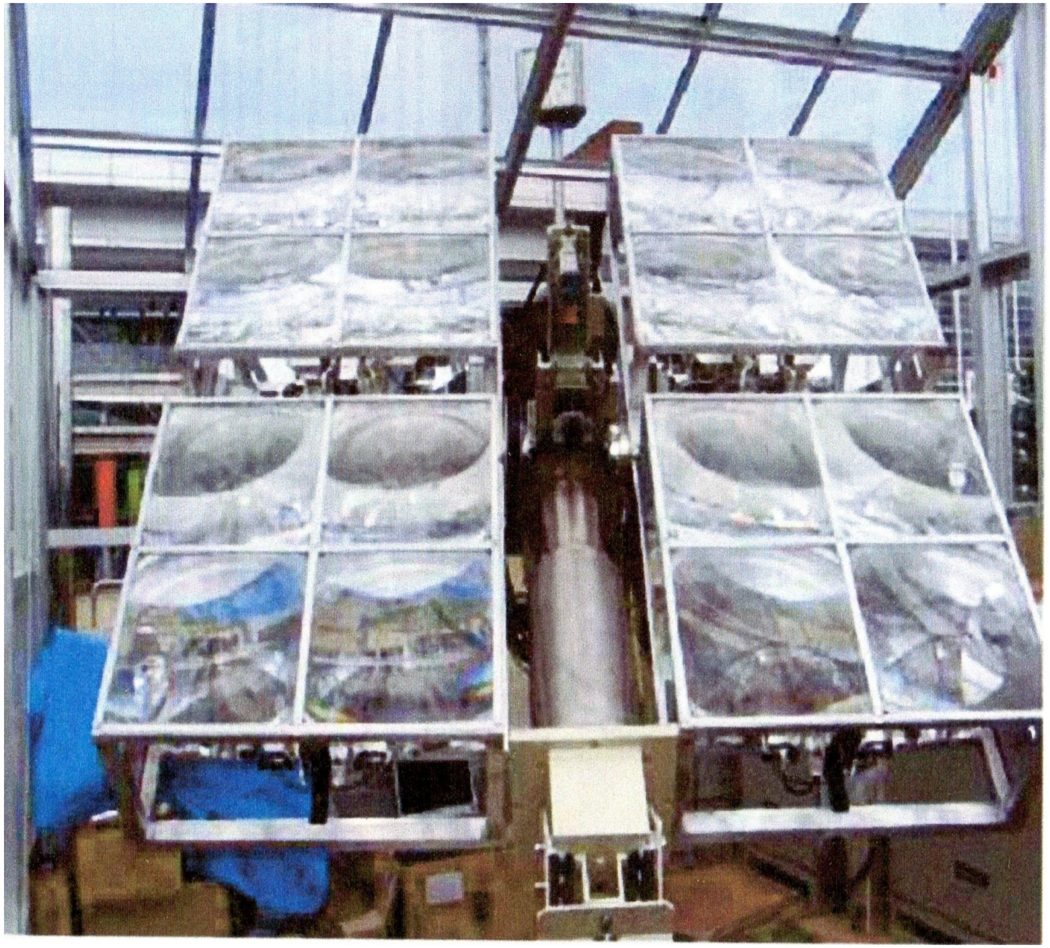
TEG System

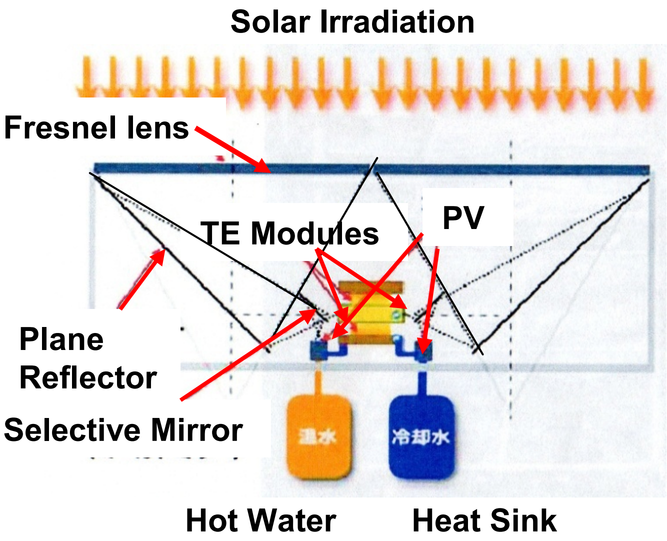


六供清掃工場に設置された熱電変換発電装置

Rokyo Incinerator Plant (Capacity: 405t/day)

TEG demonstration system using Solar Thermal energy by JAXA-ARD

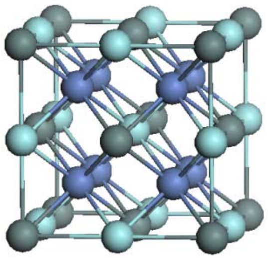




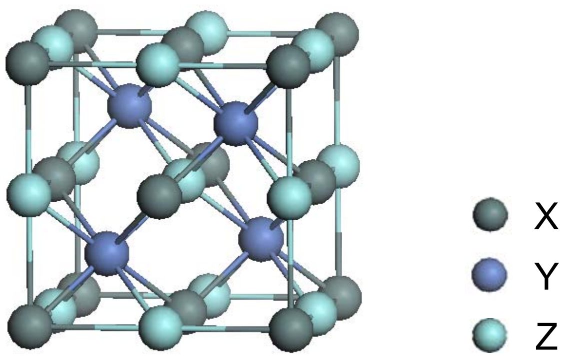
TE-PV Combined Solar System

JAXA-ARD; Japan Aerospace Exploitation Agency- Aerospace Research & Development Directrate

Half-Heusler Compounds



: Heusler type



MgAgAs structure

XYZ half-Heusler compounds

- Cubic MgAgAs type structure
- VEC=8 or 18 : semiconductor/semimetal

Reference Data:

N-type half-Heusler compounds;

ZrNiSn based	: ZT=0.5~1.5 [1-4]
TiCoSb based	: ZT=~0.3 [5]
NbCoSn based	: ZT=~0.3 [6]

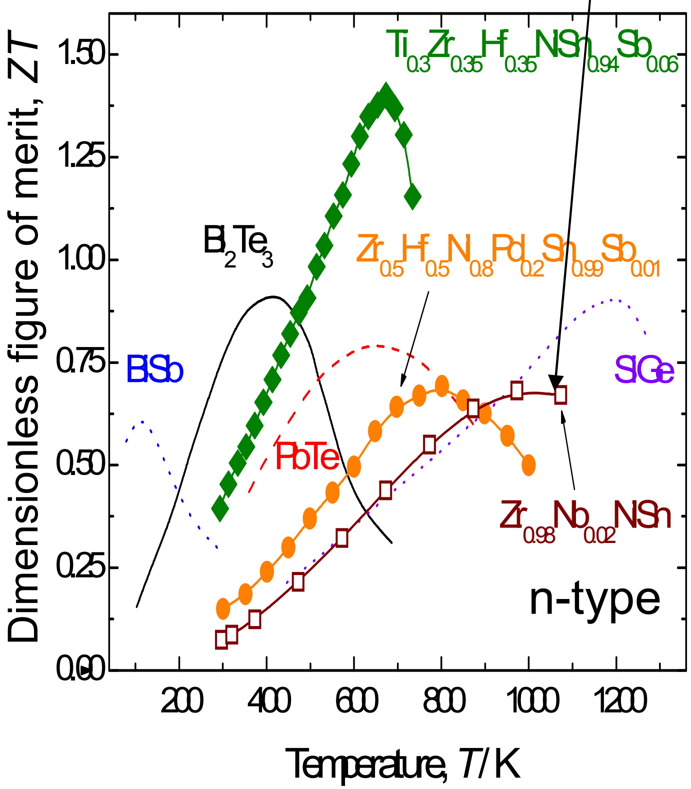
P-type half-Heusler compounds;

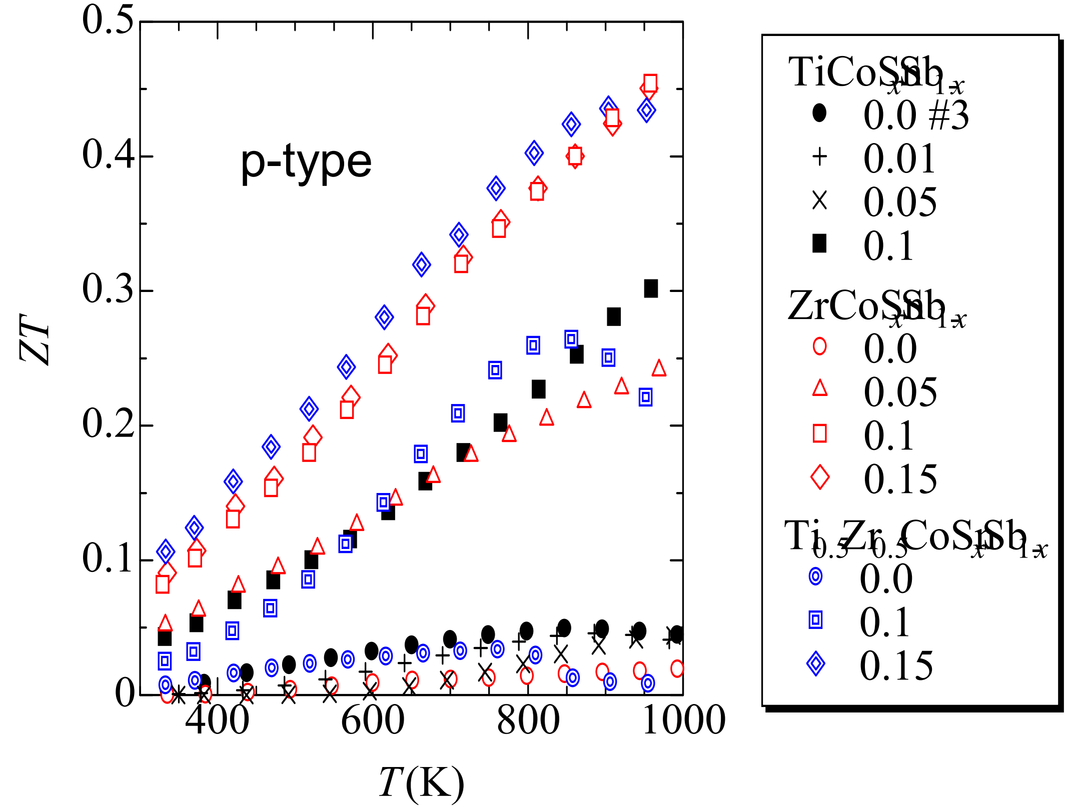
TiCoSb based	: ZT=0.3~0.9 [7,8]
ZrPtSn	: ZT=~0.1 [9]
ErPdSb	: ZT=~0.2 [10]

1) C. Uher et al, *Physical Review B*, **59** (1999) 8615-8621.
2) Q. Shen et al, *Appl. Phys. Letter*, **79** (2001) 4165-4167.
3) Sakurada et al., *Appl. Phys. Letter*, 86 (2005), 082105.
4) S.R. Culp et al., *Appl. Phys. Letter*, 88 (2006), 042106.
5) Y. Xia et al., *J. Appl. Phys.,* 88 (2000), 1952-1955.
6) Y. Ono et al, *Proc. MRS*, **793** (2003) 195-200.
7) T. Sekimoto et al, *Appl. Phys. Letter*, **79** (2001) 4165-4167.
8) Sakurada et al., *Proc. MRS* (2005).
9) Y. Kimura et al., Abst. Autumn Meeting JIM, (2005) 85-86.
10) T. Sekimoto et al., *J. Appl. Phys.,* 99 (2006), 103701.

Half-Heusler Compounds：MNiSn (M=Zr,Nb)

by Prof. Yamanaka’s Group (Osaka Univ.)





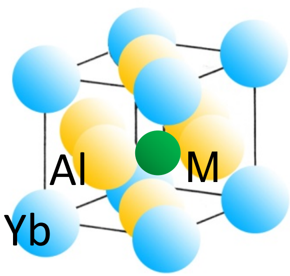
The *ZT* value was obtained 0.66 at 1000 K.

The ZT=0.45 around 1000K for Sn doped ZrCoSb without no technique for reduction of thermal conductivity

Rare-earth based heavy fermion intermetallic compounds

by S.Katsuyama's Group (Osaka Univ.)

$YbAl_3M_x$



Large effective mass:
$m^* = 15\text{-}30 m_e$

High Power factor

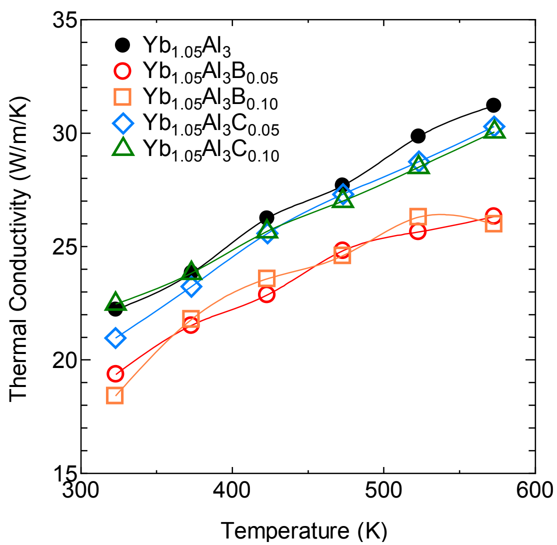
$$P = \frac{S^2}{\rho}$$

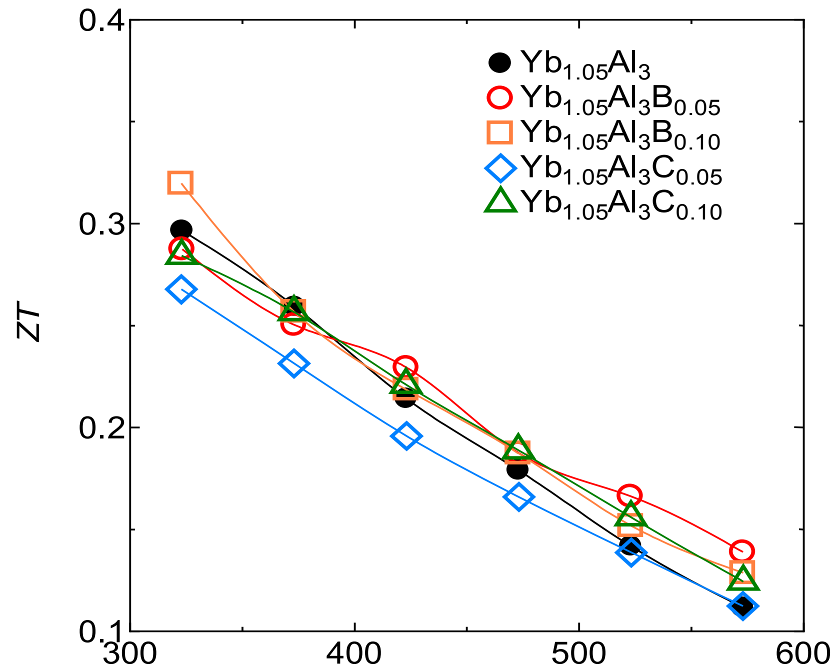
$P \sim 15000\ \mu Wm^{-1}K^{-2}$
(300K)

※Bi_2Te_3 $P \sim 5000\ \mu Wm^{-1}K^{-2}$
(300K)

Reduction of thermal conductivity

Phonon scattering due to rattling effect by M

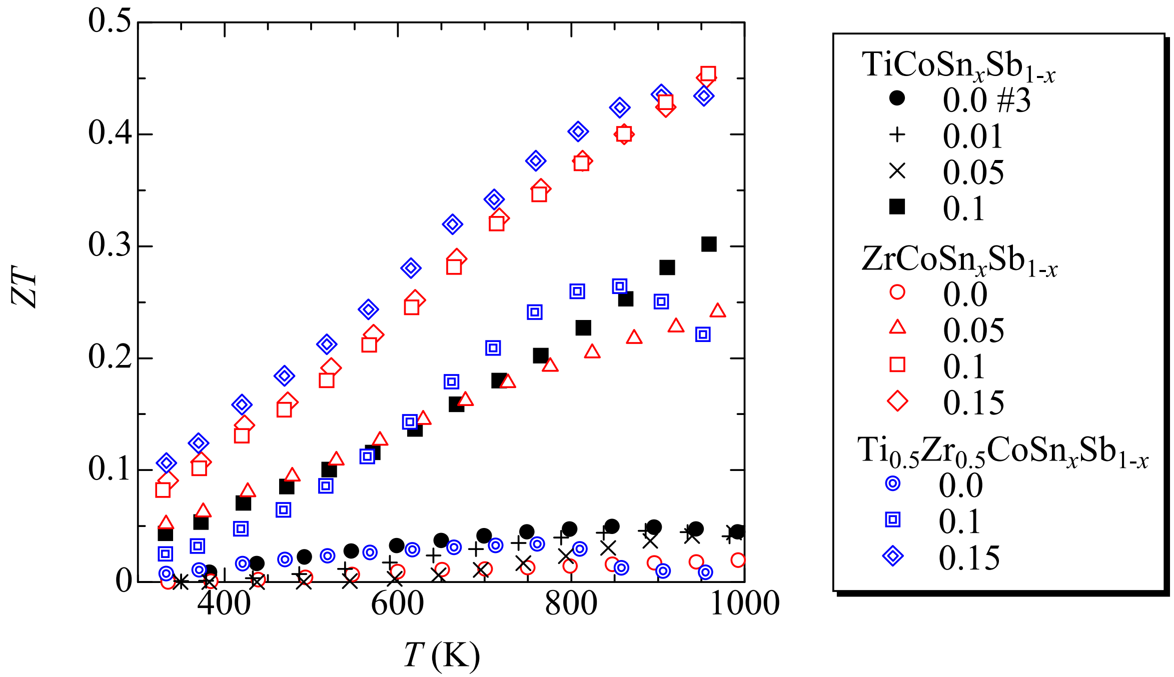




The ZT value was obtained 0.32 at 323K for $Yb_{1.05}Al_3B_{0.10}$ system.

MCoSb (p-type) : *ZT*

by Prof. Yamanaka's Group (Osaka Univ.)



Maximum *ZT*

$TiCoSn_{0.1}Sb_{0.9}$

ZT = 0.30 at 959 K

$ZrCoSn_{0.1}Sb_{0.9}$

ZT = 0.45 at 958 K

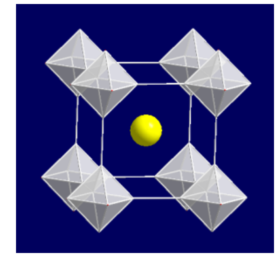
$Ti_{0.5}Zr_{0.5}CoSn_{0.15}Sb_{0.85}$

ZT = 0.44 at 904 K

The ZT=0.45 around 1000K for Sn doped ZrCoSb without no technique for reduction of thermal conductivity

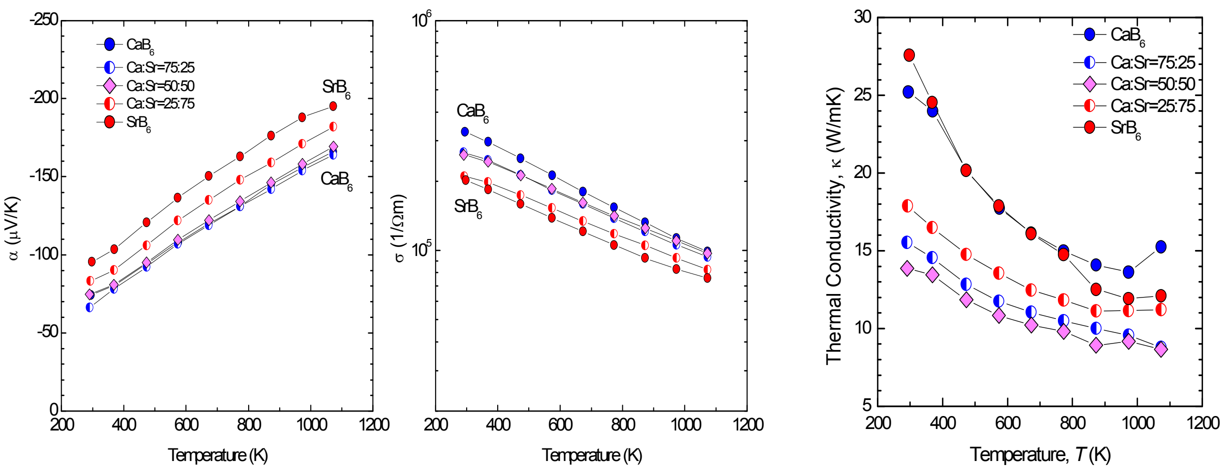
Alkaline-Earth Hexaborides

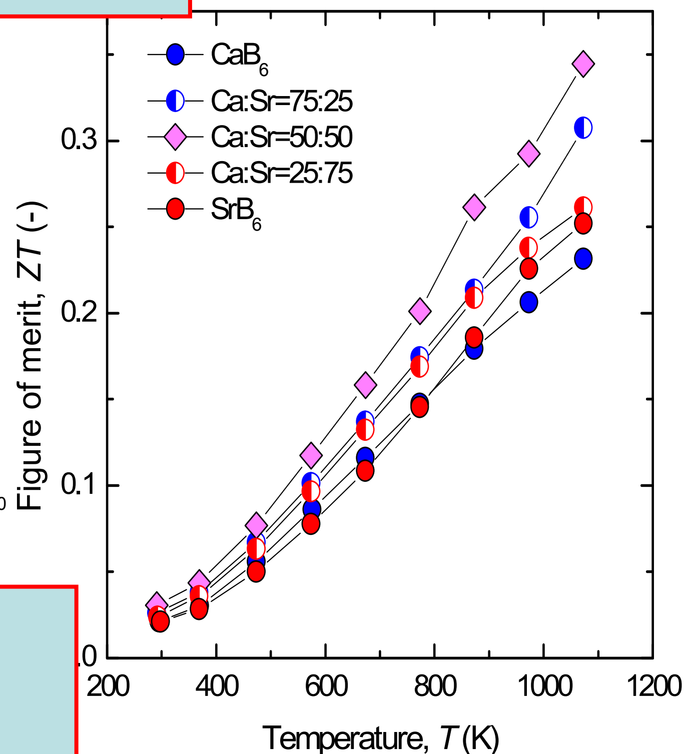
by M.Takeda (Nagaoka University of Technology)



MB_6

Thermoelectric & Transport properties:
To estimate the optimal electrical property for TE conversion
Synthesize (Ca,Sr)B6 alloys:
To reduce thermal conductivity keeping high electrical property by alloying





TE performance was successfully improved by alloying: the ZT=0.35 was obtained at 1073K.

By Solid Reaction &SPS

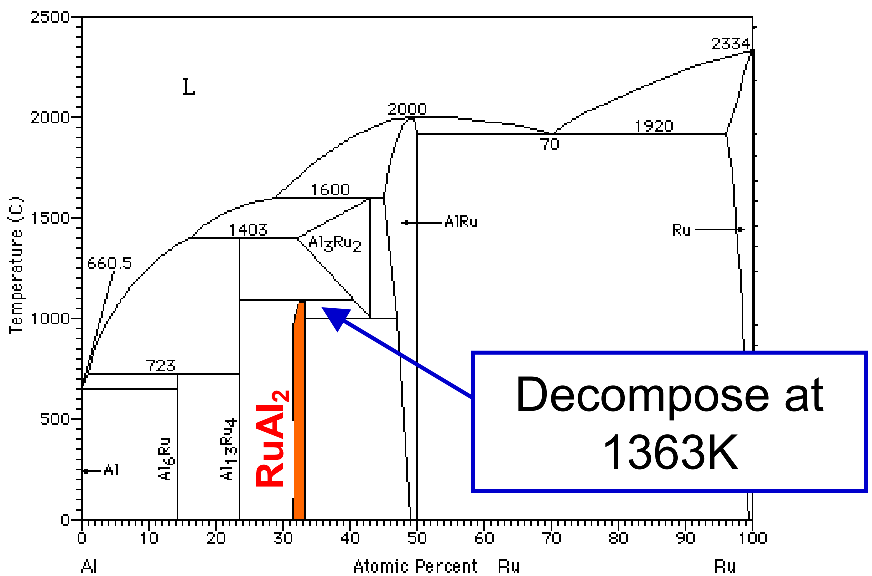
$RuAl_2$

$RuAl_2$: semimetal, Band Gap=0.1~0.6 eV

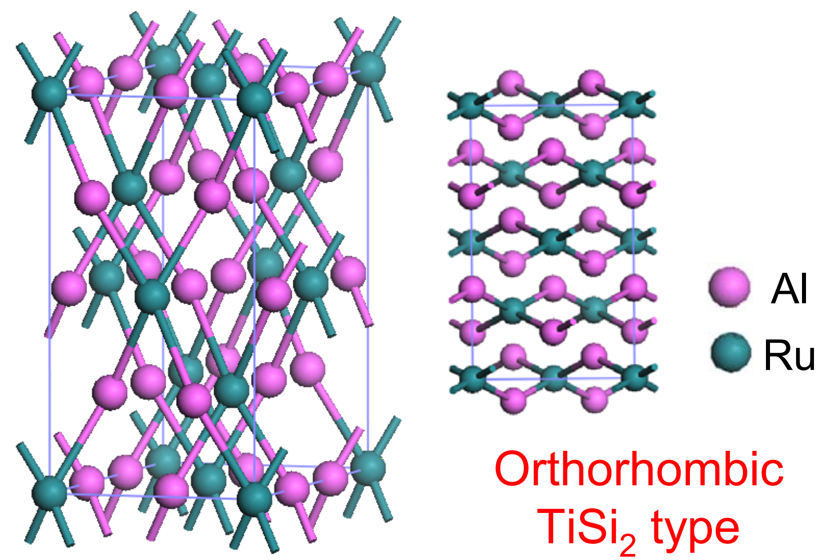
Thermoelectric properties of nondoped $RuAl_2$ have been reported*.

- The maximum *ZT* was estimated to be ~0.6 at 700 K.
- The electrical properties were not optimized yet.

*D. Mandrus, et al., *Phys. Rev. B*, 58 (1998) 3712.

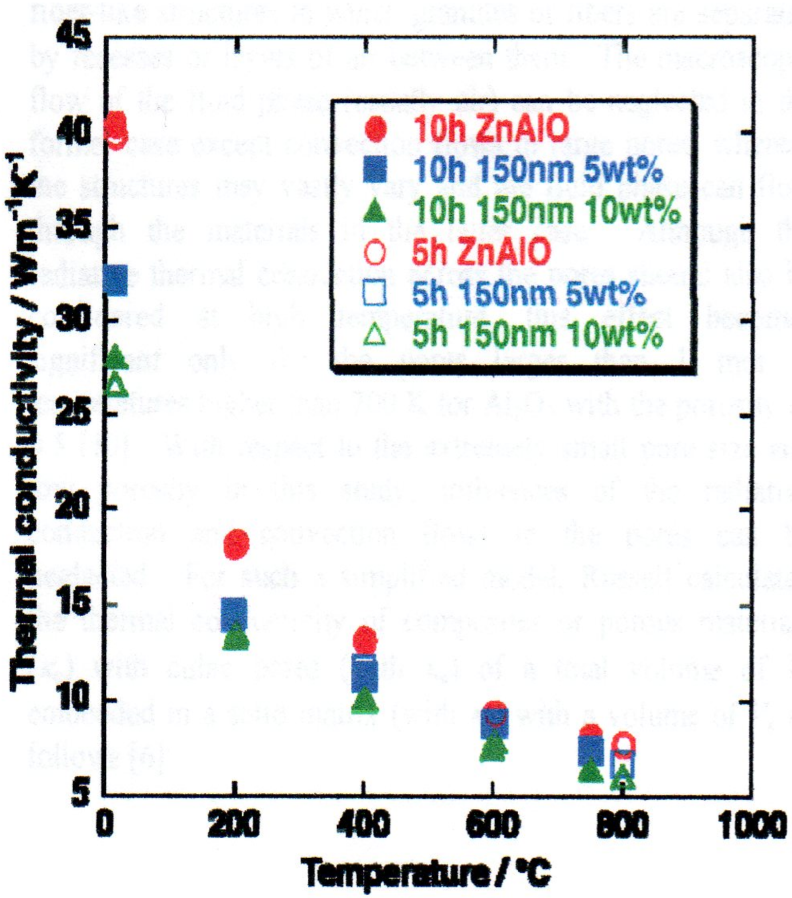


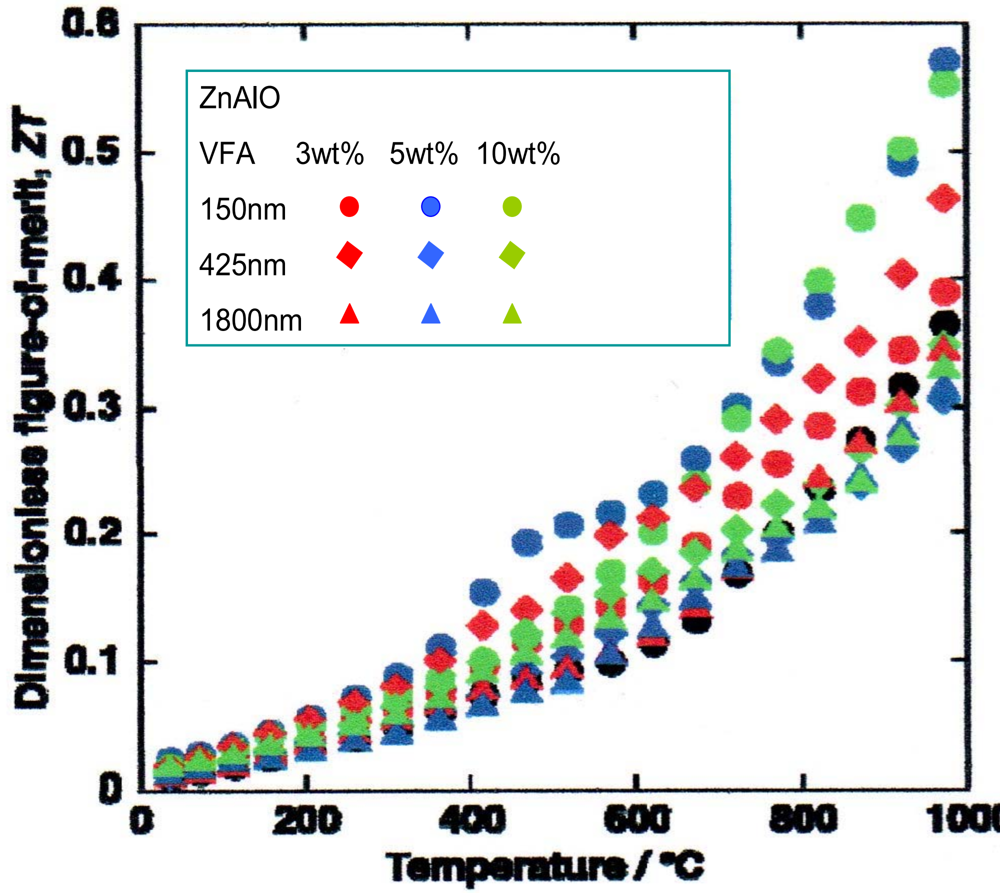
Ru-Al binary phase diagram



Crystal structure of $RuAl_2$

Nanovoid forming effect

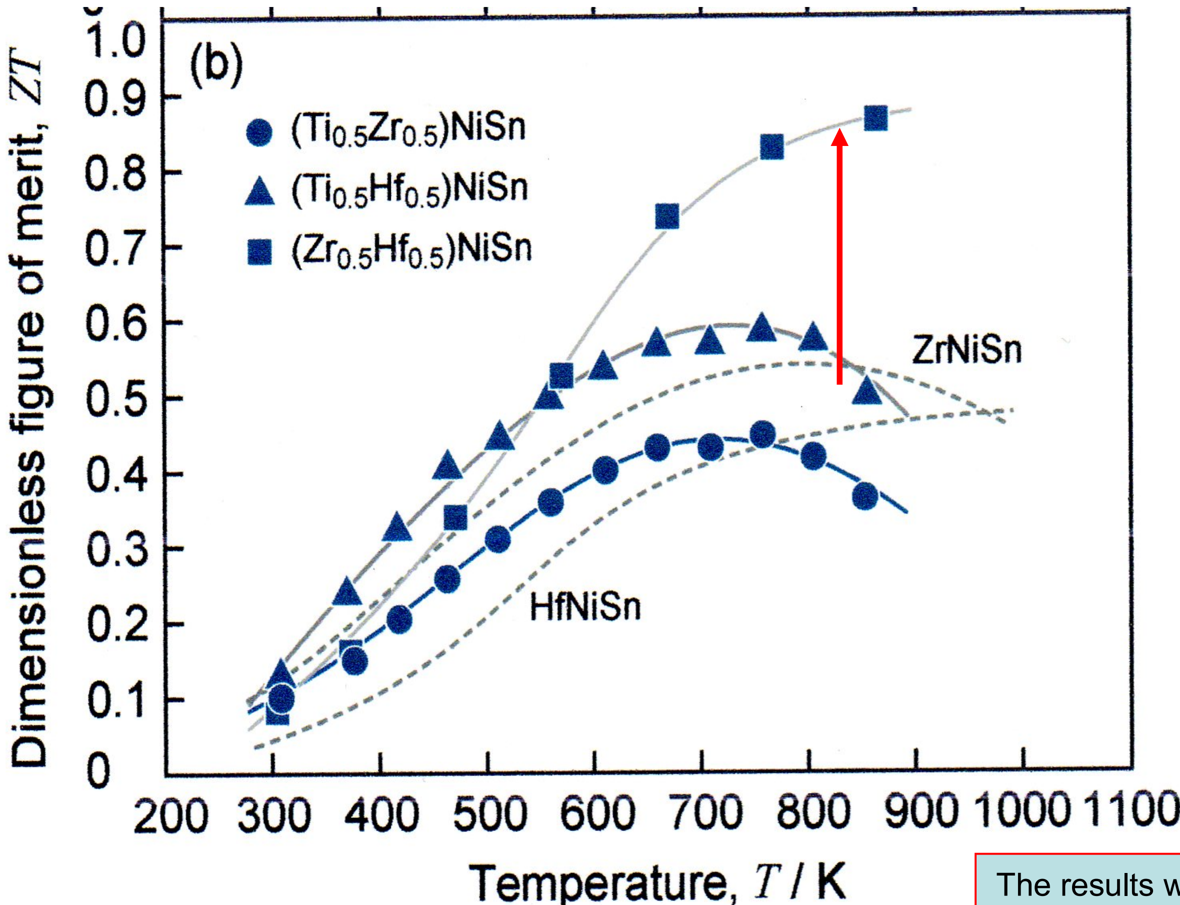




Thermal conductivity reduced by 30-35% with forming nanovoid in ZnAlO system

ZT=0.54-0.59 at 1273K: nearly two times more than that of no nanovoid dispersion samples

Nanophase separation effect for $(MA_{0.5},MB_{0.5})NiSn$ System (MA,MB=Hf,Zr,Ti)



n-type Half-Heusler

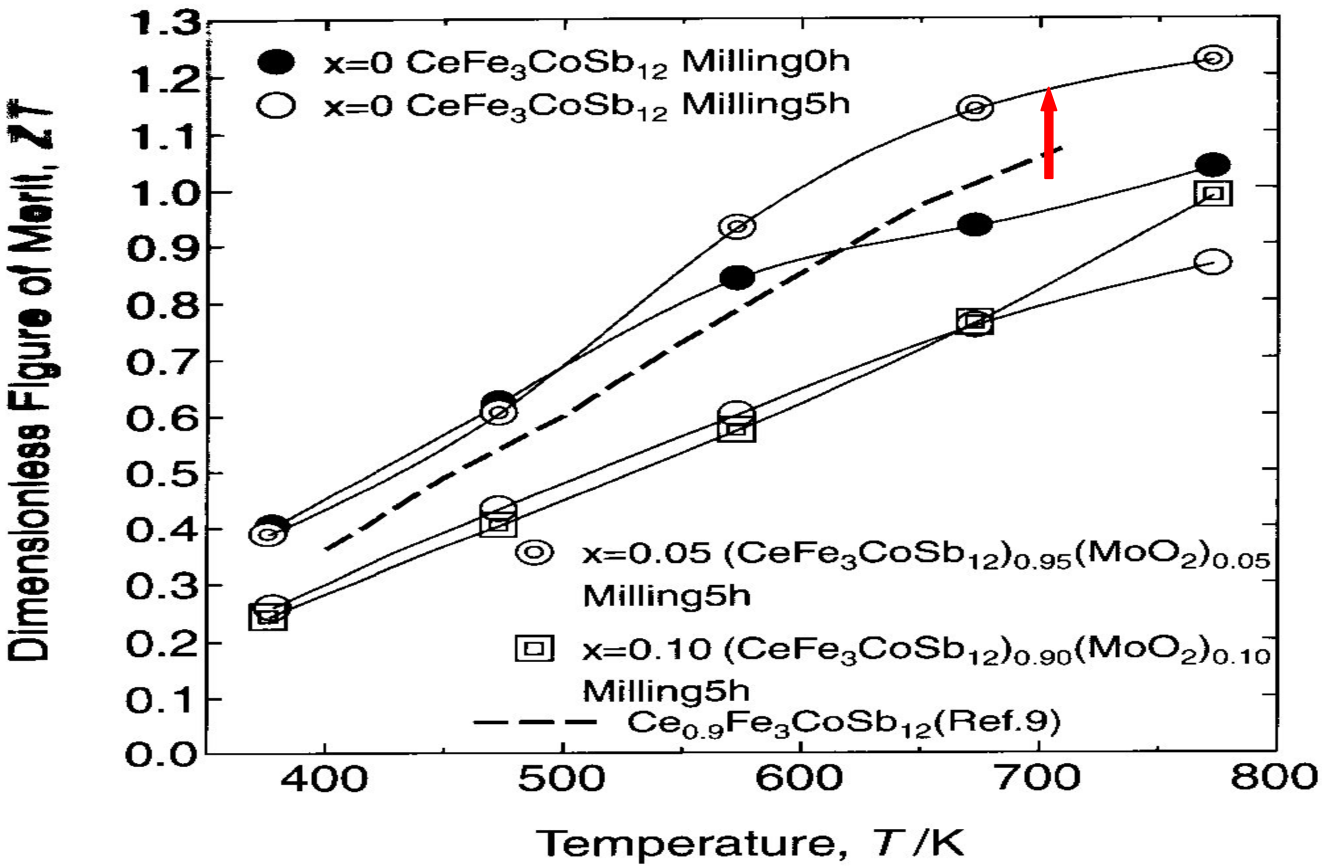
Samples are made by directional solidification.

The results would be caused by a combined effect of phase separation and solid solution.

Nanophase separation is induced with the formation of solid solution for specified combination of MA and MB.

Nanoparticle inclusion effect for filled skutterudites system

$CeFe_3CoSb_{12}$-MoO_2 composite was made by the mechanical alloying and spark plasma sintering.

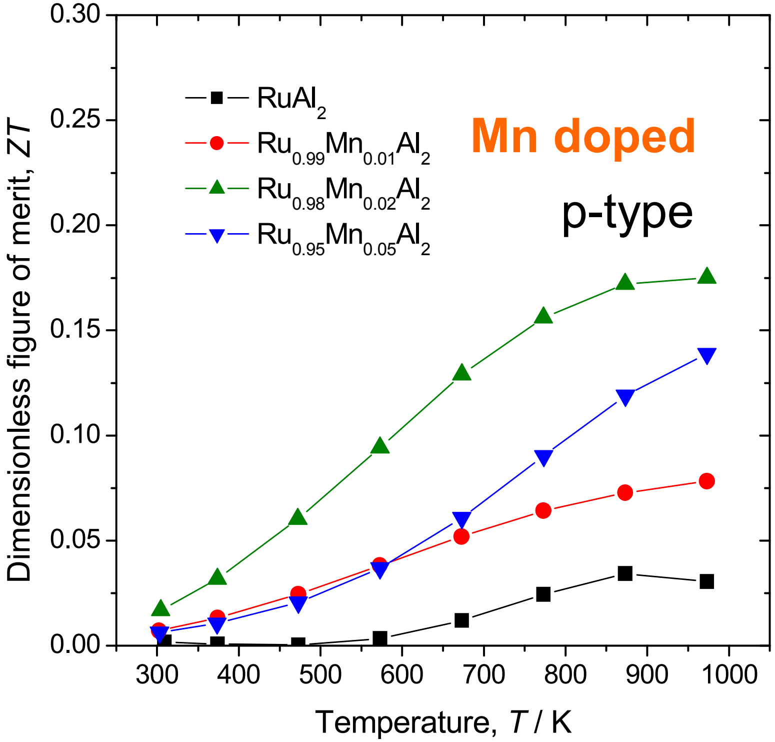


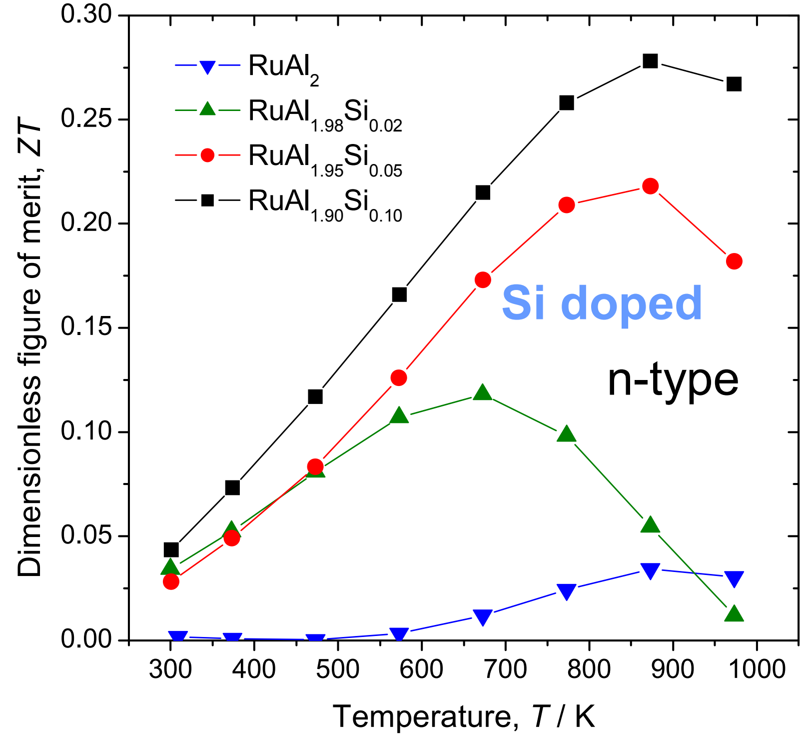
The ZT value increased from 1.1 to **1.22** at 773K.

Semimetal $Ru_{1-x}Fe_xAl_2$

by Prof. Yamanaka's Group (Osaka Univ.)

By Arc melting





The *ZT* values were 0.17 (p-type) and 0.28 (n-type) at 900 K.

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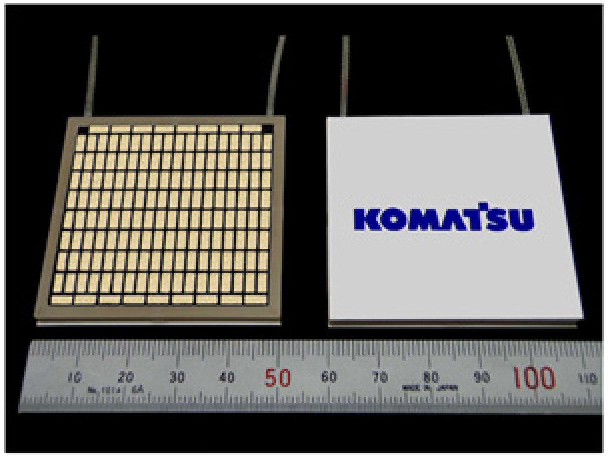
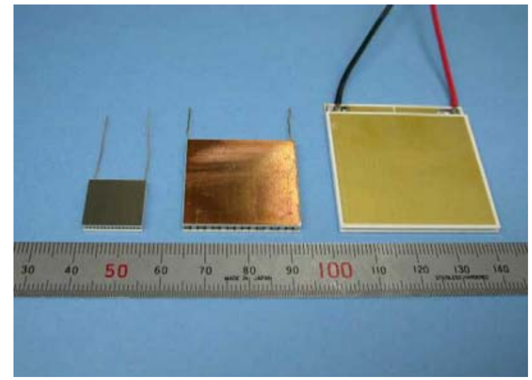
Commercial TEG modules by KELK & Komatsu , and Yamaha as the outcome with JATeCS-project

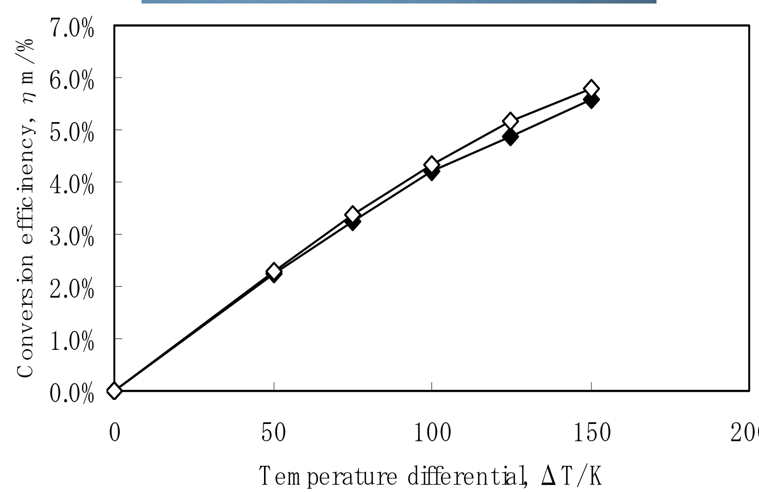


Specifications of Commercial TEG Module

Size	50mmx50mmx4.2mm
Weight	47g
Power Output	Max.24W (Th=553K,TC=303K)
Temp. Range	TH:Max. 553K, Nominal <523K,TC:Max, 423K)
TE Module Efficiency	Max.7.2%
TE Material	Bi-Te System
No. of Couples	161

Power density = 0.96 W/cm^2 and 1.95 g/W based on formal module size





Module Efficiency =5.7% at ΔT=150K.