# Overview of Progress in R&D for Thermoelectric Power Generation Technologies in Japan

Takenobu Kajikawa
Shonan Institute of Technology
Fujisawa, Kanagawa, Japan

# Outline

- Background
- Government-funding Projects
- Private Companies' Activities
- Future Prospects
- Concluding Remarks

# Background

○ Urgent Reconstruction of Overall Energy Policy in Japan due to Fukushima Nuclear Power Station Disaster

→ Urgency of the establishment of renewable energy tech.

○ Enforcement of Take-up Regulation of entire electric power from renewable energy conversion system such as PV and wind power

→ Acceleration of growing the renewable energy tech.

○ ICT2013 (June 30 – July 4,2013) will be held in Kobe, Japan.

→ Stimulation to R&D activities on TE

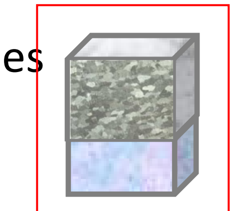
# Ongoing Government-funding R&D Projects

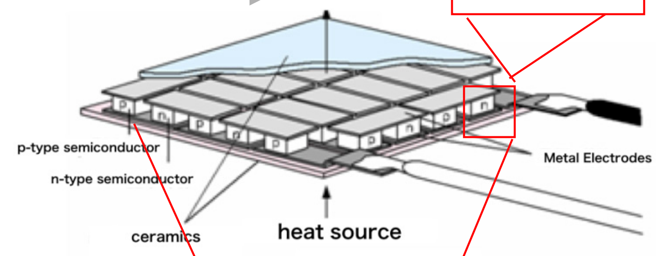
- NEDO project / Development of Nano-Structured Thermoelectric Materials using Clathrates
- JST project / Development of High-Efficiency Thermoelectric Materials and Systems

# NEDO project "Development of Nano-Structured Thermoelectric Materials using Clathrates" FY2009-2011

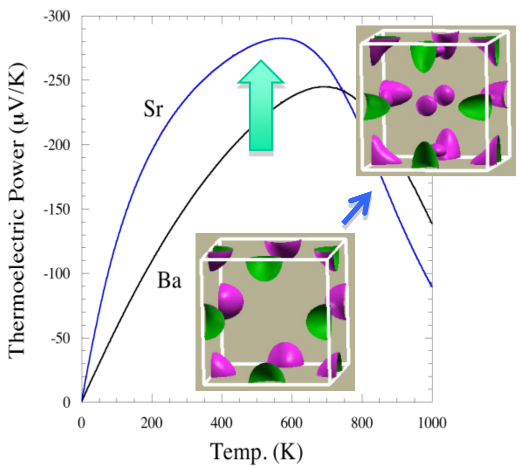
## Project Goal; *ZT*=1.3 at 200-300 °C

Optimization of Segmented TE modules
**AIST, KELK**



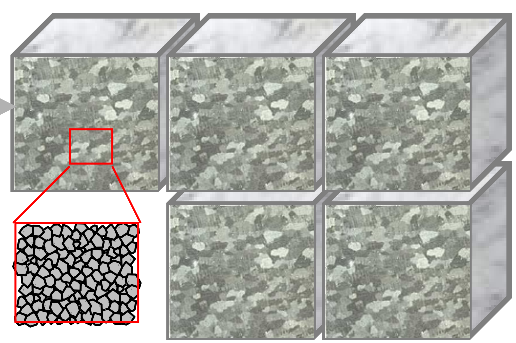



Design of novel clathrates by first-principle calculations
**Yamaguchi Univ.**

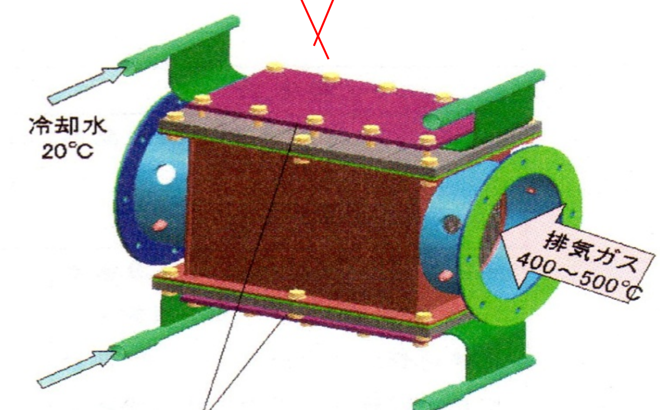



Synthesis of single crystals toward higher ZT
**Hiroshima Univ.**


Synthesis of bulk materials for modules by sintering technique
**Yamaguchi Univ.**



Design & demonstration of TE power generation unit for waste heat recovery in the furnaces
**DENSO 160W/unit**

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# Enhancement of TE Performance for Nano-structured Clathrates

- BGS: $Ba_8Ga_{16}Sn_{30}$

Saiga, Takabatake *et al.*, J. Alloys and Compds, 507, 1 (2010).

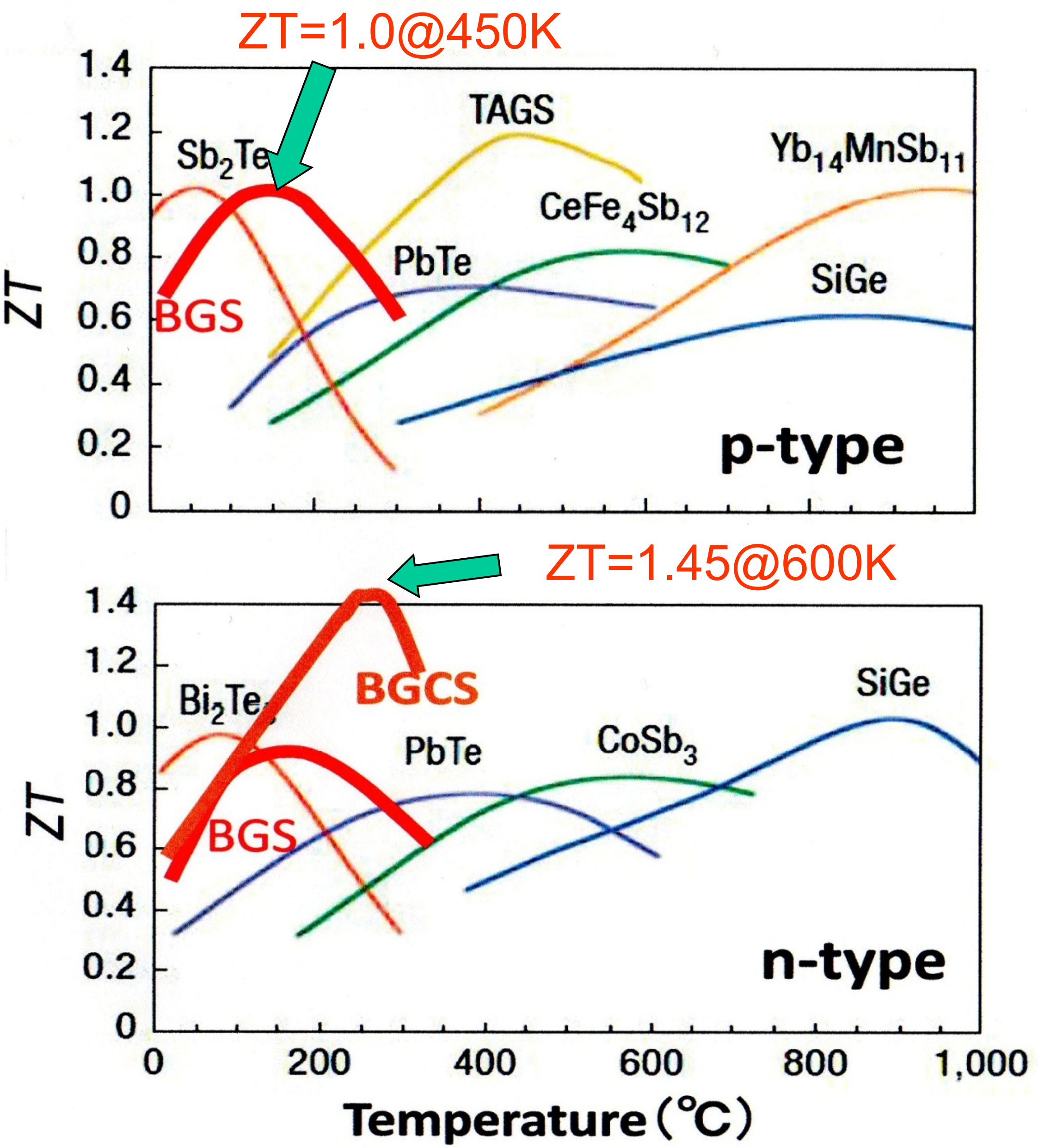
- BGCS: $Ba_8Ga_{16-x}Cu_xSn_{30}$

Deng, *et al.*, J. Appl. Phys. 109, 103704 (2011), Saiga *et al.*, unpublished.

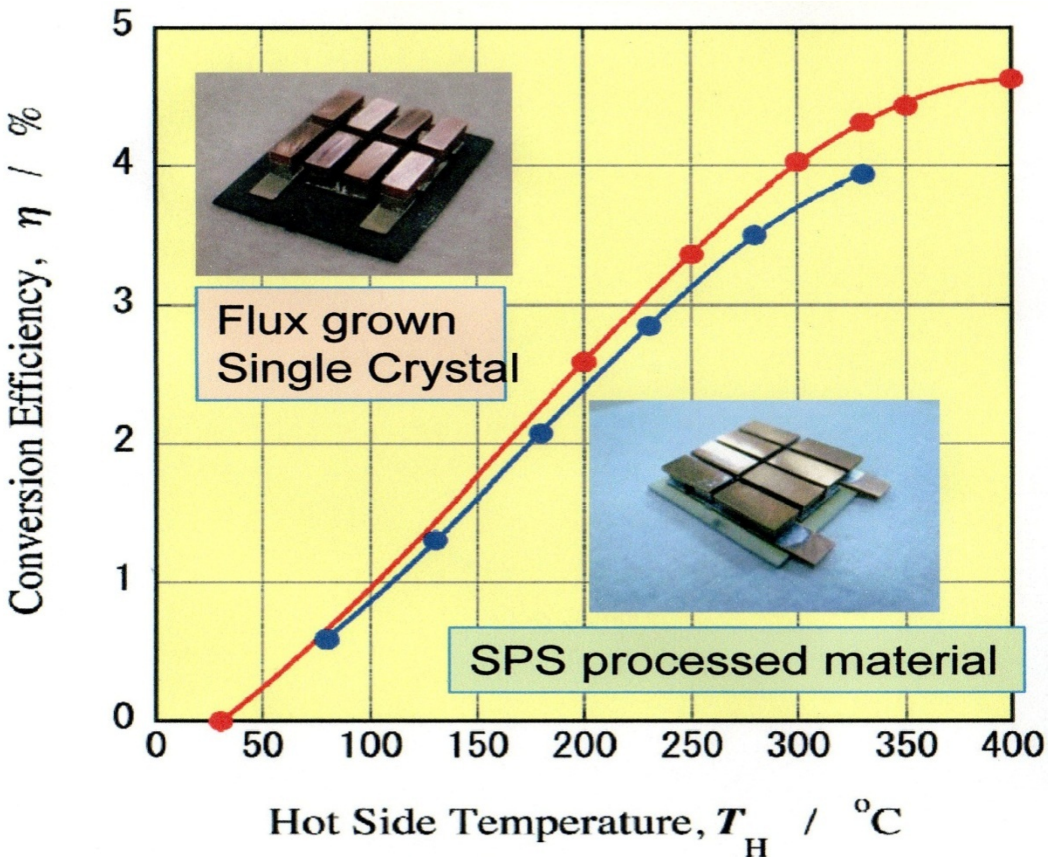
## Advantage

Both p- and n-type legs for a module can be made from the same material.

No degrading by thermal hysteresis.



# Module Efficiency for Clathrate-based TE Modules




**Made of single crystals**

module size = 18 x 15 mm$^2$

tip size = 1.9 x 1.9 x 1.4mm$^3$

pair number = 8 pairs

max. power output = 0.74W

specific power = 270mW/cm$^2$

maximum efficiency = 4.6%

**Made of SPS poly-crystals**

module size = 28 x 28 mm$^2$

tip size = 5.0 x 5.0 x 2.4mm$^3$

pair number = 8 pairs

max. power output = 1.71W

specific power = 218mW/cm$^2$

maximum efficiency = 3.9%

There are large difference between experimental results and calculation based on TE material performance. This discrepancy is attributed the imperfection in electrode technology for this material system mainly.

# Development of High-Efficiency Thermoelectric Materials and Systems
(2008.10-2014.3)

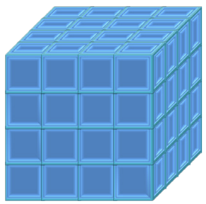
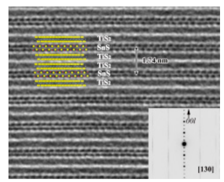
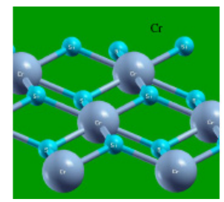
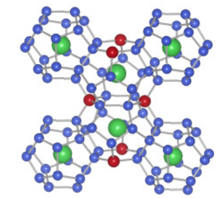
**K. Koumoto, C. L. Wan, Y. F. Wang, W. Norimatsu, M. Kusunoki, R. Funahashi***, R. Suzuki**** , H. Anno*******

***Nagoya University, Japan***
***CREST, Japan Science and Technology Agency, Japan***
****** AISТ, Japan***
******* Hokkaido University, Japan***
******** Tokyo University of Science at Yamaguchi, Japan***

◎ Development of Novel TE Materials of Non-toxic, Non-rare, Cheap, and Usable in Air for wide temperature range

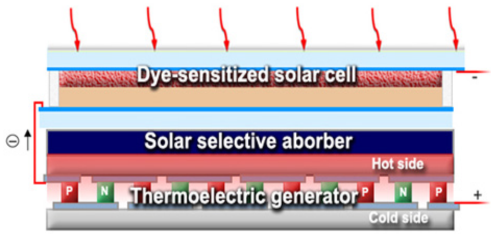
◎ Design/Development of TE Modules and Systems

# Development of Novel TE Materials (JST-CREST)

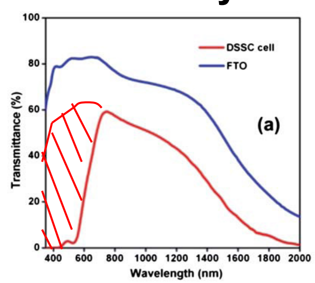
| LT<br>300-500 K | LT~MT<br>300-700 K | MT<br>500-800 K | HT<br>800-1000 K |
|---|---|---|---|
| **3D SL STO**<br><br>**Goal：*ZT*=0.8** | **$TiS_2$ NSL**<br><br>**Goal：*ZT*=0.6** | **$Mn_3Si_4Al_3$**<br><br>**Goal：*ZT*=0.6** | **Siクラスレート**<br><br>**Goal：*ZT*=0.5** |
| ・**3D SL STO** realizing <u>***ZT*~1@300K**</u> was proposed.<br><br>・**Energy filtering effect** at grain boundaries was verified.<br><br>・First succeeded in **La-STO nanocubes**.<br><br>・**3D SL ceramics** of STO are under development. | ・**$TiS_2$-based NSL** gave **world record** : <u>***ZT*=0.37@700K**</u> for sulfides.<br>（**ICT2010 Best Scientific Paper Award、ICT2011 Outstanding Poster Award**）<br><br>・Proposed quantum confinement effect in **$TiS_2$ nanosheets**.<br><br>・**$TiS_2$/Organic Hybrid SL** is now under investigation. | ・**$Mn_3Si_4Al_3$ phase** was found to give <u>***ZT*~0.2@800K**</u><br><br>・**High oxidation resistance** (<800 K in air)<br><br>・Verified the ability to generate high power with a test module.<br><br>・**Basic research** is underway among CREST Team. | ・**$Ba_8Al_{16}Si_{30}$** gave **world record** : <u>***ZT*=0.4 @900K**</u><br><br>・**$Ba_8Ga_{16}Si_{30}$**⇒ discovery of **phonon-scattering enhancement** by guest atoms in Si nanocages.<br><br>・Challenging to improve TE properties of **$Ba_8Al_{16}Si_{30}$**. |

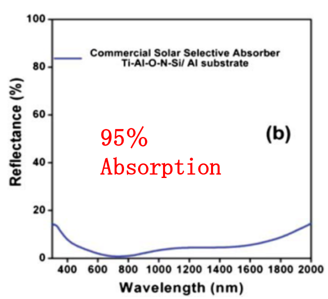
# Design/Development of TE Modules/Systems

## PV/TE Hybrid Solar Power Generator (NU+UESTC) LT Heat



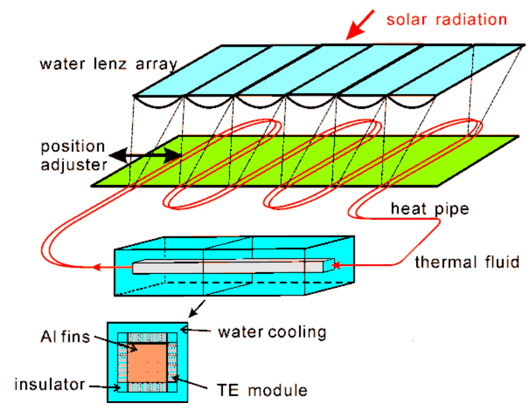

**DSSC/SSA/TE Hybrid Device**



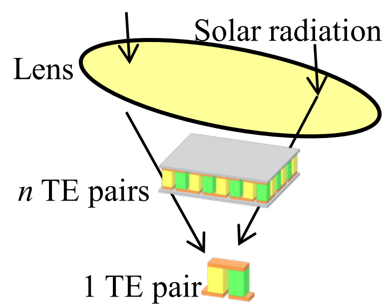




N. Wang, K. Koumoto et al., *Energy Environ. Sci.*, 4, 3676 (2011).

## TEG Design for Solar Heat Utilization (HU) LT~MT Heat

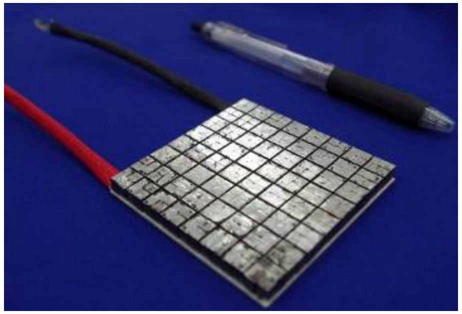



**Power Generation System (1): Water lens concentrates sunlight.**



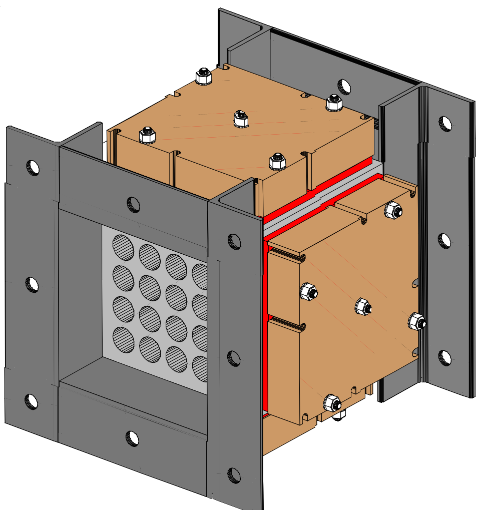

**Power Generation Systems (2): Concentrated sunlight directly irradiates TE converter.**

## Modules/Systems for Waste Heat Recovery (AIST) LT~HT Heat



**MT TE module**

**p-$MnSi_x$/ n-MnSiAl**



WHR System

# Ongoing Developments of Thermoelectric Applications promoted by private companies

○ Waste Heat Recovery Systems

Industrial furnaces

**(Komatsu/KELK, Showa Cable Systems, TEC New Energy)**

Motorcycles/Automobile **(Atsumitec, Komatsu)**

Incinerator **(Showa Denko/PLANTEC, ACTREE)**

○ Renewable Energy Sources

Solar thermal energy **(TDS group, JAXA)**

Hot springs TEG **(Toshiba)**

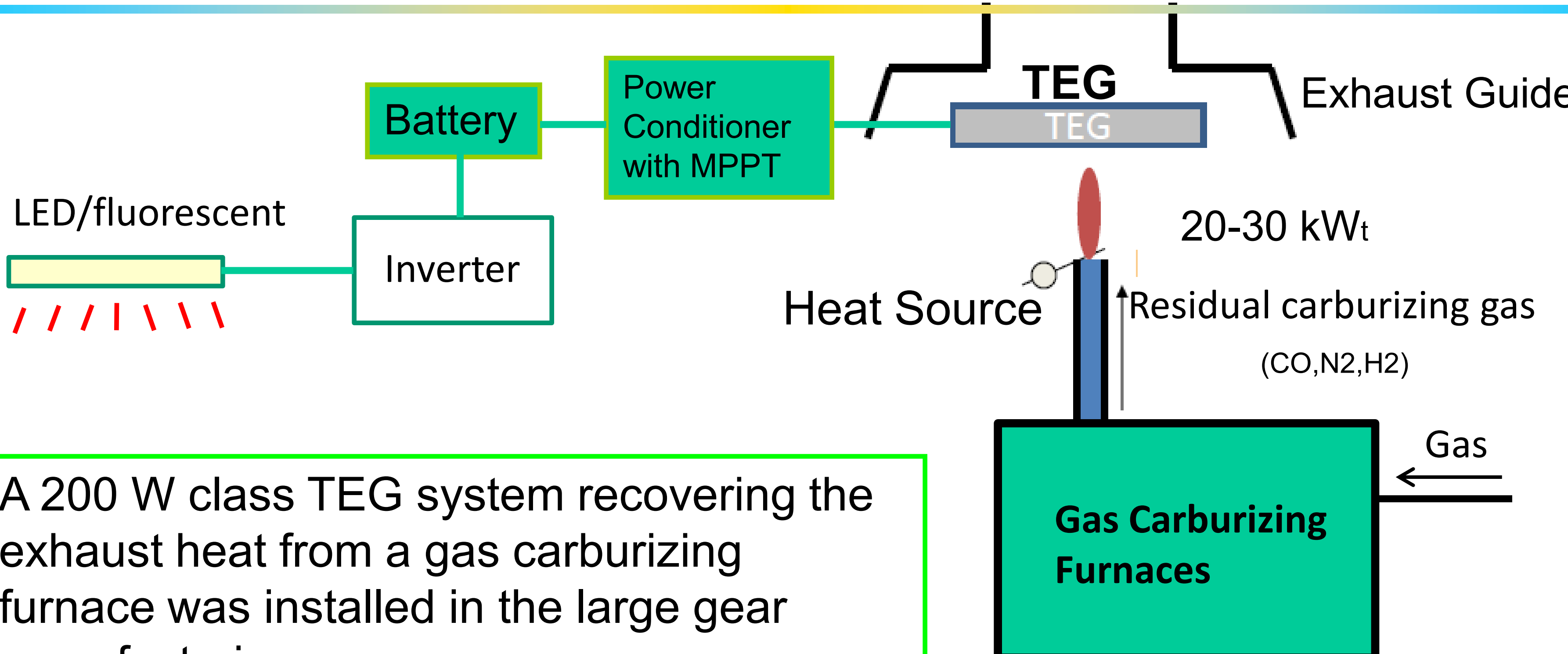
○ Energy Harvesting TEG

Monolithic micro TE Generator **(Murata Manufacturing Co.Ltd.)**

Mini-size TEG system **(YAMAHA, KELK)**

# TEG application to waste heat recovery from a gas carburizing furnace

by KOMATSU&KELK

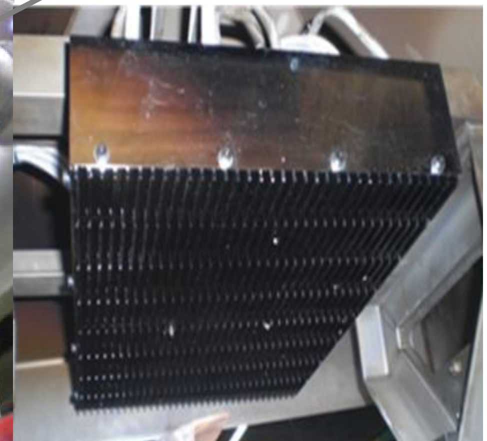


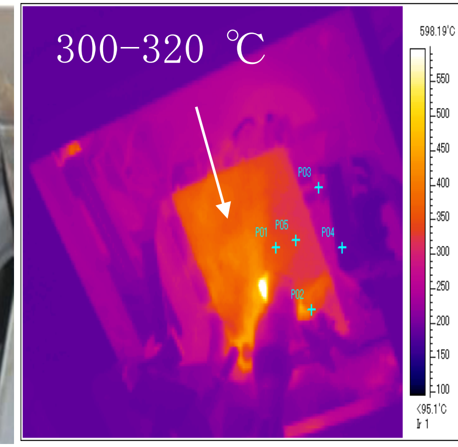

A 200 W class TEG system recovering the exhaust heat from a gas carburizing furnace was installed in the large gear manufacturing process.

Sixteen thermoelectric modules were mounted in the test facility.

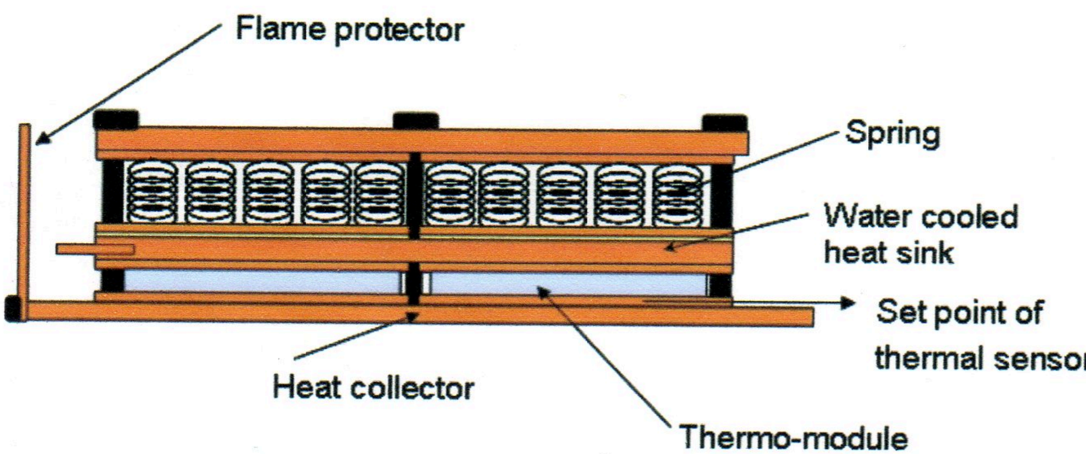
The burning power depends on flow rate of carburizing gas. One Case:10m$^3$/h in flow rate, 21kWt in thermal power.


Burner nozzle

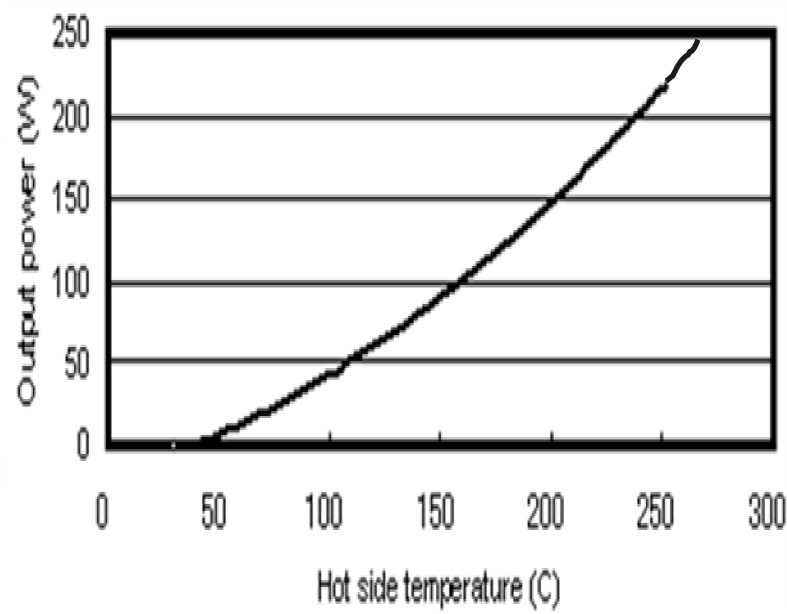





Fin type heat collector

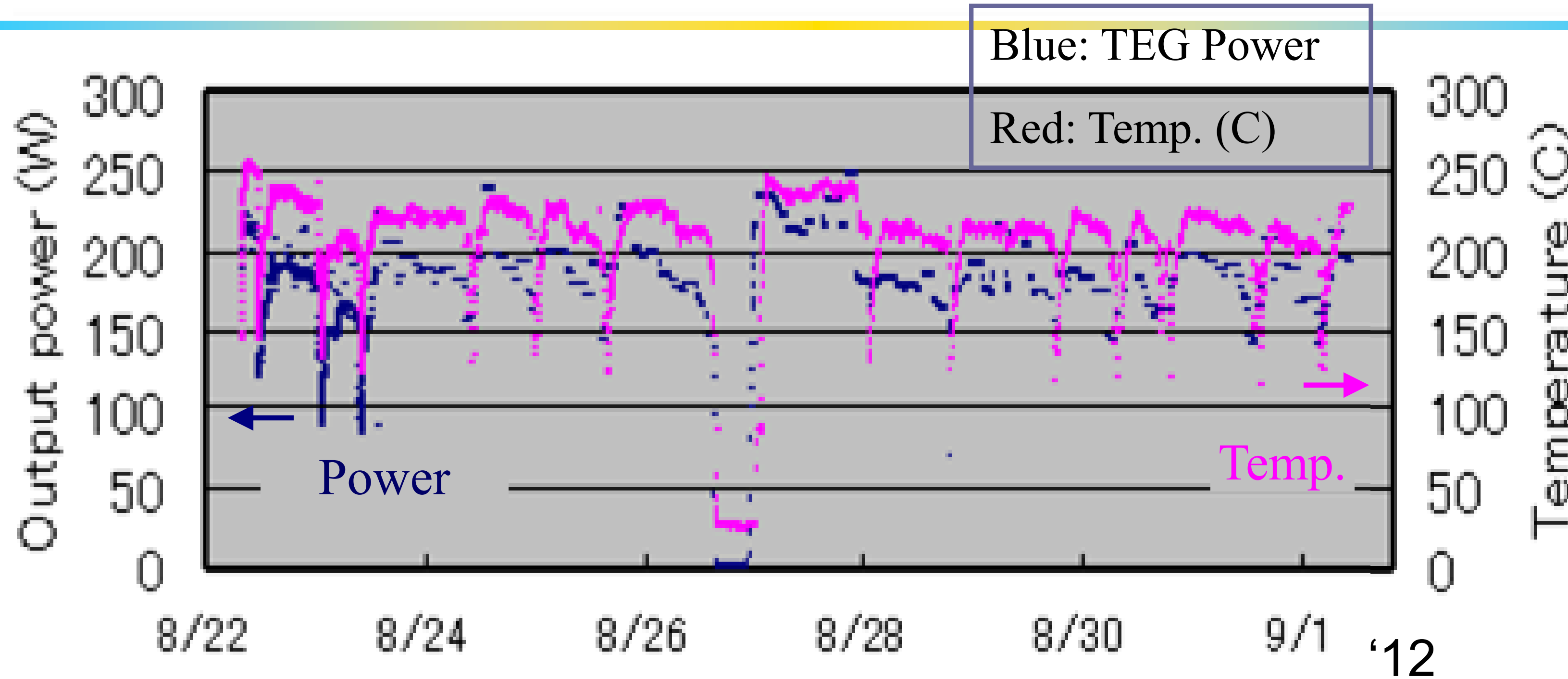



Configuration of main part for TEG system




Temperature dependence of power output

# Results for duration test




Sample data on time dependence of power output and hot side temperature for long duration test

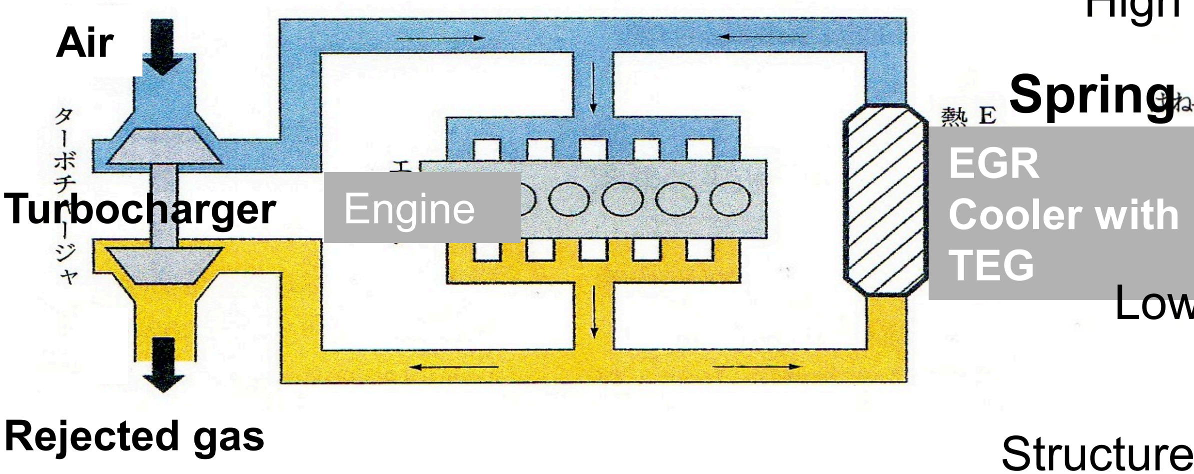
Long run test has been carried out since 2010.

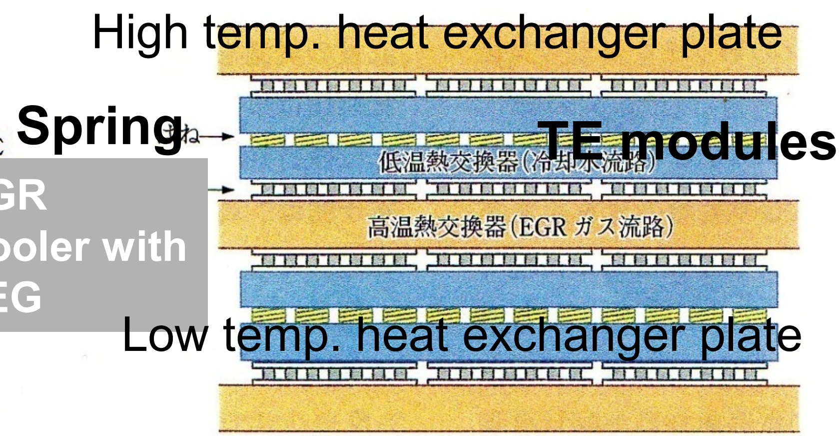
Operation time without maintenance has reached more than 12,600 h at the present stage.

TEG system will be installed to all carburizing furnaces in the factory step by step in future.

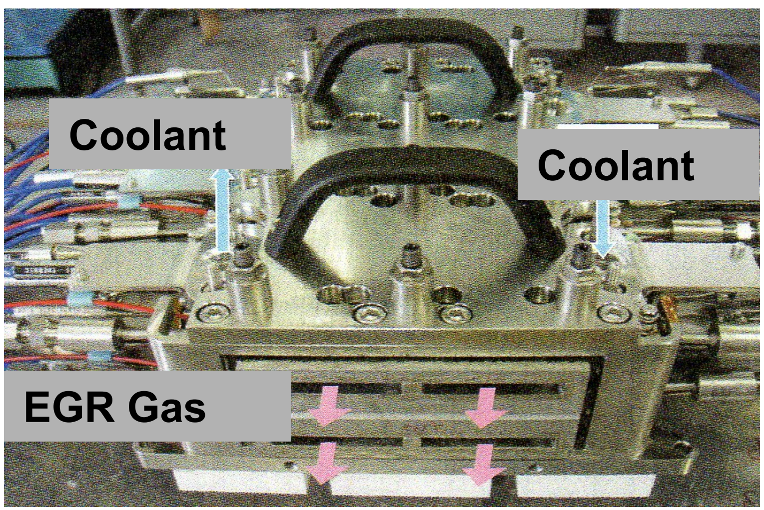
# EGR　Cooler combined with TEG

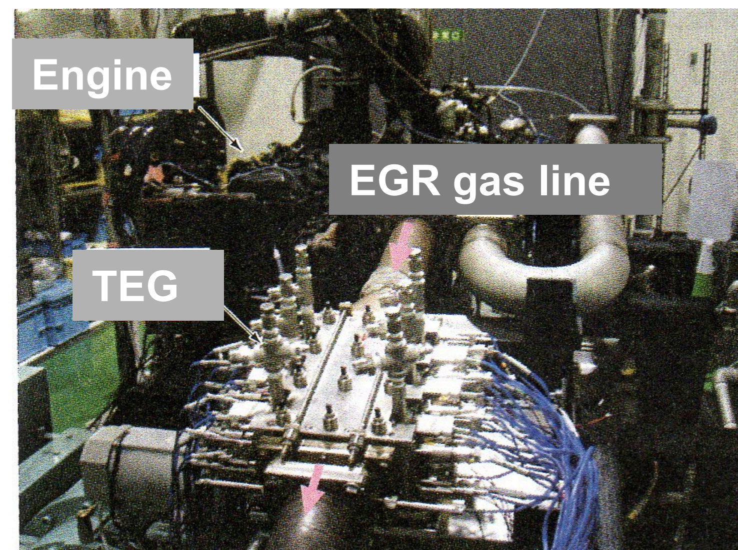
## by KOMATSU




Structure of Cooler with TE  modules

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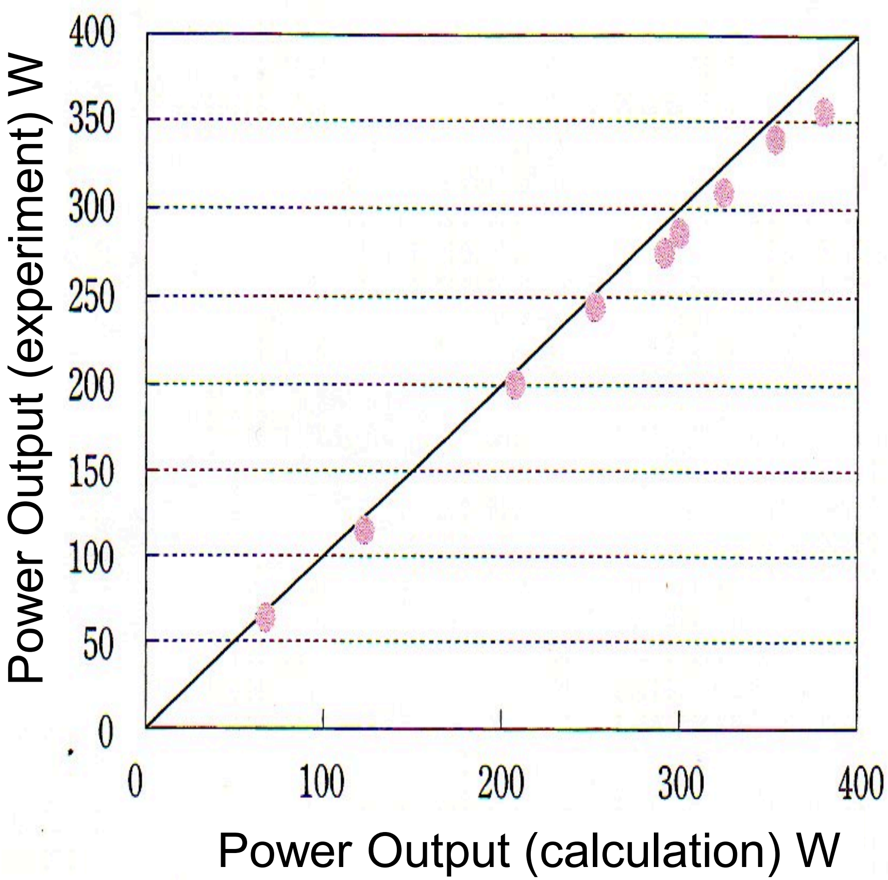
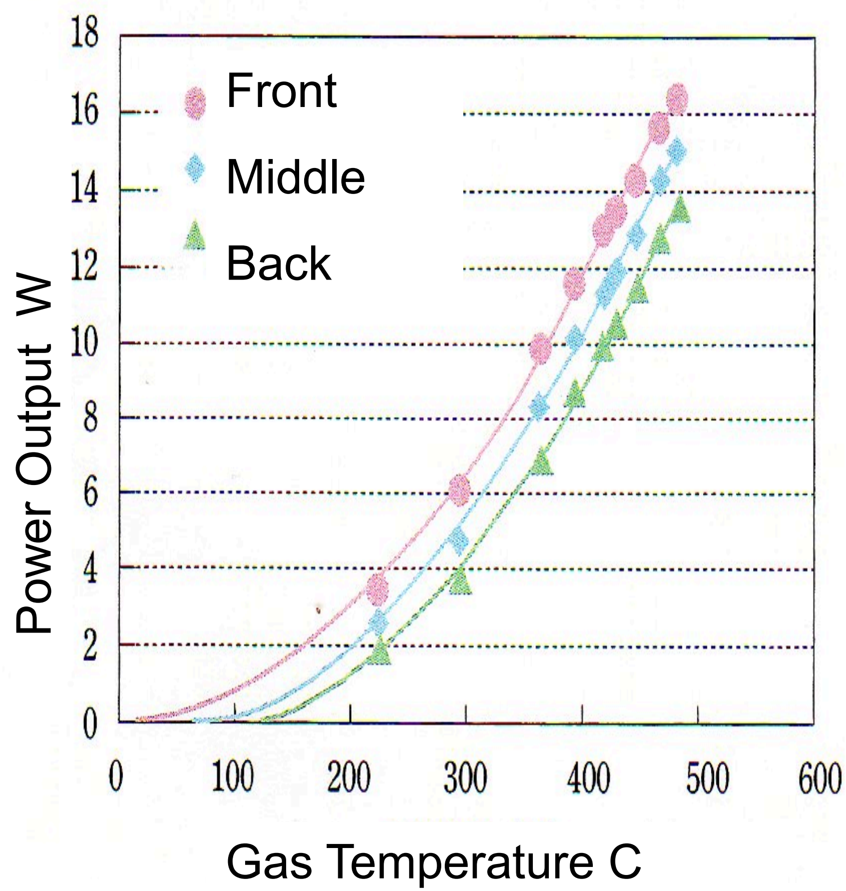
Experimental facility

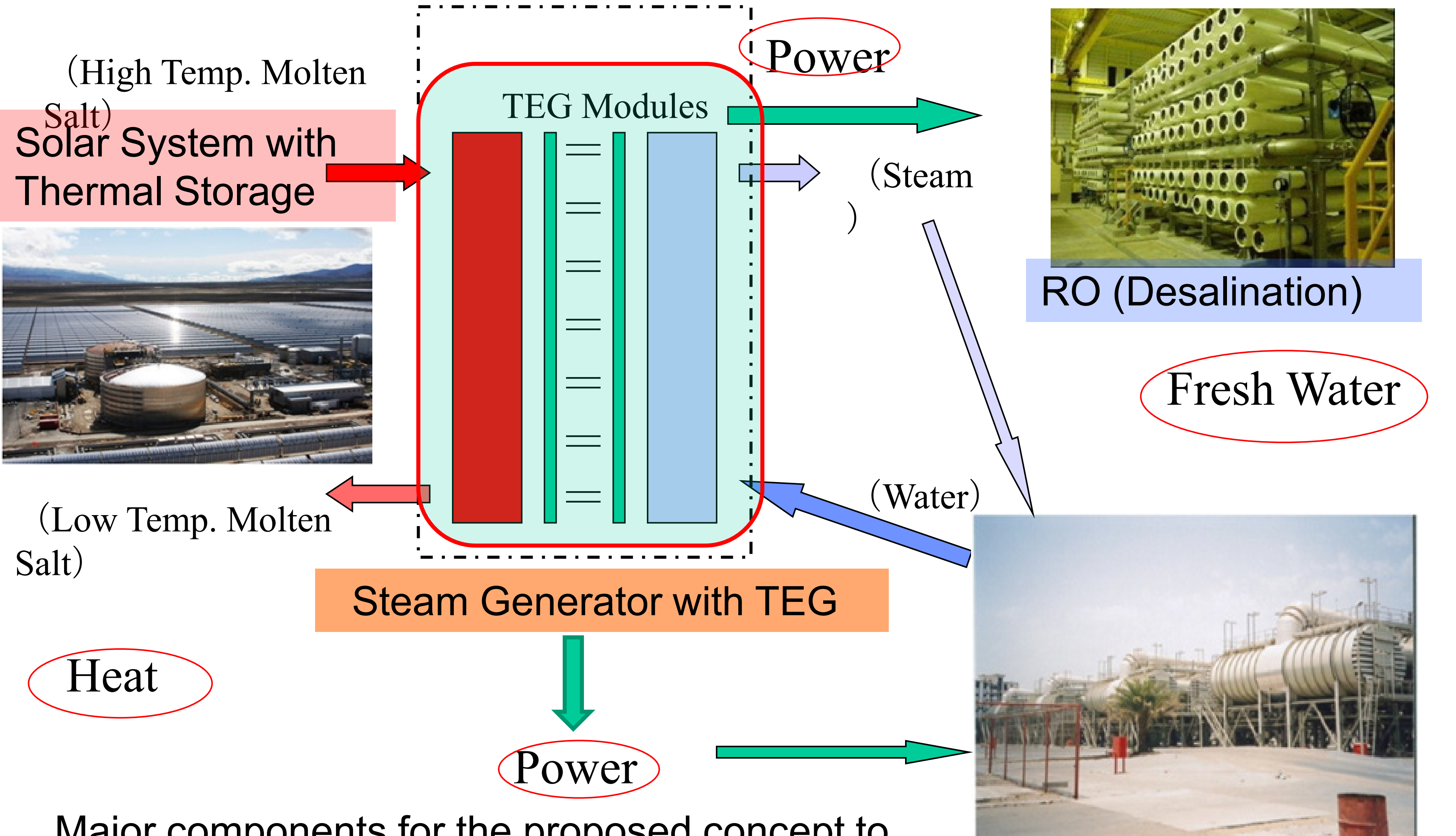
# 1/4model Test Results



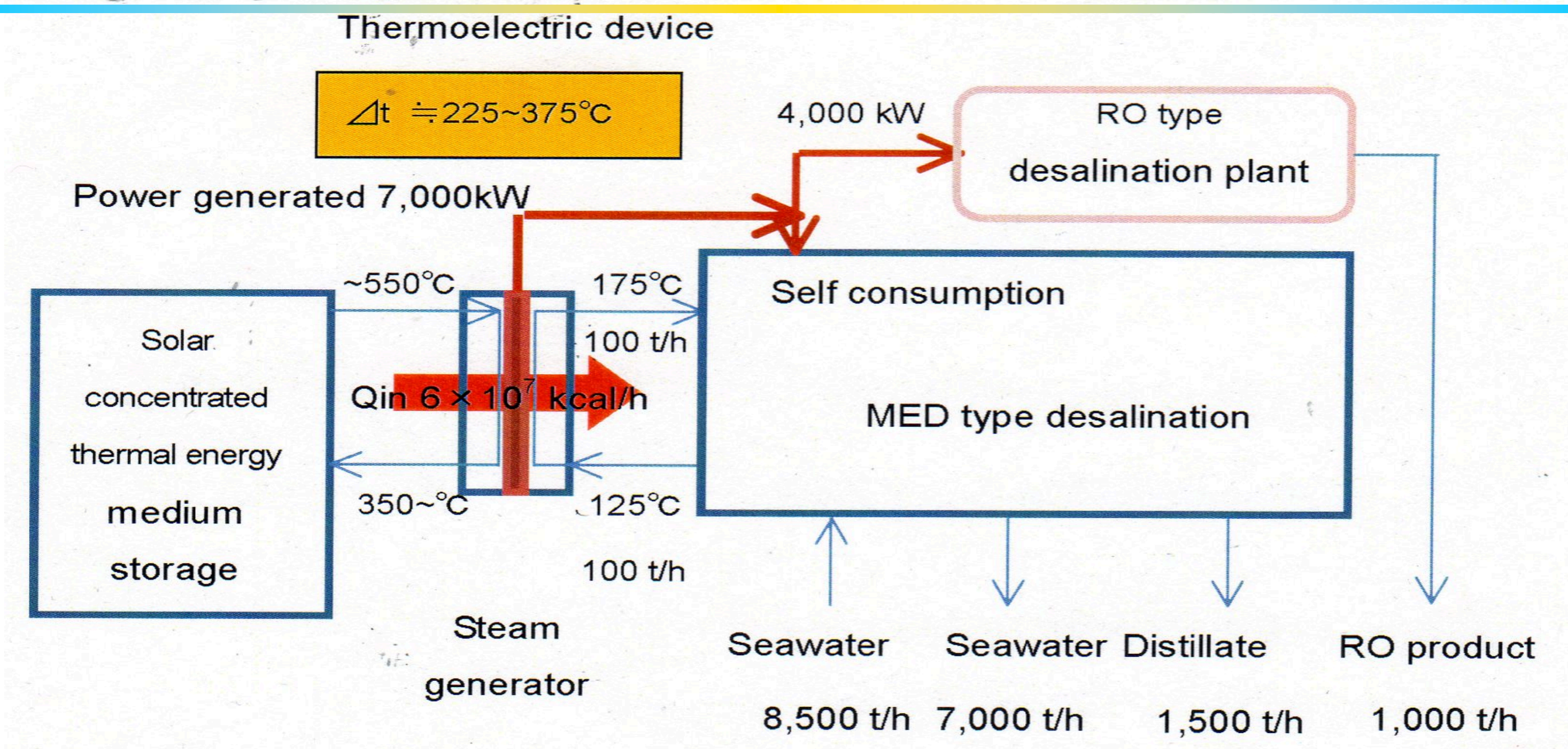

Test results show the good agreement of experiment with calculation.

# Solar powered desalination system combined with TEG    by TDS Group




Major components for the proposed concept to produce electricity, fresh water and heat

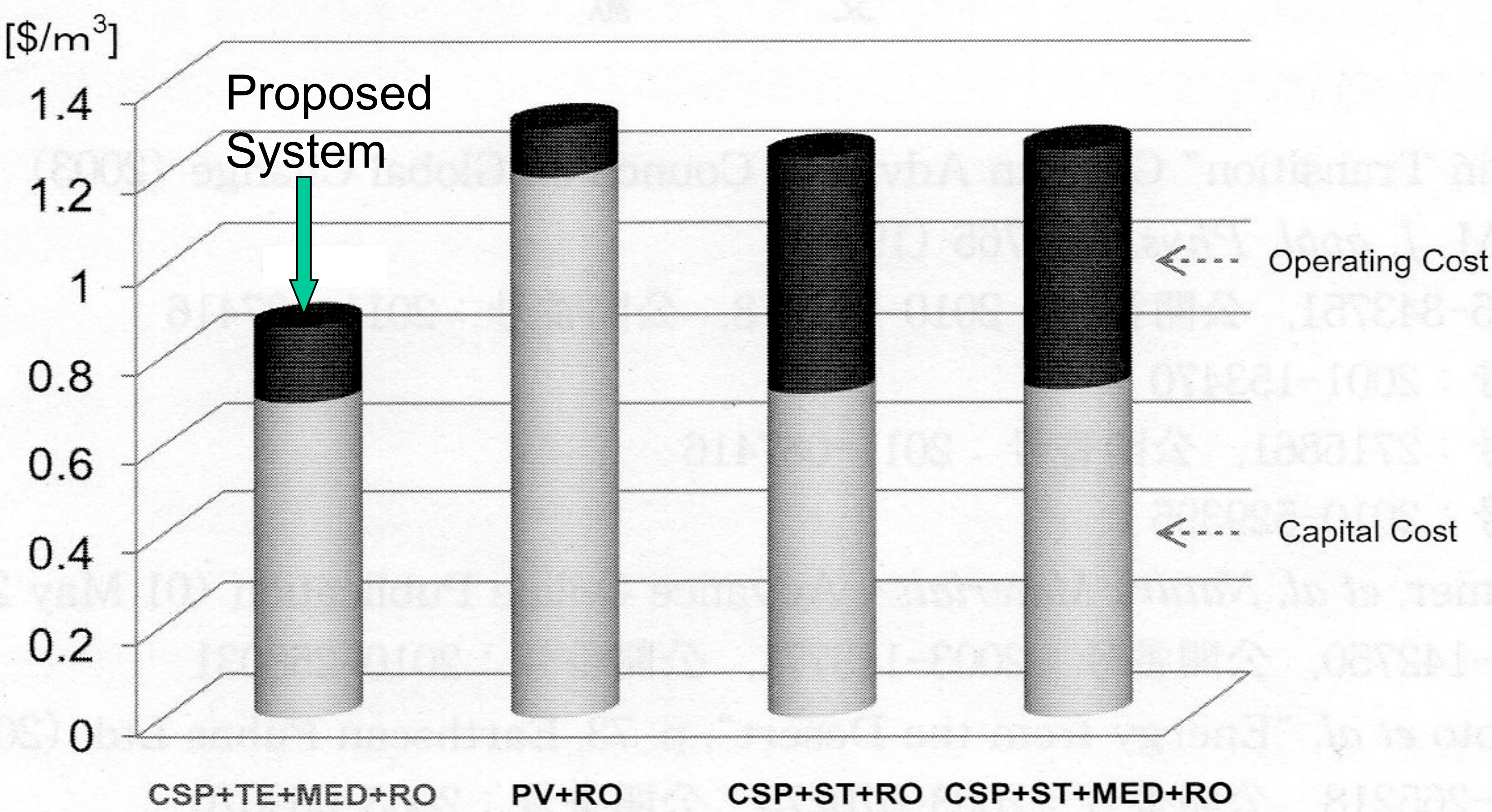
# Energy balance & temperature allocation for a conceptual design




Assumptions for fresh water production cost estimation:

Capacity:10,000t/d、 Plant availability:0.9, Site: the Middle East, Plant Life: 20years, Inflation rate:2.0%, Construction year:2010, Efficiency of TEG:7%, Efficiency of PV:20%

# Fresh water production cost competitiveness with others




PV; Photovoltaic, TE; Thermoelectric Generator, ST; Steam turbine Cycle

Assumptions

Direct Normal Irradiance: 2,500 kWh/m$^2$, Plant availability: 90%

Operation period: 20 years, Inflation rate: 2.0%, Cost index: based on year 2010,

Cost of TE modules, CSP and PV: based on mass-production volumes,

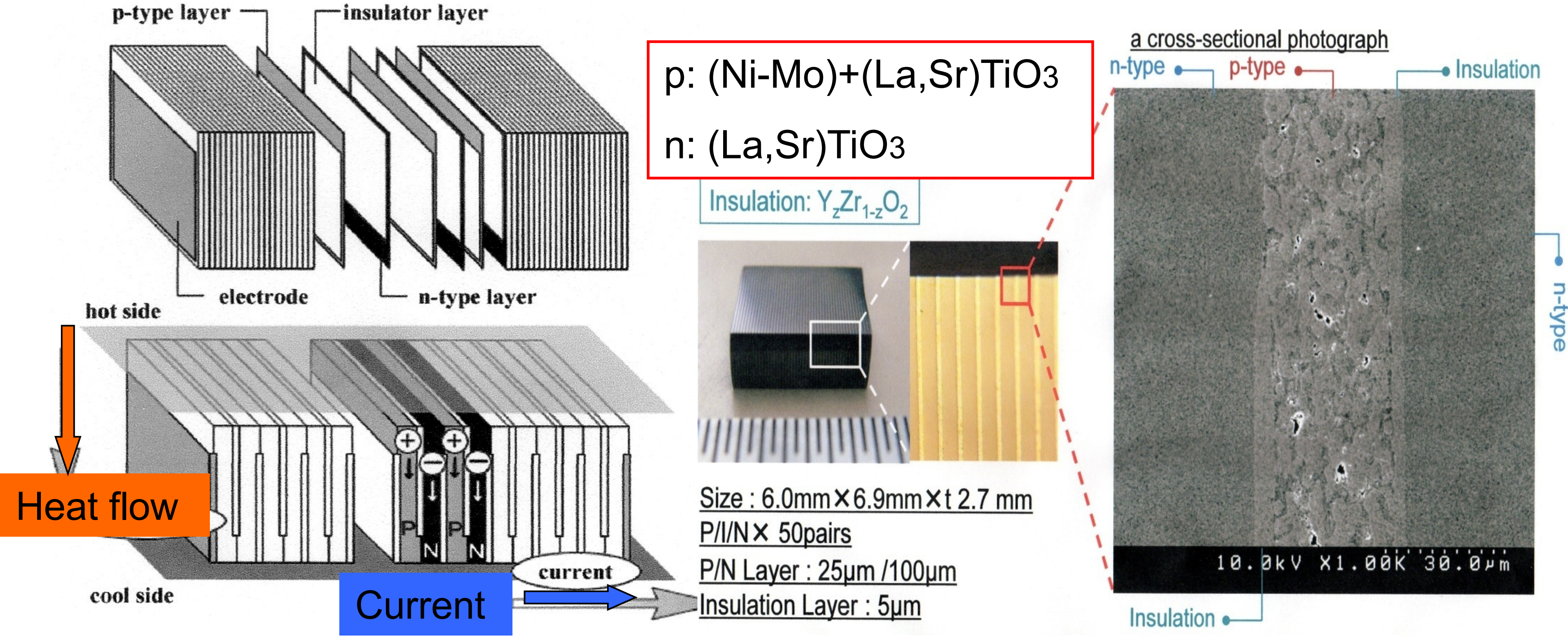
All the utilities except for sea water are self-sufficient

# Proof-of-Concept Experiment

- Design of steam generator combined with TEG
- Overall heat balance
- TEG characteristics
- Dynamic mass balance and Control in variation of temperature
- Design of Proto-type Solar Desalination System combined with TEG

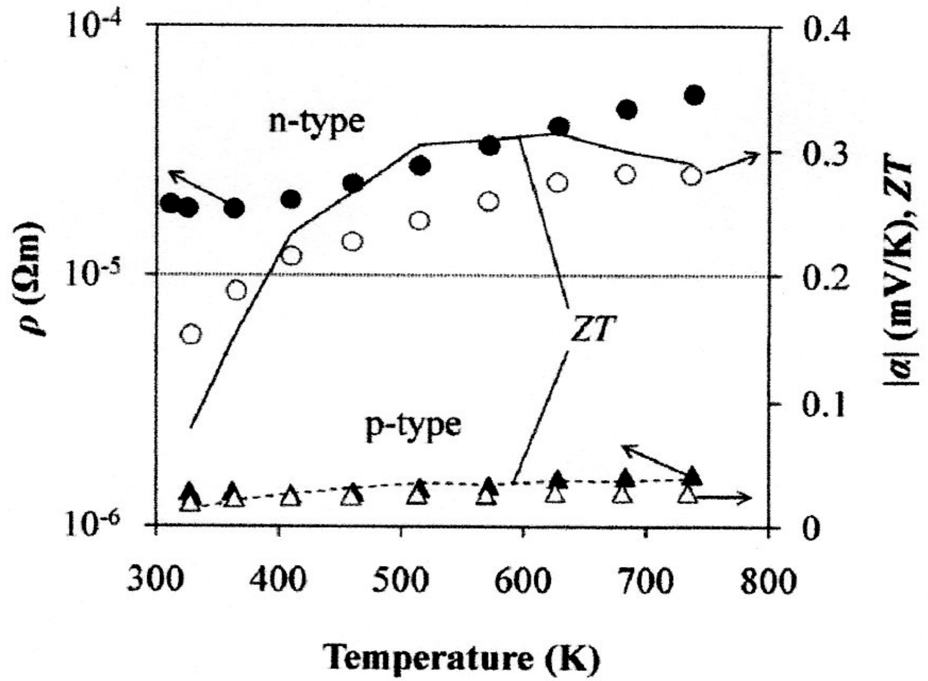
# Monolithic oxide-metal composite micro TEG for energy harvesting

by Murata Manufacturing Co.,Ltd.

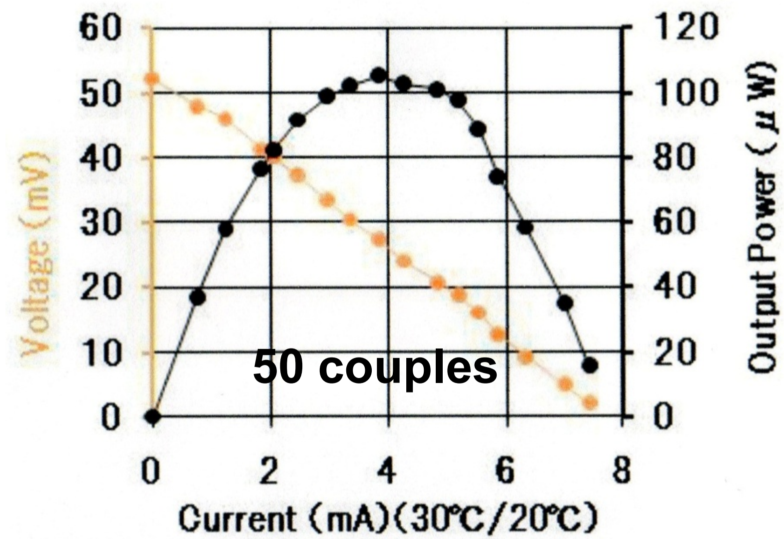



- TEG modules have been made based on multilayer ceramic capacitor technology.
- The p- and n-type layers printed on insulators are stacked and co-sintered.

# Performance of TE materials and device




Performance of TE element




| ΔT=10K | Measured |
|---|---|
| No-load output voltage | 52.3mV |
| Device resistance | 7.09Ω |
| Output power | **105μW** |

V-I characteristics of the device

- Power output is obtained about 100μW at 10K in ΔT.
- Devices can be mass-produced with MLCC process at low cost.

# Future Prospects

- New projects started in 2011

  1) NEDO project / R&D program for Innovative Energy Efficiency Technology

  2) JST projects /Advanced Low Carbon Technology R&D Program

- Academic Roadmaps revised in TSJ

  TE Materials

  TE Applications

# New NEDO Project

Development of Thermoelectric Generation Technology for Steel Plant Waste Heat Recovery

Team: JFE Steel Corporation, KELK,Ltd., Hokkaido University

Term: 2012.1-FY2015

New JST Project:

# Fabrication of Solar-Heat Thermoelectric Materials by Controlling Ordered Structures and Phase Interfaces

October 2011 ~

## Goal: Solar-heat TE power generation system

**High potential TE materials are required for the temperature range: 650～1000 K (above Bi-Te) using environmentally friendly TE materials.**

TOKYO TECH
Pursuing Excellence


**P.L.: Yoshisato Kimura**

**Associate Professor**

**Tokyo Institute of Technology**

**Materials Science & Engineering**


ALCA
Advanced Low Carbon Technology Research and Development Program
先端的低炭素化技術開発事業
アルカ

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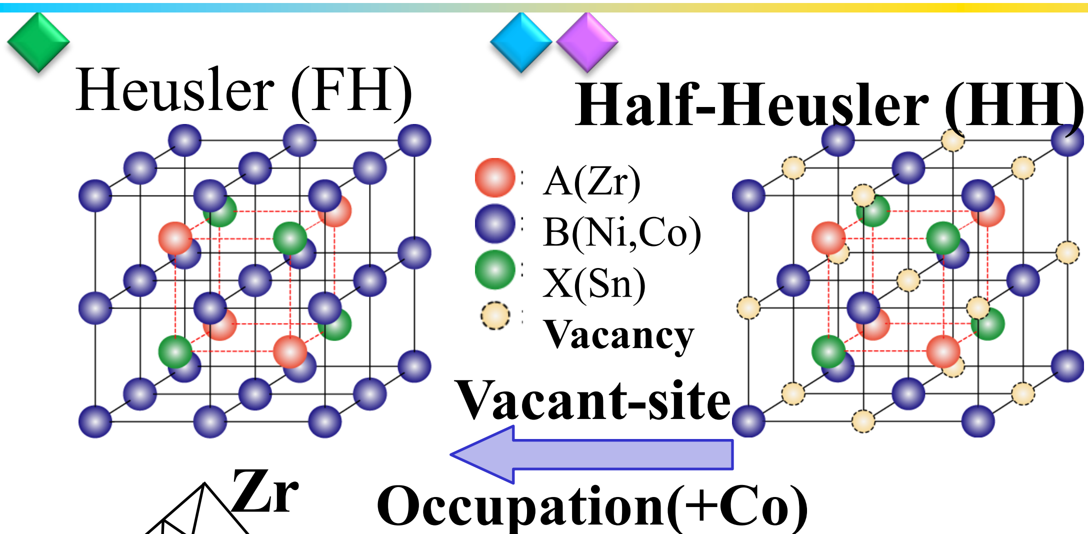
**Japan Science and Technology Agency**

JST

# 1. Controlling Ordered Structures based on Half-Heusler system

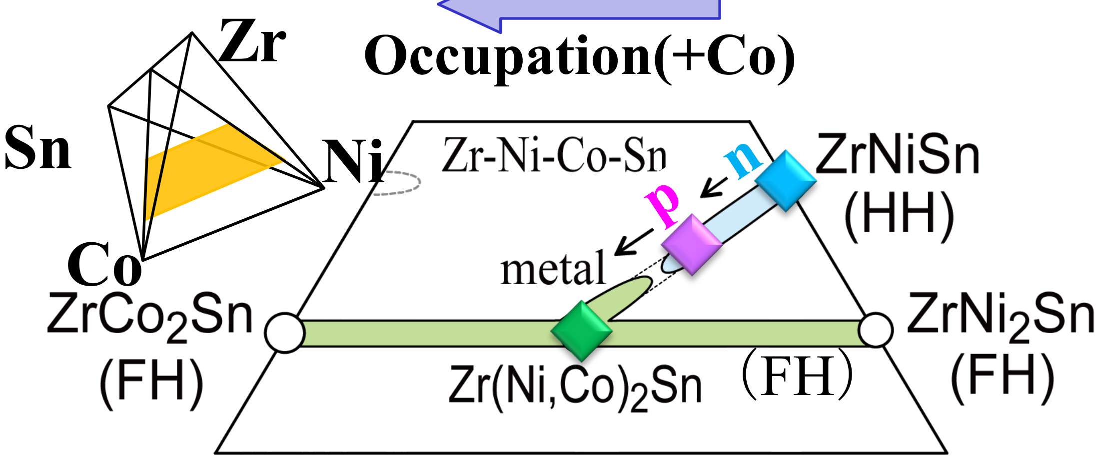



**Lattice Defects**

**Structural vacancy,**
**Anti-phase domain, etc**

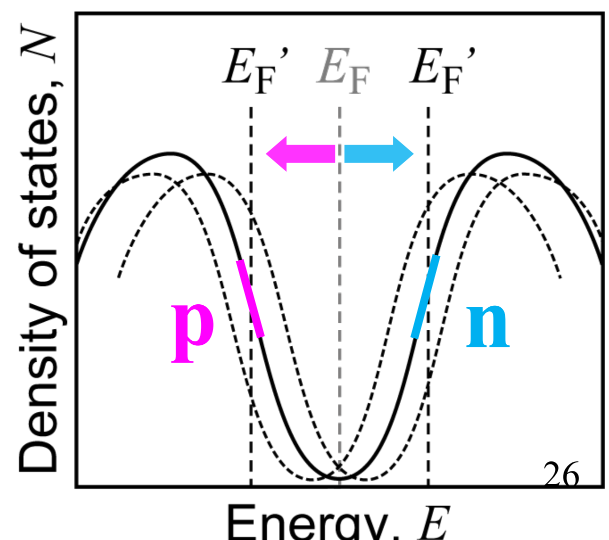
**Band structure**

**Conversion of p-n**
**Peak temperature**

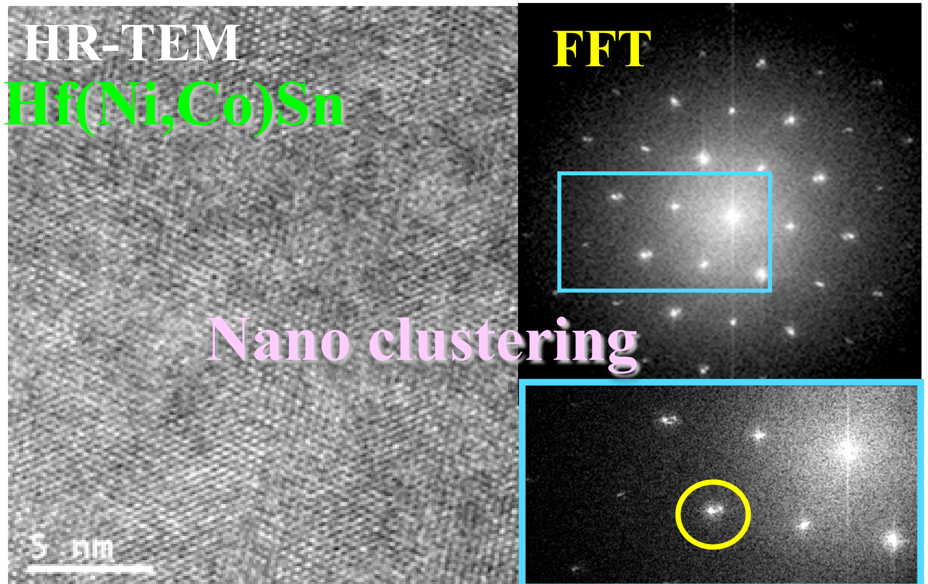



Seebeck coefficient

$$S = -\frac{\pi^2}{3}\frac{k_B^2 T}{e}\frac{1}{N(E_F)}\left[\frac{\partial N(E)}{\partial E}\right]_{E=E_F}$$

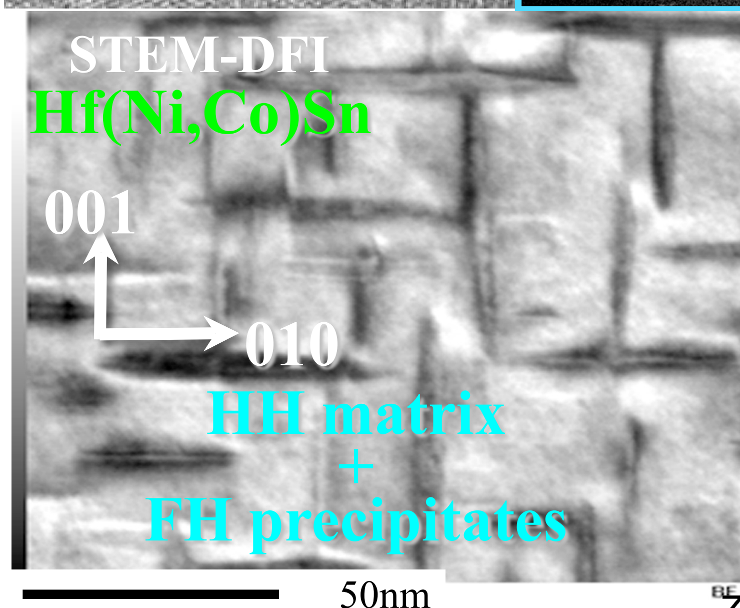


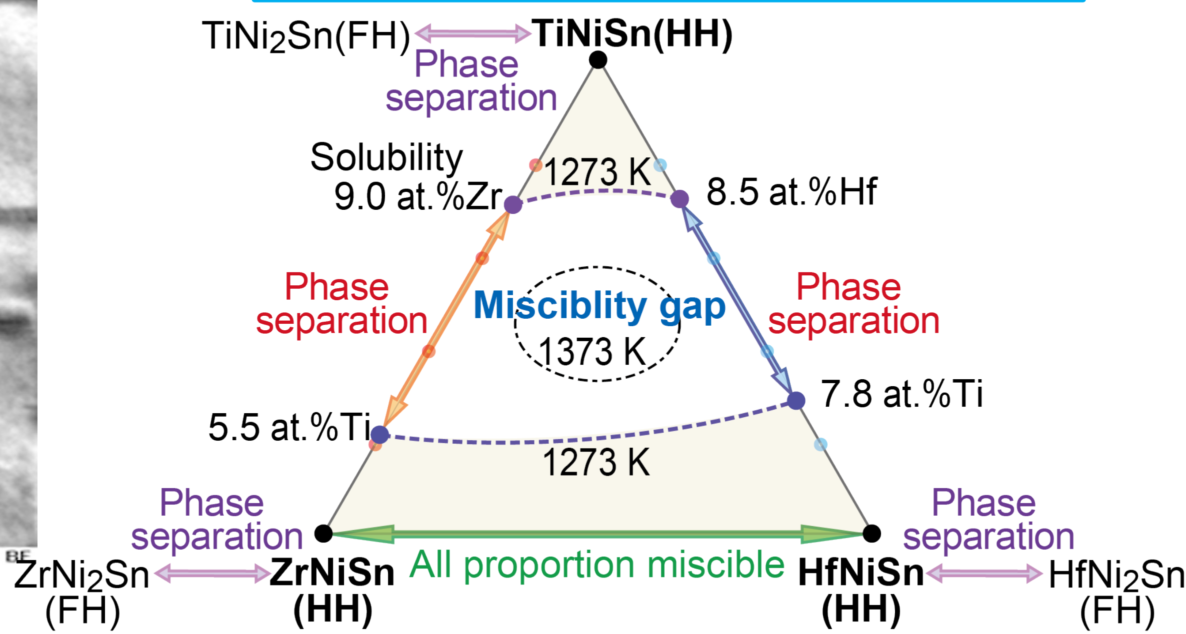
# 2. Controlling Phase Interfaces




**Phase Interfaces**
**Phase separation,**
**Precipitation, Cluster,**
**Grain Boundary etc…**

**Scattering effect**
**Lattice thermal conduction**
**Seebeck coefficient**



New JST Project:

# Development of High Efficient Silicon Thermoelectric Materials using Nanostructure Control

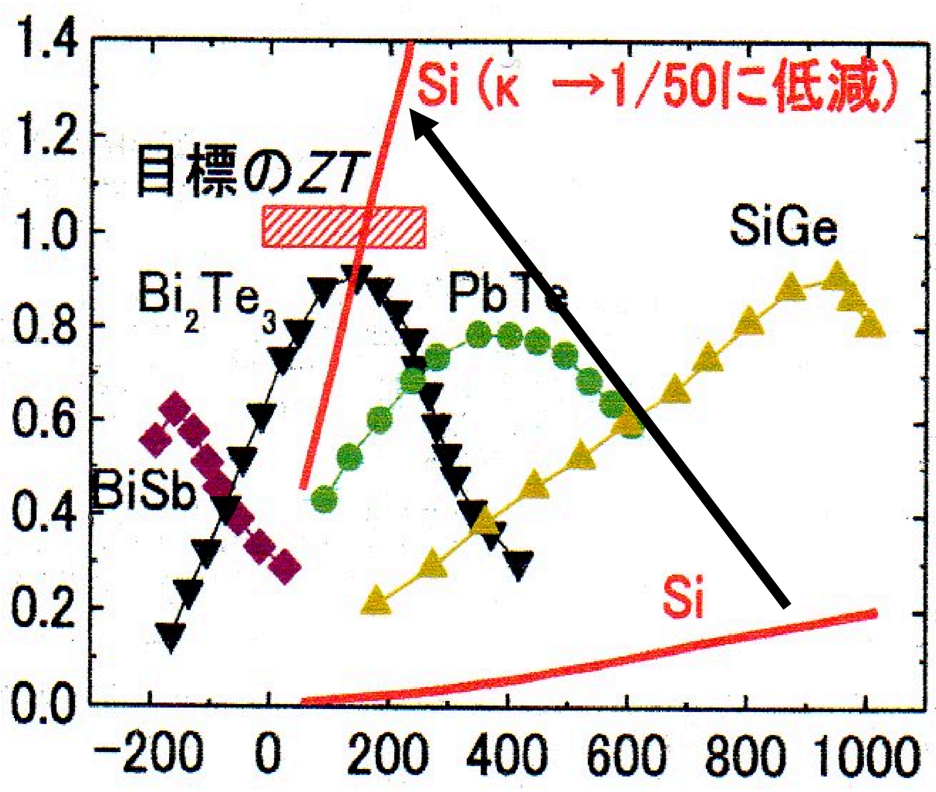
PL: Professor S.Yamanaka, Osaka Univ.

Team: Osaka University and AIST

Term: 2012-2017

Goal:

ZT~1 at RT-600K for Nanostructured Si

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# Approaches to the Goal

○ Silicide nanocomopite in Si

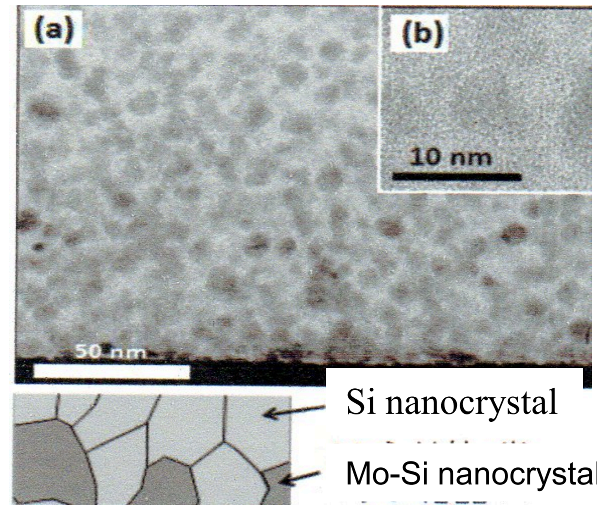
○ Nanopillar on the surface of Si

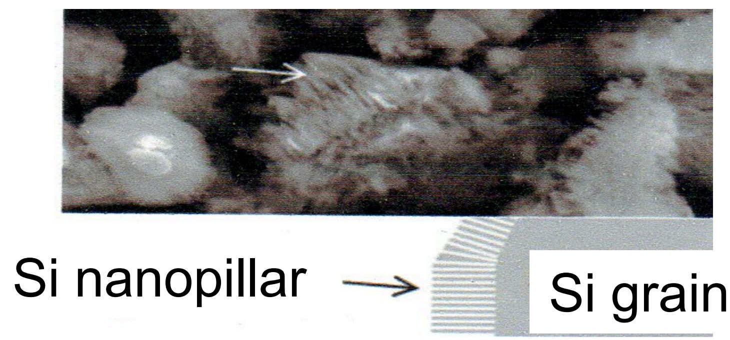
by chemical processing

○ Vacancy control in

nonstoichiometric Silicide

etc.



# Academic Roadmap on TE Materials by TSJ

### 1st Generation
ZT=1~2 in bulk

- Bi-Te
- Pb-Te
- SKD
- Heusler
- Oxide
- Silicide
- Clathrate
- Cluster
- Organic

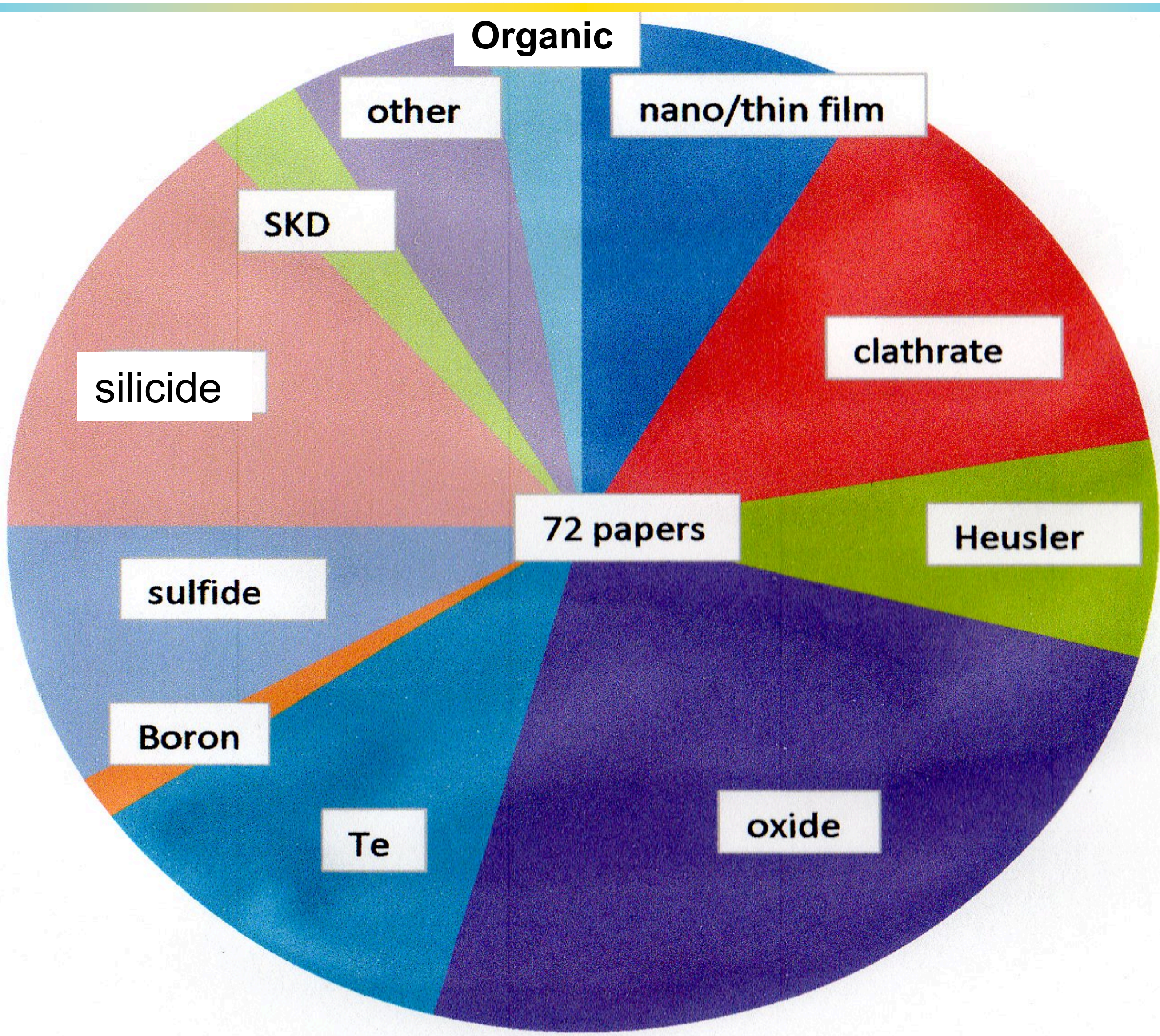
### 2nd Generation
ZT=2~3 in bulk

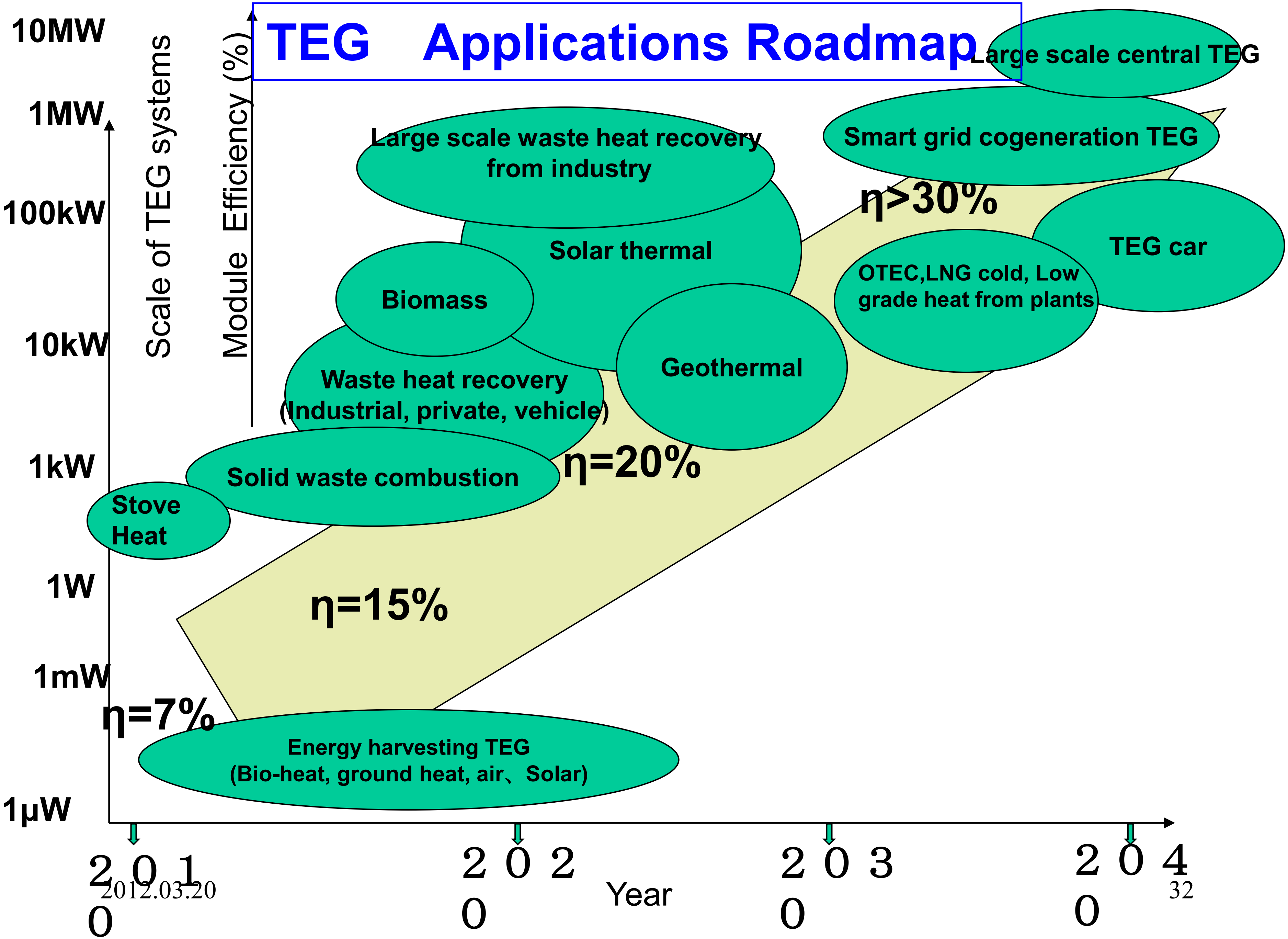
- Self assembled
- Nanostructure built-in
- Non-(Bi-Te)
- Hybrid inorganic/organic

### 3rd Generation
ZT>3 in bulk

- Fusion/Synergy Effect
- Atomic Network structure control
- Novel Condense Materials
- Novel Conduction mechanism for organic materials

# Research distribution of kinds for thermoelectric materials presented at TSJ 2011




TEG Applications Roadmap
10MW
1MW
100kW
10kW
1kW
1W
1mW
1μW
Scale of TEG systems
Module Efficiency (%)
Large scale central TEG
Smart grid cogeneration TEG
Large scale waste heat recovery from industry
Solar thermal
Biomass
TEG car
OTEC,LNG cold, Low grade heat from plants
Geothermal
Waste heat recovery (Industrial, private, vehicle)
Solid waste combustion
Stove Heat
η>30%
η=20%
η=15%
η=7%
Energy harvesting TEG (Bio-heat, ground heat, air、Solar)
2010
2020
2030
2040
Year

# Concluding remarks

- The enhancement of TE performance for nano-structured Clathrate system has been achieved. ZT value could be obtained more than 1.3 around 500K.The demonstration test of Clathrate-based modules was successful in NEDO project.
- Four novel approaches for high-efficiency TE materials have been intensively challenged in JST project.
- The progress of three kinds of TEG applications such as waste heat recovery, solar energy and energy harvesting have been introduced as private companies' activities.
- It is noteworthy that TEG system has been operated for more than 12,600 h without maintenance using a practical unstable heat source such as industrial furnaces.
- Two 5-year JST projects have just started to enhance the TE module efficiency from the viewpoints of nano and environmentally friendly technologies.
- The Thermoelectrics Society of Japan is active to promote and enlighten the thermoelectric technology in the society through the proposal of academic roadmaps of thermoelectric technology.

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