Overview of Japanese Activities in Thermoelectrics

Takenobu Kajikawa
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
Thermoelectric power generation systems can be applied to all kinds of waste heat sources in the microgrid 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


- **Reduction of Exhaust of CO₂ (NEDO --> ENAA)**
- **Eco-Energy Project to constitute high efficient energy community (NEDO --> ECC)**
- **Efficient Utilization of Unused Energy Sources such as Heat of Solid Waste (STA --> National Labs. Etc.)**
- **TE System using Solid Waste Combustion Heat (M. of H&W --> Japan Waste Research Foundation)**
- **TE System using Exhaust Gas of Gasoline Engine Vehicle (NEDO --> Technology Promotion Center, Chugoku)**
- **Advance Research on High-Efficiency Thermoelectric Technology (NEDO --> ECC, ENAA, UBE)**
- **Development for Advanced Thermoelectric Conversion Systems (NEDO --> ENAA, eco21, Hitachi, Komatsu, Toshiba, UBE, Yamaha)**

- **CREST**
- **JATeCS**

Proof of concept → Economic feasibility → Demonstration → Practical use for 1st generation → R&D for 2nd generation → 2-year Follow-up → Nano block integration project
Ongoing and Initiated Thermoelectric R&D Projects in Japan

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

1. **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, \(\210\text{M for 1}^{\text{st}} \text{ stage} / \260\text{M for 2}^{\text{nd}} \text{ stage} , ZT\sim 1.3, 12\% \Delta T \text{ of 300K by advanced cage-structured materials} \)

2. **Development of High-Efficiency Thermoelectric Materials and Systems**
   - CREST/MEXT, 2008.10-2014.3, Nagoya Univ., and 3 Institutes, \(\227\text{M}, \text{High-efficient materials such as layered oxides, Si-based Clathrates and nanostructured, } ZT>1.5, \eta_{\text{sys}}\sim 10\% \)
     - Development of Thermoelectric Materials
       - JST/MEXT, 2008.9-2013.3, Nagoya Univ., \(\40\text{M}, \text{Basic research on high performance layered oxides combined low-dimension-structured materials} \)
     - Development for High Temperature Thermoelectric Materials to recover unused waste heat sources
       - NIMS/MEXT, 2009.4-2014.3, NIMS, \(\22\text{M}, \text{Complex structured materials such as RB}_{17}\text{CN and RB}_{22}\text{C}_{2}\text{N, and Higher Borides} \)
     - Research on Spin-Seebeck Effect for Innovative Thermoelectric Materials
       - NEDO/METI, 2009.6-2011.3, Tohoku Univ., \(\25\text{M}, \text{Basic research on technology assimilation between thermal insulation material technology and spin electronics} \)
     - Development of Novel Thermoelectric Modules by Ink-jet Technique
       - MEXT, 2009.4-2013.3, JAIST and KELK, \(\26\text{M}, \text{High performance and low cost thermoelectric modules based on nanoball ink-jet technique} \)

**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.

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)
Project Goal; $ZT=1.3$ at $200-300$ °C

- Temperature range: $T_h = 400$ °C, $T_c = 100$ °C, $\Delta T = 300$ °C
- $ZT$ for previous materials has a valley at $200-300$ °C
- nano-scale caged material $\text{Ba}_8\text{Ga}_{16}\text{Sn}_{30}$: $ZT = 0.8$ for both n- and p-types

\[ ZT(200-300 \, ^\circ C) = 0.6 \sim 0.7 \]

Double $ZT = 1.3$

$\text{Bi}_2\text{Te}_3$, $\text{PbTe}$ toxic

Safe, nano-scale caged material

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 $\kappa$ to 0.4 W/Km at 300 K by controlling the structure of intermetallic clathrates.

**Important step:** Introduction of different guest ions in the two type of cages should lead to the coexistence of higher $\sigma$ and the sufficiently low $\kappa$.
Japan Science and Technology Agency - CREST Project

<2008.10.1 ~ 2014.3.31>

“Exploration of Innovative Technology to Reduce Carbon Dioxide Emission”

Development of High-Efficiency Thermoelectric Materials and Systems

K. Koumoto (Nagoya University)

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

Nontoxic, Nonhazardous, Nat. Abundant Elements!

TE module  TE system  Cars  Incinerators  Ind. furnaces

Fuel cells  Solar heat
(1) Quantum Nanostructured Bulk Materials

- Reduction in thermal conductivity
- Enhancement of power factor
- Higher ZT?

2DEG G.B.

(2) Si Clathrate Nanocomposite

- High-efficiency Bulk material
- Planetary Ball milling
- Spark Plasma Sintering
- Surface modification

(3) TE Module Development

- Oxide/Bi$_2$Te$_3$
- Cascade-type Module

(4) System Design
## Application Systems

<table>
<thead>
<tr>
<th>Temperature</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
</tr>
</thead>
</table>

### JATeCS

- **Trans.** Toshiba
- **Yamaha** Projector
- **Komatsu** Co-generation
- **Industrial Electric Heating Furnace** IHI

### Ongoing Projects

- **Hot Springs** Kusatsu (4 years operation)
- **Motorcycle** Private company (Heusler module)
- **Incinerator** Maebashi City, Ishikawa Pr. (Low Temp. application)
- **Gas Water Heater/Furnace/Topping-up** AIST (presented by Dr. R. Funahashi)
- **Solar Thermal** JAXA (China-Japan Joint Program/ Hybrid System)
Over view of TE Materials

![Diagram showing various TE materials and their temperature ranges](image-url)
Topics on TE Materials Research-1

• Environment-Friendly Materials
  
  Half Heusler
  
  \[ \text{MNiSn (M=Zr,Nb), ZT 0.66 (n), 0.45 (p), at 1000K} \]

  Heavy Fermion Intermetallic
  
  \[ \text{YbAl3Mx system, ZT was obtained 0.32 at 323K for Yb1.05Al3B0.1.} \]

  Higher Borides
  
  \[ \text{Alkaline-Earth Hexaborides (Ca,Sr)B6 ZT=0.35 was obtained at 1073K.} \]

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$_3$CoSb$_{12}$-MoO$_2$ composite. • • • Osaka Univ.

29/09/2009 DOE TE Applications Workshop
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.

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

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

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Several ongoing projects on TEG technology in Japan are summarized, in which the goals in ZT are 1.3~1.5.</td>
</tr>
<tr>
<td>2</td>
<td>The effort to proceed the TEG technology has been intensively achieved for the small-scale applications and advanced materials.</td>
</tr>
<tr>
<td>3</td>
<td>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</td>
</tr>
</tbody>
</table>
Thank you for your attention !!

Where there is heat, there is Thermoelectrics !!
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 is 1.46.

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

Thermoelectric power generation using hot springs

Photovoltaic power generation for 4kW residence

Generated energy per power generation unit area (kWh/m²)

Operating time (x10⁴ h)
Waste heat recovery from Motorcycle

On the test bench

Heusler alloy TE module

On the streets

Annual production of motorcycles: 40M/y

823K

Time variation of exhaust gas temperature

Power Characteristic
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

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

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)

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.)

Large effective mass: $m^* = 15-30m_e$

High Power factor $P = \frac{S^2}{\rho}$

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

$\text{Bi}_2\text{Te}_3 \quad P \sim 5000 \mu \text{Wm}^{-1}\text{K}^{-2}$ (300K)

Reduction of thermal conductivity

Phonon scattering due to rattling effect by M

The ZT value was obtained 0.32 at 323K for $\text{Yb}_{1.05}\text{Al}_3\text{B}_{0.10}$ system.
MCoSb (p-type) : $ZT$

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

Maximum $ZT$

- TiCoSn$_{0.1}$Sb$_{0.9}$
  \[ ZT = 0.30 \text{ at } 959 \text{ K} \]

- ZrCoSn$_{0.1}$Sb$_{0.9}$
  \[ ZT = 0.45 \text{ at } 958 \text{ K} \]

- Ti$_{0.5}$Zr$_{0.5}$CoSn$_{0.15}$Sb$_{0.85}$
  \[ ZT = 0.44 \text{ at } 904 \text{ K} \]

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)

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.

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 
\((\text{MA}_{0.5}, \text{MB}_{0.5})\text{NiSn}\) System \((\text{MA, MB}=\text{Hf, Zr, Ti})\)

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$_3$CoSb$_{12}$-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 $\text{Ru}_{1-x}\text{Fe}_x\text{Al}_2$

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

The $ZT$ values were 0.17 (p-type) and 0.28 (n-type) at 900 K.
Commercial TEG modules by KELK & Komatsu, and Yamaha as the outcome with JATeCS-project

Power density = 0.96 W/cm² and 1.95 g/W based on formal module size

Module Efficiency = 5.7% at ΔT=150K.