Development of High-Efficiency Thermoelectric Power Generation System

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As a measure against global warming, recovering waste heat and converting it into electrical energy is very effective. While there are various methods of recovering waste heat, much expectation is being entertained of the thermoelectric module that has no moving parts and that is capable of converting waste heat directly into electrical energy. Since discovery of the Seebeck effect, thermoelectric modules have been studied for more than 180 years.

Nevertheless, the thermoelectric module has not become widespread yet. The major reason for this is the low efficiencies of conventional thermoelectric modules. In recent years, however, the characteristics of thermoelectric modules have improved so much that the prospect of thermoelectric power generation has rapidly become very bright. This paper describes the current status of development and the economics of thermoelectric modules for power generation.

Key Words: *Thermoelectric Power Generation, Bi-Te, Mn-Si, Mg-Si, Cascading, Waste Heat Utilization, Thermal Stress, Generation Efficiency, Energy Recovery Years*

1. Status of development of thermoelectric element materials

With the growing public interest in environmental problems in recent years, the importance of thermoelectric power generation — an energy conversion technology — is being re-recognized. In 2002, the "development of a high-efficiency thermoelectric power generation system" was started under the leadership of the Ministry of Economy, Trade and Industry. Since then, the project has been carried on with an unprecedented scale of budget and research organization [1]. This project calls for applying thermoelectric power generation to an actual system in the near future.

Thermoelectric materials are evaluated by (figure of merit) Z $(=\alpha^2 \rho \kappa)$, which is determined by three physical values — Seebeck coefficient (α), electrical resistivity (ρ), and thermal conductivity (κ). The larger the value of Z, the better is the thermoelectric material. On the other hand, Z is a function of temperature. Namely, the value of Z of a specific thermoelectric material becomes the maximum at a certain temperature.

The national project mentioned above aims at conversion efficiency η of 12% to 15% over a wide temperature range, from room temperature to around $600°C$. To that end, the temperature range shall be divided into a "high temperature region" ($300°C$ to $580°C$) and a "low temperature region" ($30°C$ to $280°C$), and a 'cascade-type' module in which thermoelectric modules (hereinafter simply referred to as modules), the material of which has a large value of Z in the respective temperature region, are stacked one on another according to the temperature gradient shall be adopted. The overall conversion efficiency, η, of this cascade-type module roughly becomes the sum of the values of η of the individual modules.

Concerning thermoelectric materials, it is important not only to select materials having a large value of Z but also to examine carefully their thermal stability and impact on the environment, the optimum electrode construction, and the coating technology and other technologies required for modularization. **Table 1** lists the thermoelectric materials that are considered promising from the above standpoint [2]. It is unquestionable that for the low-temperature module, Bi_2Te_3-based materials whose performance has been fully demonstrated by the Peltier modules are the most suitable. For the high-temperature module, on the other hand, there are many choices both for the n-type and the p-type. They include, for example, TAGS- and PbTe-based materials [3], skutterudite-based compounds which have been energetically studied mainly by JPL (U.S.A.) and a group of researchers of Tokyo University of Science, Yamaguchi since 1990 [4], and oxide-based materials which have been derived from the high-temperature superconductor recently developed in Japan [5]. Our company has employed Mg_2Si and $MnSi_{1.73}$ which are silicide-based materials. The reason is that we attached special importance to the fact that the extensive knowledge and rich experience of Ioffe Physico-Technical Institute (Russia) [6], National Research Institute for Metals of the former Science and Technology Agency, and Dr. Isao Nishida et al. in this particular field are available to us [7] and that the materials are friendly to the environment.

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Table 1 Characteristics of various thermoelectric materials for power generation

Material	Composition	Conduction type	Optimum temperature (°C)	Production process	ZT	Mechanical properties	Thermal stability	Environmental impact
Silicides	Mn-Si	p	300 – 600	Melting & refining	0.80	Young's modulus: 12,000MPa Poisson's ratio: 0.34	○	○
	Mg-Si	n	380 – 600	Melting & refining	1.07	–	Unstable without coating.	○
Si-Ge-based	$Si_{0.8}Ge_{0.2}$	n	730	Hot press	1.00	Compressive strength: 653 MPa	Stable for over 10 years.	○
	$Si_{0.8}Ge_{0.2}$	p	730	Hot press	0.70	Compressive strength: 473 MPa		
Oxide-based	$NaCo_2O_4$	p	30 – 500	Flux	1.20	–	○	○
	$(Ca,Sr,Bi)_2Co_2O_5$	p	330 – 730	Glass annealing		–	○	○
	$(ZnO)_5(In_{0.97}Y_{0.03})_2O_3$	n	430 – 800	RTGG	0.31	–	○	○
	$Zn_{0.98}Al_{0.02}O$	n	430 – 700	Solid phase reaction	0.42	–	○	×
PbTe-based	PbTe	n	230 – 577	Hot press	0.70	–	Subject to heat history.	–
TAGS-based	$GeTe-AgSbTe_2$	p	430		1.40	–	○	–
LaTe	LaTe~1.4	n	–730		1.17 – 1.43	–	–	–
filled-Skutterudites	$YbCo_{0.9}(ptPd)_{0.1}Sb_3$	n	330 – 630	Plasma sintering	1.12	–	–	–
	$Ce_{0.12}Fe_{0.7}Co_{3.29}Sb_{12}$	p	330 – 630	Plasma sintering	0.93			–
Bi-Sb-Te-Se	Bi-Sb-Te-Se	n, p	-180 – 250	Hot press	0.3 – 1.01	–	Sufficient data available.	–
Zn_4Sb_3-based	$Zn_4(Sb_{0.97}Sn_{0.03})_3$	p	230 – 480	Plasma sintering	1.00	–	Somewhat unstable.	–
	Zn_4Sb_3	p	230 – 480	Plasma sintering	1.22	–		–

2. Improvement of performance of thermoelectric elements

2.1 Improving performance of Bi-Te-based thermoelectric elements

Thermoelectric elements have been used mainly as Peltier modules for cooling and temperature control. The representative products that apply thermoelectric elements are room temperature controls, communication laser coolers, and refrigerators. Because of their major applications, thermoelectric elements have been so designed that their characteristics become optimum at or near room temperature.

However, when a thermoelectric module is used for power generation, the optimum temperature becomes higher than room temperature. Therefore, a thermoelectric element/module suitable for power generation is such that the value of Z is large and that the optimum temperature is on the higher side.

In the present study, we made an attempt to improve the performance of a thermoelectric element/module for power generation by taking the following two approaches.

① Improving the basic characteristic (Z) of thermoelectric element

(Improve the characteristics of the element at room temperature and thereby improve them at higher temperatures.)

② Shifting the peak of Z toward the high temperature side

(Even if the value of Z in the low temperature region decreases, the overall efficiency of the element improves as the value of Z in the high temperature region increases.)

With the aim of improving the figure of merit, Z, of a thermoelectric element, we applied plasma treatment to the raw material powder as described below. Concerning the shift of the peak of Z toward the high temperature side, the experimental results obtained by our company and the University of Cardiff (U.K.) shall be introduced [8].

2.1.1 Surface treatment of powder

Fig. 1 shows the possible effects of applying various types of coating to the raw material powder. It has been predicted
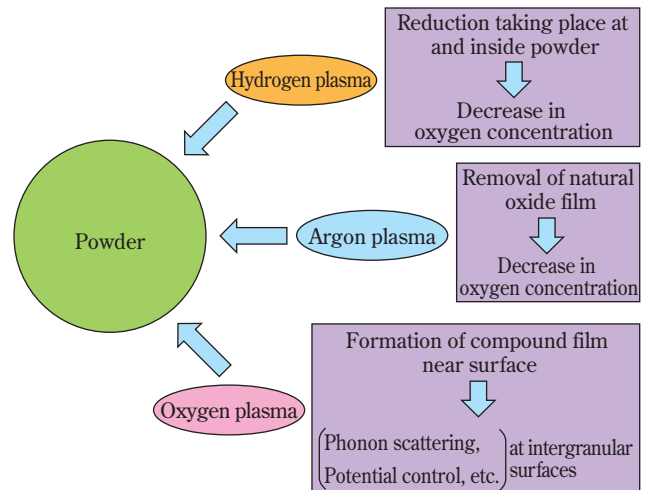
**Fig. 1** Concept of surface treatment of powder

Photo 1 Equipment for plasma treatment of powder

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that reducing powder by hydrogen will improve the powder characteristics because its oxygen concentration decreases. Actually, however, the reduction of a powder in a hydrogen furnace had not produced any marked effect. We consider that it was due to the failure to secure sufficient reducing power because of the difficulty involved in keeping the raw material powder (Bi-Te) at a high temperature.

With the aim of obtaining higher reducing power, we made an attempt to reduce the powder by hydrogen plasma. The equipment used to treat the powder is shown in **Photo 1**. It was designed and fabricated by our company.

Photo 2 shows examples of the results of powder treatment by hydrogen plasma and oxygen plasma, respectively. As a result of the plasma treatment, the powder surface changed. It can be seen that the plasma treatment removed many of micro-deposits from the powder surface. In particular, the hydrogen plasma cleaned the powder surface noticeably. It can also be seen that the hydrogen plasma decreased the oxide film on the powder surface, whereas the oxygen plasma promoted the oxidation of the powder surface.

Without surface treatment	Surface treatment by hydrogen plasma	Surface treatment by oxygen plasma
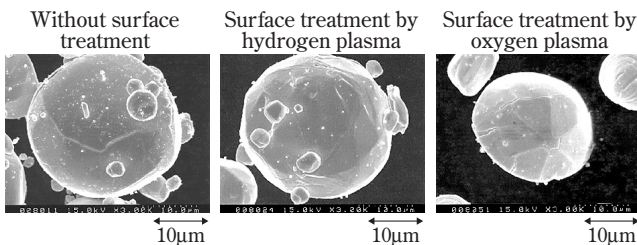
Photo 2 Examples of results of surface treatment by plasma

Fig. 2 shows the relationship between oxygen concentration and figure of merit, Z, obtained with a p-type, Bi-Te-based thermoelectric material. It can be seen that the figure of merit improves as the oxygen concentration decreases. In the present study, we shut out the open air as far as possible in the process from the plasma treatment to the sintering of powder. Actually, however, it is considered that natural oxide film was formed on the powder surface as the powder was exposed to the open air. In order to further reduce the oxygen concentration, it might be necessary to isolate the entire process from oxygen.
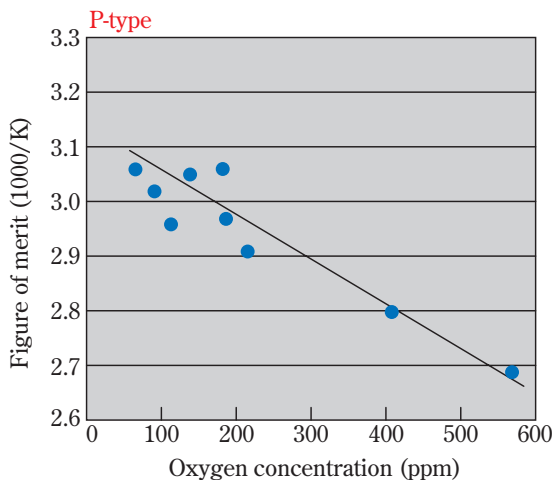

Fig. 2 Relationship between oxygen concentration and performance index

2.1.2 Peak of shift of Z toward high temperature side

It is necessary that the thermoelectric element should have high figure of merit Z in its working temperature range. As mentioned earlier, many of thermoelectric elements are used at or near room temperature. Therefore, thermoelectric elements which display high performance at room temperature have been called for. **Fig. 3** schematically shows the shifting of the peak value of Z of a thermoelectric element toward the high temperature side. Although the figure of merit at room temperature decreases, the average performance index on the high temperature side increases.

As the methods for shifting the peak value of Z of a thermoelectric element toward the high temperature side, the following two are considered.
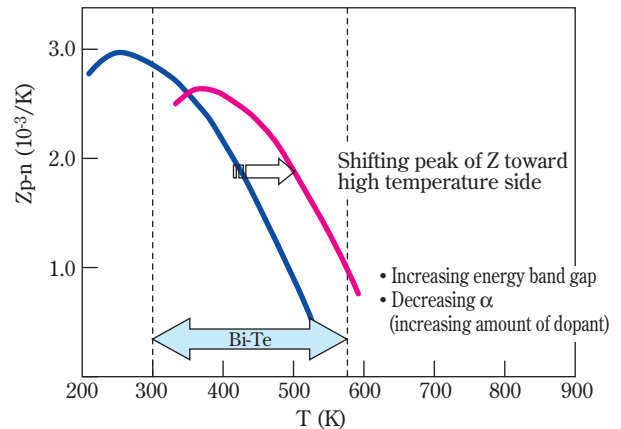
Fig. 3 Scheme of shifting peak of Z toward high temperature side

① Adjusting the carrier concentration to improve the high-temperature characteristic
② Changing the composition to control the energy band gap.

In the present study, the following two methods were applied to the n-type Bi-Te-based thermoelectric element.
① Improvement of the high-temperature characteristic by adjusting the carrier concentration
   (adjustment of amounts of Sb-I and other dopants)
② Widening of the band gap by changing the composition
   (reduction of Bi=Te bond distance; replacement of Te with homologous element having smaller atomic radius).

For the p-type, Bi-Te-based thermoelectric element, the following method was used.
① Improvement of the high-temperature characteristic by adjusting the carrier concentration
   (addition of an element of the IV group, etc.).

The material characteristic of a thermoelectric module prepared by applying the above methods is shown in **Fig. 4**.

It can be seen that the n-type maintains an improved characteristic in the high-temperature region without causing the low-temperature characteristic to decrease significantly.

The figure of merit of the p type at low temperatures decreased markedly. However, the average performance index in the entire working temperature range improved.
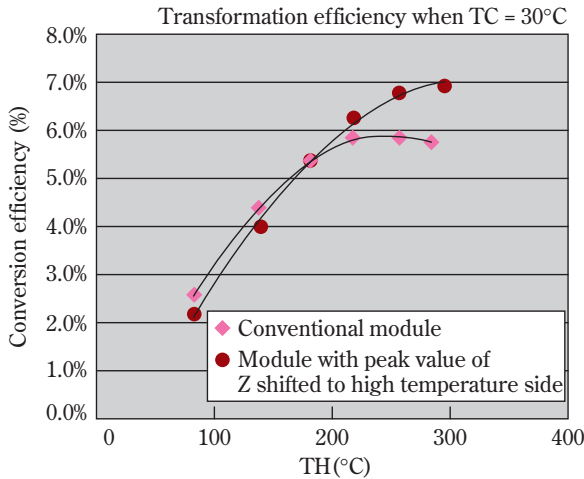
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Fig. 4 Transformation efficiency of module whose Z was shifted to high temperature side

2.2 Silicide-based thermoelectric elements
2.2.1 Mn-Si-based thermoelectric element

At present, we are developing $MnSi_{1.74}$ as an Mn-Si-based material. By optimizing the production process, it has become possible to obtain single crystals of $MnSi_{1.74}$. **Photo 3** shows an image of $MnSi_{1.74}$ under a TEM and it displays the periodic structure with monosilicide (MnSi) striation. In order to improve the performance of $MnSi_{1.74}$, it is important to control the monosilicide. A TEM image of the cross section of the interface between $MnSi_{1.74}$ and MnSi is shown at the center in Photo 3. The right-hand part is $MnSi_{1.74}$, and the left-hand part is MnSi. A marked contrast can be observed in the resolution of atomic scale, suggesting a super-lattice structure. If the layer interval and composition grading of the periodic structure of these two layers can be controlled, it might become possible to obtain so-called phonon glass electron crystal (PGEC).
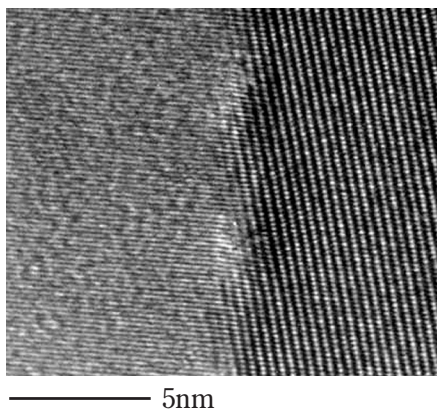

5nm

Photo 3 TEM image of cross section of $MnSi_{1.74}$-/MnSi interface

Photo 4 shows the structure of $MnSi_{1.74}$ etched by HF : HNO_3 : H_2O_2 = 1 : 6 :13 solution, observed under SEM. The striation observed in the figure is MnSi which has similar characteristics to a p-type degenerate semiconductor. Namely, it has a high electric conductivity and a low Seebeck coefficient. Because of this, the content of MnSi influences the thermoelectric characteristics of $MnSi_{1.74}$ significantly.
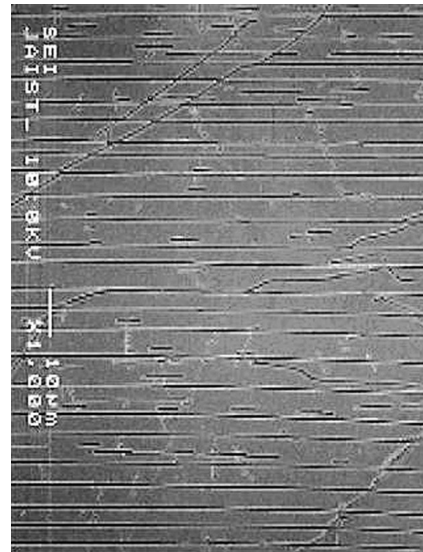

Photo 4 Lanella structure of MnSi

By optimizing the amount of dopant addition, the process conditions, etc., we could obtain the figure of merit of $MnSi_{1.74}$ as shown in **Fig. 5**. It should be noted, however, that the Z shown is an estimate based on a thermal conductivity obtained by the Widemann-Franz law. The average dimensionless figure of merit, ZeT, in the temperature range 300°C to 580°C, obtained from the figure, was 0.71.
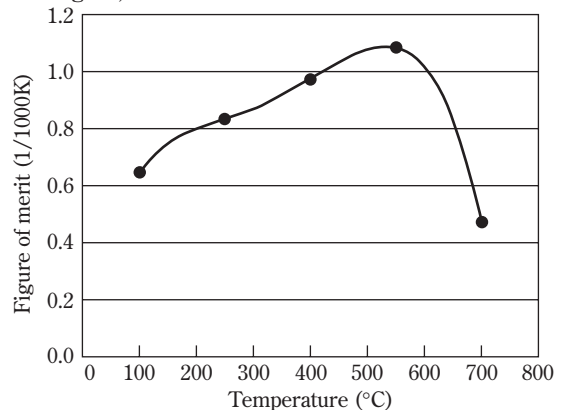

Fig. 5 Performance index of MnSi

2.2.2 Mg-Si-based thermoelectric elements

At present, we are developing $Mg_2Si_xSn_{1-x}$ as n-type thermoelectric elements. This system has a pseudo-dual system phase diagram. Because of a large temperature difference between the solid phase line and the liquid phase line, the phases can hardly be made homogeneous. Therefore, it is difficult to obtain a homogeneous phase merely by quenching and solidification. An X-ray diffraction pattern of a quenched and solidified sample shows two diffraction peaks — one for Mg_2Si and one for Mg_2Sn. Besides, there are broad diffraction lines between the peaks, suggesting the presence of various different phases. By subjecting the sample to a suitable heat treatment, we could obtain a fairly homogeneous phase.

The results of figure of merit Z measurement are shown in **Fig. 6**. The maximum value of Z was approximately $1.5 \times 10^{-3}K^{-1}$. The calculated conversion efficiency in the temperature range 300°C to 580°C was 5.5%. We consider it

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possible to further improve the Z-value by optimizing and homogenizing the material composition and optimizing the carrier density.
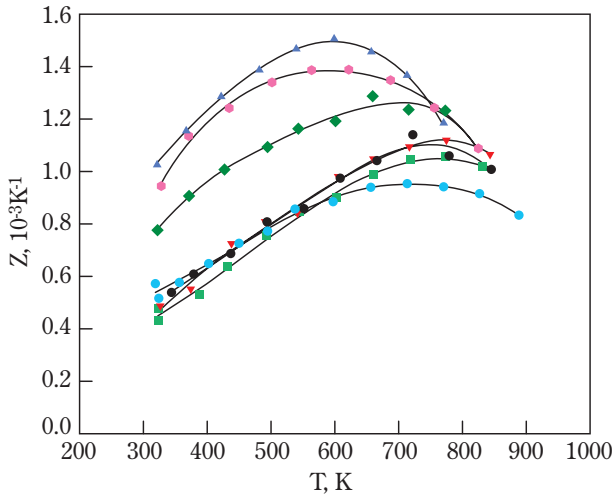

Fig. 6 Performance index of Mg-Si

As a problem with Mg-Si-based thermoelectric elements, the unstable thermoelectric characteristic at high temperatures can be cited. We, therefore, subjected a sample to a test in which it was left in a 600°C vacuum for 15 hours. As a result, it was found that both the Seebeck coefficient (α) and electric resistivity (ρ) of the sample had changed markedly. This change in characteristics is considered ascribable to an insufficient solid phase reaction of $Mg_2Si_xSn_{1-x}$, which caused the segregation of Mg in part of the sample and the volatilization of the segregated Mg. In order to avoid this phenomenon, it is necessary to homogenize the phase and form a protective coating film.

Fig. 7 shows the power factors (at 580°C) of MgSi with and without coating, as a function of time. When the coating is effective, the power factor remains almost the same for about 15 hours and the thermal stability of MgSi with coating is higher than that of MgSi without coating. However, the test time was not long enough and the thermal stability is still insufficient for practical use of MgSi. Since the test was carried out in a vacuum atmosphere, it is important to study the thermal stability of MgSi in the open air and in an actual environment in the future.
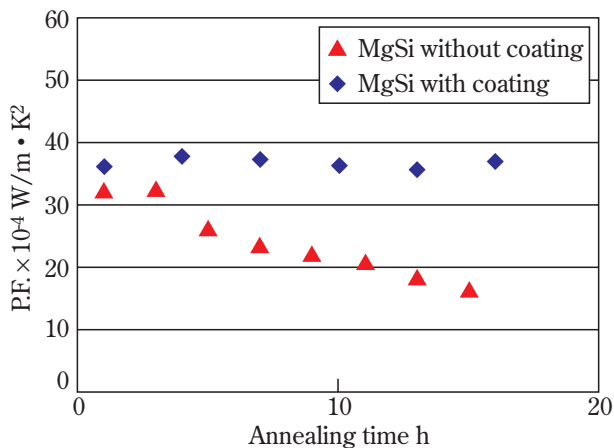

Fig. 7 Time-serial change in power factor of MgSi at 580°C

3. Economics

3.1 Energy recovery

In the effort to save energy by using a thermoelectric module, it is important that the amount of energy produced by the thermoelectric module during its life time should be larger than the amount of energy required to fabricate it.

Fig. 8 shows the energy recovery years (i.e., the number of years in which the amount of energy consumed to build a specific power generation system is recovered by electric power generated by the system) for various methods of electricity generation [9], [10]. The energy recovery years are 0.1 year or less for thermal and nuclear power generation currently in use, 2 years or less for wind power generation which is spotlighted in recent years, and 10 years for fuel cell power generation. In the case of thermoelectric power generation by a Bi-Te-based module of 200°C class, the energy recovery years are 0.85 year. Thus, thermoelectric power generation is considered to have sufficient competitiveness.
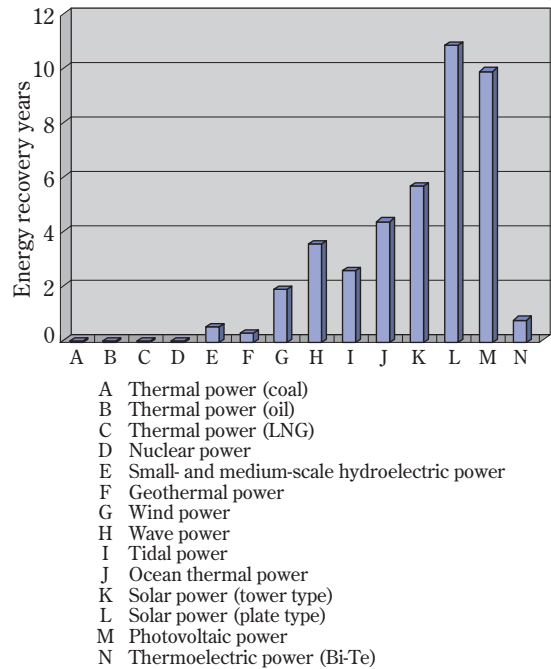

A Thermal power (coal)
B Thermal power (oil)
C Thermal power (LNG)
D Nuclear power
E Small- and medium-scale hydroelectric power
F Geothermal power
G Wind power
H Wave power
I Tidal power
J Ocean thermal power
K Solar power (tower type)
L Solar power (plate type)
M Photovoltaic power
N Thermoelectric power (Bi-Te)
Fig. 8 Comparison of energy recovery years

3.2 Module price

Estimating the manufacturing costs of thermoelectric modules is extremely difficult because the materials, processes, etc. vary widely. **Fig. 9** shows the selling prices of Bi-Te-based thermoelectric modules we checked on the Internet.

The selling prices range from $7 to $42. The most expensive module ($42) is a power generation module manufactured by I Company. The maximum output of the company's 40 mm × 40 mm module is estimated to be 12 W, hence the cost of power generation is estimated to be around $3.5 (¥420)/W.

The maximum output of our Bi-Te module (40 mm × 40 mm) shown in Fig. 4 is 21 W. If this module can be mass-produced and sold at the same price as offered by I Company, the cost of power generation will be ¥240/W.
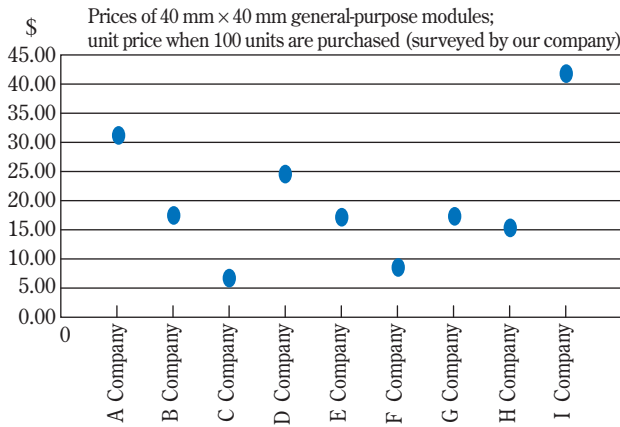
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Fig. 9 Selling prices of various modules

3.3 System price

Table 2 shows the cost of a 3kW solar cell system for general home (2001) [11]. The major peripheral device is the inverter, which is considered necessary for a thermoelectric power generation system too. Assuming the cost of the thermoelectric module as ¥240/W (shown above), the cost of the inverter and other peripheral devices as ¥155/W, and the cost of the heat exchanger as ¥110,000/kW, the system price comes to approximately ¥505/W. This level is considered attainable without so much difficulty.

Table 2 Cost of solar cell system

	Solar cell
Module price	¥520/W
Peripheral devices	¥155/W
Standard installation work	¥110/W
Total	¥785/W

The economics of the system can be roughly calculated as follows.

Yearly operating hours = 365 days year × 24 hours × 0.65
(the rate of operation)
= 5,694 hours/year
Electric energy generated = 5,694 (hours/year) × 1 W
= 5.7kWh/year
Saving of energy = 5.7kWh/year × ¥10/kWh
= ¥57/year · W
Recovery years = ¥505/W ÷ ¥57/year = 8.9 years
Cost of power generation = ¥505/W ÷ 5.7kWh/year ÷ 10 years
= ¥8.9/kWh

Table 3 lists the costs of electric power for various generation methods (2001) [12], [13].

The cost of thermoelectric power generation is ¥8.9/kWh as calculated above, and hence thermoelectric power generation is quite competitive. The above calculations assume that there is sufficient heat source. If this condition is satisfied, we consider that the possibility of power generation by a BiTe thermoelectric module being put into practical use is very strong. When a cascade-type module which allows for more effective utilization of the high temperature side is developed, the economics of a thermoelectric power generation system will be improved still better.

Table 3 Comparison of cost of electric power generation

	Cost per kWh	Service life
Hydropower	¥13.6	
LNG	¥6.4	40 years
Oil	¥10.2	40 years
Nuclear power	¥5.9	40 years
Wind power	¥10 – ¥24	
Photovoltaic power	¥66	20 years
Thermoelectric power		10 years

3.4 Market

We aim at an energy conversion efficiency of 12% by improving the performances of Bi-Te-based and silicide-based thermoelectric modules and by cascading modules. Then, by introducing them into a thermoelectric conversion system properly, it should become possible to obtain a thermoelectric conversion system efficiency of 6%. This is a significant progress in view of the thermoelectric conversion efficiency of 3.6% of conventional waste incinerators. Therefore, the way toward practical application of thermoelectric power generation will open wide.

Concerning the energy-saving effect of thermoelectric power generation, we shall study the application of a high-efficiency thermoelectric system to a diesel engine for cogeneration.

We estimate the overall effect in Japan as follows. It is expected that diesel engine-based cogeneration will reach 2,848MW by the end of 2010. The quantity of waste heat is nearly equal to the electric power generated. Therefore, when thermoelectric power generation is applied to all the cogeneration systems, the energy recovered will be 2,848MW × 6% = 171MW. It is also expected that 120MW of cogeneration will be added annually. Assuming that thermoelectric power generation is introduced to all the new cogeneration systems in 2010, it will be applied to 720MW, resulting the 25% of coverage.

The market will be ¥36,400 million by 2010, with ¥6,000 million in 2010 alone.

The energy-saving effect will be 43MW/h, or 167GWh assuming the yearly operating hours as 3,900 hours. This corresponds to the saving of 40,600 kℓ of crude oil per year and the reduction of approximately 20,200 tons of CO_2 per year.

5. Acknowledgements

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Introduction of the writers

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[A few words from the writers]
We would like to commercialize thermoelectric power generation early.