High performance thermoelectrics for power generation using earth-abundant and low toxicity elements

— Toward developing an innovative waste heat recovery system —

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We have successfully realized greater thermoelectric performance through nanotechnology and developed alternative materials that are more abundant and less toxic than the conventional materials. These studies were conducted in collaboration with domestic and overseas research institutions. A comprehensive effort to all aspects of thermoelectrics, *i.e.* from materials to module, has realized high-performance and environmentally friendly technologies. A startup company was founded in order to develop the thermoelectric market for these technologies. This article describes the research and development strategies employed to achieve practical use of thermoelectric power generation.

Keywords : Thermoelectric power generation, nanostructuring, element strategy, technology transfer, international collaborative research

1 Introduction

While it may not be easy to notice in daily life, a massive amount of waste heat is generated by many sources, such as vehicles, industrial processes, computers. According to a statistical study by the Lawrence Livermore National Laboratory, 66.4 % of primary energy supplied in the United States in 2016 was rejected; only 30.8 % of this energy was used for human activities.[1] Because energy eventually becomes heat, unused energy primarily takes the form of waste heat. A similar situation was found in the estimated energy flow in Japan in 1998, where the amount of waste heat reached 66 % of the primary energy.[2] Since the primary energy in Japan in 1998 was 18×10^{18} J according to the Energy White Paper of Agency for Natural Resources and Energy,[3] the amount of waste heat in this case can be represented as 12×10^{18} J. We lose an enormous amount of energy in the form of waste heat. Therefore, an important strategy that can diminish a serious global energy crisis and environmental burden is improving thermal energy management. Thermoelectrics[Term1] can provide a new approach to this problem. An enormous amount of unused waste heat can be directly converted to useful electricity by using thermoelectric generators. This article describes our longstanding efforts to advance thermoelectric technologies.

Thermoelectrics have only been found in niche applications, for example for use in space exploration. From the 1950s to the present, when space probes explore dark areas without sunlight, radioisotope thermoelectric generators (RTGs) have been used to supply power to the probes.[4] In RTGs, heat released as a result of radioactive decay has been used as the heat source for thermoelectrics. These thermoelectric generators have decades of proven reliability as mission critical applications in space missions. The current focus of energy and environmental sustainability has recently begun to promote the development of commercial thermoelectric applications. If thermoelectric modules[Term2] with a conversion efficiency of 12 % harvest waste heat from exhaust gases in a vehicle, fuel efficiency is estimated to increase by 7 %.[5] In these cases, thermoelectric modules are placed on a vehicle's exhaust pipe surface after the catalytic converters. The surface temperature reaches ~720 K.

There are obvious differences in thermoelectric performance requirements for space and commercial uses. Improved thermoelectric conversion efficacy is required for commercial applications. Further, thermoelectric materials, the key technology in thermoelectrics, should be composed mainly of earth-abundant and low toxicity elements. To realize thermoelectric waste heat recovery, it is necessary to develop thermoelectric modules and associated peripherals, such as a system for the harvesting of waste heat and the transport of heat to modules. It is then important to accumulate operating experience to validate the prototypes. It is also essential to develop rules and guidelines for these processes, including standards for efficiency evaluation. In collaboration with researchers in the National Institute of Advanced Industrial

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Science and Technology (AIST) (of which the author is a member) and at domestic and overseas research institutes, he has steadily addressed the technical challenges of thermoelectrics in interdisciplinary studies that span several research fields. Our longstanding efforts and future strategies are shown in Fig. 1. This article discusses an improvement in thermoelectric conversion efficacy through nanostructuring, the development of thermoelectric materials composed of earth-abundant and low toxicity elements, and the establishment of a startup for developing the thermoelectric market. Further study on the prototype validation is being undertaken.

2 Enhancement in thermoelectric performance through nanotechnology under international collaboration

2.1 Technical barriers between the development of thermoelectric materials and modules

Solid-state devices based on thermoelectrics can directly convert temperature difference (heat) between the hot and cold sides of thermoelectric materials into useful electrical energy through a physical phenomenon called the Seebeck effect. An enhancement in the performance of thermoelectric materials is principally required to achieve high efficiency in thermoelectric modules; therefore, the development of high-performance thermoelectric materials is the most popular field in thermoelectrics. Yet, the development of high-temperature electrodes and the design of electrical and thermal circuits are also important for module fabrication but are low profile fields in thermoelectrics. Extensive efforts have been devoted to enhancing materials performance; however, there has been little effort made to apply this progress in the materials to module development.

To overcome technical barriers, an integrated approach combining materials development and module fabrication has been conducted under international collaboration supported as part of the Japan-United States Cooperation Project for Research and Standardization of Clean Energy Technologies (Japan-United States Clean Energy Cooperation, FY2010–FY2014) funded by the Ministry of Economy, Trade and Industry (METI). As a result, we have successfully demonstrated exceptionally high performance in materials and corresponding high conversion efficiency in the modules.

2.2 Development of thermoelectric materials and modules through technological interaction between Japan and the United States

Good thermoelectric materials need to possess two key properties: low electrical resistivity and low thermal conductivity. Low electrical resistivity (*i.e.*, high electrical conductivity) results in high electrical output because of reduced Joule heating. The thermal conductivity must be low to inhibit heat flow and maintain the temperature difference across materials. Recall that electric power is induced through the temperature difference in thermoelectrics. However, both electrical and thermal transport property needs lead to a conflict in material design. Metals typically exhibit low electrical resistivity but high thermal conductivity. Typical glasses exhibit low thermal conductivity but high electrical resistivity. Therefore, metals and glasses show poor thermoelectric properties. One strategy to optimize these conflicting material properties is based on the concept of a phonon glass–electron crystal (PGEC).[6] In a PGEC material, an electron crystal region allows efficient transmission of charge carriers while inhibiting the heat flow in a phonon glass region. Before the end of the 20th century, it was difficult to realize this concept.

In 2000, then-President Bill Clinton launched the National Nanotechnology Initiative to boost the United States' competitiveness in nanotechnology. As in other fields, attempts had been made to end the trade-off between electrical and thermal transport properties through nanotechnology to enhance performance in thermoelectrics. For almost all

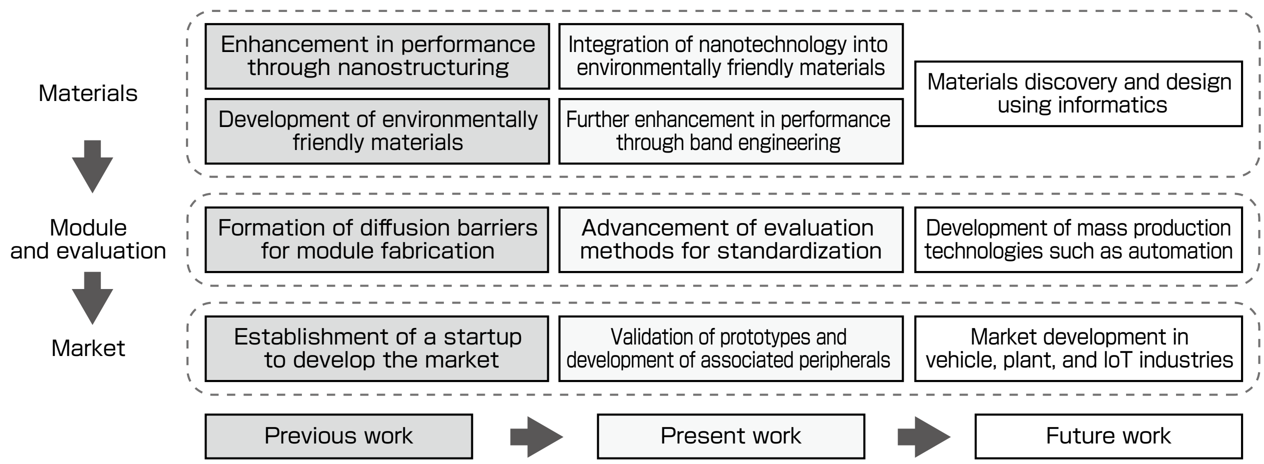

Fig. 1 The author's longstanding studies and future strategies in thermoelectrics
Interdisciplinary studies combining materials, module, and market development.

fields including thermoelectrics, nanotechnology initially got a boost from the development of low-dimensional materials, such as zero-dimensional quantum dots, one-dimensional nanowires, and two-dimensional nanolayer films. Thermoelectric materials used in products are normally three-dimensional bulk forms aimed to distribute the temperature difference across materials; therefore, in this early stage, thermoelectrics benefited little from nanotechnology. Single-phase lead telluride (PbTe)-based thermoelectric materials have been used in several space missions. In 2004, a team led by Mercouri Kanatzidis of Michigan State University (present affiliations: Argonne National Laboratory (ANL) and Northwestern University (Northwestern Univ.)) successfully embedded nanoscale secondary phases (nanostructures) in PbTe bulk through the addition of silver (Ag), bismuth (Bi), and extra tellurium (Te).[7] The insertion of nanostructures causes the effective scattering of heat-carrying phonons and correspondingly reduces the lattice thermal conductivity, enhancing the thermoelectric figure of merit *ZT*.[Term3] Scientific validation of this process took a lot of time and effort because of difficulty in the forming of nanostructures in bulk materials. Recently, several groups including the present team have demonstrated that high performance is observed with the reduction in lattice thermal conductivity through nanostructuring.

Around the same time (FY2002–FY2006), a Japanese national project called the Development for Advanced Thermoelectric Conversion Systems was conducted under the support of New Energy and Industrial Technology Development (NEDO). The author does not know the details because this project was launched prior to his joining AIST. More resources had been devoted to the development of thermoelectric systems than to the development of thermoelectric materials, because this project began before the trend toward nanotechnology.[8] In this project, AIST researchers, Haruhiko Obara and Atsushi Yamamoto, developed thermoelectric modules and measurement systems and accumulated necessary knowledge in AIST.[9]

As mentioned above, Kanatzidis *et al.* first demonstrated that the insertion of nanostructures in bulk thermoelectric materials causes an enhancement in the figure of merit. AIST researchers have successfully developed thermoelectric modules and measurement systems. Since FY2010, in a five-year project under the Japan-United States Clean Energy Cooperation funded by METI, a team of researchers from AIST, ANL, and Northwestern Univ. have developed a high efficacy thermoelectric module based on nanostructured materials by combining both technologies. Figure 2 shows an overview of this joint research. To promote technological interaction, the author had joined the Kanatzidis group at ANL and Northwestern Univ. as a visiting scholar for one year and two months from 2011 to 2012. This stay has led to close coordination with colleagues at these institutions and the consequent achievement of innovative results.

2.3 Improvement in the thermoelectric figure of merit through insertion of nanostructures in bulk materials

The nanostructuring of bulk thermoelectric materials was not investigated in detail before the present study. Under the Japan-United States Clean Energy Cooperation, the experimental condition of melt growth process for PbTe was thermodynamically investigated, allowing for the formation of nanostructures. As shown in Fig. 3(a), nanostructures were embedded in PbTe possessing p-type electrical transport properties through the addition of a very small amount (2.0 at.%) of Mg and the optimization of heating and cooling rates and holding temperature and time in the preparation process.[10] It is well known that sodium (Na) is an acceptor for PbTe. In this study, we doped 4.0 at.% sodium (Na) to yield a suitable p-type carrier concentration for thermoelectric properties.

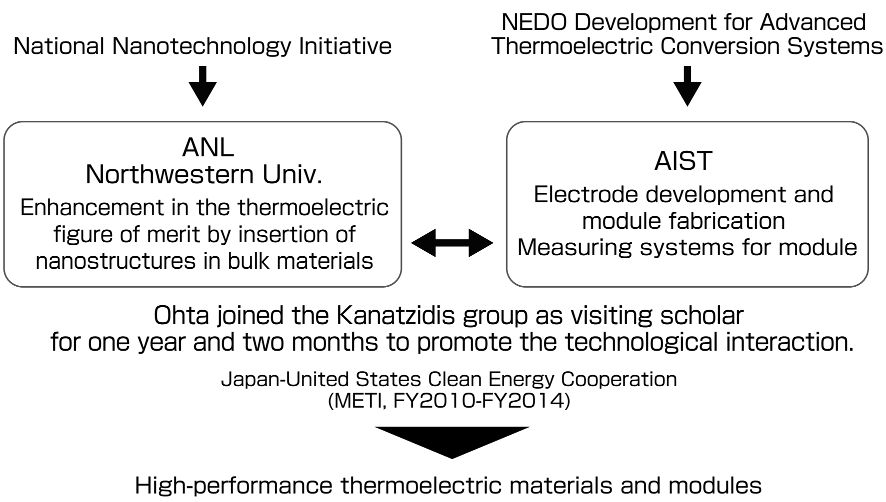

Fig. 2 International joint research between AIST, ANL, and Northwestern Univ. has led to development of high-performance thermoelectric materials and modules.

Figures 3(b) and (c) show a schematic representation of phonon scattering and charge carrier transmission and simplified energy band diagrams, respectively, in the nanostructured thermoelectric materials. The lattice strain fields surrounding nanostructures, induced by the addition of Mg, effectively scatter the nano-order wavelength phonons, resulting in reduced lattice thermal conductivity (Fig. 3(b)). Nonetheless, the lattice strain fields have only a small effect on the system's electrical transport properties. This is most likely due to the coherent (endotaxial) nature of the interface between the nanostructure and the PbTe matrix. In other words, the charge carriers, holes in this case, can propagate without significant scattering in a defect-free interface between two endotaxial components. Moreover, the small valence-band offset between the nanostructures and the PbTe matrix allows for seamless charge carrier transmission[Term4][11] (Fig. 3(c)). Further, the nanostructure is too big for scattering of the charge carriers. A mean free pass of the charge carriers is typically shorter than that of phonons. An important finding here is that the nanostructures induced through the addition of Mg in p-type PbTe selectively reduce lattice thermal conductivity and maintain excellent electrical transport properties, dramatically enhancing the thermoelectric figure of merit *ZT*. A *ZT* of 1.6 at 780 K achieved for $(Pb_{0.94}Mg_{0.02}Na_{0.04})Te$ is 1.8 times higher than that achieved without nanostructures (Fig. 4).[10]

The nanostructured PbTe developed is stable. In this study, the ingots of nanostructured PbTe were hand-ground to fine powders; the samples were then sintered at 773 K for 1h under a uniaxial pressure of 30 MPa in a vacuum (7.0 × 10^{-3} Pa). The nanostructures are maintained after sintering (Fig. 5(a)).[12] As shown in Fig. 5(b), an energy dispersive spectroscopy analysis carried out on the nanostructures confirmed the clear presence of Mg and the absence of Pb and Na. It is noted here that this high performance was maintained in the sintered compacts, which are favorable for processing into thermoelectric modules.

In this article, we focus on the enhancement in thermoelectric performance of p-type PbTe through nanostructuring. We have shown that the performance of n-type PbTe doped with lead iodide (PbI_2) is enhanced through the same nanostructuring approach.[13]

2.4 Comprehensive development from materials to modules: achieving the world's highest level of conversion efficiency

We have successfully enhanced the *ZT* value of both p and n-type PbTe through nanostructuring. The articles describing these results and observations have been published in high impact journals.[10]–[13] This progress in nanostructured thermoelectric materials aroused our interest in future work in materials science. However, in this work, we advanced the development of thermoelectric modules using newly developed nanostructured materials, aiming to inspire innovation in thermoelectric applications. One of the important missions of AIST is to bridge the gap between basic research and commercial production;

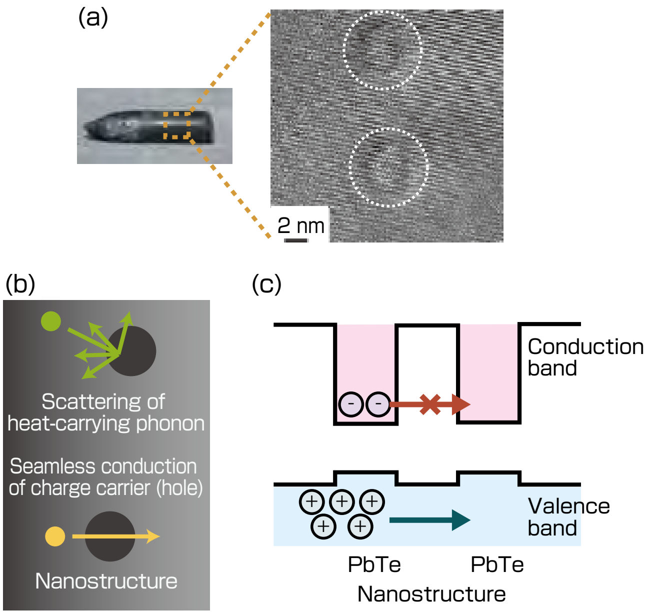

Fig. 3 (a) Typical photograph and high-magnification transmission electron microscopy image of the melt-grown ingot of p-type $(Pb_{0.94}Mg_{0.02}Na_{0.04})Te$,[10] (b) conceptual diagram of the enhancement in the thermoelectric figure of merit *ZT* through nanostructuring, and (c) expected band alignment of nanostructure in the p-type PbTe matrix.[11]
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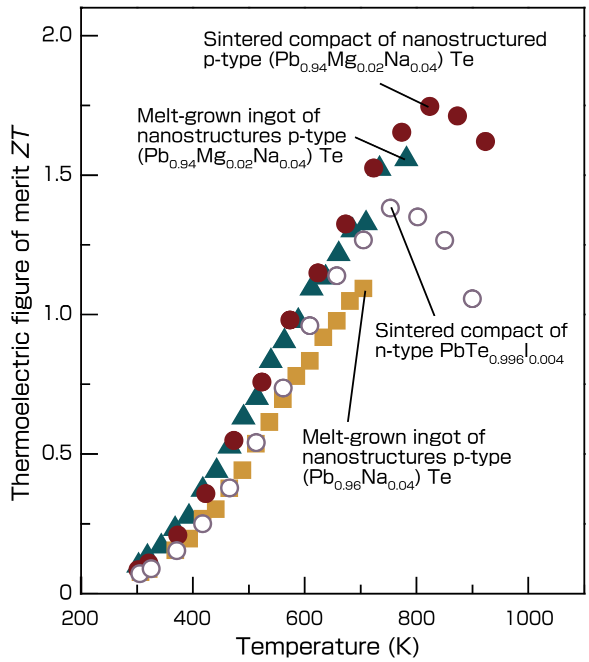

Fig. 4 Temperature dependence of the thermoelectric figure of merit *ZT* for the melt-grown ingots and sintered compacts of p- and n-type PbTe[10][12]

therefore, the author decided to respond to industrial and social expectations for thermoelectrics. In this study, he took advantage of the existing knowledge of thermoelectric modules and measurement systems developed at AIST in the previous NEDO project.

A thermoelectric module is composed mainly of thermoelectric materials and electrodes. The electrodes should have low electrical resistivity to efficiently extract electrical energy from the materials and a high thermal conductivity to efficiently provide heat to the materials. The hot side of the module is subject to high temperatures, such as 720 K in vehicle applications. In high temperatures, the diffusion of atoms generally occurs at the interface between different materials, *i.e.*, thermoelectric materials and electrodes, reducing the module's efficiency. Therefore, in module development, it is particularly important to prevent interface diffusion. Single-phase PbTe is one of the traditional thermoelectric materials. It has been reported that for single-phase PbTe an iron (Fe)-based diffusion barrier formed between the thermoelectric materials and the electrodes prevents interface diffusion.[14] However, in the case of nanostructured PbTe, a high electrical resistance layer has been found to form in the Fe-based diffusion barrier between the thermoelectric materials and the electrodes. In this study, we investigated several Fe-based alloys and mixtures as possible diffusion barriers. As a result, a cobalt (Co)-Fe based diffusion barrier has been successfully developed to improve electrical and thermal contact between the nanostructured PbTe materials and the electrodes.[12]

Figures 6(a) and (b) show the single-stage module fabricated in this study. In this module, we used the sintered compacts of nanostructured $(Pb_{0.94}Mg_{0.02}Na_{0.04})Te$ for p-type legs, $Pb(Te_{0.996}I_{0.004})$ for n-type legs, and a mixture of Co-Fe for the diffusion barriers. As shown in Fig. 4, the *ZT* of $(Pb_{0.94}Mg_{0.02}Na_{0.04})Te$ and $Pb(Te_{0.996}I_{0.004})$ are ~1.8 at 810 K and ~1.4 at 750 K, respectively. The cross section of thermoelectric elements composed of the legs and the diffusion barriers is 2.0 mm × 2.0 mm. The lengths of the thermoelectric legs and diffusion barriers are 2.2 mm and 0.3 mm, respectively; the total length of the legs is 2.8 mm. The module comprises eight p–n couples (sixteen elements) interconnected by copper (Cu) electrodes. As listed in Table 1, the maximum power output and maximum conversion

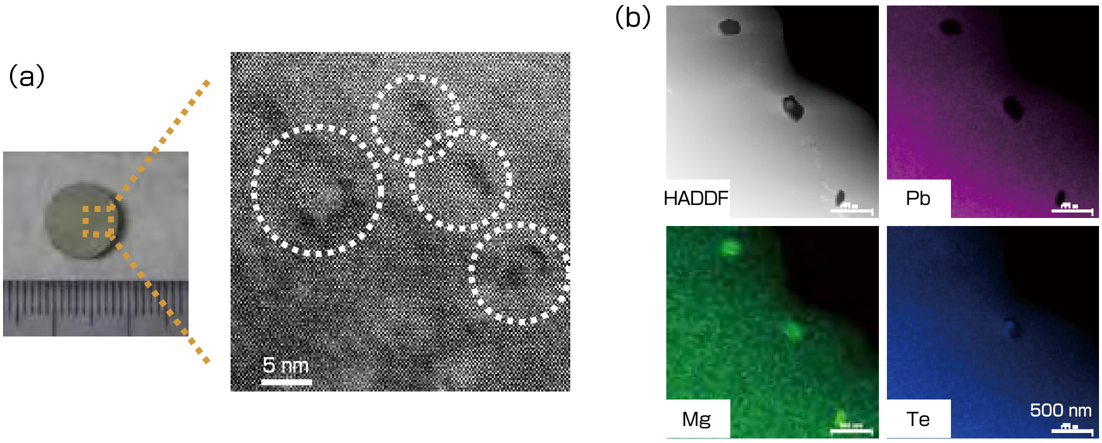

Fig. 5 (a) Typical appearance and high-magnification transmission electron microscopy image[12] and (b) energy-dispersive X-ray elemental mapping of the sintered compact of p-type $(Pb_{0.94}Mg_{0.02}Na_{0.04})Te$.[12]
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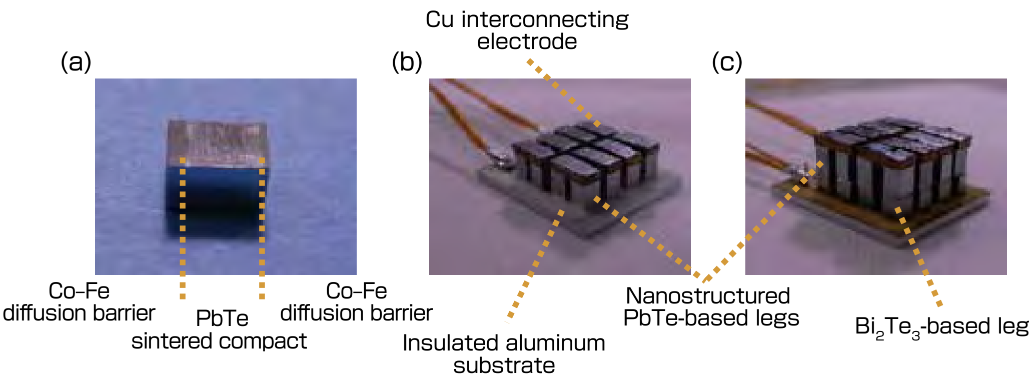

Fig. 6 Nanostructured PbTe-based (a) thermoelectric element, (b) single-stage thermoelectric module, and (c) two-stage (segmented) thermoelectric module using Bi_2Te_3[12]
(b) and (c) Reproduced with permission.[12] Copyright 2016 Royal Society of Chemistry

Table 1. Measured and simulated values of the maximum power output and maximum conversion efficiency of single- and two-stage thermoelectric modules[12]

	Hot-side temperature (K)	Cold-side temperature (K)	Maximum power output (W)		Maximum conversion efficiency (%)	
			Measured value	Simulated value	Measured value	Simulated value
Single-stage thermoelectric module	873	303	3.55	4.71	8.8	12.2
Two-stage thermoelectric module	873	283	2.34	2.55	11	15.6

efficiency achieved are 3.55 W and 8.8 %, respectively, at a hot-side temperature of 873 K and a cold-side temperature of 303 K.

The sintered compact of PbTe shows a high *ZT* over the temperature range of 573 K to 973 K and a low *ZT* below at temperatures below 573 K (Fig. 4). Therefore, conventional bismuth telluride (Bi_2Te_3), which shows a high *ZT* (~1.0) at 373 K, was used in the cold-side thermoelectric elements to develop a two-stage (segmented) thermoelectric module (Fig. 6(d)).[12] The module also comprises eight p–n couples. The size of the PbTe-based thermoelectric elements is the same as that of the single-stage type. The Bi_2Te_3-based thermoelectric elements are 2.0 mm long, 2.0 mm wide, and 2.0 mm tall. The improvement in performance on the cold-side boosts maximum power output. The very high value of 11 % is achieved at a hot-side temperature of 873 K and a cold-side temperature of 283 K (Table 1). If this two-stage module is used for a waste heat recovery system in vehicles, as mentioned above, fuel efficiency is estimated to increase by 7 %.

The power generation characteristics of our nanostructured PbTe-based modules were investigated in a three-dimensional finite-element simulation using the measured thermoelectric properties of the legs and the diffusion barrier.[12] As listed in Table 1, the simulations predict that the maximum conversion efficiency of the single- and two-stage modules would reach 12.2 % and 15.6 %, respectively. The comparison between the simulated and the measured values shows that the differences in maximum power output and maximum conversion efficiency are due to the large contact resistances at the interfaces between the legs and the interconnecting electrodes and heat losses such as radiation which do not contribute to power generation. Therefore, as a next step, we will focus on the further optimization of interfaces and geometrical configuration in order to achieve a maximum conversion efficiency significantly greater than 11 %.

When the author started studying thermoelectrics in 2002, it was challenging to develop a module with a greater than 10 % efficiency. Thermoelectric generators are semiconductor-based devices. Similarly, solar photovoltaics semiconductors convert solar energy into electricity. The photovoltaic market expanded after solar cell efficiency reached 10 %. Although thermoelectric and photovoltaic technologies cannot be directly compared, when the efficiency of semiconductor-based thermoelectric modules exceeds 10 %, this likely promotes the growth of the market. Of course, it is necessary to combine the associated peripherals with high-efficiency thermoelectric modules and technically validate the prototypes for realizing a thermoelectric waste heat recovery system, as discussed in Chapter 5. In collaboration with the researches from ANL and Northwestern Univ., and Osaka University, the author has recently focused on engineering electrical properties in thermoelectric materials to enhance performance. Materials science is actually the author's primary field. This work has been supported as part of the Development of Thermal Management Materials and Technology funded by NEDO.

3 Substitution of rare and toxic elements: environmentally friendly thermoelectric sulfides

3.1 Advantages of thermoelectric sulfides and the difficulty of their preparation

The exceptionally high thermoelectric figure of merit in materials and corresponding high efficiency in modules achieved in this work probably meet those required by commercial markets. Unfortunately, the PbTe-based thermoelectric materials mainly consist of the toxic element Pb and the scarce and expensive element Te. The use of Pb is tightly restricted not only in Japan but also worldwide. The abundance of Te in Earth's crust is low (0.005 ppm), comparable to that of platinum (Pt). Note that the toxicity of Pb has no direct relation to the toxicity of PbTe. The restriction of the use of PbTe should be considered carefully because the high toxicity of Pb is not a sufficient reason for this restriction. It is necessary to scientifically investigate the toxicity of PbTe; however, this takes a great deal of time and effort. At this stage, the use of PbTe is hard to be accepted in the market. Therefore, to explore the market, efforts to develop environmentally friendly thermoelectric materials and modules using less toxic and more earth-abundant elements should be considered in parallel with efforts to develop PbTe-based materials and modules.

Numerous alternative materials to PbTe have recently been investigated. Among these are sulfide systems, which we have studied for over ten years. Thermoelectric sulfides would be widely accepted in society because of the abundance and low toxicity of sulfur (S). Moreover, both sulfur and tellurium belong to the chalcogen family in the periodic table; therefore, sulfides and tellurides tend to have similar chemical and physical properties. Finally, the electronegativity of S is less than that of oxygen (O), which also belongs to the same element group. This means that sulfides generally have low electrical resistivity. However, there are difficulties to developing thermoelectric sulfides. For example, it is difficult to control the chemical reaction for synthesizing sulfides because of the large difference in vapor pressure between metals and sulfur.

This study has made attempts to develop the synthesis and processing of thermoelectric sulfides. For example, in collaboration with a team led by Shinji Hirai of the Muroran Institute of Technology (Muroran IT), several sulfide systems have been successfully prepared through sulfurization.[15]–[21] Because carbon disulfide (CS_2) is a powerful sulfurizing agent, we have used it for sulfurization. The CS_2 sulfurization leads to the low temperature formation of sulfides. The thermodynamic investigations on the synthesis and processing of sulfides have brought about the development of various thermoelectric sulfides. For instance, rare-earth sulfides have been developed for n-type high-temperature applications (above 873 K).[16][17] The titanium disulfide developed is a candidate for n-type intermediate-temperature thermoelectric applications (~673 K).[18] Layered sulfides have been developed as high-temperature thermoelectric materials. In this system, the charge carrier type (p or n) is tunable through the change in the chemical composition.[19][21] p-type Chevrel-phase sulfides exhibit high potential for high-temperature applications.[22][23] However, as summarized in Fig. 7, the thermoelectric figure of merit *ZT* has been limited to 0.6 for these systems.

There are limitations on the development of thermoelectric sulfides through studies based only on inorganic chemistry. We fully acknowledge that studies of condensed matter are also required to look for promising systems within the very large sulfide family. An integration of chemistry and physics is obviously needed for thermoelectric study. The author has noted the benefits of such integration through direct experience. Since 2010, he has collaborated with the following condensed matter physicists, who have investigated the thermoelectric sulfides: Koichiro Suekuni of the Japan Advanced Institute of Science and Technology (JAIST) (at Hiroshima University (Hiroshima Univ.) from 2013 to 2016 and since then at Kyushu University (Kyushu Univ.)), Mikio Koyano of JAIST, and Toshiro Takabatake of Hiroshima Univ. To promote the development of thermoelectric sulfides through joint research, the following three strategies have been integrated into the substitution of Te for S, which is a key direction of AIST studies.[24] In the first strategy, the crystal structure of thermoelectric sulfides should belong to a cubic system, because high valley degeneracy in electronic bands is conducive to a high thermoelectric power factor and a high corresponding power output. In the second strategy, the thermoelectric sulfides should have a complex crystal structure such as a large unit cell containing a large number of atoms, because structural complexity enables low lattice thermal conductivity. The third strategy is to use chemically stable minerals as references for developing thermoelectric sulfides. To carry out these strategies, we have focused on copper (Cu)-containing sulfides; these would be widely

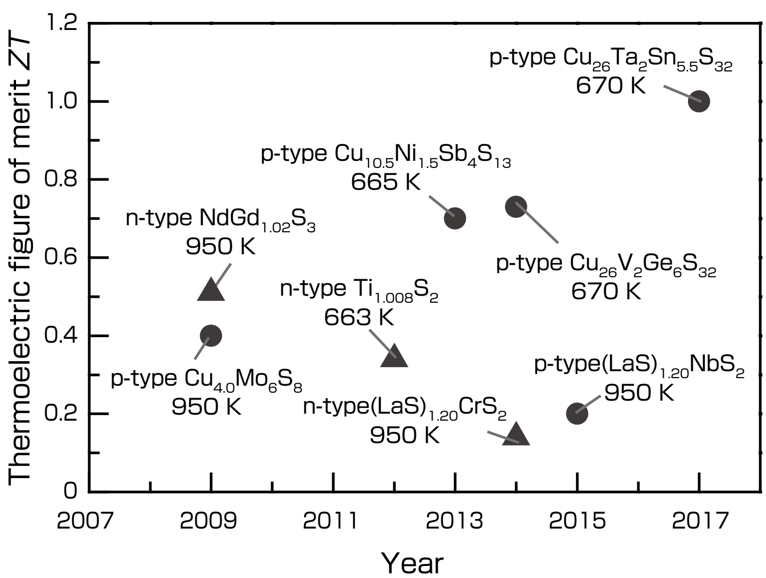

Fig. 7 Thermoelectric sulfides developed in this study:
rare-earth sulfide $NdGd_{1.02}S_3$,[16] titanium disulfide $Ti_{1.008}S$,[18] layered sulfides $(LaS)_{1.20}CrS_2$[19] and $(LaS)_{1.20}NbS_2$,[21] Chevrel-phase sulfide $Cu_{4.0}Mo_6S_8$,[22] tetrahedrite $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$,[26] and colusites $Cu_{26}V_2Ge_6S_{32}$[29] and $Cu_{26}Ta_2Sn_{5.5}S_{32}$[31]

accepted in society because of their abundance and low toxicity of S and Cu.

3.2 Successful development of new thermoelectric tetrahedrites

Thermoelectric sulfides have been explored through the four strategies mentioned above. In 2012, JAIST researchers found low lattice thermal conductivity at room temperature in $Cu_{12}Sb_4S_{13}$, whose chemical composition is similar to a sulfosalt mineral called tetrahedrite.[25] In 2013, a team of researchers from JAIST, AIST, and RIKEN successfully enhanced the *ZT* of the thermoelectric tetrahedrites at around 673 K by substituting Ni for Cu.[26] These systems are excellent candidates for use in vehicle applications. In this study, materials were first developed for thermoelectrics by physicists at JAIST. Inorganic chemists at AIST investigated the processing for the preparation of these materials. At RIKEN, the crystal structure was examined using synchrotron radiation at SPring-8.

Thermoelectric tetrahedrites exhibit a PGEC behavior, namely, low electrical resistivity and low lattice thermal conductivity. The crystal structure of tetrahedrites belongs to a cubic system. The concentration of the charge carrier can be tuned by substituting Ni for Cu, resulting in an improved thermoelectric power factor.[26] Lattice thermal conductivity is low, below 0.5 W K^{-1} m^{-1} over the temperature range of 300 K to 673 K (Fig. 8). To understand lattice thermal conductivity, the synchrotron powder X-ray diffraction data measured were used to carry out crystal structure refinements. The result reveals the low-energy vibration of some Cu atoms in the crystal structure.[26] The vibration effectively scatters phonons, yielding the low lattice thermal conductivity. The enhancement in the *ZT* achieved have come both from the improvement in power factors and the reduction in lattice thermal conductivity. In $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$, the *ZT* reaches ~0.7 at 665 K as shown in Fig. 7.

At the same time, a team led by Donald Morelli of Michigan State University has also successfully developed thermoelectric tetrahedrites.[27] In 2015, they demonstrated high *ZT* ~ 1.03 at 723 K in $Cu_{10.5}Ni_{1.0}Zn_{0.5}Sb_4S_{13}$.[28] The successful development of tetrahedrites in these studies has proven our strategies, demonstrating the potential of sulfides for thermoelectrics. The high *ZT* achieved in the Cu-containing sulfide has significant impacts for the thermoelectric community. The citation of our paper on the thermoelectric tetrahedrite[26] is greater than 90 (accessed July 2017). However, the high toxicity of antimony (Sb) in tetrahedrites is an obstacle to practical use.

3.3 Materials development and module fabrication in colusites

Since our strategies have been demonstrated through the development of tetrahedrites, we have continued to explore thermoelectric sulfides based on mineral-based systems under joint research. In 2014, we demonstrated that Pb, Te, and Sb-free thermoelectric sulfides $Cu_{26}V_2M_6S_{32}$ (M = Ge, Sn) called colusites show a high *ZT* at around 673 K.[29] Colusites also crystallize in a cubic structure. Like tetrahedrites, the high *ZT* in colusites arises from their metal-like high power factor and glass-like low lattice thermal conductivity. As shown in Fig. 8, the lattice thermal conductivity of $Cu_{26}V_2Ge_6S_{32}$ is low, below 0.5 W K^{-1} m^{-1} over the temperature range of 300 K to 673 K. It remains an open question why colusites show low lattice thermal conductivity. To address this question, lattice thermal conductivity is compared between colusite and sulvanite. The chemical composition of sulvanite is

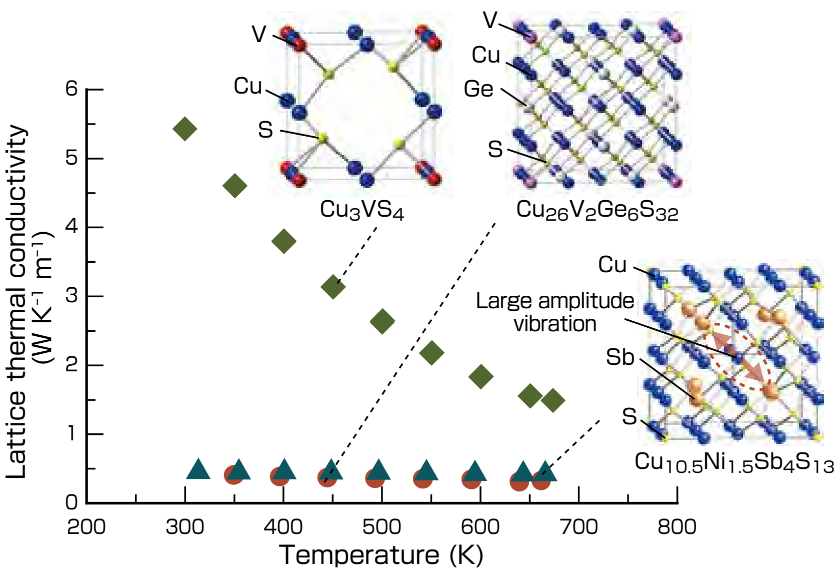

Fig. 8 Temperature dependence of thermal conductivity for tetrahedrite $Cu_{10.5}Ni_{1.5}Sb_4S_{13}$,[26] colusites $Cu_{26}V_2Ge_6S_3$,[29] and sulvanite Cu_3VS_4,[29] along with their crystal structures.

Cu_3VS_4 ($Cu_{24}V_8S_{32}$), similar to that of colusite $Cu_{26}V_2Ge_6S_{32}$. Both of these sulfides belong to a cubic system. On the other hand, there is a large difference in the number of atoms per unit cell between $Cu_{26}V_2Ge_6S_{32}$ (66 atoms) and Cu_3VS_4 (8 atoms). As shown in Fig. 8, the lattice thermal conductivity of Cu_3VS_4 is higher than that of $Cu_{26}V_2Ge_6S_{32}$. For example, the room-temperature value of Cu_3VS_4 is ten times as high as that of $Cu_{26}V_2Ge_6S_{32}$. This comparison implies that the much lower lattice thermal conductivity in $Cu_{26}V_2Ge_6S_{32}$ is due to its structural complexity, including the large number of atoms per unit cell.

A certain company pointed out that there is still concern regarding the oxidation of V for production processes and practical use, because V-oxides are toxic. We have therefore reworked our strategy using the periodic table of elements to address the problem. Like in the substitution of S for Te, an attempt was made to substitute the low toxicity elements Nb and Ta for V in colusites.[30] The Nb and Ta-substituted samples have been successfully prepared without a significant change in the processing, because all the elements belong to the same element family. The important finding here is that high thermoelectric performance is maintained with full substitution of Nb and Ta for V. Therefore, it can be said that the fully substituted colusites are environmentally friendly thermoelectric materials. In our recent study, the concentration of charge carriers can be tuned by changing the Sn content, leading to an improved thermoelectric power factor.[31] As a result, the *ZT* has been enhanced to 1.0 for $Cu_{26}Ta_2Sn_{5.5}S_{32}$ at 670 K. In PbTe, nanostructuring is proven to result in the dramatic enhancement of *ZT*; therefore, further study is currently in progress to boost the thermoelectric performance of colusites through nanostructuring (Fig. 1). This work has been supported as part of the International Joint Research Program for Innovative Energy Technology funded by METI. We will also promote the development of materials using data-driven study such as materials informatics (Fig. 1).

We have not only enhanced the materials performance of colusite systems but have also fabricated a thermoelectric module for practical use. Au-based diffusion barriers have been developed in our recent study. Figure 9 shows the recently fabricated colusite-based thermoelectric elements.

4 Establishment of a startup through technology transfer from AIST for developing the market

Thermoelectrics have recently received increasing attention with growing concerns over the global energy crisis and associated environmental burdens. As a result, there is increased need in downstream and end-user companies to test thermoelectric prototypes with their products. We possess high-efficiency thermoelectric modules and environmentally friendly materials developed at AIST. The studies are now in progress to improve their mechanical properties and chemical stability. There is also increased demand to evaluate thermoelectric products and buy measurement systems in upstream and manufacturing companies. We have mastered the measurement of thermoelectric materials and modules. As shown in Fig. 10, the seeds created by AIST seem to match the needs of industry. However, for AIST, it is hard to sufficiently meet demands from industry for various reasons, such as the difficulty of mass production. To bridge this gap, we had to create a new framework beyond the activities of AIST. One possibility was to transfer technologies from AIST to an established company. However, negotiations broke down because almost all companies did not have enough certainty in regard to how the thermoelectric market would grow. Furthermore, the author hoped to introduce the technologies into the market himself, improving them through feedback from the market. In June 2016, a startup company named Mottainai Energy was founded through transfer of technologies from AIST. The author is now the technical advisor to Mottainai Energy while he continues to work for AIST as a senior researcher.

Although it is difficult for a startup company to survive in Japan, two reasons prompted the establishment of

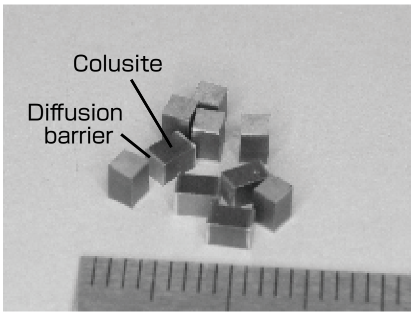

Fig. 9 Colusite-based thermoelectric elements. Au-based diffusion barriers are formed on both sides.

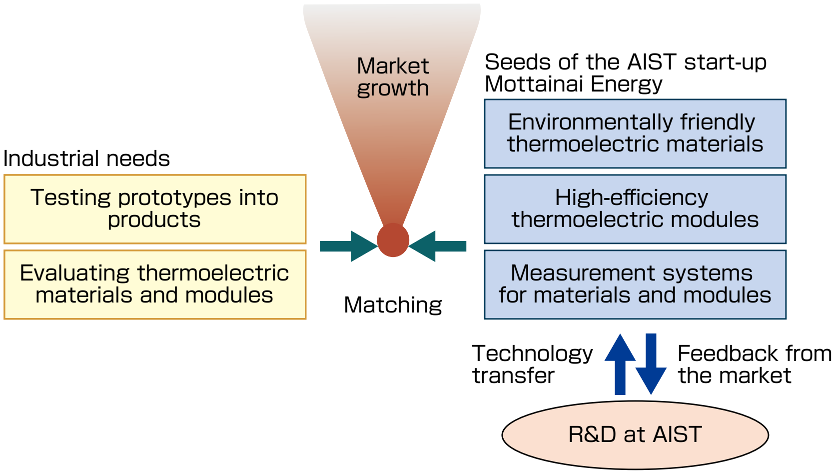

Fig. 10 Industrial needs and the AIST startup's seeds in thermoelectrics.

the Mottainai Energy. The first reason has already been mentioned above. And here is the second reason. In Japan, several national projects supported by METI, the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and related agencies are now in progress. In this project, many companies and research institutes, including AIST, have focused on various subjects covering the basics and applications of thermoelectrics. Almost all of these projects target the development of applications for large markets such as the vehicle market. Because thermoelectrics provide new approaches to improving energy, in the future thermoelectric markets will grow and provide benefits and returns to government and the companies who invest in them. On the other hand, the use of thermoelectrics is currently limited to space applications such as RTGs; therefore, the quality of products is expected to gradually improve for commercial markets. The first market for thermoelectrics is probably small. US startups have initially introduced niche products such as outdoor gear to small markets. In Japan, there are less projects and support for targeting niche applications. Mottainai Energy, to keep up with world trends, aims to first develop niche applications for commercial markets and then grow the market in Japan.

Taking into consideration the factors mentioned above, the following main products are being developed through Mottainai Energy: High-efficiency thermoelectric modules and environmentally friendly materials will be supplied for downstream and end-user companies. Measurement systems and services will be supplied for upstream and manufacturing companies. The supply of the former provides a good opportunity to inform people about thermoelectrics, thereby developing the market. In the latter, the measurement systems and services improve the reliability of products at each company, as mentioned in Chapter 5. The company passed its first anniversary without deviation from its original purposes during the writing of this article.

5 Challenges in prototype validation and advanced measurements

To develop the thermoelectric market, we have focused on the following studies, in addition to the materials and module developments discussed above: prototypes should be made and validated to promote commercialization and implementation. Common measurement methods must be established as part of the rules. For prototype validation, the design and development of a system of technical integration between the thermoelectric module and associated peripherals, particularly for vehicles, are needed to meet growing industrial demand. As an example of associated peripherals, a heat exchanger is needed to transfer heat from waste heat sources to thermoelectric modules. Moreover, it is necessary to validate the thermoelectric system in a vehicle test bench for finding and solving technical problems. Like the materials and module developments, the project is being promoted in international collaboration with researchers who are familiar with vehicles.

For measurements, common methods must be established as standard before the wide spread of thermoelectrics. If the thermoelectric efficiency of modules is measured with different methods and systems of each company and country, it is easy to imagine that the lack of compatibility will cause confusion. A measurement method and system for thermoelectric modules were developed at AIST in collaboration with Japanese companies and research institutes before the author joined AIST.[9] The efficiency of ~370 modules was measured through the AIST system for the past decade. The AIST system has become a de facto standard in Japan. On the other hand, because the modules have been used in space missions for many years, other high-quality measurement systems were developed for this field. Therefore, the joint research between AIST and research institutes for space programs will lead to the development of high-accuracy measurement systems. Specifically, there are plans for cross-checking of the measurement systems, to be performed by a team led by A. Yamamoto, who is mainly responsible for the development of the AIST system. The members of this team would include the author and experts from space technology research institutes and equipment manufacturing companies. The measurement of heat flow and the reduction of the effect of thermal radiation will be particularly improved through cross-checking.

An example of the collaboration in prototype validation and advanced measurement is the joint research between AIST and the German Aerospace Center (DLR) supported as part of the International Joint Research Program for Innovative Energy Technology funded by METI. The DLR research covers transportation and energy as well as aeronautics and space. The DLR is therefore an appropriate collaboration partner for both prototype validation and advanced measurement. On 19 March 2017, AIST and DLR concluded a memorandum of understanding (MOU) to start joint research. The author will steadily improve thermoelectric technologies through various frameworks, including through the AIST and DLR joint research.

6 Conclusion

Although the author’s interdisciplinary activities from materials development to startup establishment have made an impact on thermoelectrics, the growth of the market remains a distant goal. His effort will continue to be devoted to achieving this goal, using current knowledge, including the discussions in this journal, *Synthesiology*. The importance of international collaboration, interdisciplinary study, and technology transfer addressed in this paper was already recognized through various past discussions. The important aim of this work was to integrate these discussions in the development of the study. Each knowledge element has been deeply understood in full research proposed by AIST after a great deal of discussion. The author believes that the discussion of the full research should be shifted to the integration and advancement of elements of knowledge.

7 Acknowledgments

The author expresses my deep appreciation to Prof. Mercouri Kanatzidis, Senior Researcher at ANL and Professor at Northwestern Univ., and Dr. Priyanka Jood, Researcher at ATSI, for plentiful stimulating discussions in the development of PbTe-based thermoelectric materials. The author is sincerely grateful to Prof. Koichiro Suekuni, Associate Professor at Kyushu Univ., Prof. Shinji Hirai, Professor at Muroran IT., Prof. Toshiro Takabatake, Professor at Hiroshima Univ., and Prof. Mikio Koyano, Professor at JAIST, for productive collaboration on the development of thermoelectric sulfides. The author also thanks Dr. Haruhiko Obara, Deputy Director General at AIST, and Mr. Atsushi Yamamoto, Group Leader at AIST, for lending their expertise on thermoelectric module and their evaluations in PbTe and sulfide. Mr. Hirotaka Nishiate, CEO at Mottainai Energy, made enormous contribution to starting the company. The author would like to thank his colleagues for in-depth discussions and the postdoctoral fellows for strenuous efforts. Their names appear in the various publications cited in this article. The work was supported as part of Japan-United States Cooperation Project for Research and Standardization of Clean Energy Technologies funded by METI, International Joint Research Program for Innovative Energy Technology funded by METI, and Development of Thermal Management Materials and Technology funded by NEDO. Financial support from JSPS KAKENHI Grant Number 25420699, Thermal and Electric Energy Technology Foundation, and Iketani Science and Technology Foundation also are gratefully acknowledged.

Terminologies

Term 1. Thermoelectrics: Figure a shows an electric circuit consisting of two dissimilar materials. In this case, one is an electrode and the other is a semiconductor thermoelectric material. When one of the two junctions is heated, the voltage V is produced in electric circuits by the temperature difference dT: $V = SdT$. The phenomenon and proportionality constant, S, are known as the Seebeck effect and Seebeck coefficient, respectively. A thermoelectric generator directly converts heat into electricity through the Seebeck effect.

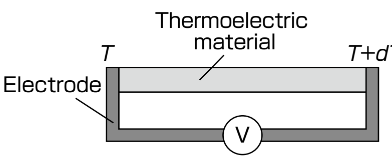

Fig. a Seebeck effect

Term 2. Thermoelectric module: Figure b shows the thermoelectric module made from one couple of p- and n-type thermoelectric materials. The charge carriers of the p- and n-type materials are positively-charged holes and negatively-charged electrons, respectively. Both charge carriers, holes and electrons, diffuse from the hot side to the cold side. As a result, the electrical current flows form the cold side of n-type material to that of p-type material by passing through the interconnecting electrode. Thermoelectric modules normally contain many couples. For example, the modules shown in Figs. 6(b) and (c) contain eight p-n couples. The power output and conversion efficiency obtained changes with the electrical load. The power output reaches a maximum (maximum power output) when the impedance is matched between the load and the internal resistance. In conversion efficiency, the maximum value (maximum conversion efficiency) slightly shifts from the value at the impedance matching because of the effect of heat.

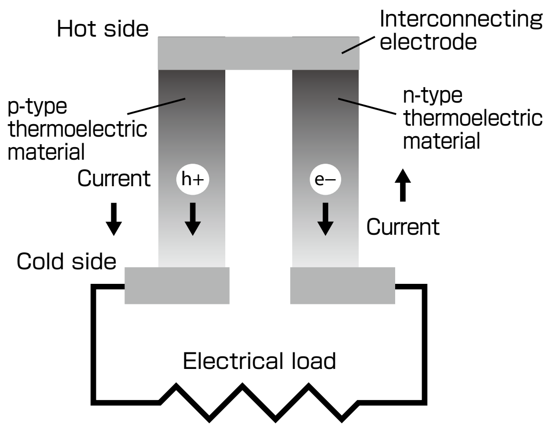

Fig. b Thermoelectric module made from one couple of p- and n-type thermoelectric materials

Term 3. Thermoelectric figure of merit: The performance of a thermoelectric material is determined by the thermoelectric figure of merit ZT, defined as $ZT = S^2T/\rho\kappa$, where T is the temperature, S is the Seebeck coefficient, ρ is the electrical resistivity, and κ is the thermal conductivity. The performance of a thermoelectric material increases with increasing ZT. Their units are T [K], S [V K^{-1}], ρ [Ω m], and κ [W K^{-1} m^{-1}], respectively. Thermal conductivity arises from two sources, phonons and charge carriers; therefore, it is the sum of lattice (lattice thermal conductivity, κ_{lat}) and electronic (electronic thermal conductivity, κ_{el}) contributions: $\kappa = \kappa_{lat} + \kappa_{el}$. A high Seebeck coefficient and low electrical resistivity lead to a high-power output. Low thermal conductivity, particularly low lattice thermal conductivity, helps to maintain the temperature difference.

Term 4. Band offset: In this case, this means the energy difference between the top of the valence bands in dissimilar materials.

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Discussions with Reviewers

1 Overall

Comment (Toshihiko Kanayama, AIST)

This paper discusses the author's consistent strategy to work from original materials development and module fabrication to social implementation for thermoelectrics. The content of this article meets the editorial policy of *Synthesiology.* International collaboration with a team of experts from various research institutes has been actively conducted, achieving meaningful results. This article gives a good example for others.

Comment (Shigeki Naitou, AIST)

The utilization of unused heat energy will greatly contribute to energy conservation and have significant effects on industries' activities, including power generation, steel, vehicle, and chemical industries. Therefore, this study will play an important role in society. The author's concept and the design of R&D and the efforts to establish a startup for social implementation meets the editorial policy of *Synthesiology.*

2 Industrial significance of thermoelectrics

Comment (Shigeki Naitou)

Thermoelectric waste heat recovery in industries including power generation, steel, vehicle, and chemicals should be discussed in more detail. With regards to social implementation, the future outlook should be provided in this article. Public support would be received through improvement in the outlook to be shared with these industries.

Answer (Michihiro Ohta)

A technology roadmap for thermoelectric waste heat recovery in industrial use should be provided as you indicated. For the introduction of thermoelectrics, it is necessary to develop associated peripherals such as a heat exchanger as well as thermoelectric materials and modules. For example, a heat exchanger should be designed and developed for each product. We have started to develop a thermoelectric system, including a heat exchanger, for use in vehicles, as mentioned in Chapter 5. Figure 1 and relevant sentences have been modified to clarify the importance of developing the associated peripherals as well as the thermoelectric technologies.

3 Social implementation

Comment (Toshihiko Kanayama)

The important point of this work is that the establishment of the startup and the development of advanced measurements, as well as the development of materials and modules, have been promoted for social implementation and the spread of thermoelectrics. There is a need for more concrete discussion of the establishment of the startup and the development of advanced measurements in Chapters 4 and 5, respectively. The startup's business activities and missions should be particularly emphasized in Chapter 4. In Chapter 5, the author should address how advanced measurements and prototype validations will be developed through international collaboration with research institutes and companies. These discussions would help to clarify the author's intentions.

Answer (Michihiro Ohta)

As suggested by the reviewer, the startup's activities and missions have been included in Chapter 4. Moreover, future plans and the purpose of international collaboration have been added to Chapter 5. However, because both activities are at an early stage, these discussions need to be deepened in further work. On the other hand, the profound discussions on the materials and module development in previous works have been provided in Chapters 2 and 3.

4 Configuration and properties of the thermoelectric module

Comment (Toshihiko Kanayama)

An explanation for the configuration of the thermoelectric module is needed to better understand the discussion in this article. I recommend that the schematic representation of the basic configuration is shown in a figure and an explanation is added to the text. The reasons why both p- and n- type semiconductors are needed in the module should be particularly noted.

In addition, the meaning of the following technical terms used is unclear. Definitions and explanations should be added: a) Nanostructure: Because this generally has a very broad meaning, a definition should be provided. b) Bulk: This technical term is used in specific fields. c) Maximum power output: The meaning of maximum is unclear. d) Maximum conversion efficiency: The meaning of maximum and conversion efficiency should be explained.

Answer (Michihiro Ohta)

Thank you for your valuable suggestions. In term 2 of Terminologies, the configuration of thermoelectric module, maximum power output, and maximum conversion efficiency have been explained. The meaning of nanostructure and bulk has been defined in the main text.