2021

NIMS NOW INTERNATIONAL

NATIONAL INSTITUTE FOR MATERIALS SCIENCE

No. 1

21st "THERMAL SCIENCE" CENTURY

Significant advances in efforts to control heat

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Humans have benefitted from the effective use of heat. Heaters, boilers and internal combustion engines are all examples of heat-based technologies that have made our lives more comfortable and convenient.

However, heat can also cause many problems and difficulties. For example, heat generated by personal computers can cause mechanical failure and shorten product life, and waste heat from vehicles and industrial plants gives rise to environmental issues, such as heat island effects. To address these issues, a succession of heat-related materials has been developed.

This trend has been accelerating since the dawn of the 21st century. The understanding of thermal conduction mechanisms is progressing and the flow of heat can now be manipulated with nanoscale precision. One of the current focuses of thermal science is the development of technologies capable of capturing thermal energy before it dissipates and efficiently exploiting it. To achieve this, NIMS has been taking advantage of every available scientific approach: theory, simulations, experiments and materials informatics.

This NIMS NOW issue features some significant achievements in the quest to completely control heat.

Major advances in thermal science:

New technologies will help make our lives more comfortable and convenient

Most electronics and appliances, including lamps, vacuum machines and smartphones being used to watch videos or being charged, generate heat. Heat is always produced when electric power is used to operate machines and devices. Naoki Ohashi at NIMS has been researching and developing functional materials capable of controlling heat.

"Electrical and electronic devices warm while they are being used because some of the electrical energy flowing through them transforms into heat and dissipates through such mechanisms as electrical resistance, leakage current and friction," Ohashi said. "A lamp cannot covert all of the electric power supplied to it into light. When a battery is being charged, some of the electric power fed to it escapes as heat. In addressing heat-related issues such as global warming, effective thermal control and more efficient energy usage are essential."

In October 2020, the Japanese government announced its policy to reduce Japan's greenhouse gas emissions to net zero by 2050. To achieve this goal, thermal control materials and technologies need to be developed with extreme urgency.

Human attempts to effectively use heat led to the development of thermally functional materials

Humans had learned to effectively use heat even before the advent of science. For example, thermal insulation materials, such as stones and straw, have been used to form the exterior walls of houses in order to keep the rooms cooler in the summer and warmer in the winter, and sun-heated water has been used to store heat. People then began to seek greater comfort using synthetic materials such as thermal insulation materials—used to prevent heat dissipation and conduction—and heat-resistant materials used under high-temperature conditions.

"Expanded polystyrene foam (EPS) is probably the most well-known synthetic thermal insulation material," Ohashi said. "EPS with numerous pores can store a large volume of air—a poor thermal conductor—making it an effective thermal insulator. More recently, aerogel with much higher thermal insulation performance than EPS was developed. Research is currently underway to determine the applicability of aerogel for use as a thermal insulation material in buildings and electronic devices."

Increased demand for thermal power generation has stimulated the development of heat-resistant materials.

"The temperature of combustion gas in thermal power plant turbines may reach as high as 1,500°C," Ohashi said. "The fuel efficiency of the turbine increases with an increase in combustion gas temperature. To help increase the turbine's fuel efficiency, NIMS has been working to discover alloys with outstanding heat-resistant capability and has been developing techniques to coat alloys with ceramics with melting points higher than those of the coated alloys."

Physical properties of heat-related materials need to be optimized depending on their intended use in applications such as regulating temperatures in indoor spaces and electronic devices and increasing combustion performance in rocket engines. Global efforts have been made to develop high-performance materials for different heat-related purposes.

Advanced understanding of phonons led to a breakthrough in thermal science

"The phonon is the fundamental thermal conduction mechanism," Ohashi said. "Significant progress in the understanding of phonons has substantially advanced thermal science R&D."

In essence, heat is conducted by atomic and molecular vibrations, particularly in solids. The phonon is a concept describing these vibrations.

"The understanding of phonons is crucial in studying the thermal conductivity of materials, determining the amount of thermal energy required to raise their temperatures and optimizing materials design based on these parameters," Ohashi said. "However, ways in which atoms in a material vibrate and conduct heat in relation to their types and arrangements are difficult to determine through experiments alone. In addition, not all scientists can easily access large facilities such as SPring-8 to conduct phonon-related experiments. These limitations are becoming less of an issue with recent advances in condensed matter physics, computers and computer software. These tools have enabled us to perform simulations with high precision, allowing us to quantitatively analyze the behavior of phonons. Moreover, rapid technological enhancement in recent years has made it feasible for us to design desirable synthetic microstructures and actually create them. We then may be able to manipulate phonons in these microstructures in an intended manner. Through this approach, we might be able to gain greater control and freedom in applied thermal science."

R&D concerning thermoelectric materials is one of the scientific fields that has greatly benefitted from advances in simulation techniques and nanotechnology. The 2020 NIMS Award recognized achievements in this field. These materials, capable of direct conversion between heat and electricity, may potentially be used to convert waste heat—approximately 90% of which is less than 200°C—into electrical energy. However, their conversion efficiency is very low. Bismuth telluride is known to have the highest thermoelectric conversion performance at near room temperature. This material was discovered by Hiroshi Julian Goldsmid in 1954, a winner of the 2020 NIMS Award (see p. 12). Practical materials with higher thermoelectric conversion performance than bismuth telluride are yet to be discovered.

However, significant progress in this endeavor is being made. Kunihito Koumoto—another 2020 NIMS Award winner (see p. 14) who has been a Japanese leader in the field of thermoelectricity—has devised and fabricated a unique nanostructure and demonstrated a new method of improving materials' thermoelectric conversion performance by manipulating phonons. NIMS is also making a major effort to develop a thermoelectric material with new mechanisms (e.g., magnetism is used to increase thermoelectric conversion efficiency; see the boxed text on p. 7). In addition, another NIMS group has succeeded in developing a thermoelectric device composed entirely of abundant chemical elements. This device is currently in the process of commercialization by a private company.

Increasing thermal science applicability

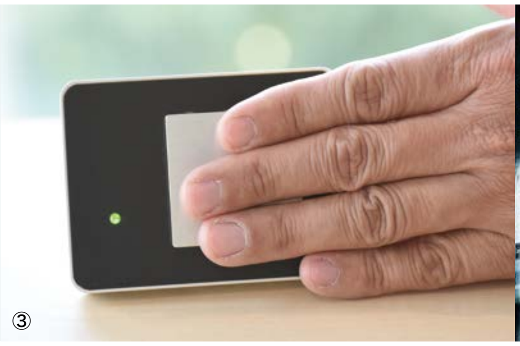
"The applicability of thermal science is increasing," Ohashi said. "For example, magnetic refrigeration technology, which manipulates the spin of a magnetic material, can be used to cool objects, and thermal radiation (i.e., heat transfer through infrared radiation) can be used to control the temperature of objects (see the boxed text on p. 8)."

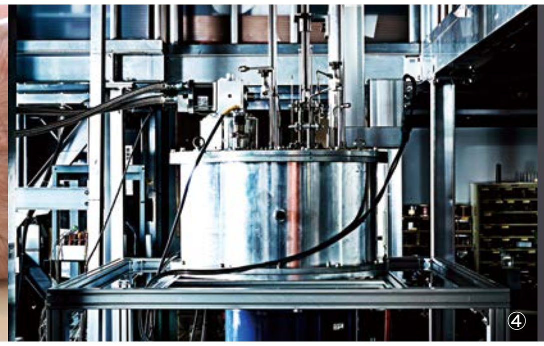
Materials informatics (MI) is another powerful tool that has become available in recent years. MI is a machine learning-based technique to select candidates of materials with desirable characteristics. The use of MI has actually led to the discovery of high-performance thermal insulation materials and its usefulness has been convincingly proven (see the boxed text on p. 9).

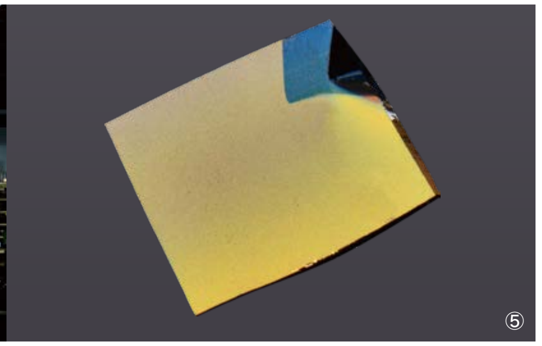
"The use of MI may potentially enable us to invent new materials," Ohashi said. "This is achievable even for the types of materials that have a long history of development, including thermal insulation, heat storage and heat-resistant materials. I believe that technologies capable of precisely controlling heat can be used to make our lives more comfortable and convenient. I hope that NIMS will be able to help create such technologies through materials development." NIMS will continue to tackle this challenge using every means available: theory, simulations, experiments and MI.

Naoki Ohashi

Director of the Research Center for Functional Materials







① Aerogel, a porous material with high thermal insulation performance.

② Aircraft engine turbine blades made of a highly heat resistant nickel-based superalloy. These blades are designed to enable high-temperature combustion.

③ Prototype thermoelectric device capable of turning body heat into electricity, causing green LED to glow. This device contains FAST material, a thermoelectric material composed of iron, aluminum and silicon.

④ Magnetic refrigeration system capable of generating extremely low temperatures using magnetic materials that release and absorb heat.

⑤ Thin film material composed of silicon and bismuth capable of delivering one of the highest thermal insulation performances in the world.

Technological and strategic approaches to controlling thermal behavior

Controlling heat is one of the major challenges of the 21st century.
Thermal science researchers have been tackling it in a variety of ways.
Among them are three NIMS researchers attempting to achieve high-precision thermal control who would like to share their research activities and strategic visions with us.

Takao Mori
Leader of the Thermal Energy Materials Group, International Center for Materials Nanoarchitectonics (MANA)

Yibin Xu
Deputy Director of the Research and Services Division of Materials Data and Integrated System, Leader of the Data-driven Inorganic Materials Group

Hideki T. Miyazaki
Leader of the Plasmonics Group, Research Center for Functional Materials

Issues with handling heat

——Could you briefly describe your research activities?

Mori: I have been researching thermoelectric materials. About two-thirds of primary energy (e.g., petroleum, coal and natural gas) used by humans is lost in the form of waste heat. We could save significant amounts of energy if waste heat could be converted into electricity using thermoelectric generators. On a different note, sensors used to collect data on various human activities are expected to play a vital role in bringing Japan's Society 5.0 initiative for an IOT Society into reality. Thermoelectric materials may be effective in generating electricity from various heat sources, including human bodies, and supplying it to these sensors.

Thermoelectric materials need to possess high electrical conductivity but also low thermal conductivity. Materials with these characteristics are difficult to create. It's important to be able to achieve a high degree of control of the heat that flows through them.

Xu: My main research focus has been to understand thermal conduction mechanisms through experimental, theoretical and simulation approaches. I've also been involved in the development of materials capable of dissipating, storing and insulating heat. I also have been working to build MatNavi—a database on the structures and physical properties of various materials—since 2002. In addition, I have incorporated materials informatics (MI) (i.e., identification of optimum material compositions by analyzing large amounts of data using machine learning techniques) into my research since around 2013 in an effort to accelerate the discovery of new materials with desirable physical properties.

Miyazaki: I have been researching and developing optical devices for many years. As such, unlike Mr. Mori and Ms. Xu, my area of expertise is optics rather than heat-related materials. However, a common ground was recently found between these two areas of expertise: over the past 10 years, it became technically feasible to fabricate materials with nanostructured surfaces capable of emitting only specific wavelengths when heated. We have also come to know that materials can be cooled by allowing them to radiate heat. These new findings have led optics researchers, including myself, to step into heat-related research without even noticing it. I hope to make further contributions to heat-related research.

——Heat is something common in everyday life. Why is it so difficult to control?

Mori: We now can control electrons and photons—quanta of light—with a high degree of precision. However, phonons, which carry heat, are still difficult to control. Phonons transfer heat across a solid through the propagation of atomic vibrations (i.e., lattice vibrations). Phonons have a dispersive nature, making their manipulation difficult. Phonons are difficult to be coherent and therefore have a "poor memory", so to speak.

Xu: The flow of electrons and photons can be stopped completely. This means they can be switched on and off. By contrast, the flow of phonons cannot be stopped completely unless they are exposed to absolute zero temperature. Moreover, thermal conduction involves not only phonons, but they also interact with electrons and photons in a complex manner. These three entities, therefore, need to be controlled simultaneously. This is why thermal control is difficult.

Miyazaki: Optical scientists use Maxwell's equations—named after James Clerk Maxwell, a 19th-century theoretical physicist—when they design optical devices. Because these equations work very accurately, we are able to manipulate photons in extreme precision. On the other hand, phonons and heat are exceptionally difficult to control.

Focus: Mori's Research

Creating a thermoelectric material with a new mechanism superior to bismuth telluride

For more than 60 years, bismuth telluride (Bi_2Te_3) has been known to be the best performing thermoelectric material at near room temperature. Active research efforts have been made worldwide to develop thermoelectric materials superior to Bi_2Te_3 by identifying new mechanisms and structures. In 2012, while studying a chalcopyrite-based magnetic semiconductor, Mori and his colleagues discovered a promising new mechanism: strong interactions between magnetic ions and electrons enhance the thermoelectric performance of a material. This phenomenon, named paramagnon drag, has since been a focus of intense thermoelectric research around the world. Mori's research group recently discovered a material as effective as Bi_2Te_3 in thermoelectric performance between room temperature and 300°C. "This new material is composed of more abundant chemical elements than Bi_2Te_3," Mori said. Mori's group is currently working to optimize a thermoelectric device they have developed using this material.

Thermoelectric device containing chalcopyrite-based magnetic semiconductors.

Powerful 21st century tools

——Is precise thermal control becoming more feasible with advances in nanotechnology and computer simulations?

Mori: With respect to thermoelectric materials, this year, 2021, marks the 200th anniversary of the 1821 discovery of the Seebeck effect: the direct conversion of temperature differences into electricity. However, power generation devices capable of exploiting this effect still remain largely unavailable. Science and technology previously available were unable to significantly improve the performance of thermoelectric generator devices.

A major breakthrough came in the 1990s, when significant progress was made in our understanding of phonons, simulation techniques and techniques to fabricate and evaluate the performance of nanostructures. These advancements led to the creation of a series of materials with new mechanisms and structures. Our group has also been working to develop innovative materials: materials with nanopores and crystalline defects capable of selectively scattering phonons, thereby increasing the materials' thermal insulation capacities through thermal transport control. I imagine that Dr. Miyazaki and Dr. Xu are also actively leveraging nanotechnology and computer simulations.

Miyazaki: Perhaps optical device researchers, including myself, have benefitted the most from nanotechnology and simulations. When I was a college student, the wavelengths of light were generally recognized as unimaginably tiny and uncontrollable physical entities. However, we can now easily create periodic nanopatterns with an interval narrower than the wavelength of light using simulations and computer-aided design (CAD) software. We can precisely control the absorption and emission of light at the surface of a material by modifying the shape, arrangement and interval of nanopatterns (see the boxed text on p. 9).

Among the full range of wavelengths, infrared radiation has long been known to be able to carry heat in the form of thermal radiation. This phenomenon can now be precisely controlled to convert heat into light, which can then be transmitted over a long distance. The development of this technology was enabled through a combination of optics and thermal science and by the advances in nanotechnology and computer simulations.

Xu: I've been amazed by the fact that the results of optical experiments always closely match simulation results. Because theories to explain thermal conduction are still under development, not all heat-related problems can be solved using computer simulations. Even so, the use of simulations is immensely helpful in understanding the mechanisms behind thermal phenomena.

Heat can be transferred via different pathways. Analyzing experimental measurements alone cannot enable us to determine exact thermal conduction pathways or the sources of heat. By contrast, the use of first principle calculations allows us to simulate the behavior of atoms and electrons without bias and enable us to separate a group of heat-related phenomena into individual phenomena. This approach also allows us to determine the relationship between different phenomena, such as the relationship between electrons and phonons. This type of study gives us great insights into fundamental thermal conduction mechanisms.

——How useful do you think MI would be in heat-related materials research?

Xu: The application of MI requires a huge amount of data to be processed by machine learning algorithms. A large amount of data on the thermal properties of materials has been accumulated through many years of experiments. In addition, a large amount of computational data has also been amassed by performing large-scale automated calculations (i.e., high-throughput calculations). According to research literature, some new thermoelectric materials and highly thermally conductive polymers have been developed by exploiting these data resources. Our group has also succeeded in discovering a highly thermally insulating material using MI. The key to our success was the fact that we incorporated data on thermal resistance at interfaces between different materials into our analysis (see the boxed text on p. 8).

Advances in nanotechnology have greatly increased the performance of MI. For example, the temperature of a material is usually quantified by measuring heat-related phenomena, such as the wavelengths emitted by the material and the thermal expansion of the material. These measurements could previously only allow to obtain an average of temperature across a macroscale material. With the use of nanotechnology, we can now precisely measure materials' temperature. For example, even an instantaneous temperature change occurring in a nanoscale area can be measured. Because the accuracy of MI predictions is influenced by both the quality and quantity of data, nanotechnology is very complementary to MI.

Interdisciplinary approach to the development of thermal management systems

——What strategies do you think will be needed to win the competition in thermoelectric R&D?

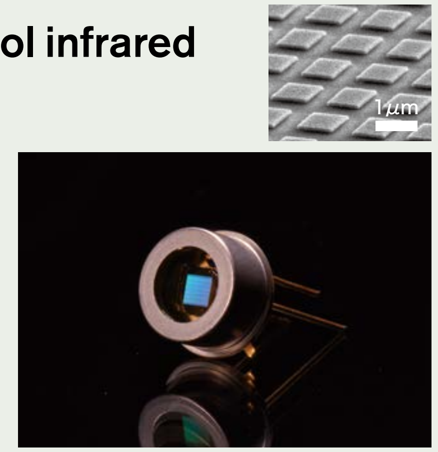
Mori: My approach is to search for high-performance materials with new mechanisms and structures. In 2012 our group discovered a chalcopyrite-based material composed of iron, sulfur and copper with high thermoelectric power generation ability at near room temperature. We then found that the magnetic properties of the material enhanced its thermoelectric performance. We were the first to discover this striking enhancement mechanism and this discovery had a global impact. We have since made more achievements, including the discovery of a magnetic semiconductor with even higher thermoelectric performance. These achievements have stimulated research teams overseas and intensified global research competitions (see the boxed text on p. 7).

I also think that active interaction and learning from scientists in other disci-

Focus: Miyazaki's Research

Metamaterials: engineering materials to control infrared emission and absorption

Infrared waves are able to transfer heat. Metamaterials—artificially engineered materials—can be designed to manipulate infrared radiation in a desirable manner. The emission and absorption of light at the surface of a metal material can be controlled by embossing it with periodic patterns with an interval narrower than the wavelength of light. This recently developed technique of achieving fine-tuned infrared manipulation has been exploited to advance both thermal and optical technologies. Miyazaki has been particularly focused on its optical applications and is developing a device capable of measuring gaseous molecules in an atmosphere. Many of these molecules absorb only a specific range of infrared wavelengths. The device can determine the type and concentration of gaseous molecules present in an atmosphere by emitting infrared radiation and sensing the wavelengths that have passed through the molecules. Miyazaki has succeeded in measuring two types of polluting gases (CO_2 and nitrogen oxides (NOx)) using these devices.



Infrared emitter containing a metamaterial and a close up of the micropatterned metamaterial surface.

Focus: Xu's Research

Development of a world-class thermal insulation material using materials informatics

Thermal insulation materials are intended to interrupt the flow of heat. One effective design strategy for achieving this is to exploit thermally resistant interfaces between different materials. Heat flow tends to be disrupted at material interfaces where heat-carrying phonons and electrons may scatter and bounce back. However, materials with thermally resistant interfaces are extremely difficult to design through theoretical and computational approaches. This is because the thermal resistances of materials are influenced by myriad different factors, including compositional ratios, crystalline structures and the presence/absence of crystalline defects.

To overcome these challenges, Xu adopted a materials informatics approach. She first selected 12 parameters related to interfacial thermal resistance from data collected from existing databases and the research literature. She then determined the three most accurate models, used each of them to find interfaces with high thermal resistance respectively and extracted the common parts of the results. Using this method, she was able to narrow about 80,000 candidate interfaces down to the most promising 25. Of these 25 materials, she selected a silicon-bismuth composite that is relatively easy to synthesize and fabricated it. She created many samples of this composite under slightly different synthesis conditions. This effort eventually enabled her to develop one of the highest performance thermal insulation materials ever devised, with a thermal conductivity of 0.16 $Wm^{-1}K^{-1}$.

plines is important. Magnetic materials research in Japan is very strong internationally. Learning from domestic scientists researching magnetic materials may benefit us, for example, in fine-tuning the physical properties of materials. A proper integration of materials with different physical properties is also critical. In order for practical thermal management systems to achieve high energy efficiency, thermoelectric materials and thermal insulation materials need to be skillfully integrated.

Miyazaki: Speaking of materials integration, I believe that the performance of thermoelectric materials can be increased by controlling their thermal radiation. To enable a material to convert heat into electricity, a temperature gradient needs to be created across the material. Most naturally occurring materials lack cooling capability, and artificial cooling requires a large amount of energy and is costly. Despite these constraints, a US research team demonstrated about five years ago that the thermal radiation toward a cool object can be used to efficiently cool a distantly located target object. A material capable of intensely emitting long-wave radiation (i.e., mid-infrared radiation) from its surface has been found to be able to significantly cool itself through so-called radiative cooling without requiring electric power.

The ultimate cool object is located a great distance from here. Can you guess what it is? Outer space. It's vast and extremely cold: -270°C.

Mori: I suppose that we can efficiently cool a specific portion of a thermoelectric conversion material if we can achieve the following: The portion intended to be cooled has a surface structure capable of intensely emitting only long-wave radiation which can penetrate the atmosphere and reach outer space. Is this how it works?

Miyazaki: That's correct. Radiative cooling research was recently launched at NIMS as well. Dr. Satoshi Ishii, a young researcher, is leading the effort and the team has already produced some promising results.

——Finally, what are your future research goals?

Mori: I really hope to develop a practical thermoelectric generator. We'd like to keep improving the thermoelectric performance of materials with magnetic and nanostructured enhancement principles we have developed so that they can be integrated into such a device. In addition, a comprehensive thermal management technique (e.g., enabling better thermal input on the hot side and effective cooling on the cold side) needs to be applied to create larger temperature differences across a device. The development of mass production strategies for devices is also essential. All necessary tools are now available to address these issues and I'm eager to achieve a thermoelectric breakthrough 200 years after the discovery of the Seebeck effect.

Takao Mori

Xu: Curiosity has always been the driving force behind my research. My utmost interest at present is to investigate heat-related mechanisms. New thermal conduction channels (i.e., heat transfer media and pathways) were recently discovered. There are probably other types of thermal conduction channels yet to be discovered and I hope to identify them. In regard to materials development, I'm willing to try out any tools and means available to us for the sake of creating high-performance materials. I intend to take full advantage of theoretical, experimental, simulation and MI approaches for the development of materials with thermal insulation, heat dissipation and heat storage capacities.

Miyazaki: My goal is to bring innovation using infrared radiation. Among the full range of electromagnetic wavelengths, shorter wavelength radiation, such as ultraviolet and visible light, has been studied extensively. Notably, the invention of the blue LED was awarded a Nobel Prize. By comparison, infrared has been studied less extensively and its research still has great potential to bring innovation. I hope to expand the application of infrared so that people would recognize its value as much as the value of other wavelengths. Achieving thermal control using infrared is part of this effort.

(By Kumi Yamada)

NIMS
AWARD
NATIONAL INSTITUTE FOR
MATERIALS SCIENCE

Winner Interview

NIMS Awards are annually bestowed on individuals and groups who have made significant contributions to materials science.

The 2020 award focused on energy and environmental materials science. Two researchers—Professor Hiroshi Julian Goldsmid and Professor Kunihito Koumoto—won this year's awards in recognition of their pioneering work on the research and development of thermoelectric materials: materials capable of converting thermal energy into electrical energy.

Professor Goldsmid discovered materials that are outstanding both in cooling and power generation performance —the two primary purposes of thermoelectric materials.

Professor Koumoto is one of the first scientists to take the initiative in developing a new type of thermoelectric material composed entirely of abundant and non-toxic chemical compounds.

We conducted special interviews with these two NIMS Award recipients.

A pioneer in thermoelectric materials with profound influence on society

Prof. Hiroshi Julian Goldsmid

Professor Emeritus, University of New South Wales

He joined the General Electric Company (GEC) in the United Kingdom in 1951. During his tenure at GEC, he earned his Ph.D. from the University of London in 1958. After resigning from GEC in 1964, he worked at the University of Bath as a reader in solid state physics until 1969. He then served as a visiting professor at many universities. He is currently working in R&D to promote advances in thermoelectric conversion materials at the University of New South Wales.

Dr. Hiroshi Julian Goldsmid identified bismuth telluride as a practical material for thermoelectric cooling in 1954. He succeeded in creating a large temperature difference (26℃) using bismuth telluride (Bi_2Te_3) as the p-type leg and bismuth (Bi) as the n-type leg in a thermoelectric device.

Since that development, bismuth telluride-based Peltier devices have been integrated into laser oscillators to precisely control their temperatures, leading to increased optical communication transmission capacity and distance. These and other accomplishments have had a profound influence, through commercialization and innovation of thermoelectric devices that play essential roles in the core technology to support the coming “Internet of Things” (IoT) society.

Dr. Goldsmid spoke with NIMS Now after receiving his NIMS Award for advancements in the field of materials for thermal energy conversion and thermal management.

Welcome, Dr. Goldsmid, and congratulations on your NIMS Award.

Thank you. This award means a lot to me, because although I've won awards in the past, from organizations like the International Thermoelectric Society, for advances in thermoelectric technology, the NIMS Award recognizes my work as part of the broader field of materials science, which is very gratifying.

Your first name is Hiroshi. Do you have a strong connection to Japan?

Yes, my father was Japanese and lived in England, and my mother was English. After World War II broke out, he had to return to Japan, so I didn't see him for many years. But he always wanted me to be a scientist and was pleased to see me succeed in his ambition.

What inspired you to pursue research on thermoelectric energy conversion?

I joined the General Electric Company (GEC)* in 1954 as a researcher under the leadership of Dr.R.W. Douglas, head of the semiconductor research group. It was his idea to work on thermoelectricity. He was aware of thermoelectric cooling, and knew it to be inefficient, so he asked me to see if I could boost its performance using standard conductors.

What challenges did you face in achieving these successes?

At the start, I knew only the basic physics of the phenomena, so I really oversimplified things. I knew about the properties and capabilities of charge carriers in semiconductors, and about heat carried by the lattice vibrations. I expressed my ideas in quite basic language, but luckily the ideas worked out — I had decided to select a compound with a high atomic weight and bismuth telluride satisfied this requirement. I could, I suppose, have chosen lead telluride and probably would have moved on to that compound if bismuth telluride had not turned out to be so promising. If I'd known more semiconductor physics, I might have been overwhelmed. It was a case of beginner’s luck, because the very first material I looked at turned out to be the best for the application.

I was also lucky to be working in a group where other people were looking at other aspects of semiconductors. They gave me advice on how to conduct my experiments, and helped me make samples of the bismuth telluride. At that time, I didn’t have a PhD yet, but most of the members of the group did, and were much more established in the field. We weren't competing — we were looking to support each other.

What was the response to your accomplishment?

There was very little work being done on this elsewhere, except for a few people working in the USSR, more or less in parallel with what we were doing in Britain. After my paper was published in 1954, things started to move fast in Britain, the U.S. and Europe, and it became a hot topic. Eventually, it generated hundreds of papers in Europe alone.

At GEC I was working in an industrial laboratory, and the management there wasn't too keen on their members talking to people from other labs. But they soon realized that cooperation with other laboratories was good for everyone.

How did your successes influence competition in product development?

The company wasn’t really set up to take advantage of an application like that. Thermoelectricity didn't really fit into any of the established products. So they were unsure of what to do with the new developments. Large electrical companies like GEC were not terribly interested; they were happy to see the advances be taken up and developed by much smaller organizations. I couldn't find an application for it at first, but I'm glad it has been put to practical use thanks to the development of other technologies.

Bismuth telluride is still, years after you developed it, the most efficient material for thermoelectric power generation. Is that surprising to you?

It's surprising given how many materials have been investigated since then — perhaps hundreds of thousands. The variants used nowadays are similar to the materials we used years ago. It is perhaps disheartening that better materials have not been discovered, but one thing I've learned is that specifying a chemical formula does not necessarily close the book on a material. For example, we might develop a material that has the same chemical composition but different properties, so there may be other developments related to bismuth telluride. Nanostructured materials may turn out to be one of those developments.

What roles could these thermoelectric materials play in the future?

I've always thought that one day they will be used in converting low-grade heat into electricity. Ordinarily, if your heat source is low-grade, you'll never get very high efficiency. Thermoelectrics solve that problem and hold out the possibility of using novel sources of energy. Ocean thermal gradients, for example, haven't been explored yet. There's an enormous amount of low-grade heat sources available, and hopefully this will lead to a way of making use of it.

These materials would be used in small-scale technology such as off-grid power for remote scientific instruments, in spacecraft, and for harvesting waste heat in vehicles, industrial processes, microprocessors, etc. They could also be used in conjunction with photovoltaics, because thermoelectrics can use wavelengths outside of the solar spectrum.

What have been the ultimate goals of your research?

My personal goals reflect the goals of the whole thermoelectric community, such as finding worthwhile projects related to thermoelectricity. My previous work has led to research on the aspects of these materials that have an effect on magnetic fields, or the effect of these materials in amorphous form. Bismuth telluride is a strongly anisotropic material in single crystal form, so there could be many interesting and rewarding topics coming up.

Finally, what would you say to a young researcher, just starting out?

I have spent a long time working in this field. I don't forget that when I was young and inexperienced, I tried not to be intimidated by the fact that I was working with so many knowledgeable people. Luckily, my boss, Dr. Douglas, let me go ahead so my work could show whether something was worthwhile. That was a great thing — having a boss who was supportive, and didn’t interfere too much. I learned that if you have an idea, follow it through, because even if it doesn’t pan out the first time, that doesn't mean it won’t work. And it’s probably better than just taking over what other people have done.

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* The General Electric Company (GEC) was a manufacturer of general electric and defense equipment in the United Kingdom.

Generating electricity directly from heat using environmentally friendly materials

Prof. Kunihito Koumoto

Professor Emeritus, Nagoya University
Senior Researcher, Nagoya Industrial Science Research Institute
Distinguished Adjunct Professor, King Abdulaziz University

In the early days of thermoelectric materials R&D, the use of scarce and toxic elements was considered necessary to increase the performance of these materials. Despite this general belief, Dr. Kunihito Koumoto has promoted the development environmentally friendly thermoelectric materials. He demonstrated ways by which non-toxic materials could be developed by proposing and fabricating revolutionary nanostructures and demonstrating their adequate performance. He developed various types of new materials, including flexible thermoelectric materials composed of organic and inorganic compounds. We asked Dr. Kunihito Koumoto to share some of the inspirations he gained during his research career and talk to us about the ways his research has transformed.

Earned a doctorate degree from the University of Tokyo, Graduate School of Engineering in 1979. After working as a researcher at the university for 13 years, he became a professor at Nagoya University. In March 2015, he earned the title of professor emeritus from Nagoya University upon his resignation. He has since been engaged in thermoelectric materials R&D at various universities and institutions, including the Toyota Physical and Chemical Research Institute and research institutions in China, South Korea, Australia and Saudi Arabia.

Congratulations for winning a NIMS Award!

Thank you. It's a great honor for me to be a corecipient of this award with Professor Julian Goldsmid, who is known as a founding father of the field of thermoelectricity. What really makes me happy is the fact that NIMS selected thermoelectric materials as the area of consideration for this year's NIMS Award.

What made you enter into thermoelectric materials research?

It happened by chance. When I was a research associate at the University of Tokyo in the 1980s, my area of research was defect chemistry of ceramics. One day we were preparing to study physical properties of silicon carbide (SiC) as part of a student's dissertation research. When we sintered SiC powder to create SiC ceramic samples the sintering process did not turn out properly, failing to firmly densify the powder compact. Although we were disappointed with the result, we proceeded to measure the physical properties of the porous samples anyway. When I noted the thermal and electrical conductivities of the samples, I had a hunch that this material may have promising thermoelectric properties.

The Seebeck effect explains the fundamental mechanism behind the conversion of heat into electricity: when temperatures differ between the two ends of a material, this difference may be converted into electric voltage (thermoelectromotive force) in a directly proportional manner. Having both poor thermal conductivity (which creates a large temperature difference between the two ends) and high electrical conductivity is desirable for materials intended to generate a large thermoelectromotive force. However, highly electrically conductive materials, such as metals, also tend to be highly thermally conductive. In other words, thermoelectric materials are required to possess inversely related thermal and electrical conductivities. The SiC sample mentioned above happened to be a poor thermal conductor probably because of its high porosity but was highly electrically conductive. I published a paper to report the potentially effective thermoelectric properties of porous SiC materials. Professor Kakuei Matsubara, a Japanese authority in the field of thermoelectricity, was intrigued by this finding and encouraged me to pursue in-depth research on this subject.

Did you already have a vision to create environmentally friendly materials early in your research career?

Professor Matsubara was strongly advocating the use of solar heat and human-activity-generated waste heat and the development of thermoelectric materials that can be used to achieve it. I shared the same vision with him. However, as an unglamorous field, thermoelectric materials R&D had been underappreciated for years because the effort to develop thermoelectric materials superior to bismuth telluride was fruitless. Bismuth telluride had poor heat resistance and its production required scarcely available and toxic tellurium, preventing its widespread practical use. However, increased public awareness of environmental pollution caused by toxic elements greatly encouraged materials developers to create environmentally safer products.

We imagine that your endeavor to make thermoelectric materials environmentally safer has been a great challenge.

Invention of the nanoblock integration concept became a turning point to me. Simply put, this concept is to create a periodic structure consisting of a combination of electrically conductive nanoblocks and thermally insulating nanoblocks.

The performance of thermoelectric conversion materials is determined by three physical parameters: electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (κ). The higher the σ and S values and the lower the κ value, the higher the thermoelectric performance. However, it is extremely difficult to control these three parameters independently. To address this issue, I envisaged the creation of an artificial superlattice (i.e., hybrid crystal) composed of a combination of two or more types of nanoscale materials (nanoblocks) whose physical properties can be separately controlled.

This idea developed from everyday research activities. SiC were susceptible to oxidation and had limited applicability. I therefore switched my research focus to metallic oxides after I transferred to Nagoya University in 1992. Among the metallic oxides studied, I found that an alternate stack of two-dimensional zinc oxide and indium oxide layers exhibits relatively high thermoelectric performance. This discovery made me suspect that a stacked layered structure is the key to increasing the thermoelectric performance of materials.

At around this time, Professor Mildred Dresselhaus in the United States, a notable nanomaterials scientist, theoretically demonstrated a mechanism of the performance of thermoelectric materials. According to her theory, when a thermoelectric material is processed into a film less than one nanometer in thickness, its electrons are confined within a narrow field, causing them to transform into a two-dimensional electron gas with unique behavioral properties, which leads to a significant increase in the material's thermoelectric performance.

The stack of zinc oxide and indium oxide layers we developed are also very thin with each layer having atomic or molecular level thickness. The relatively high thermoelectric performance observed in the stacked layered structure was consistent with Professor Dresselhaus' theory. Moreover, publications by Dr. Ichiro Terasaki at the University of Tokyo and others indicated that a layered cobalt oxide exhibits high thermoelectric performance. These publications convinced me that the nanoblock integration concept—controlling physical properties of materials by creating a stacked layered structure—can be put into practice.

What types of materials have you actually developed using the nanoblock integration technology?

To enable thermoelectric conversion materials to efficiently generate electricity, positive charge carrying materials (p-type) and negative charge carrying materials (n-type) need to be alternately connected. P-type materials were already available in the form of layered cobalt oxides. Our group therefore launched a project to develop an n-type material.

We focused on strontium titanate ($SrTiO_3$ or STO for short), a commonly used electrically insulating oxide. However, adding a small amount of niobium modifies its electronic state, causing it to exhibit relatively high electrical conductivity even at room temperature. Unfortunately, this material also had high thermal conductivity—an undesirable characteristic for it to be used as a thermoelectric material. To address this issue, we fabricated two types of extremely thin STO layers using a high-precision film forming technique: niobium-added electrically conductive STO and niobium-free electrically insulating STO. We then created a superlattice composed of alternately stacked layers of these two types of STO. The thermoelectric performance of this material (ZT = 2.4) was found to be 30 times larger than that of single crystal STO*. This study published in 2007 turned out to be the first direct experimental demonstration of Professor Dresselhaus' theory.

However, fabrication of two-dimensional superlattices required extremely fine-scale processes and high production cost. We therefore tried to find ways to reduce production cost by increasing the size of superlattices. As a result, we developed a three-dimensional superlattice: a Rubik's Cube-like three-dimensional material composed of a stack of numerous STO nanocube particles. Our group finally succeeded in developing a technique to fabricate three-dimensional superlattices, although reproducibility remains to be an issue.

In another project aiming to develop a flexible thermoelectric conversion material, we produced unexpectedly good results. One of my research associates focused on titanium disulfide (TiS_2), a layered inorganic compound, and inserted a variety of different molecules in the interlayer spaces to see if its thermoelectric performance increased. When hexylamine was inserted, he found that the thermoelectric performance of TiS_2increased. This approach also made the material soft and flexible because hexylamine was an organic compound. Another research associate in our group subsequently developed a process to mass-synthesize this material. She is currently using this material to develop a self-powered electronic skin (e-skin) capable of generating electricity from human body heat.

What are your expectations for the developers of thermoelectric materials?

I'd like to see advances in effective heat utilization. I'm currently conducting research with a university in Saudi Arabia in which we are aiming to synthesize carbon nanotubes made of ash resulting from petroleum combustion and incorporate them into thermoelectric materials. On another note, active efforts are being made in research and development of flexible thermoelectric devices around the world, particularly in South Korea and China. I hope Japan will keep up with these countries and develop innovative materials and devices.

(by Akina Horikawa)

* Thermoelectric figure of merit $(ZT) = S^2\sigma T\kappa^{-1}$, where T is absolute temperature. The Seebeck coefficient S of a material is a measure of the magnitude of an induced thermoelectromotive force in response to a temperature difference of 1 K across that material.

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NIMS NOW International 2021. Vol.19 No.1
National Institute for Materials Science
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photo by Michito Ishikawa (p5 Dr.Ohashi's face photo, p6-10)
editorial design by Barbazio Inc.

To subscribe, contact:
Dr. Yasufumi Nakamichi, Publisher
Public Relations Office, NIMS
1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047 JAPAN
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