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Research Center for
Electronic and
Optical Materials

Revolutionizing Electronic and Optical Materials: New Initiatives

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Moving society forward technologically

The transition from vacuum tubes to transistors enabled groundbreaking advances in electronics. Likewise, the invention of optical fibers and their integration into the internet and other networks have made the world a smaller place as global communications have become dramatically faster and more convenient. These examples illustrate the effect of advances in electronic and optical materials on social development.

These materials leverage the properties of electrons, ions and photons, often within crystals. Established in April 2023, the Research Center for Electronic and Optical Materials has been researching and developing these sophisticated, globally important materials.

The Center has been carrying out two major projects since its inception. They aim to bring about social innovation by strategically producing electronic and optical materials with new functions through precisely designed crystals.
This NIMS Now issue highlights these new projects in detail.

Photo: A phosphor composed of rare earth elements and organic molecules able to withstand temperatures higher than 320°C (see p. 15) being dissolved in a solvent. The phosphor emits green or red light depending on which rare earth element—terbium or europium, respectively—it contains.

Data : **Research Center for Electronic and Optical Materials**

Managing Director: Naoki Ohashi

Number of permanent researchers: 61

Functional Materials Field

- Ultra-wide Bandgap Semiconductors Group
- Next-generation Semiconductor Group
- Environmental Circulation Composite Materials Group
- Nano Electronics Device Materials Group
- Electro-ceramics Group

Optical Materials Field

- Optical Single Crystals Group
- Optical Ceramics Group
- Advanced Phosphor Group
- Semiconductor Epitaxial Structures Group
- Quantum Photonics Group
- Nanophotonics Group
- Semiconductor Defect Design Group
- Polycrystalline Optical Material Group

Key Projects

The Research Center for Electronic and Optical Materials has launched two new projects. Let' s take a look and learn about its activities.

#1 Development of sustainability-enhancing functional materials

The next-generation electronics needed to make society more sustainable will have to withstand higher voltages and temperatures and respond more quickly than those in current use. Developing these technologies will require materials that can outperform existing semiconductors. In addition, the materials scientists working on this project are committed to solving environmental issues through various approaches, such as replacing the toxic chemical elements used in current materials with less toxic ones. NIMS is working to make society more sustainable in many different ways.

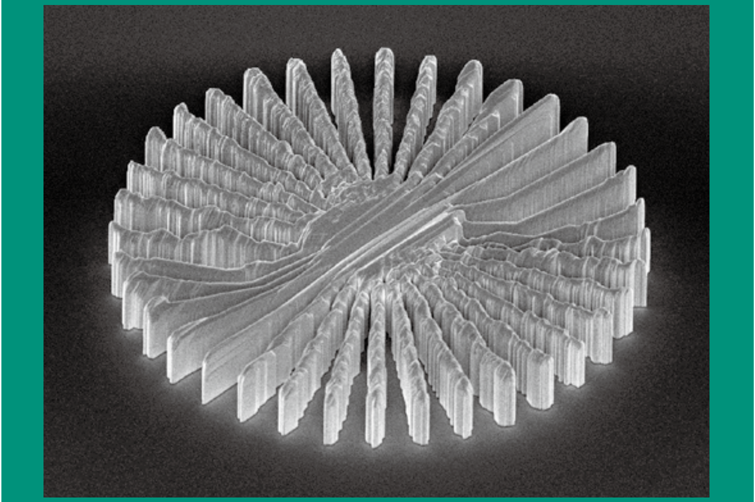
Project leader

Naoki Ohashi

Putting theory into practice: realizing the full potential of promising materials

Some materials could, in theory, exhibit outstanding physical properties. However, actually bringing these properties out of them often requires skillful manipulation. This is because the physical properties of semiconductor devices are greatly influenced by the configuration of crystalline defects and junction structures between the different materials within them. Gallium nitride (GaN), diamond, gallium oxide (Ga_2O_3) and a few other compounds are considered to be promising materials for use in high-powered, energy-efficient next-generation semiconductor electronics because of their ability to withstand higher voltages and temperatures than silicon. This project aims to bring out the full potential of these promising materials by developing high-purity crystal growth techniques, controlling junction structures and developing microfabrication techniques. In addition, we will develop analytical techniques capable of accurately measuring electronic states within crystals, advancing our understanding of the unique crystalline physical and chemical properties that emerge only from high purity crystals.

See Research 1 on **p. 6**



Three-dimensional β-gallium oxide structure fabricated using a selected area growth technique

The clay filter placed in the pipette adsorbs only the pigment in the liquid material.

Creating novel materials for innovation and sustainability

We are pursuing two approaches to solving social issues: designing novel materials / crystalline structures and modifying existing crystals to impart new functions. Our current research focuses include lanthanum oxyhydride—a material that enables high-speed hydrogen anion (H^-) conduction—and Ca_3SiO, an oxysilicide compound with direct-band-gap in near infrared range and composed entirely of cheap and non-toxic chemical elements. We will promote conservation of natural resources by identifying effective ways of utilizing these novel materials and removing toxic substances from the environment using chemically active materials—a layered material with the ability to take up ions through adsorption. We are also incorporating automation into our research to reduce time for innovation and to compensate for the decrease of population in our country. As part of these efforts, we are developing a machine capable of automatically fabricating a series of thin films with slightly different compositions. We are also adopting artificial intelligence (AI) techniques able to automatically collect and analyze data.

See Research 2 on **p. 8**

#2 Basic research into innovative optical materials

Infrared sensors play an important role in making society safer and more secure. Their key components are optical semiconductor devices that convert infrared radiation into electrical signals. We are also developing optical window materials to protect semiconductor devices. In addition to infrared sensor R&D, NIMS has been researching and developing a wide variety of optical materials that could be used to significantly improve social systems. These include LED backlights for lighting devices and liquid crystal displays and light sources indispensable to quantum cryptographic communications.

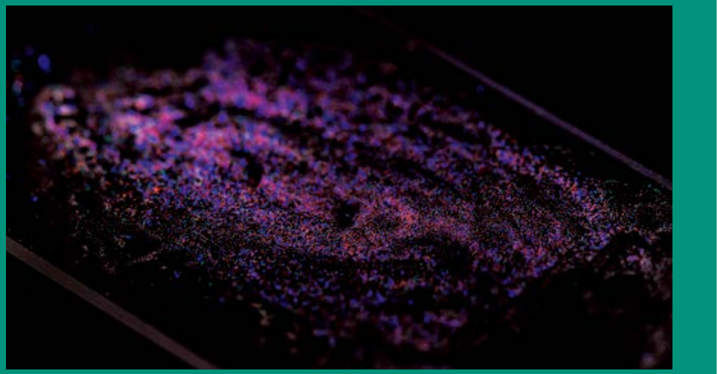
Project leader

Kiyoshi Shimamura

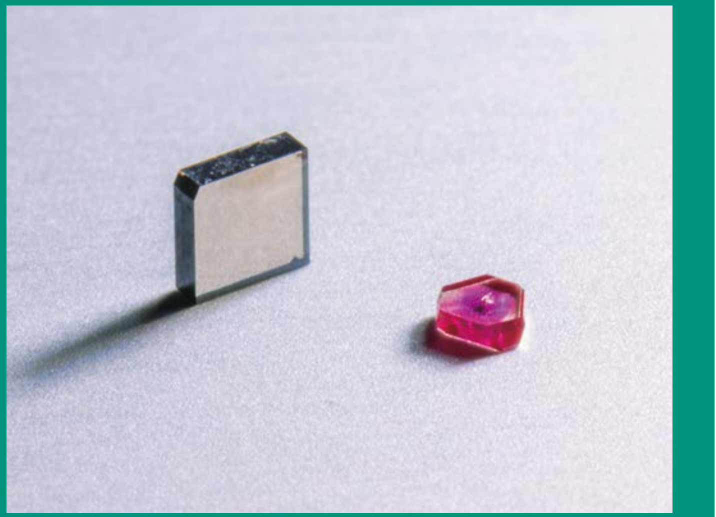
Bulk photonics: light-manipulating crystalline compositions and structures

We are developing transparent ceramics for use as optical window materials in infrared sensors. Optical properties of polycrystals, such as its light transparency and emission characteristics, are influenced not only by a material's intrinsic physical properties but also by many other factors (e.g., the structure of the interfaces between adjacent crystals and particle aggregation states). As part of these efforts, we are attempting to optimize both the transparency and mechanical properties of these materials by aligning their crystallographic orientations using strong magnetic fields and other methods. We are also developing optical single crystal materials needed for optical wavelength conversion and optical intensity modulation. In this subproject, we are focusing mainly on oxides, halides and nitrides and developing techniques to grow high-quality single crystals of these materials at low cost. In addition, we are developing phosphors for use in lighting devices and liquid crystal display panels. We are designing a wide variety of materials—ranging from inorganic materials to organic-inorganic hybrid materials—to achieve brighter emissions and a wider spectrum of colors. Finally, we are currently streamlining our materials search schemes by building a diagnostic system capable of automatically selecting promising phosphors from a large number of candidate powder samples and through other efforts.

See Research 3 on **p. 10**



A phosphor developed for use in an LED light source emits visible light when subjected to ultraviolet irradiation.

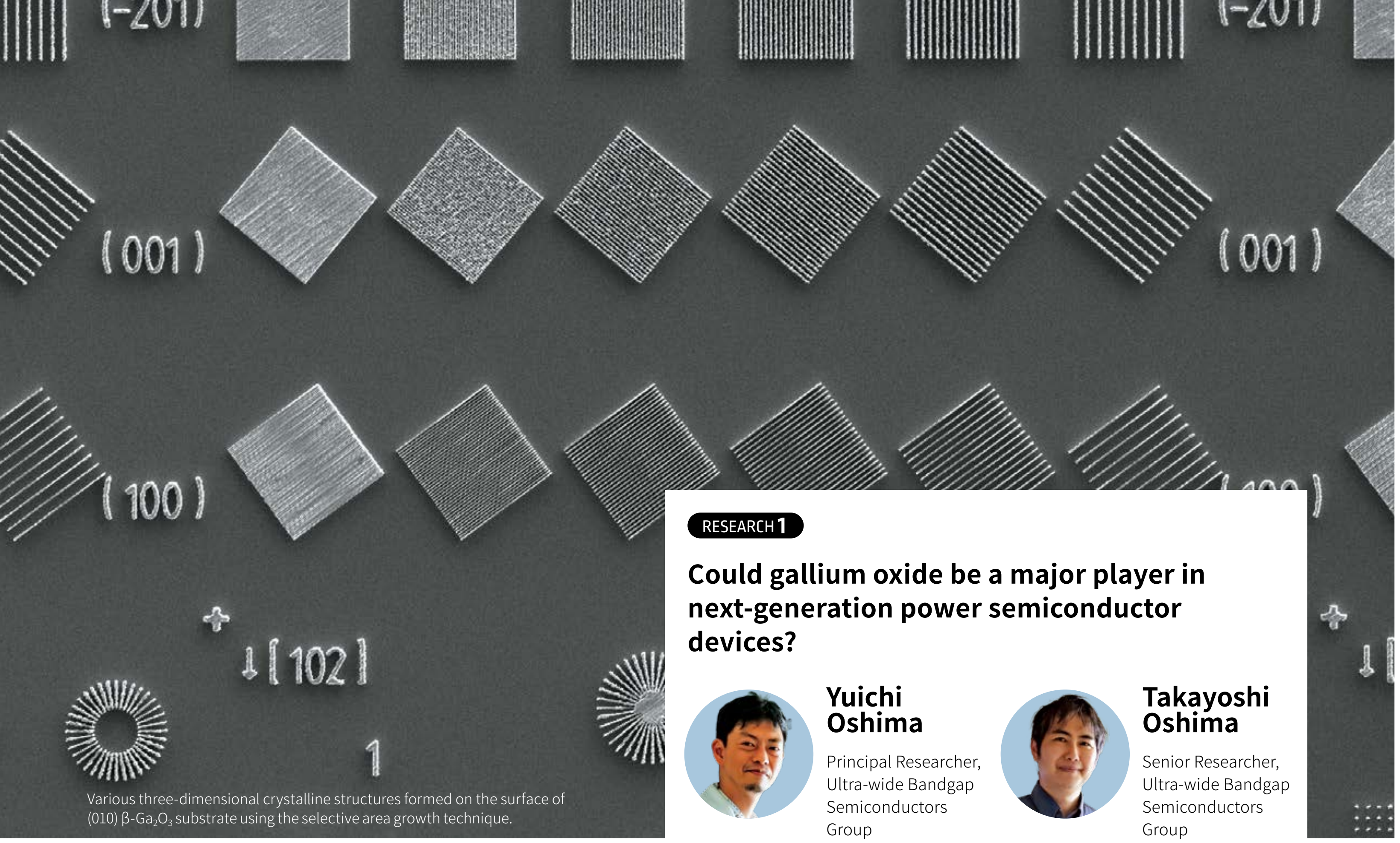


Ultrapure diamonds vital to quantum sensors

Nanophotonics: fine tuning optical behavior

Nanophotonics is the study of nanometer-scale optical behavior, including interactions between light and nanoscale materials. This is a clear contrast with bulk photonics, which is mainly concerned with controlling light within relatively large crystals. Metamaterial substrates with repeated patterns on their surfaces at scales smaller than optical wavelengths can be used to control light radiation and absorption. We are developing these nanostructured materials for use in infrared detectors and biosensors and many other applications. We are also developing semiconductor devices—key components in high-sensitivity infrared sensors—and investigating techniques for fabricating light-emitting quantum dots capable of generating pairs of entangled photons, a vital quantum cryptographic communications technology. Moreover, we are further refining NIMS' ultrapure diamond synthesis techniques as part of an effort to develop ultrasensitive quantum sensors. Through these and other efforts, we hope to develop optical materials that can be used to fundamentally improve social systems.

See Research 4 on **p. 12**



Various three-dimensional crystalline structures formed on the surface of (010) β-Ga_2O_3 substrate using the selective area growth technique.

RESEARCH 1

Could gallium oxide be a major player in next-generation power semiconductor devices?

Yuichi Oshima

Principal Researcher,
Ultra-wide Bandgap Semiconductors Group

Takayoshi Oshima

Senior Researcher,
Ultra-wide Bandgap Semiconductors Group

Power semiconductor devices control electricity by acting as switches or rectifiers in industrial equipment and consumer electronics. Gallium oxide (Ga_2O_3) has the potential to serve as an outstanding power semiconductor material because it could, in theory, outperform the other two major candidate compounds, silicon carbide (SiC) and gallium nitride (GaN). Yuichi Oshima and Takayoshi Oshima (no relation) are working together closely to put β-Ga_2O_3 into practical use. We asked them about their research activities.

β-Ga_2O_3 in the spotlight

Efforts to research and develop next-generation power semiconductor materials have been intensifying. Ga_2O_3 has a wider bandgap than either SiC or GaN, potentially making it compatible with higher voltages. This compound can be divided into several polymorphs, such as α- and β-phases, based on its crystal structure.

"Because the α-phase has a wider bandgap than the β-phase, it has the potential to outperform the β-phase as a power semiconductor material," said Yuichi Oshima, who has been working on techniques for growing high-quality crystals. "However, α-Ga_2O_3 single crystal substrates are difficult to fabricate due to the metastability, making it very challenging to put the α-phase into practical use. By contrast, β-Ga_2O_3 single crystal substrates are much easier to produce because β-phase is the most stable and bulk single crystals can be grown from the melt. Therefore, at this point, I believe that β-Ga_2O_3 is more suitable for practical use, despite its narrower bandgap." Y. Oshima has been working to put β-Ga_2O_3 into practical use while also trying to find ways of producing high-quality α-Ga_2O_3.

"High-quality β-Ga_2O_3 thin films can be grown on the surface of a β-Ga_2O_3 substrate using an epitaxial growth technique," Y. Oshima said. "Furthermore, technologies already exist for producing large, high-quality, single crystal β-Ga_2O_3 substrates from the melt—the same technique used to produce silicon and gallium arsenide substrates already in widespread use. A Japanese company recently began manufacturing and selling β-Ga_2O_3 substrates, making them available to researchers and developers around the world. This has made Ga_2O_3 more attractive for R&D."

Optimizing the quality-cost balance

In addition to improving crystalline quality, it is also important to increase crystalline film production in order to achieve commercial use. β-Ga_2O_3 films suitable for use in power semiconductor devices may need to be as thick as 100 µm. Growing crystals to this thickness without significant production cost increases will require techniques for growing crystals quickly without compromising their quality.

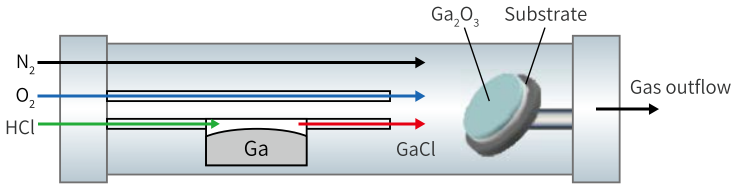


Figure 1. Schematic diagram showing the halide vapor phase epitaxy (HVPE) technique in action

Gallium (Ga) and hydrogen chloride (HCl) first react to produce gallium monochloride (GaCl), which then reacts with oxygen gas (O_2) on the substrate surface to form gallium oxide (Ga_2O_3). "During these chemical reactions, crystalline growth can be speeded up by supplying larger amounts of source gases," Yuichi Oshima said. "However, excess supply will also cause these gases to react with each other in midair, transforming them into unwanted particles. This problem can be effectively prevented by introducing HCl gas, but too much HCl can deter crystalline growth on the substrate. Growing high-quality crystals requires precise refinements."

To satisfy these requirements, Y. Oshima's group has been developing a halide vapor phase epitaxy (HVPE) technique, a type of epitaxial crystal growth technique (figure 1). This technique allows crystals to grow 100 to 1,000 times more quickly than using other epitaxial growth techniques.

"The HVPE technique, with its higher crystalline growth rate, is a promising means of synthesizing higher quality crystals at lower cost," Y. Oshima said. "However, taking full advantage of this technique will require the use of a crystalline substrate with an optimum crystallographic orientation. This is crucial because the growth rate and quality of β-Ga_2O_3 crystals are greatly influenced by the crystallographic orientation of the substrate on which they are grown. The Japanese company I mentioned earlier that produces and sells β-Ga_2O_3 substrates currently offers substrates with either (010) or (001) surfaces. These are not necessarily optimum substrates for the HVPE technique as they represent only two of the many crystallographic orientations that exist. There's still room for research to identify better substrates that could allow high-quality β-Ga_2O_3 crystals to grow even more quickly. I'm currently conducting a number of studies to determine optimum combinations of film deposition conditions and substrate crystallographic orientations for β-Ga_2O_3 synthesis using the HVPE technique."

The growth rate can also be increased by supplying larger amounts of source gases to growing crystals. However, caution is required, as excess supply could cause problems. Y. Oshima has been attempting to determine the precise amounts of source gases to supply while making structural modifications to the HVPE system to optimize his HVPE technique.

Minimizing damage to crystals: two microfabrication methods

Microfabrication is another crucial step in making β-Ga_2O_3 crystals suitable for use in power semiconductor devices. Takayoshi Oshima has been developing microfabrication techniques.

"There are two basic types of semiconductors: p- and n-types. Due to the nature of a Ga_2O_3 semiconductor, its p-type is difficult to produce," T. Oshima said. "When a device is created using only n-type semiconductors, leakage current will occur at increased voltages, undermining the material's ability to withstand high voltages. I have been developing microfabrication techniques to address this issue."

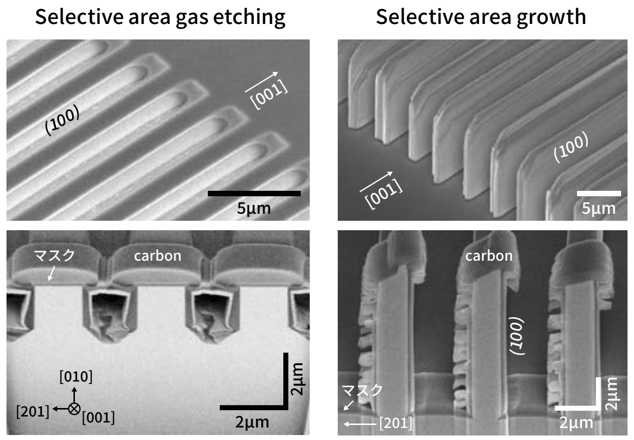


Figure 2. β-Ga_2O_3 substrates with micropatterned (010) surfaces fabricated using the selective area gas etching and selective area growth techniques. (Top) Top views. (Bottom) cross-sections. In both techniques, the lateral faces of the micropatterns are running parallel to the (100) facets—the chemically most stable crystalline planes—making them highly flat and smooth.

Leakage current in semiconductor devices could be minimized by processing a crystal into a three-dimensional microstructure consisting of fins (long, thin projections) and trenches (long, narrow depressions), thereby restricting the movement of electrons. Microfabrication of semiconductors is usually performed using plasma etching. However, this method often damages crystals, diminishing their quality and functionality.

T. Oshima has been developing two non-plasma microfabrication techniques: selective area gas etching and selective area growth.

Selective area gas etching is a technique in which the surface of a grown crystal is covered by a mask with openings (windows) at intended locations. The crystalline areas exposed by these windows are then selectively etched using an HCl gas. On the other hand, in selective area growth, the surface of the substrate is covered with mask with windows in it before crystals are grown on it. Source gases are then supplied to allow crystals to grow on the substrate only through the windows. This technique enables a crystal to grow in a predetermined pattern, although certain skills are needed to form fins and trenches with smooth and flat faces.

"Both microfabrication techniques can be performed using an HVPE system," T. Oshima said. "This is possible because the system is equipped with an HCl gas injection capability needed for selective area gas etching."

T. Oshima actually applied microfabrication on the (010) surfaces of β-Ga_2O_3 crystals using both techniques within an HVPE system. "I confirmed that both techniques were able to create fins and trenches with nicely flat and smooth faces, which is impossible to achieve using plasma etching (figure 2)," T. Oshima said. "In future research, I will investigate optimum crystalline microstructures for controlling electric currents and will aim to put the two microfabrication techniques into practice."

Techniques for growing high-quality crystals and high-precision microfabrication techniques are indispensable in developing practical β-Ga_2O_3 crystals for use in power semiconductor devices. Yuichi Oshima and Takayoshi Oshima intend to accelerate their collaborative R&D activities.

Yuichi Oshima (left) has previously achieved mass production of GaN single crystal substrates using the HVPE technique when he worked for a private company. "Mass production using an HVPE system requires all of the steps in substrate synthesis—from crystalline growth to microfabrication—to meet high standards," Y. Oshima said. "I have been working to improve the HVPE system and optimize the relative amounts of Ga_2O_3 ingredients while consulting with Takayoshi Oshima, who is very knowledgeable about crystalline microfabrication."

RESEARCH 2

Extracting useful resources from CO_2 using hydrogen-conducting crystals

Soshi Iimura
Senior Researcher,
Electro-ceramics Group

Iimura's lab is equipped with the full range of instruments needed to develop H^- conductors, including a sintering furnace able to precisely control the amount of source gas supplied and systems that can be used to evaluate samples' characteristics. "Our uniquely customized systems allow us to efficiently synthesize and evaluate sample materials without exposing them to air," Iimura said.

The international community is engaged in urgent efforts to achieve carbon neutrality by reducing carbon dioxide (CO_2) emissions. One innovative approach to reducing these emissions is allowing CO_2 to react with hydrogen gas (H_2), thereby converting it into useful compounds, such as methane (CH_4) and methanol (CH_3OH). Soshi Iimura has developed a material capable of rapidly conducting hydrogen anions (H^-). He is now seeking to find effective ways of leveraging H^- as a powerful reducing agent.

H^-: an underappreciated ion

Hydrogen is the most abundant chemical element in the universe, and is stabilized in either molecular (i.e., bonded with other chemical elements) or ionic (i.e., positively charged cations (H^+) or negatively charged anions (H^-)) forms. On the other hand, most hydrogen on Earth exists as H^+ and makes a bond with other elements to form stable compounds. For example, in water molecules two H^+ are bonded to oxygen. By contrast, H^- is much less common on Earth.

Soshi Iimura recently developed a material highly conductive to H^-—a unique characteristic—which may cast a new spotlight on H^-.

H^-: a strong reducing agent

In January 2022, Iimura and Tokyo Institute of Technology (Tokyo Tech) published a research article reporting that the lanthanum oxyhydride ($LaH_{3-2x}O_x$)—a ceramic material they co-developed—exhibited the world's highest H^- conductivity. When placed between two electrodes, the material rapidly conducted H^- between them. Its ionic conductivity was found to be more than 1,000 times that of any other H^- conductor at approximately 20°C—a temperature at which no thermal energy was available to assist the conduction.

These impressive results aside, what are the benefits of using H^- conductors, given that fast, room temperature ionic conductors are already in practical use for H^+ and lithium ions (Li^+)?

"Near-room-temperature H^+ conductors require high humidity and don't work at temperatures higher than the water evaporation temperature," Iimura said. "By contrast, our H^- conductor does not require humidity and is able to operate even in the intermediate temperature range of around 300°C. Another remarkable quality of H^- is its efficient reduction capability. Unlike H^+, H^- is chemically active and able to remove oxygen from compounds or add hydrogen, in other word, H^- can upgrade substance. For example, using H^- to reduce oxidized iron, aluminum and other metals should, in theory, be able to remove rust from these metals, thereby restoring them to their original condition. Similarly, adding H^- to CO_2 should theoretically be able to produce methane (CH_4) and methanol (CH_3OH)."

CO_2-derived methanol—if successfully produced—could be used as fuel or converted into propylene (C_3H_6), a raw material for plastics production. One of Iimura's goals is to deliver H^- to CO_2 generation source and produce desirable chemical there, thereby contributing to the meeting of carbon neutrality targets.

"A fast H^- conductor is now available that could be used to deliver H^- wherever desired," Iimura said. "I'm now focusing on identifying effective ways of optimally utilizing the delivered H^-. My current goal is to develop such a 'killer app' by leveraging H^-'s unique ability to add hydrogen and upgrade chemicals."

Mechanism behind rapid H^- conduction

Alloys capable of storing H^- have long been known. In fact, these materials have been used as nickel–hydrogen battery electrodes installed in certain hybrid vehicles. However, these hydrogen storage alloys are incapable of conducting H^-. This is because when voltage is applied to them, they readily conduct electrons, rather than H^-.

"One key feature that makes rapid H^- conduction possible in lanthanum oxyhydride is the oxygen atoms incorporated into the material's crystalline structure," Iimura said. "These oxygen atoms restrict the movement of electrons, greatly increasing the mobility of H^-. In addition, simulations performed by a research collaborator revealed that H^- conduction takes place through spaces in the crystalline lattice of lanthanum and oxygen atoms, and occur in the form of a chain of H^- bumping into each other rather than individual anions traveling a long distance across the material."

Another unique feature of the lanthanum oxyhydride is that its constituent elements—oxygen and hydrogen atoms—are able to coexist, although they in general form water. How is this possible?

"Because lanthanum is a powerful electron donor, it readily donates electrons to hydrogen atoms and forms negatively-charged H^-. The electrostatic repulsion between negatively-charged oxygen and H^- prevents the water formation," Iimura said.

A source of inspiration: developing superconducting materials as a student

Iimura was inspired to develop lanthanum oxyhydride during his previous experience as a Tokyo Tech student researcher. While a student, he researched lanthanum iron arsenide oxide (LaFeAsO)—an iron-based high-temperature superconductor—at the laboratory of Professor Hideo Hosono (currently a Professor Emeritus at Tokyo Tech; also a Distinguished Fellow at NIMS). Iimura discovered that replacing some of the oxygen atoms in LaFeAsO with H^- enabled the material to exhibit superconductivity at even higher temperatures. He received the Young Scientists' Award from MEXT (Ministry of Education, Culture, Sports, Science and Technology) in 2020 in recognition of this achievement.

"During my superconductor research, I was particularly intrigued by the fact that oxygen and H^- can coexist within a material, rather than reacting with each other to produce water," Iimura said. "In this iron-based superconductor, electrons are able to travel without resistance through the $[FeAs]^-$ layer sandwiched by $[LaO]^+$ layer. This insight generated a new idea: I might be able to convert this superconductor into an H^- conductor by replacing the $[FeAs]^-$ with H^-. This idea led me to launch the lanthanum oxyhydride R&D."

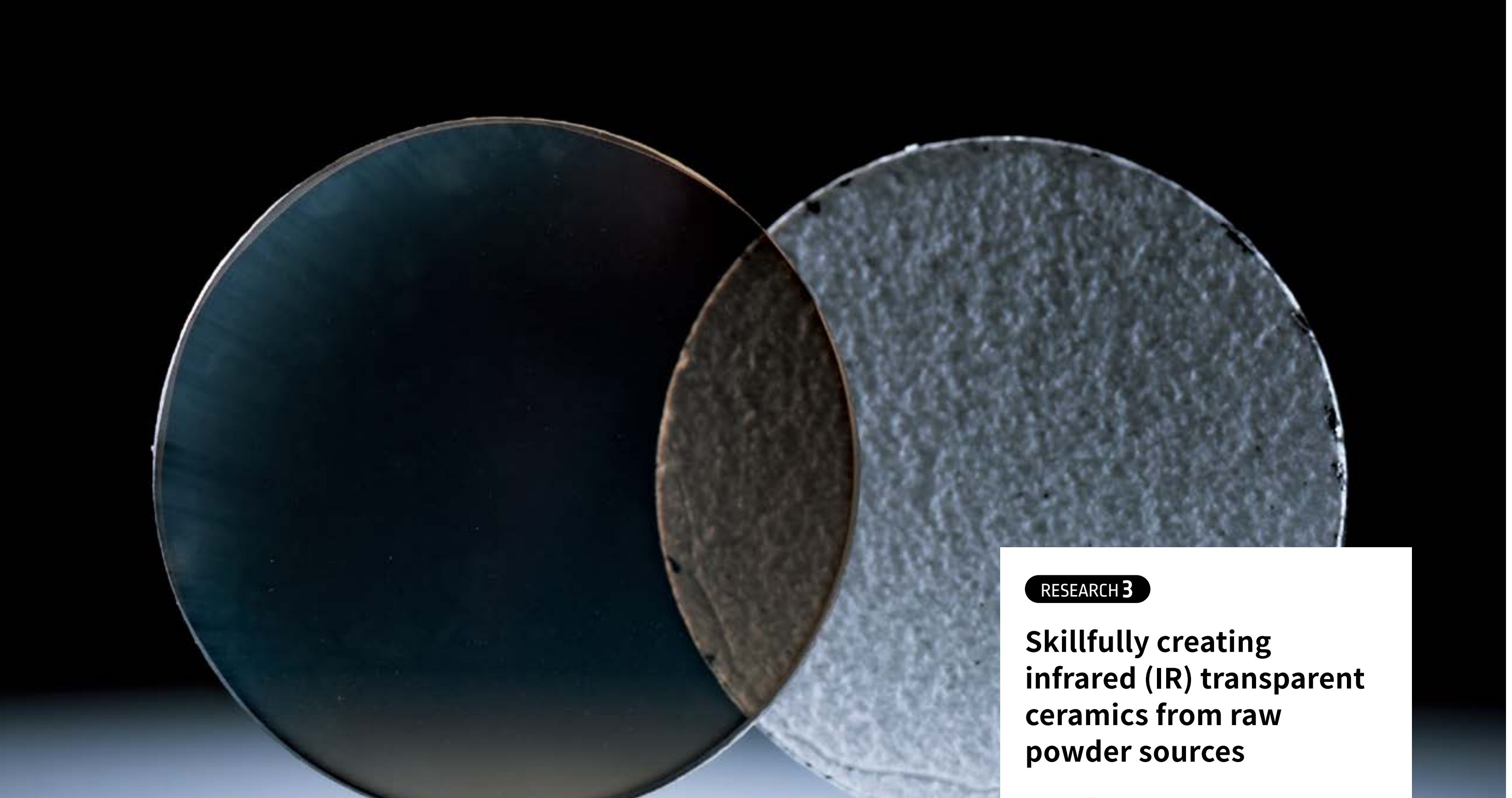
Since successfully developing the H^- conductor, Iimura has been primarily working to identify beneficial functions that could be exhibited by materials in which oxygen and H^- coexist stably. As part of these efforts, Iimura is currently carrying out a number of research projects to find ways of converting CO_2 into useful resources.

"Using lanthanum has a disadvantage as well," Iimura said. "This element reduces too much hydrogen atoms, making the crystal unstable. For this reason, I'm also developing other H^- conductors using chemical elements other than lanthanum. Another issue I'm tackling is figuring out how to extract pure hydrogen from commonly available compounds without expending large amounts of energy. I see photosynthesis as an ideal model. Plants produce H^- from water using solar energy. They then produce organic compounds and oxygen by allowing the water-derived H^- to react with CO_2. I'm working to develop materials able only to produce H^- from water using only small amounts of energy, like photosynthesis."

Iimura is making steady progress on designing new materials to help Japan meet its carbon neutrality goals.

Almost all of the chemical elements Iimura needs are readily available in his lab cabinets. "I always keep my periodic table close by when I design materials," Iimura said. "I consult with the table to gain insights into the characteristics of chemical elements I plan to use in formulating materials."

Lanthanum oxyhydride powder (left) and the product formed after it was compacted and sintered (right). Lanthanum oxyhydride can be synthesized by mixing lanthanum oxide with lanthanum hydride and heating the mixture.



The spinel ($MgAl_2O_4$) disc on the left was produced by sintering a raw material at 1300°C for 20 minutes. By comparison, the spinel disc on the right was created by sintering the same raw material at 1275°C for 20 minutes. A difference of only 25°C made a big difference in transparency.

RESEARCH 3

Skillfully creating infrared (IR) transparent ceramics from raw powder sources

Koji Morita

Leader,
Polycrystalline Optical
Material Group

Infrared (IR) sensors are indispensable in making our lives safer and more secure. Koji Morita has been researching and developing ways of fabricating transparent ceramics for use in optical windows—a vital IR sensor component—in an effort to create high-quality window materials at lower cost.

Fabrication processes impact ceramics' characteristics

The two discs shown in the photo above are both made of spinel ($MgAl_2O_4$), a type of ceramic. They display quite different transparencies and qualities despite having been created through sintering technique from exactly the same raw powder source.

"Sintering is the process of compacting and forming a bulk material from raw powders using pressure and/or heat without melting it to the point of liquefaction," said Koji Morita, who has been working to develop ceramics with higher transmittance and other desirable mechanical properties. "Slight changes in the sintering conditions—such as the temperature, duration and heating rate—have a great impact on the optical and mechanical properties of sintered ceramics (e.g., transparency, strength and heat resistance). That's the real thrill of ceramics research."

"A transparent ceramic could serve as an effective material for optical windows—important IR sensor components that protect sensors while conveying a full spectrum of incident light," Morita continued. "Some IR sensors are capable of simultaneously detecting IR light in addition to visible light. For example, a synthetic image created by combining a visible light image and an IR thermal image can be used to visually determine thermal distributions. These sensors therefore require optical window materials that can transmit light at wide wavelength range. The silicon and germanium lenses currently in practical use as optical window materials for IR sensers are incapable of transmitting visible light. Similarly, the lenses used in ordinary visible light cameras do not transmit IR light. Although diamonds can transmit both visible and IR lights, they are quite expensive, and hence, their applications are highly limited. Glasses and plastics are cheap to produce and transmissible to visible and some IR lights, but they are not strong and are also susceptible to heat. Spinel is a relatively inexpensive ceramic material that could have desirable mechanical properties while also being highly transmissible to both visible and IR lights. Hence, spinel is one of the materials could be used as an optical window material in a wide range of sensors, from general purpose optical sensors to sensors that need to be highly reliable, such as IR sensors to be mounted on aircraft."

Morita's group has developed a transparent ceramic (spinel) material as clear as glasses with approximately 75% near IR transmittance (see the photo at left above). This material is also about five times stronger than general-purpose glasses and about twice as strong as preexisting spinels. In addition, it can withstand temperatures as high as 700 to 800°C. The group has been working to further improve the physical properties of the optical ceramics with the goal of developing it into a high-performance optical window material for use in IR sensors.

Higher transparency achieved using NIMS' unique techniques

What was remarkable about the transparent ceramic Morita's group developed was that it was made from raw powder sources. A polycrystalline material is a solid consisting of many microscopic crystals ("grains"). These materials are usually opaque as incident light is scattered by both the grain boundaries and the tiny spaces ("pores") between the grains. This is the reason why general-purpose ceramics are not transmissible to light.

To prevent the spinel material from light scattering, Morita's group reduced the crystalline grain sizes to create "nano-grains" smaller than optical wavelengths. The group also made some modifications to the sintering processes that both successfully prevented the nanograins from enlarging and completely closed the pores between them. As a result, light scattering was greatly reduced, improving the spinel's transparency. Its strength was also significantly increased by the reduction in grain size.

"Transparent ceramics can also be created using single crystals—a material in which the crystal lattice of an entire sample is continuous and unbroken with no grain boundaries," Morita said. "In fact, they are already being produced and sold commercially as components for x-ray and gamma ray scintillators and laser diodes. However, creating single crystals is a very costly process. Their raw materials first need to be melted at high temperatures (≥2,000°C) within a container called as a crucible. The single crystals must be then slowly grow-up from the molten materials using a seed crystal."

Producing polycrystalline ceramics is much easier than producing single crystals: their powder raw sources simply need to be sintered. While their transparencies are to some extent lower as compared to those of single crystals, they are more practical for mass production and can be formed into complex shapes. Another major advantage is that sintering polycrystalline ceramics is a substantially quicker process than producing single crystals from the molten materials.

"The transparency of polycrystalline ceramics can be greatly influenced by differences in sintering temperatures of as little as a few dozen degrees," Morita said. "Deviating even slightly from the optimum sintering temperature would form more pores between crystalline grains or cause crystalline overgrowth, degrading transparency. The key objectives of my research are therefore to first understand transparency degradation mechanisms and then identify optimum sintering conditions."

Creating higher performance ceramics through close collaboration

In another project, Morita's group has been developing polycrystalline ceramics composed of multiple materials.

"For example, we are developing a composite polycrystalline ceramic material with a layered structure consisting of a spinel phase layer sandwiched between layers of alumina (Al_2O_3) phase—a common ceramic material (figure)," Morita said. "Spinel can generally show higher transparency than other ceramic materials, but its mechanical properties are inferior. By contrast, alumina has superb mechanical properties but is unsuitable for transparency. We combined these two contrasting materials into a composite polycrystalline ceramic material in an attempt to address these shortcomings."

In this project, Morita's group used an innovative approach to align the crystalline orientation of the alumina grains into the same direction before sintering. The orientation of polycrystalline grains is ordinarily random, increasing light scattering at grain boundaries and degrading the material's transparency. Its anisotropic crystalline structure of alumina ceramics makes it even less susceptible to being made higher transparent due to the more severe light scattering occurring at its grain boundaries.

The group used a magnetic field aligning technique developed by NIMS to align the crystalline grains in alumina. Strong external magnetic fields were applied to alumina powder while it was being shaped, aligning its grains. A spinel powder layer was then sandwiched between two align processed alumina layers. Simply sintering this composite material resulted in a transparent polycrystalline ceramic with a layered structure. This technique was performed by collaborating with the Optical Ceramics Group of the Research Center for Electronic and Optical Materials—the same affiliation to the Polycrystalline Optical Material Group which Morita serves the leader.

"The powder raw source's particle size and shape also greatly influence sintering outcomes," Morita said. "We consult with researchers with expertise in powder processing to optimize our sintered products. We are also conducting collaboration research aimed at creating high-intensity LED light sources with members of the Advanced Phosphor Group. In this project, we're developing a thermally conductive, transparent ceramic material in which LED phosphor powder is dispersed. Adding the phosphor is intended to help dissipate excess heat generated by the light source as its light emission intensity increases."

These collaborative exchanges of skills and expertise with other groups have enabled Morita's group to make a series of improvements to its ceramic fabrication processes. The group hopes to develop innovative ceramics by working closely with its collaborators.

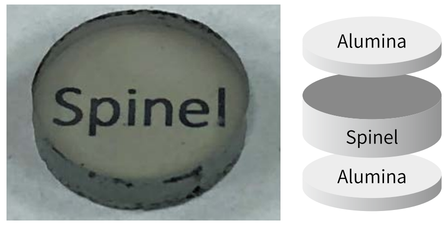


Figure. Transparent ceramic composed of alumina and spinel layers

Morita has been responsible for guiding students enrolled in the Kyushu University–NIMS Joint Graduate School Program. One of his students is shown in this photo working on a research project in Morita's lab. "I actively engage my students. I act as an academic advisor for some while others are from other groups participating in joint research projects in which I' m involved," Morita said.

RESEARCH 4

New insights enable development of a cheap, low-toxicity optical semiconductor device

Takaaki Mano
Leader,
Semiconductor Epitaxial Structures Group

Semiconductor devices are a vital component in high-sensitivity infrared (IR) sensors. Achieving widespread use of these sensors will require the development of cheaper, less toxic next-generation semiconductor devices. Takaaki Mano has been working on semiconductor devices with novel operating principles.

Growing high-quality InAs crystals on low-cost GaAs substrates

Demand for IR sensors—used in for example night vision cameras and gas sensors for environmental monitoring—is growing every year. The semiconductor devices currently used in high-sensitivity IR sensors have issues: they contain highly toxic chemical elements (e.g., mercury and cadmium) and/or are costly to produce because they need expensive substrates. Takaaki Mano has been researching and developing highly sensitive yet less toxic and cheaper semiconductor devices for IR sensors.

"The semiconductor device I've been focusing on is composed of indium arsenide (InAs) deposited on the (111)A surface of a gallium arsenide (GaAs) substrate," Mano said. "Both InAs and GaAs are less toxic than mercury or cadmium. I began this research after reading a 1997 research article reporting that InAs crystals grown in this way may develop fewer defects. I surmised that this technique could be used to develop IR sensing semiconductor devices with desirable characteristics."

In general, when one semiconductor crystal (e.g., InAs) is grown on the surface of another (e.g., GaAs) whose lattice constant is different (i.e., a lattice mismatch system), the crystal grows in layer-by-layer mode with strained state until it reaches a certain critical thickness. Further growth accumulates the strain in the crystal due to the lattice mismatch, causing it to develop threading dislocations finally—linear crystallographic defects that run through the whole crystal. Preventing this problem requires intricate fabrication processes, including the creation of a thick buffer layer on the substrate.

However, to Mano's surprise, results reported in a 1997 article were contrary to this general expectation: when InAs was deposited directly on the (111)A surface of a GaAs substrate, dislocations developed only during initial InAs crystalline growth within the limited area around the InAs-GaAs interface. However, a high-quality InAs crystal grew beyond the initial area of growth.

Mano initially thought after reading the article that this crystal growth technique could be used to deposit an InAs crystal on the surface of an inexpensive GaAs substrate without the need to create an elaborate buffer layer, potentially offering a simple way of fabricating high-sensitivity, low-cost semiconductor devices for IR sensors. Mano launched his semiconductor device R&D in 2018.

"Things didn't go as expected," Mano said. "I grew an InAs on the (111)A surface of a GaAs substrate using molecular beam epitaxy—a crystal growth technique. I then observed the surface of the InAs semiconductor under a transmission electron microscope, and to my disappointment, found many threading dislocations on it. I grew the crystals again and again under different conditions (e.g., different temperatures), but the results were mostly unsatisfactory. After this long period of trial and error, a breakthrough suddenly emerged in an unexpected way."

A surprising phenomenon

When the ground state electrons in a semiconductor IR sensor absorb IR radiation, they become excited and cross the band gap or other barriers into the excited state, generating electric current. The greater the amount of photocurrent the IR sensor can generate, the higher the sensitivity of the sensor.

Mano had been trying to reduce the number of defects in InAs crystals in order to fabricate electrically conductive semiconductor devices from them. As part of this effort, he routinely measured the optical responsivity and electric current characteristics of the semiconductor devices he fabricated. While taking these measurements, he always applied voltage in such a way to ensure that electrons traveled from the InAs crystal to the GaAs substrate. However, he made a mistake one day, reversing the voltage and causing the electrons to travel in the opposite direction—from the GaAs substrate to the InAs crystal. He then noticed something odd: when the device was irradiated with light, it generated a larger amount of electric current.

"I was really surprised by this," Mano said. "Even when a semiconductor device is not irradiated with light, 'dark current' is always flowing through it. Dark current is a small electric current that flows through photosensitive devices even when no photons are entering them. The electrons that generate dark current normally flow from a crystal with a wider band gap to an adjacent crystal with a narrower band gap, similar to the way in which water flows downhill. Because GaAs has a wider bad gap than InAs, it's natural to expect that electrons will flow easily from GaAs to InAs. Applying voltage to cause electrons to flow from GaAs to InAs should then increase the amount of dark current, which in turn should reduce the sensitivity of the device to IR radiation because the larger dark current would restrict the range within which IR-induced electric current could be detected. However, my experiments found that these assumptions were false."

Moreover, the experiments indicated that hardly any dark current was present in the semiconductor device Mano fabricated.

"I Initially had no idea what to make of these results," Mano continued, "so I asked Akihiro Ohtake and Takuya Kawazu—my colleagues in the same research group—to analyze the results in detail. Their analysis found that the flow of electrons was obstructed by defect-induced barrier at the interface between the GaAs substrate and the InAs crystal, explaining why almost no dark current flowed in the device."

This insight completely changed Mano's approach to developing semiconductor devices.

"My efforts before this discovery focused on developing InAs/GaAs semiconductor devices in which electrons were designed to flow from InAs to GaAs and techniques for fabricating them with fewer crystalline defects," Mano said. "However, the new insight caused me to do a 180 in my R&D approach. From that point onward, I aimed to develop InAs/GaAs semiconductor devices in which electrons were designed to flow from GaAs to InAs using lower voltages. I also actively exploited the benefits of introducing crystalline defects at the interface into my semiconductor devices."

These changes were intended to significantly improve the sensitivity of his semiconductor devices to IR radiation.

His efforts bore fruit in 2022 when he succeeded in developing an IR sensor with increased sensitivity to IR wavelengths—ranging from 2.6 to 3 micrometers—by controlling the doping concentrations of GaAs and InAs, thereby achieving his goal of developing a high-sensitivity, low-cost semiconductor device for IR sensors.

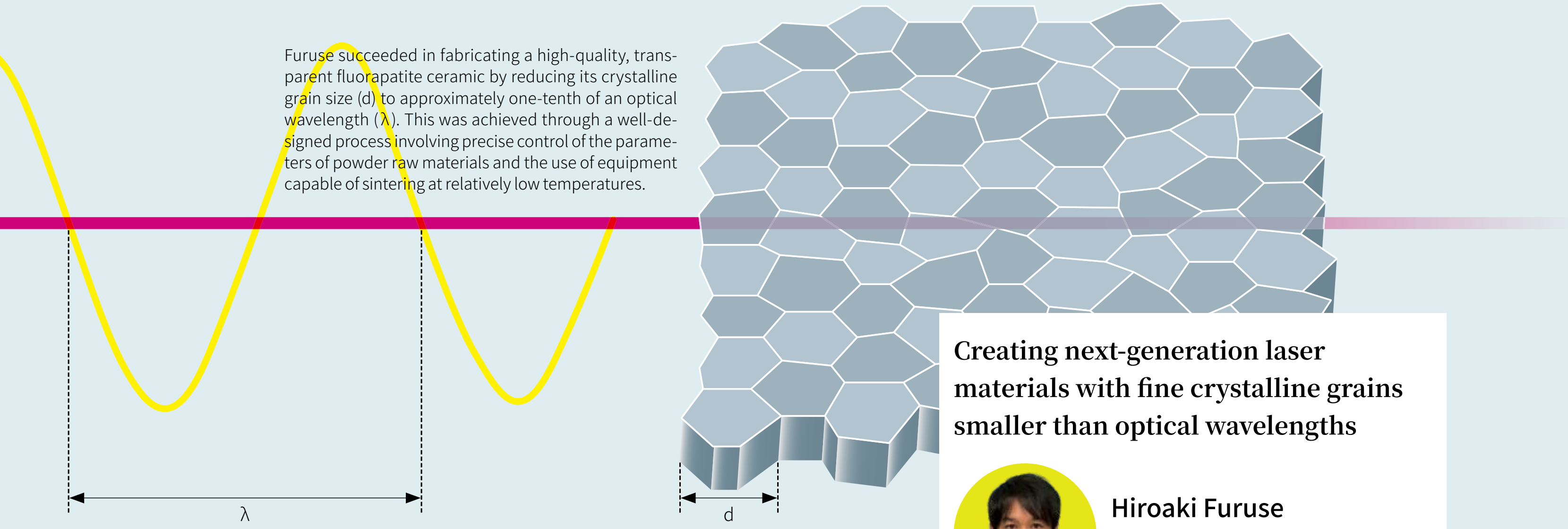
Developing new materials sensitive to a wider range of wavelengths

Mano is now trying to put his semiconductor device into practical use by further improving its sensitivity. In addition, he plans to develop different semiconductor devices sensitive to a wider range of IR wavelengths—a requirement for gas sensors capable of detecting CO_2 and other gases—using other materials, such as indium antimonide (InSb).

"InAs is a fascinating material," Mano said. "Despite being a crystalline solid, it is very flexible and strain-resistant. I found that depositing InAs on the (111)A surface of a GaAs substrate is the best combination for reducing the number of defects in the InAs. By contrast, InSb is inflexible and rigid and has a mismatched lattice, causing it to readily develop defects when it is grown on other materials. I hope to leverage the desirable characteristics of InSb by skillfully overcoming these issues. I've found that the most rewarding challenges in semiconductor research are bringing out the full potential of each type of crystal and identifying its suitable applications." Mano has been diligently engaged in IR sensor R&D as a way of making society safer and more secure.

Mano usually works independently when engaged in the development of crystalline growth techniques. However, he needed all the help he could get from a range of collaborators during his recent development of the optical semiconductor device. "Several colleagues at the Research Center for Electronic and Optical Materials helped me a great deal in thoroughly analyzing my prototype devices, including their interfacial structures and the activities taking place within them," Mano said. The photo on the previous page shows Mano (right) and two other group members: Yoshiki Sakuma (Special Researcher, left) and Akihiro Ohtake (Principal Researcher, middle).

CRYSTALS
Key to future technologies

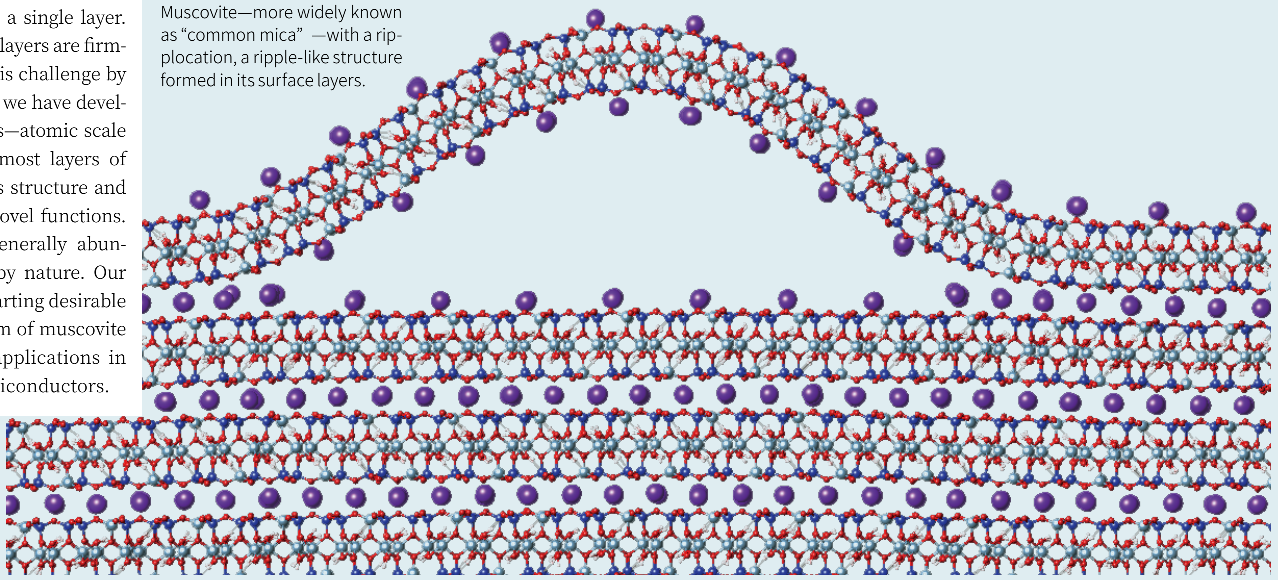


Furuse succeeded in fabricating a high-quality, transparent fluorapatite ceramic by reducing its crystalline grain size (d) to approximately one-tenth of an optical wavelength (λ). This was achieved through a well-designed process involving precise control of the parameters of powder raw materials and the use of equipment capable of sintering at relatively low temperatures.

Could ordinary clay be a next-generation device component?

Hiroshi Sakuma
Principal Researcher,
Environmental Circulation Composite Materials Group

Clay minerals are layered materials composed of stacks of nanosheets. They are commonly used as adsorbents due to their ability to adsorb ions and retain them within their interlayer spaces. Our research group has recently been focused on muscovite—a type of clay mineral. We began this line of investigation after reading a recent research article reporting that muscovite's electrical conductivity significantly increases when its number of constituent layers are reduced from 20 to 10. We wondered what new physical properties might emerge from muscovite if more of its layers were removed. To answer this question, we are working to develop a means of stripping muscovite down to a single layer. This is very challenging given that muscovite layers are firmly bonded to one another. We are tackling this challenge by reexamining the layer separation techniques we have developed. We are also interested in ripplocations—atomic scale ripple-like structures formed in the uppermost layers of muscovite (see the illustration at right). This structure and its physical properties may be a source of novel functions. Clay minerals—including muscovite—are generally abundant, heat-resistant and chemically stable by nature. Our goal is to add new value to muscovite by imparting desirable electrical and/or other properties to it. A form of muscovite with new functions may have advanced applications in devices such as next-generation power semiconductors.

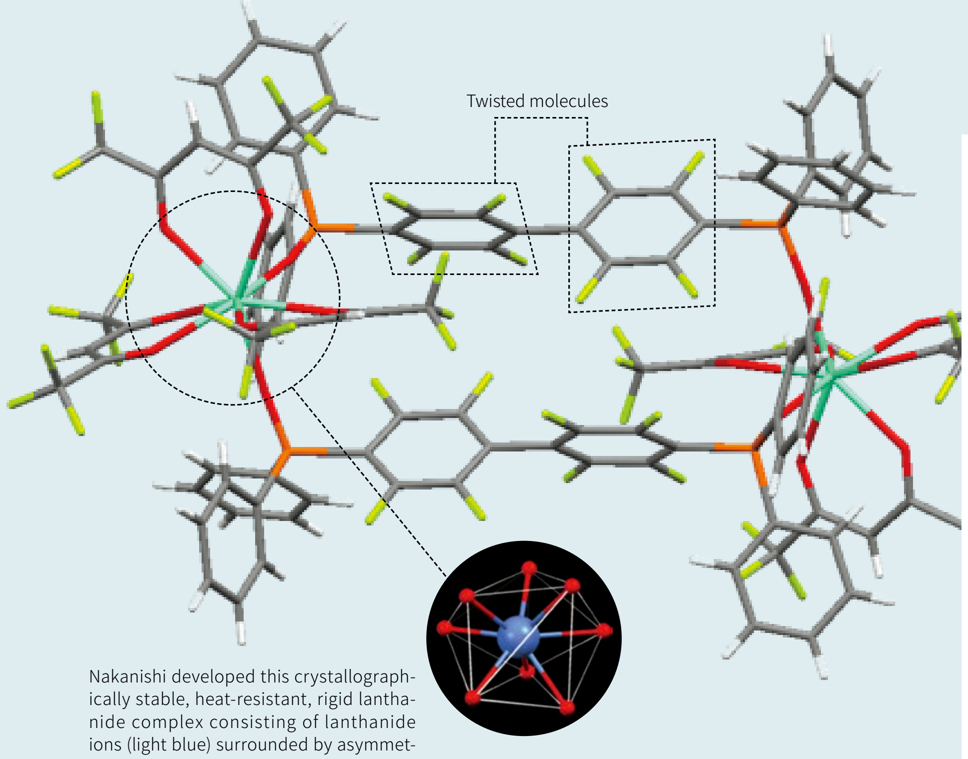


Muscovite—more widely known as "common mica" —with a ripplocation, a ripple-like structure formed in its surface layers.

Creating next-generation laser materials with fine crystalline grains smaller than optical wavelengths

Hiroaki Furuse
Independent Scientist,
Optical Ceramics Group

Transparent ceramics have been used as lasing media—a vital component in high-power lasers. Because even small imprecisions in crystals can cause them to scatter light—an undesirable characteristic for lasers—single crystals have generally been used as lasing media in typical lasers. Polycrystalline ceramics—composed of many minute crystals (i.e., grains)—are also viable alternatives as they can be used to create larger diameter lasing media at lower cost. However, they are susceptible to the formation of light scattering due to air voids and grains of different composition within their crystalline structures. Ceramics with non-cubic crystalline structures are particularly difficult to develop into lasing media because refractive index discrepancies can easily crop up between their individual grains. One way of overcoming this issue is making the grains sufficiently smaller than optical wavelengths, enabling the spaces between them to close during sintering (see the schematic diagram above). I have been working to determine optimum conditions for fabricating transparent polycrystalline ceramics using my expertise in laser engineering. I also use micromeritics methods to control the shapes and particle diameters of powder raw materials and powder metallurgy techniques to design sintering processes. I was previously able to successfully generate laser oscillation using a lasing medium made of a fluorapatite (FAp) ceramic with a hexagonal crystalline structure. I fabricated the ceramic by first preparing fine FAp particles approximately 50 nm in diameter via liquid-phase synthesis and sintered them using a spark plasma sintering technique. This achievement defied the common belief that only polycrystalline lasing media with a cubic crystalline structure is conducive to generating laser oscillation. I hope to develop polycrystalline lasing media at least equal in quality to its monocrystalline counterparts for next-generation lasers.



Nakanishi developed this crystallographically stable, heat-resistant, rigid lanthanide complex consisting of lanthanide ions (light blue) surrounded by asymmetrically arranged oxygen atoms (red) and other components. This was achieved by asymmetrically positioning the oxygen atoms and controlling the bond angles and distances between molecules.

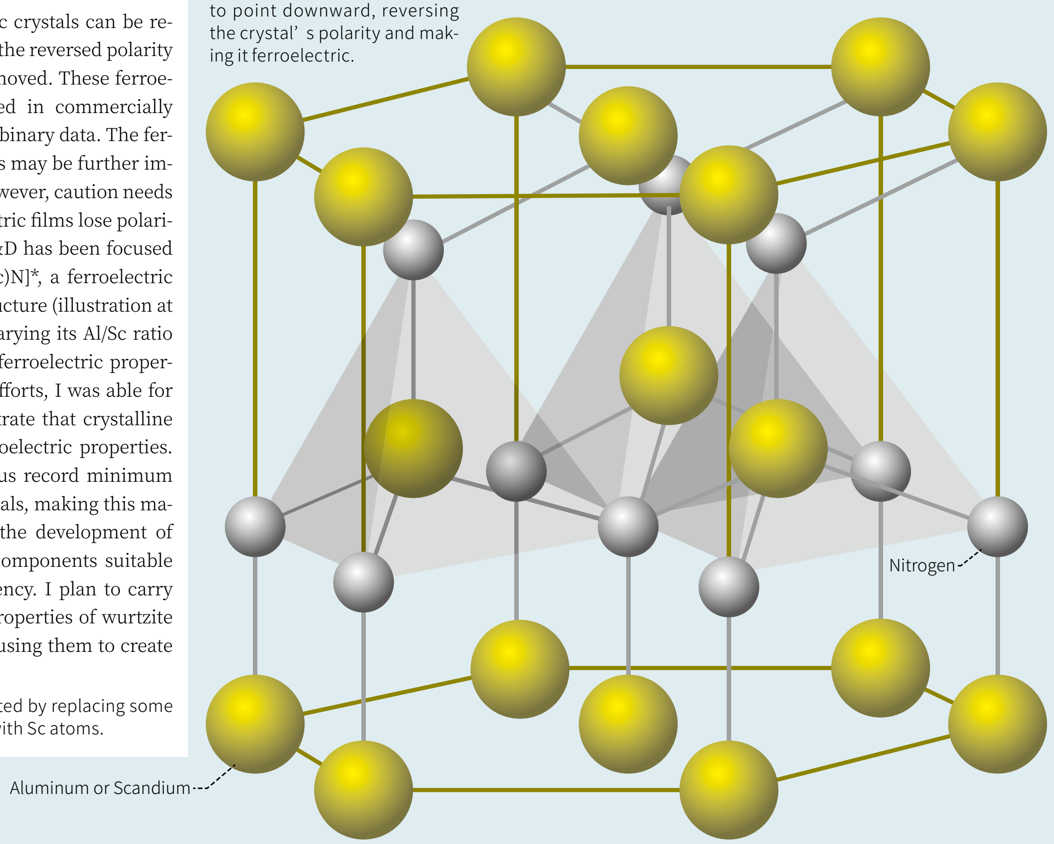
Ferroelectric materials potentially suitable for use in brain-like computers. Crystals with reversible polarity

Takao Shimizu
Independent Scientist,
Electro-ceramics Group

Some electrically polar crystals (i.e., crystals in which electric charge is unevenly distributed) also exhibit ferroelectric properties. The polarity of ferroelectric crystals can be reversed by applying voltage to them, and the reversed polarity is retained even after the voltage is removed. These ferroelectric properties have been leveraged in commercially available non-volatile memory to store binary data. The ferroelectric properties of crystalline films may be further improved by reducing their thickness. However, caution needs to be observed because many ferroelectric films lose polarity when thinned to nano levels. My R&D has been focused on scandium aluminum nitride [(Al,Sc)N]*, a ferroelectric material with a wurtzite crystalline structure (illustration at right). I fabricated this crystal while varying its Al/Sc ratio and film thickness and measured the ferroelectric properties of these samples. Through these efforts, I was able for the first time in the world to demonstrate that crystalline films as thin as 9 nm can exhibit ferroelectric properties. This is less than one-tenth the previous record minimum thickness achieved using (Al,Sc)N crystals, making this material a serious candidate for use in the development of brain-like computers, which require components suitable for tight integration and energy-efficiency. I plan to carry out further research on the physical properties of wurtzite crystalline structures with the goal of using them to create revolutionary devices.

* Scandium aluminum nitride can be created by replacing some of the Al atoms in aluminum nitride (AlN) with Sc atoms.

All of the tetrahedra in a wurtzite hexagonal crystalline structure point upward when no voltage is applied to the crystal. Applying voltage causes them to point downward, reversing the crystal' s polarity and making it ferroelectric.



Making the world more colorful using twisted molecules

Takayuki Nakanishi
Senior Researcher,
Advanced Phosphor Group

The phosphors used in liquid crystal displays emit light of different colors. My R&D focuses on enhancing the color purity and emission efficiency of phosphors using lanthanide complexes. A lanthanide complex consists of two main components: lanthanide ions—which convert radiant energy into light and emit it—and organic molecules, which capture radiant energy from external sources and pass it to the lanthanides in a manner similar to antennas receiving signals. The specific arrangement of these components determines the performance of lanthanide complexes. For example, the positions of the atoms directly bonded to the lanthanide ions influence energy transition efficiency. Moreover, the types and number of interactions taking place between the different components directly affect crystalline stability. I have been creating my original phosphors by designing molecules based on carefully formulated hypotheses. Phosphors I have developed include a binuclear lanthanide complex with a fluorine-based backbone (see the illustration at upper left). In this phosphor, the oxygen atoms surrounding the lanthanide ions were positioned asymmetrically by slightly twisting their arrangements. The structures of fluorine-containing molecules were also twisted to adjust the intermolecular interactions. As a result, I succeeded in developing a high-emission-efficiency phosphor able to withstand temperatures higher than 320°C which can also be dissolved in a solvent (see the photo on p. 2). I am now exploring various potential applications for this phosphor, ranging from transparent light-emitting displays to cosmetics.

Dierk Raabe

Director, Department Microstructure Physics and Alloy Design & Sustainable Synthesis of Materials,
Max-Planck-Institut für Eisenforschung GmbH
Professor, RWTH Aachen University, Germany

Interview with the 2023 NIMS Award winner

This year's winner has made outstanding achievements in structural materials research.

> *"I'm committed to advancing environmentally sustainable metallurgical practices."*
>
> *—Dierk Raabe*

Research Summary

Professor Raabe has designed a number of highly functional, workable structural metals by investigating the correlations between metallic materials' microstructures and chemical properties and how their physical characteristics affect workability. His pioneering efforts include the development of techniques for analyzing metallic materials at multiple scales by combining atomic-scale analysis using atom probe tomography, electron microscopes and other methods, in part in conjunction with machine learning analysis. These techniques enabled Raabe to develop strong, durable steels. Raabe has also studied environmentally sustainable metallurgy and produced results that could eventually help to revolutionize the metals industry. These include the development of crude steel production processes with significantly reduced CO_2 emissions, the design of recyclable, hydrogen-resistant alloys and an in-depth study of the hydrogen-based reduction of iron ores.

— How do you feel about receiving a NIMS Award?

I'm greatly honored to receive this award. It would not have been possible without the contributions of the superb young researchers and dedicated colleagues I worked with and the metallurgical experts around the globe who have helped me. This award is also a testament to the collective efforts of the metallurgical research community to push the boundaries of knowledge in pursuit of sustainable solutions to the global challenge of reducing CO_2 emissions.

— What inspired you to focus your metallic materials research on sustainability?

Currently, about two billion tons of metals are produced annually, with steel production alone accounting for about 1.85 billion tons. Global metal production is expected to nearly double by 2050. Most metals require large amounts of energy for extraction and refining, and these processes emit huge amounts of CO_2, accounting for about 40% of all industrial CO_2 emissions. This means that commercially successful metal product industries are obliged to take responsible actions to address environmental issues. Sustainability is not a mere buzzword but a moral imperative. I feel a profound sense of responsibility to continue advancing sustainable metallurgical practices through research.

— What are your future goals?

I'd like to advance our understanding of fundamental metallurgical phenomena and mechanisms related to sustainability, especially with regard to steels and aluminum alloys. The global metals industry has started developing and investing heavily in various technologies, including those enabling hydrogen-based reduction of iron ores and more efficient coal-fueled blast furnace processes. However, further research is needed to better understand the fundamental redox reactions and kinetic mechanisms involved in these technologies and processes. Due to the enormous size of the steel industry, even small advances and changes can result in major sustainability advantages, greatly motivating metallurgical researchers to go deeper into basic research in this sector. I believe that NIMS—one of the world's leading materials science research institutes—could be a fantastic partner in achieving this objective.

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on the cover: "Metamaterial light sources" that manipulate light
with a periodic structure smaller than the wavelength of light

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