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Designing Fine Particles

Development and Application of Particle Processing That Enables the Fabrication of New Materials

New Year's Greetings

When I was a graduate student in the United States more than 30 years ago, my thesis advisor said to me, "Is it common that Japanese people don't like discussions? Discussion and interaction are very important not only for research, but also for anything that involves creativity. When Einstein was alone, he used to have discussions by mumbling to himself." I realized how true this is, looking back at my own career as a researcher; I always had good discussion partners.

As the President of NIMS, my goal is to create an ideal environment for people-interaction, which I believe is important for innovation. How can we make this happen? There are two essential factors: people and shared space.

People are the first and most obvious requirement. Not everyone is capable of holding a lively discussion with him or herself, as Einstein is said to have done. It is important to be surrounded by good partners and fellow researchers with whom one can hold open-minded discussions.

Researchers in cutting-edge fields gather at NIMS, and we are committed to leading the world in materials research. This environment also contributes significantly to developing human resources. Although the number of female researchers is still small in Japan, NIMS is making a positive effort to hire more of them. We are also looking for talented engineers.

The other factor is shared space. Construction of the Structural Materials Research Building has started at NIMS, which

will assemble structural-materials researchers specialized in focused research. Similar to the Nano-GREEN/WPI-MANA Building, which was completed two years ago, we have chosen a design that would encourage people to communicate informally with each other. Theoretical Research Building at the Namiki site, which was rebuilt to assemble the experts in theory and computational research, is also expected to provide a comfortable space for daily discussions. In this manner, NIMS is

attempting to advance innovation by bringing together diverse minds of people from a wide range of disciplines and cultural backgrounds. We strongly encourage interaction and discussion among them.

Furthermore, NIMS promotes research collaboration and actively seeks outside partnerships. In our effort to promote collaboration with the private sector in 2013, we added three collaborative research centers in Japan, and a third international joint research center at National Taiwan University. We also signed several collaboration agreements with academic and public research institutions within and outside Japan, including the University of Rennes 1 in France and the

Public Works Research Institute in Japan.

We are going to enter the fourth year of the Third Five-year Program (FY2011 – FY2015). It is therefore time to work towards completing the projects for the current Five-year Program. I would greatly appreciate your continued support and cooperation in making NIMS a success in 2014.



Prof. Sukekatsu Ushioda
President, National Institute for Materials Science

A handwritten signature in black ink that reads "S. Ushioda".

A hand is shown from the palm side, holding a cluster of glowing, irregularly shaped particles. The particles are bright yellow and orange, with a red glow around them, suggesting heat or energy. The background is dark, making the glowing particles stand out. The hand is positioned in the center of the frame, with fingers slightly spread.

Designing Fine Particles

Development and Application of Particle Processing That Enables the Fabrication of New Materials

There is a somewhat interesting substance that exists in the form of an "assembly."
It is an "assembly of fine particles," whose coupling mechanism and nature differ from those of metal that melts into a mass or polymer materials that are flexible.

Some materials made of an assembly of fine particles show greater resistance to ultra-high temperature, allow light transmission over a farther distance and show greater corrosion resistance, as compared to metal. A typical, well-known example is ceramics.

Earlier research on these materials mostly focused on "what to assemble."

Now, let us take one step forward.

When we control the arrangement or structure of an assembly of fine particles, how will their nature change?
Each one particle contains several elements.
Then, what will we see if we shed light on "how" these elements are contained, rather than "what kind of elements" are contained and "how much" they are contained?

Particle processing, featured in this issue, is an attempt to discover new functions and properties of materials that are made of an assembly of fine particles, by designing the arrangement or structure of fine particles as well as the combination and configuration of elements in each one particle.

Designing of fine particles will make currently somewhat interesting materials more interesting.



Development and Application of Fine Particle Processing That Enables the Fabrication of New Materials

Unit Director, Materials Processing Unit,
Advanced Key Technologies Division

Yoshio Sakka

Five subthemes for promoting research on particle processing

We are working on the precise structure control at all levels from the nanometer order to the micrometer order through more advanced particle processing, with the aim of creating environmentally-friendly multifunctional inorganic materials (especially optical devices, fuel cells, secondary battery materials) that will contribute to solving issues related to the global environment and energy, using ubiquitous elements.

Particle processing involves such processes as synthesis, surface modification, shaping, and sintering of fine particles. By putting these essential technologies together, we are engaged in (1) development of advanced processing with the use of nanoparticles, nanotubes and mesopores, and creation and functionalization of nanostructures, (2) development of advanced processing for fabricating highly structure-controlled inorganic materials by applying external fields such as a high magnetic field or electromagnetic field and ultra-high pressure, and (3) elucidation of the relationship between microstructures and various functional properties, as well as elucidation of the relationship between crystalline structures and functional expressions

using techniques in computer science. We also promote mutual feedback of the results obtained in the respective research areas.

In order to promote these research activities comprehensively, we set the following five subthemes. Figure 1 is a schematic diagram indicating the connections between the research elements and the research goals. The titles of the respective subthemes and researchers assigned thereto are as follows.

1. Synthesis of nanoparticles and mesopores, and their functionalization (Yoshihiko Takeda: Ion Beam Group, Quantum Beam Unit)
2. Development of novel nanocarbon materials and their functionalization (Kun'ichi Miyazawa: Fullerene Engineering Group, Materials Processing Unit)
3. Development of advanced ultra-high pressure techniques and their application to materials science (Takashi Taniguchi: Ultra-High Pressure Processes Group, Materials Processing Unit)
4. Fabrication of highly structure-controlled ceramics (Yoshio Sakka: Advanced Ceramics Group, Materials Processing Unit)
5. Search for functions and creation of multifunctional materials (Naoto Hirotsaki: Sialon Group, Sialon Unit)

Subtheme 1:

Synthesis of nanoparticles and mesopores and their functionalization

On this subtheme, we work on the synthesis of nanoparticles by various techniques and the arrangement and integration thereof, as well as the fabrication of regularly arranged pores of uniform size and the use thereof. Si or Ge-based luminescent nanoparticles described in the special feature are an example of the use of such nanoparticles. We also engage in presenting the guidelines for optimal designs of chemotherapy of cancer cells with the use of magnetic nanoparticle materials, and studying the formation of metal nanoparticles in silica by fast heavy ion irradiation and the characterization of optical properties.

Subtheme 2:

Development of novel nanocarbon materials and their functionalization

On this subtheme, we focus on the development and functionalization of environmentally-friendly novel nanocarbon materials. With regard to shape-controlled fullerene compounds developed by NIMS such as fullerene nanofibers, in particular, we carry out research on their

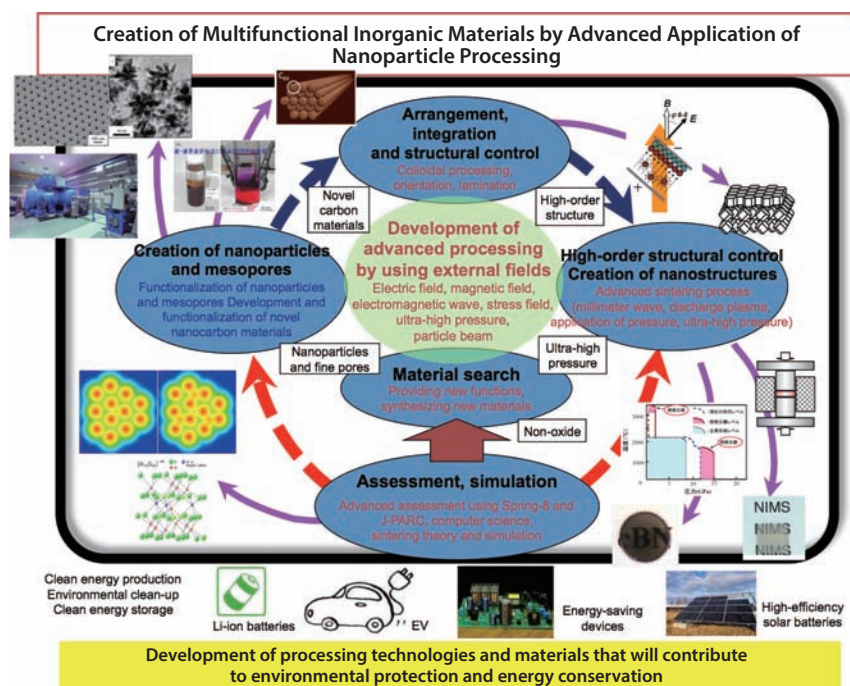


Fig. 1 Schematic diagram indicating the relationship between the research elements and the research goals.

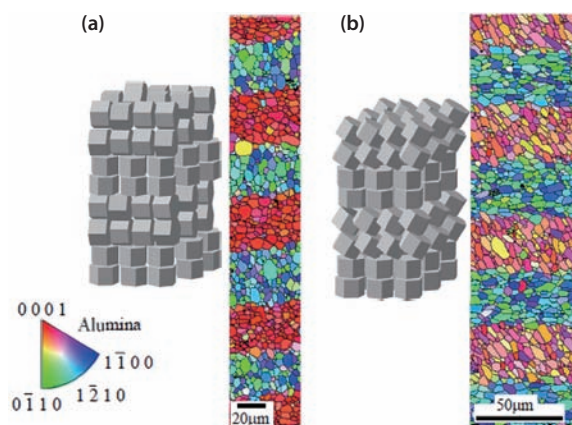


Fig. 2 Minute schematic diagram of oriented alumina laminates produced by depositing alumina particles in an electric field and a high magnetic field, imposed at different angles by turns, and the analyzed organization structure thereof.

(a) Oriented laminates produced in an electric field and a high magnetic field imposed at an angle of 0° and 90°. (b) Oriented laminates produced in an electric field and a high magnetic field imposed at an angle of 0° and 45°.

use as superconducting materials or materials for photovoltaic devices. NIMS NOW previously featured research on super capacitors using carbon-based materials such as carbon nanotubes and carbon fullerene.

Subtheme 3: Development of advanced ultra-high pressure techniques and their application to materials science

On this subtheme, we promote the improving of the ultra-high pressure technology that NIMS has developed over many years, and its application to materials processing. The special feature describes the research on achieving the single-phase synthesis of new transition metal nitrides such as tungsten nitride crystal (δ -WN, h- W_3N_4) by applying metathetical reactions to high-pressure synthesis, and developing high-purity hexagonal boron nitride (hBN) monocrystal as a substrate material for graphene devices.

Subtheme 4: Fabrication of highly structure-controlled ceramics

On this subtheme, we promote the develop-

ment of advanced processing for fabricating highly structure controlled ceramics using various external fields. The special feature focuses on oxyapatites as a new oxygen ion conductor, and discusses the development of a new method for fabricating easily-sintered particles, orientation for high conductivity, and elucidation of the composition phase diagram.

Production of translucent ceramics is an example of a process from synthesis of fine particles to fabrication of densely sintered ceramics. Pores remain in ordinary sintered ceramics and cause the reflection of light, so it is necessary to fabricate densely sintered ceramics with as few pores as possible. To achieve this, adjusting fine particles to ensure that they are not aggregated is extremely important.

Another effective method is pressure sintering performed by applying a high pulsed current. For example, translucent alumina is usually produced at 1800°C or higher. Through the new sintering method, we were able to produce the same material at 1150°C under pressure of 80MPa, and at 950°C under pressure of 500MPa. Thus, we succeeded in fabricating ceramics with a smaller grain size and higher strength at a lower temperature and in a shorter time.

New sintering methods have various advan-

tages, but many things about the sintering mechanisms of these methods are still unclear, and the elucidation thereof is imperative for the future development of new sintering methods. Furthermore, imposing an electric field or high magnetic field from outside enables advanced microstructure control. For example, textured materials can be produced by using the rotation and alignment of particles that take place when a high magnetic field is imposed to form and consolidate a suspension in which fine particles are dispersed. Oriented laminates can also be produced by superimposing an electric field and high magnetic field (Figure 2).

Subtheme 5: Search for functions and creation of multifunctional materials

On this subtheme, we particularly target non-oxide ceramics which still have unexploited areas, and explore the relationship between the development of advanced processing and the structure and functional expressions, with the aim of fabricating new multifunctional ceramics. The special feature describes a new efficient approach for searching functions by establishing methods for crystalline structure analysis and optical characterization using fine-particle monocrystal.

Figure 3 shows the development of multifunctional inorganic materials achieved through the collaboration of the research activities based on these five subthemes and the ripple effects thereof. We hope that the publication of these special features will further enhance collaboration in research.

The details of the research activities under this project are featured in the following publications.

- [1] NIMS Project, Advanced Particle Processing: Realizing Higher Functionality in Fine Ceramics, Material Integration, 25, No.10 & 11 (2012).
- [2] Special issue on particle processing technology, Science and Technology of Advanced Materials, No.5, 6 (2013) and No.1 (2014).

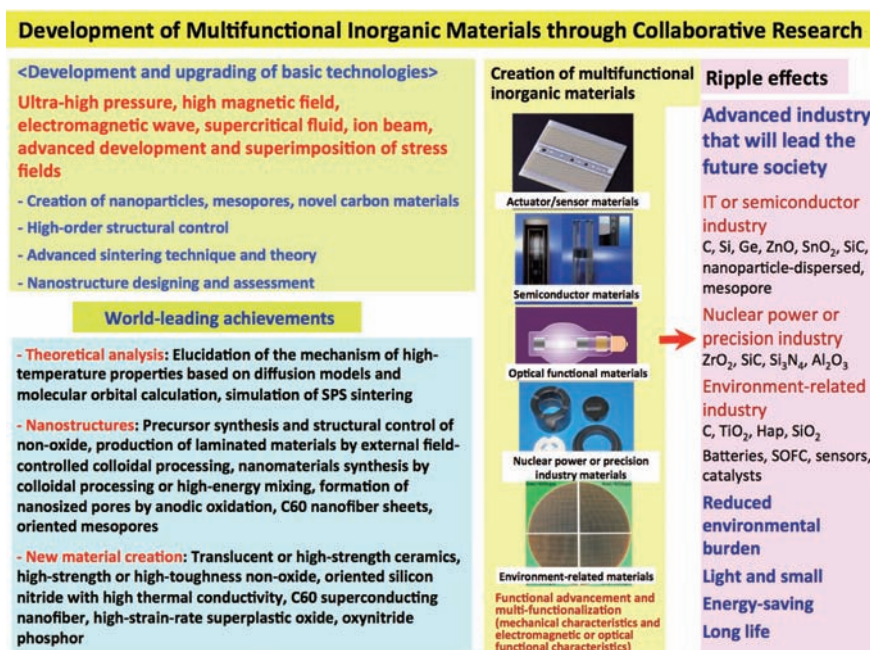


Fig. 3 Development of multifunctional inorganic materials through collaborative research, and the ripple effects thereof.

Profile

Yoshio Sakka PhD (Engineering). Joined the National Research Institute for Metals (NRI; currently NIMS) in 1983. After serving as the Managing Director of the Nano Ceramics Center in 2006, assumed the current position in 2011. Concurrently holds the position of professor at the University of Tsukuba.



Luminescent Nanoparticles in Harmony with the Environment and Recycling-Oriented Society

MANA Independent Scientist,
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Naoto Shirahata

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Batu Ghosh

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Yoshio Sakka

Substances that become luminescent when reduced to nanometer size

Electromagnetic waves have the nature of both electricity and magnetism. As shown in the Figure, there are various types of electromagnetic waves which can be classified by wavelength. An electromagnetic wave with a wavelength of 1 nm to 1 mm is called "light," and an object that emits light is called a "light source." Electromagnetic waves perceivable by the human eye are called "visible light," which has a limited range of wavelength, 380–780 nm. In order to enjoy an affluent life and society, we make use of the interactions between various substances and visible light, which makes up most of the electromagnetic waves that are emitted by the sun and reach the surface of the earth.

One such interaction is "emission of light." For example, fireworks get their beautiful colors from flame color reactions, and most light sources used in LED lamps, which are increasing their share as room lamps by replacing filament bulbs, take advantage of a phenomenon called "luminescence" caused by photoexcitation or by applying an electric field. Furthermore, in basic research in the medical field, bioimaging using luminescent materials plays an important role in making specific bio-intermolecular interactions visible.

In general, each substance has its own fixed emission wavelength, so we use different light sources according to the purpose and situation. However, we have found that by processing silicon and germanium, which belong to Group 14 of the periodic table, into particles, and reducing their size to nanometer scale, we can obtain a desired emission of light from a wide range of wavelength covering near-ultraviolet, visible and near-infrared light.

Make effective use of recyclable materials

Figure shows a typical photoluminescence image. The emission wavelength of silicon and germanium can be controlled within the following range by transforming the structure of their nanoparticles.

Silicon (Si): 300-1000 nm^{1,2)}
Germanium (Ge): 350-1280 nm³⁻⁵⁾

No substances other than Si and Ge allow continuous control of their emission wavelength, which is as long as 1 μm, solely by way of structural transformation of their particles. Furthermore, as Si and Ge are composed of a single element, they do not require precise composition control. These substances are unique in terms of the characteristics derived from their elements, in addition to their emission function. For exam-

ple, Si and Ge can be combined by covalent binding with the major components of organic matter, namely, carbon, nitrogen and oxygen, and become various types of derivatives.²⁾ Therefore, it is possible to make them colloiddally dispersed, that is, water or oil-soluble. It is also possible to design molecules using these substances so that they are joined with conducting polymers or show high affinity with specific cells.²⁾ Although only a few successful cases of application to laser devices have been reported thus far, these substances are extremely interesting in view of the recent research progress involving them, such as the improved luminous efficiency and other functions.

There are some substances which are not toxic to organic matter when they exist as bulk crystals but become toxic to organic matter when they are reduced in size to nanoscale. Si and Ge are a rare type of substance in a sense that their nanostructures do not show toxicity to organic matter.¹⁾ In addition, Si, with a large Clarke number,* is applicable to industry without the fear of its depletion. We believe that we can contribute to building an environmentally-friendly society by bringing out latent functions of substances which exist in abundance such as Si by way of artificial manipulation, and linking these functions to application of materials.

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- 2) N. Shirahata, *Phys. Chem. Chem. Phys.* (Perspective) 13 (2011) 7284.
- 3) B. Ghosh, Y. Sakka, N. Shirahata, *J. Mater. Chem. A* 1 (2013) 3747.
- 4) N. Shirahata, D. Hirakawa, Y. Masuda, Y. Sakka, *Langmuir* 29 (2013) 7401.
- 5) B. Ghosh, M. Ogawara, Y. Sakka, N. Shirahata, *J. Nanosci. Nanotech.* 14 (2014) 2204.

* Clarke number: the percentage by weight of an element that exists near the surface of the earth, estimated based on the results of chemical analysis of igneous rocks.

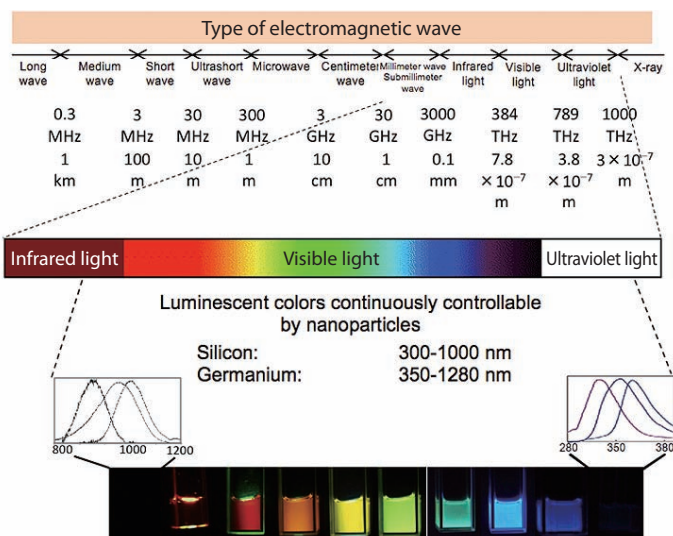


Figure Correlation between electromagnetic waves and light, and luminescent colors that have become continuously controllable by manipulating nanoparticles. (Photoluminescence image obtained from silicon)

Profile

Naoto Shirahata PhD (Engineering). Joined the National Institute for Materials Science in 2006 after working under the fellowship program of the Japan Society for the Promotion of Science (JSPS), etc., and assumed the current position in 2011. Concurrently holds a position as JST PRESTO researcher since 2009. / **Batu Ghosh** PhD (Science). Completed the doctoral course (experimental physics) at the graduate school of the University of Calcutta, India, and assumed the current position in November 2011. / **Yoshio Sakka** See p.5 for his profile.

Superconducting Fullerene Nanowhiskers

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Superconductivity in C₆₀ Fullerene

Carbon 60 (C₆₀) is a soccer ball-shaped molecule composed of 60 carbon atoms, and it is a type of a cage-like hollow molecule called fullerene (Figure 1). C₆₀ molecules become aggregated and crystallized by weak van der Waals forces and form a face-centered cubic lattice, but between C₆₀ molecules exist large interstices such as octahedral interstices and tetrahedral interstices. In 1991, Hebard and others demonstrated that by heating potassium (kalium, K) at 200 °C for 36 hours and making it diffusively intrude into these interstices, they obtained K₃C₆₀ powder which exhibits superconductivity at a transition temperature (T_c) of 18K.¹⁾ However, in their research, only one percent by volume of the powder displayed superconductivity.

Superconductivity of C₆₀ Fullerene Nanowhiskers

Fullerene nanowhiskers (FNW) are fine wire-like crystals made of an aggregate of fullerene molecules, and many types such as C₆₀ FNW (Figure 1) and C₇₀ FNW have been synthesized thus far.²⁾ Hollow FNW are called fullerene nanotubes. FNW can be synthesized by diffusively mixing a saturated liquid that is a good solvent of fullerene with a poor solvent that can be mixed well with the former. For example, C₆₀ nanowhiskers (C₆₀

NW) can be synthesized by mixing a C₆₀ saturated toluene solution with isopropyl alcohol, removing the solvent inside of it, to obtain C₆₀NW in the form of face-centered cubic crystal.

We thought that it must be possible to realize superconductivity in C₆₀NW by adding potassium to it, and we actually found that by vacuum-encapsulating C₆₀NW powder (4.4 μm in average length, 540 nm in average diameter) into a silica tube together with potassium and heating the mixture at 200 °C for only 24 hours, we can make more than 80 percent of the mixture into a superconductor with T_c of 17K.³⁾ We also found that the high critical current density in this superconducting material is more than 300,000 A/cm² and it can be maintained in a high magnetic field of up to 50 kOe (Figure 2).

Superconducting C₆₀NW, which we have successfully developed, is a porous material containing a number of nanosized fine pores (Figure 3). We presume that this porous structure helps the diffusion of potassium to make C₆₀NW in whole doped with potassium, which thereby enabled us to obtain a superconducting C₆₀NW at a high percentage by volume.

Future vision for application of superconducting C₆₀NW

Superconducting C₆₀NW is the world's first achievement in realizing superconductivity in

linear fullerene. Unlike copper oxide superconductors such as Bi-Sr-Ca-Cu-O which are made by using liquid nitrogen (boiling point: 77K) as a freezing medium, superconducting C₆₀NW needs to be cooled using liquid helium (boiling point: 4.2K). However, the density of C₆₀NW is as small as about 2g/cm³, which is about one-third of that in niobium-titanium superconductors which also need liquid helium and are most frequently put to practical use. Furthermore, superconducting C₆₀NW is favorable in terms of availability of resources because it is made of common elements, carbon and alkali metal, and C₆₀ is a recyclable material.

As C₆₀NW is soft, it may be used to create superconducting materials which are flexible and light. We believe that superconducting C₆₀NW will be applied in various fields related to energy, transportation and medical equipment, to make light and superconducting motors, generators and magnetic shielding materials.

- 1) A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, A. R. Kortan, *Nature* 350 (1991) 600.
- 2) Kun'ichi Miyazawa, ed., Fullerene Nanowhiskers (Pan Stanford Publishing Pte. Ltd., Singapore, 2011)
- 3) H. Takeya, K. Miyazawa, R. Kato, T. Wakahara, T. Ozaki, H. Okazaki, T. Yamaguchi, Y. Takano, *Molecules* 17 (2012)4851.

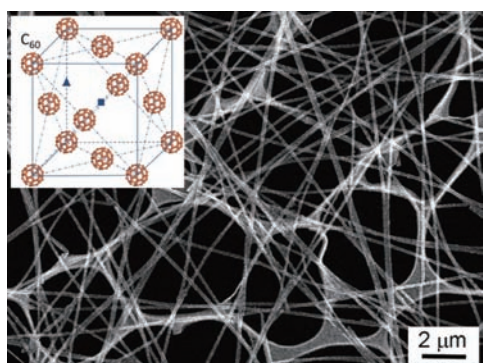


Fig. 1 C₆₀NW observed with a scanning electron microscope (SEM). The drawing in the upper left represents a model of a face-centered cubic crystal in which C₆₀ molecules (of about 0.71 nm in diameter) are arranged on lattice points. ■: octahedral interstices; ▲: tetrahedral interstices

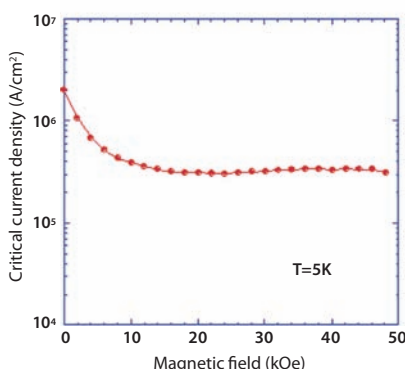


Fig. 2 Critical current density in superconducting C₆₀NW (5K).

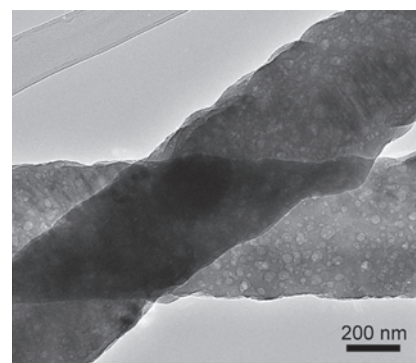


Fig. 3 Porous C₆₀NW showing excellent superconducting properties, observed with transmission electron microscope (TEM).

Profile

Kun'ichi Miyazawa PhD (Engineering). Became an engineering official of the Ministry of Education after leaving the doctoral course at the School of Engineering of the University of Tokyo in 1985. After serving as an assistant and lecturer at the Faculty of Engineering of the University of Tokyo, joined NIMS in 2002. / **Takatsugu Wakahara** PhD (Science). Became an assistant at the Graduate School of Science and Technology of Niigata University in 1998 and a lecturer at the Center for the Tsukuba Advanced Research Alliance of the University of Tsukuba in 2002, and joined NIMS in 2007. / **Hiroyuki Takeya** PhD (Science). Became an assistant at the Institute for Solid State Physics of the University of Tokyo in 1987 (and after serving as a doctoral research fellow at Iowa State University), joined the National Research Institute for Metals (NRI; currently NIMS) in 1993. / **Yoshihiko Takano** PhD (Science). Became a research fellow at the Institute for Solid State Physics of the University of Tokyo in 1995, and after working under the JST fellowship program, joined the National Research Institute for Metals (NRI; currently NIMS) in 1999.

Hexagonal Boron Nitride for Graphene Devices

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Graphene electron devices

An atomic layer of graphite is called graphene and it has very interesting properties such as unique electrical conduction. It is well-known that the Nobel Prize in Physics in 2010 was awarded to researchers who succeeded in obtaining graphene exfoliated from graphite with the use of adhesive tape. However, in reality, it is significantly difficult even by applying the exfoliation method to obtain a carbon atomic layer which has perfectly flat planes on the atomic layer level and which is electronically isolated.

SiO₂ substrate, which is ordinarily used, has such features as an uneven atomic order and a polar bond or unbonded state of atoms on the surface, which prevent graphene from exhibiting its original properties. To overcome this problem, a suspended structure over a substrate was developed. However, it was not easy to produce this structure, and there was a limit to the length of the device to be made because the suspended structure tends to hang down at its center. These restricted graphene from exhibiting its true properties.

Hexagonal boron nitride (hBN) is an insulator which has a 2D-plane crystalline structure comprised of nitrogen and boron atoms in sp² bonding and which does not have an unbonded state of atoms on the flat surface of the atomic layer. With these features, hBN was thought to be suitable for use in graphene substrates, but conventional hBN crystals did not provide the desired results due to constraints in terms of purity and size.

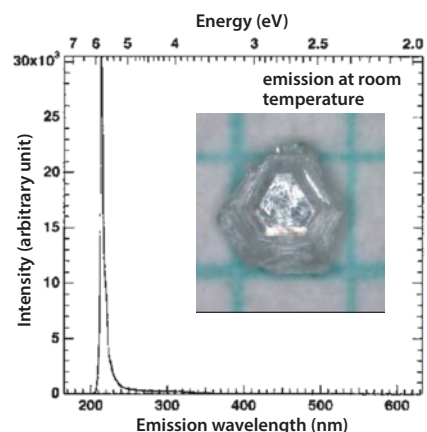


Fig. 1 hBN single crystal and far-UV emission spectrum.

High-purity hBN crystals

The authors have been engaged for many years in studying high-pressure synthesis of cubic boron nitride (cBN) and diamond as superhard materials and wide-gap semiconductor materials. In particular, with regard to the former target materials, earlier studies have not been sufficiently accumulated and synthesis of high-quality and high-purity single crystal is itself a key subject of study.

Through trial and error in technological development focusing on high-purity single crystal growth, in 2004, we succeeded in synthesizing cBN single crystal with relatively high purity that exhibits band edge emission, which is a criteria of the purity of a crystal. At the same time, we obtained hBN single crystal and found that it also has interesting optical properties as a high-purity crystal (high-intensity far-ultraviolet (far-UV) emission)¹⁾ (Figure 1).

Although hBN has been applied in industry from a long time before as a heat-resistant material and lubricant agent, its optical properties have scarcely been studied. Through a series of studies, various properties of hBN such as evaluation of its band gap, the origin of its high-intensity emission (Jahn-Teller distortion), its stacking fault, and the effect of impurities such as oxygen and carbon have been elucidated. Based on these findings, we developed a method for achieving liquid-phase growth of high-purity crystal at normal pressure,²⁾ and produced a prototype of a compact, electron beam-excited far-UV emitting device,³⁾ and then inspected a bactericidal effect using this device.

Development of hBN monocrystals for use in substrates of graphene devices

Meanwhile, in 2009, we were approached by a research group led by Professor P. Kim of Columbia

University in the U.S.A., who expressed the hope to use hBN crystal as a substrate material in graphene devices. In the next spring, the utility of hBN crystal (e.g. graphene mobility of 140,000cm²/Vs⁴⁾ was made public at the American Physics Society meeting, and following this, more than 50 research institutes at home and abroad, including MIT and the University of Manchester, have been working together on this subject.

Figure 2 shows AFM images of graphene on the conventional SiO₂ substrate and on the hBN crystal substrate. They are clearly different in terms of flatness on the surface. The process of controlling the atomic layer by exfoliation and transfer requires precision and patience in work. Nevertheless, efforts are currently being made in the development of multi-layer materials composed of hBN and graphene and the application to MoS₂ device substrates, toward the optimization of the technology to construct these laminated structures.⁵⁾

In order to achieve practical application, it is necessary to make graphene larger without using the exfoliation and transfer method. In this respect as well, we consider the combination of graphene and hBN a key concept. In parallel with the study on vapor-phase synthesis of graphene that is being vigorously carried out at present, we expect that the synthesis study aimed at creating high-quality and large hBN substrates and thin films by the vapor-phase synthesis and liquid-phase growth methods will be accelerated in the future.

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- 2) Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, *Science*, 317, 932 (2007).
- 3) K. Watanabe, T. Taniguchi, A. Niiyama, K. Miya, M. Taniguchi, *Nature Photonics* 3,591 (2009).
- 4) C.R. Dean, K. Watanabe, T. Taniguchi, P. Kim, et.al, *Nature. Nanotech.*, 5,722-726 (2010).
- 5) L. Wang, T. Taniguchi, K. Watanabe, O. Kim, C. Dean, et.al, *Science*, 342,614(2013).

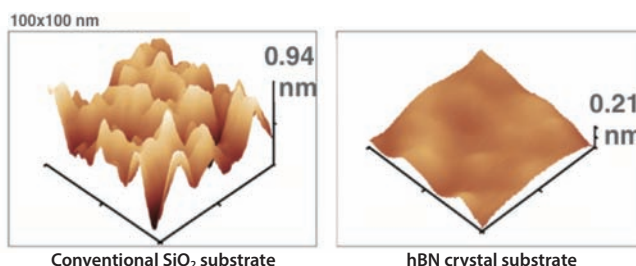


Fig. 2 Example of improved flatness of graphene: Evenness is extremely improved on the hBN crystal substrate (right) (AFM images).

Profile

Takashi Taniguchi PhD (Engineering). Group Leader, Graduated from the Faculty of Engineering of Tokyo University of Agriculture and Technology in 1982. Completed the doctoral course at the Interdisciplinary Graduate School of Science and Technology of Tokyo Institute of Technology and became a research associate at the Department of Inorganic Materials of Tokyo Institute of Technology in 1987. Joined the National Institute for Research in Inorganic Materials (NIRIM) established under the auspices of the former Science and Technology Agency (reorganized into NIMS in 2001) in 1989. Specializes in materials synthesis at high pressure. / **Kenji Watanabe** PhD (Science). Graduated from the Faculty of Science of Shizuoka University in 1985. Earned credit and left the doctoral course of the Graduate School of Science of Hokkaido University and joined Oki Electric Industry Co., Ltd. in 1990. Joined the National Institute for Research in Inorganic Materials (NIRIM) established under the auspices of the former Science and Technology Agency (reorganized into NIMS in 2001) in 1994. Specializes in semiconductor physics.

Creating New High-Density Nitride Material: Toward Development of New Ultra-hard Materials

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Expectations for new hard materials

In recent years, there have been growing expectations for the development of hard materials that exhibit excellent characteristics. "Cemented carbide" which is representative of the current hard materials, refers to sintered compact mainly composed of tungsten carbide (WC). It is a material suitable for cutting metal, since it is not only very hard, but is also chemically and thermally stable. Recently, however, materials such as carbon fiber reinforced plastic (CFRP), which are difficult to cut even by using cemented carbide, have been developed, prompting calls for improvement in the characteristics of cutting materials.

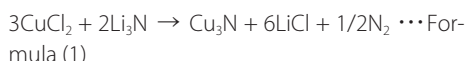
In developing new hard materials, a search for hard nitride materials has become active since theoretical calculations have predicted the existence of extremely hard materials among transition metal nitrides.

Our group is creating "nitrides with a high-density crystal structure" which are essential for developing hard materials, by using high pressure.

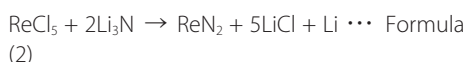
Creation of new materials by using metathesis reactions

"Metathesis reaction" is a generic term for synthesis methods using an exchange reaction between elements or functional groups, as exemplified by $AB + CD \rightarrow AC + BD$. It has been known that, when using this method in synthesizing nitrides, various nitrides can be synthe-

sized easily by reacting chloride with alkali metal nitride.¹⁾ As early as 1902, the synthesis of copper nitride was reported as shown in Formula (1).



Therefore, we attempted to apply a metathesis reaction to the synthesis of rhenium nitride (ReN_2). ReN_2 is a material that has been predicted by theoretical calculations as being an ultra-hard material comparable to diamonds.



As a result, by gradually advancing the Formula (2) reaction at a pressure of 7.7 GPa, we succeeded in confirming the synthesis of a new material, rhenium nitride (ReN_2) (Fig. 1). The elastic property of the synthesized crystal can be measured by a synchrotron X-ray diffraction experiment under high pressure by using a diamond-anvil cell.

When we derived the bulk modulus, which is correlated with hardness, from this measurement, we were unable to obtain a high value as had been theoretically predicted. However, structural analysis by X-ray diffraction revealed that the material has a layered structure as shown in Fig. 2, and we found that it is a new layered nitride material.²⁾

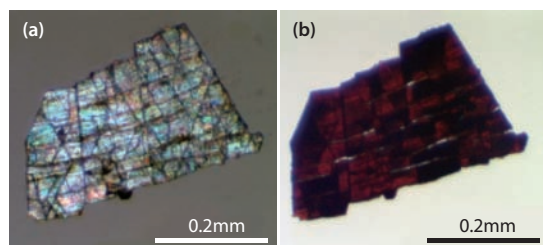


Fig. 1 Optical micrographs of the ReN_2 crystal synthesized for the first time (a. reflected light microscope, b. transmitted light microscope).

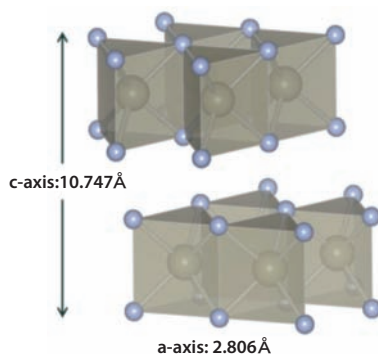


Fig. 2 Crystal structure of new material ReN_2 .

Synthesis of tungsten nitride

In the same manner as the synthesis of ReN_2 , we attempted to synthesize tungsten nitride (WN) crystal under high pressure. WN has the same crystal structure as WC, which is the main component of cemented carbide, and is expected to exhibit extremely high hardness for only replacing its carbon with nitrogen. The existence of WN crystals had been known in the past, but since it could only be synthesized in trace amount, its physical property had not been clarified. If WN crystals can be synthesized with a metathesis reaction, it will be possible to elucidate its detailed physical property and to create its sintered compact.

We reacted tungsten chloride (WCl_6) with sodium azide (NaN_3) at a pressure of 7.7 GPa, and confirmed that almost single-phase WN crystals can be synthesized at 1,700°C or above. As a result of measuring the bulk modulus of the obtained WN crystal, we confirmed a high bulk modulus (342 GPa), which is comparable to WC (Fig. 3).

In the future, we plan to investigate the possibilities of this material as a new ultrahard material by creating its sintered compact.

- 1) Gunts, A, Compt. Rend. Acad. Sci. 135(ser.3) 738 (1902)
- 2) F. Kawamura, H. Yusa, T. Taniguchi, Appl. Phys. Lett. 100, 25, 251910 (2012)

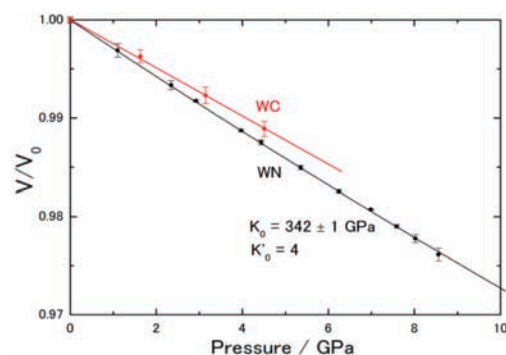


Fig. 3 Compression curve of WN (compared with WC) and bulk modulus measured by using a diamond-anvil cell.

Profile

Fumio Kawamura PhD (Engineering). Completed the doctoral course at the Department of Applied Chemistry, School of Engineering, the University of Tokyo in 2000. After serving as a Visiting Associate Professor at Graduate School of Osaka University, joined NIMS. Specializes in single crystal growth mechanism in flux growth. / **Hitoshi Yusa** PhD (Science). Completed the doctoral course at the Graduate School of Science, the University of Tokyo in 1994. After becoming a Senior Researcher at the National Institute for Research in Inorganic Materials, assumed the current position. Specializes in high-pressure synthesis and research on physical property of high-pressure structures. / **Takashi Taniguchi** See P8 for the profile.



Oxide-Ion Conductive Apatite: From the Development of Synthesis Process toward Application

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Advanced Key Technologies Division
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Tohru S. Suzuki

Fine Particles Engineering Group,
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Yoshio Sakka

Elucidating the functions of synthesized apatite—oxyapatite

Apatite is known as a material composing bones and teeth. The material we specifically focused on in our research was called “synthetic apatite” by artificially changing the elements constituting natural apatite to another elemental-combination that does not generate in natural mineral, without changing the original crystal structure.

Apatite comprised of rare-earth oxide and silicon oxide is called “oxyapatite.” Oxyapatite itself has been known since the 1960s; however its high oxide-ion conductivity around intermediate temperature was not discovered until 1995. The high oxide-ion conductivity is the key property of solid electrolyte for solid oxide fuel cell (SOFC) applications. Even though the excellent oxide-ion conductivity was revealed, the practical use of the oxyapatite as a solid electrolyte has been limited due to the difficulty in fabricating the dense bulk ceramics.

Focusing on the difficult-to-sinter property of the oxyapatite, we started our research from developing a novel synthesis process to obtain easy-to-sinter powder. As the result, we succeeded in synthesis of oxyapatite-type lanthanum silicate fine powder and synthesis of ceramics (Fig. 1). In addition, we have evaluated the solid-state electrochemical properties using our ceramics, and clarified that they have comparable oxide-ion conductivity as typical solid electrolytes.

Furthermore, we have revealed that the oxyapatite-type lanthanum silicate compounds are ideal solid electrolytes having high oxide-ion conductivity as well as good chemical stability under strong reducing atmosphere such

as in hydrogen. We have also found that they shows a low reactivity with many oxides compared to zirconium oxide based solid electrolytes, thus being excellent in practicability for fabrication of solid state devices.

Further enhancing the ion conductivity of oxyapatite

Extending our desire involves the further enhancement of the ion conductivity. In the case of oxyapatite-type lanthanum silicate, crystallographic direction in which the oxide-ion can be conducted easily is known to exist; and therefore, a possible methodology to enhance the ion conductivity is to fabricate crystal-orientation controlled sintered ceramics. But fabrication of such ceramics is very difficult by usual technology.

Fortunately, we have a technique to fabricate crystalline-orientation controlled ceramics by colloidal processing using a high magnetic field. By applying this processing technique, we have succeeded in producing highly c-axis oriented oxyapatite ceramics. We have confirmed that the oxygen ion conductivity of this highly c-axis oriented oxyapatite is about three times higher than non-oriented oxyapatite.

Another methodology is to control the concentration of lattice defects associated with oxygen ion conduction by dissolving oxides with different valence numbers to the lanthanum (+3) and silicon (+4). In particular, magnesium oxide was reported to be effective, no basic

data exist about the solid solubility of magnesium oxide in the lanthanum silicate oxyapatite phase. Therefore, we synthesized the samples with various compositions in lanthanum oxide, silicon oxide, and magnesium oxide to clarify the composition map of the formed phases. This map is called quasi-ternary phase diagram (Fig. 2), which shows the relationship between the compound phases formed and the composition, for the first time in the world.

This article¹⁾ had excellent reputation, and won the Richard and Patricia Spriggs Phase Equilibria Award of the American Ceramic Society in 2013.

At present we are evaluating the oxide-ion conductivity of the obtained oxyapatite in an effort to find the optimum composition as a solid electrolyte.

In order for a new material to be practically applied, an environment where data for someone who searches the new material to their purpose can be found and therefore, various data should be opened widely. We are pursuing basic research for inspiring the application of oxyapatite electrolytes and developing application technologies on a trial basis.

1) K. Kobayashi and Y. Sakka, “Phase relationships in the quasi-ternary $\text{LaO}_{1.5}\text{-SiO}_2\text{-MgO}$ system at 1773K”, *Sci. Tech. Adv. Mater.*, 13 (2012) 045006.

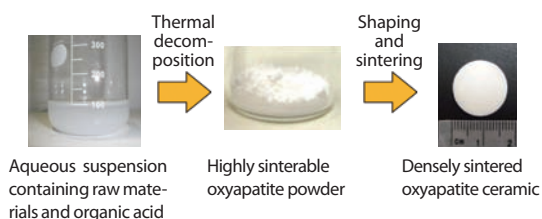


Fig. 1 Adjustment process for densely sinterable powder of oxyapatite-type lanthanum silicate and the sintered compact produced.

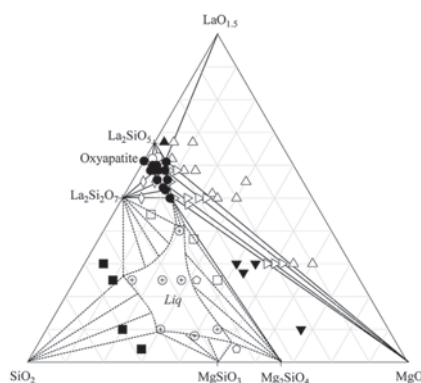


Fig. 2 Relationship between composition of lanthanum oxide-silicon oxide-magnesium oxide and formation phase (composition phase diagram) at 1,500°C. The part inside the equilateral triangle shows the composition consisting of three constituents ($\text{LaO}_{1.5}$, SiO_2 , and MgO), while the lines inside the triangle are conjugate lines representing the border lines across which the type of the formed compound changes. Black and white circles, and small graphics, such as squares, are composition points derived by experimentally investigating the formed compounds. Single-phase composition of oxyapatite phase (●), two-phase mixture composition of oxyapatite phase + La_2SiO_5 phase (○), two-phase mixture composition of oxyapatite phase + La_2SiO_7 phase (◇), three-phase mixture composition of oxyapatite phase + La_2SiO_5 phase + La_2O_3 phase (▲), two-phase mixture composition of oxyapatite phase + MgO phase (▷), three-phase mixture composition of oxyapatite phase + La_2O_3 phase + MgO phase (△), three-phase mixture composition of oxyapatite phase + MgO phase + Mg_2SiO_4 phase (▼), liquid phase forming composition (⊕), three-phase mixture composition of oxyapatite phase + Mg_2SiO_4 phase + La_2SiO_7 phase at room temperature (□), three-phase mixture composition of SiO_2 phase + MgSiO_3 phase + La_2SiO_7 phase (■), and three-phase mixture composition of La_2SiO_5 phase + MgSiO_3 phase + Mg_2SiO_4 phase (◇).¹⁾ Liq. indicates the region in which a liquid phase is formed at 1,500°C.

Profile

Kiyoshi Kobayashi PhD (Engineering). Became NIMS Senior Researcher in 2006. NIMS Principal Researcher since 2013. Visiting Associate Professor at Tokyo University of Science since 2013. / **Tohru S. Suzuki** PhD (Engineering). Became Research Associate at Waseda University in 1994. Joined the National Research Institute for Metals (current NIMS) in 1996. Visiting Researcher at Lawrence Berkeley National Laboratory during 2000–2001. NIMS Chief Researcher since 2012. / **Tetsuo Uchikoshi** PhD (Engineering). Joined the National Research Institute for Metals (current NIMS) in 1987. Fine Particles Engineering Group Leader since 2011. Visiting Researcher at McMaster University during 1997–1998. Visiting Professor at Kumamoto University during 2009–2012. Visiting Professor at Hokkaido University Graduate School since 2011. Visiting Professor at Hosei University Graduate School since 2013. / **Yoshio Sakka** See P.5 for his profile.

Development of a New Phosphor using One Particle

Sialon Group, Sialon Unit,
Environment and Energy Materials Division
Takashi Takeda

Sialon Group, Sialon Unit,
Environment and Energy Materials Division
Naoto Hirosaki

Need for a new phosphor

White LEDs, which are rapidly becoming popular as a component of energy-saving lighting and liquid crystal backlights, comprise phosphors and LEDs. Thus far, we have developed sialon phosphors suitable for white LEDs and led them to practical application. In order to further improve the performance of white LEDs such as efficiency and color rendering properties, it is necessary to improve the properties of phosphors and there is a call for the development of new phosphors.

The conventional phosphor development process was carried out by powder synthesis, and the effort to make a new phosphor more like a single-phase* material by changing the starting compositions or synthesis conditions was essential because this would make it possible to elucidate the luminescence properties, crystal structure and composition of the new phosphor. However, in actual synthesis, it requires a great deal of labor and time to make a single-phase material due to composition deviation resulting from vaporization of some starting compositions or uneven reactions within the crucible. Furthermore, some of the existing phosphors are so stable that once such phosphors are generated in the course of synthesis, they remain as impurities within the product and make it significantly difficult to obtain a single-phase material.

Development of a phosphor using one particle

In this project, with the aim of solving the above problem and developing new phosphors efficiently, we have worked on a new approach for the development of a phosphor using one particle. Even when it is difficult to make a single-phase material, particles of the target material must be contained in the product. One such particle is of course in a single phase, and we have developed a new phosphor by using this one particle (Figure 1).

Understanding even a small particle's properties

As in the conventional phosphor development process by powder synthesis, in the development process using only one particle, we should identify the crystalline structure and composition of the target material and also probe into its emission properties. Due to the small size of one particle, less than 100 μm , a problem may arise as to whether it is possible to obtain sufficiently strong signals from analytical instruments, but this problem can be solved by using X-ray structural analysis or electron beam probing to identify the crystalline structure and composition. The emission properties, which represent the most important factor, can now be measured in the same manner as the ordinarily measure-

ment of powder by using both a microscope and a spectroscope.

Figure 2 shows the spectrum of the excitation and emission from one particle of a phosphor of less than 100 μm , and the changes in the temperature of the emission of another phosphor. It is possible to measure these properties of a far smaller particle.

This approach has other characteristics. Specimens that have been treated as single-phase materials actually have slightly different compositions and properties for each particle, and what is observed in powder is the average among particles. In addition, the observation of powder may contain an influence of the emission from one particle being reabsorbed into another particle. In the new approach, we focus on one particle, so we can eliminate the influence of other particles and obtain the true emission properties of that one particle.

By applying this new approach, we have worked on the development of new phosphors and have already discovered many new phosphors. We will aim to apply these new phosphors and lead them to improving the performance of white LEDs and developing new applications of phosphors.

* Single-phase: the state of a substance with a single structure and uniform composition.

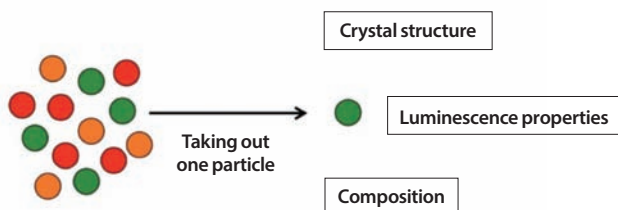


Fig. 1 Development of a phosphor using one particle.

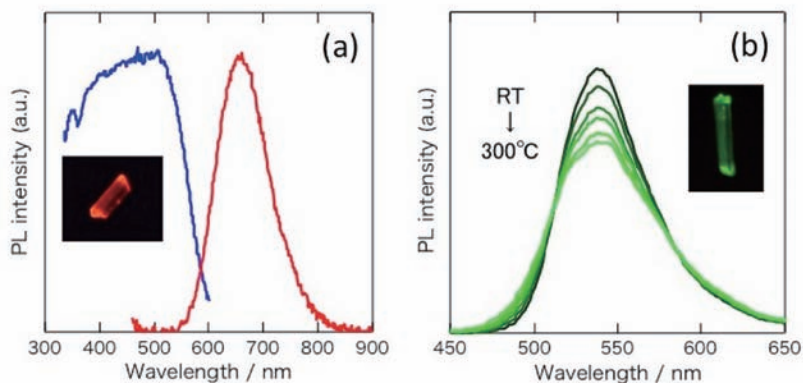


Fig. 2 (a) Spectrum of excitation and emission of one particle of a phosphor, and (b) changes in the temperature of the emission. Each photograph shows the emission of one particle of a phosphor.

Profile

Takashi Takeda PhD (Science). After completing the doctoral course at the graduate school of Kobe University in 2000, served as a researcher at Sumitomo Chemicals, an assistant at Tohoku University and an assistant professor at Hokkaido University, and assumed the current position in 2007. Associate professor at the Hokkaido University-NIMS graduate school. / **Naoto Hirosaki** PhD (Engineering). Joined Nissan Motor Co. in 1980 and the National Institute for Research in Inorganic Materials in 1998. Professor in the cooperative field of the Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology.

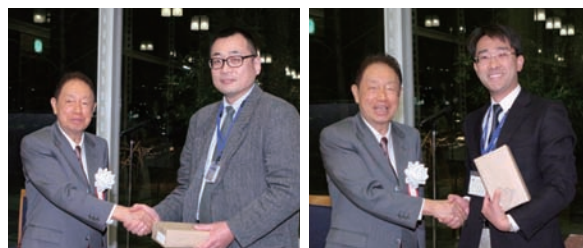
NIMS NEWS

1 NIMS Researchers Receive World's Top Poster Award and Best Presentation Award for Opening New Frontier at SAT Technology Showcase 2014

On January 24, SAT Technology Showcase 2014 was held at the International Congress Center, Epochal Tsukuba (sponsored by: the Science Academy of Tsukuba (SAT) of the Science and Technology Promotion Foundation of Ibaraki; co-sponsored by 27 organizations and associations including NIMS; supported by 16 organizations and associations), and in this event, the poster presentation by Dr. Kazuhiro Kimura, Director of the Materials Reliability Unit, titled "Long-time Creep Strength Characterization and Creation of Creep Datasheet," won the "World's Top Poster Award," and the presentation by Dr. Izumi Ichinose, Di-

rector of the Polymer Materials Unit, titled "Diamond-like Carbon Filter," won the "Best Presentation Award for Opening New Frontier." The award winners had the honor of receiving the awards from Dr. Reona Esaki, SAT President, in the award ceremony. Under the slogan of "Intellectual Inspiration in Tsukuba through Transmission and Exchange of World's Top Research," a total of 100 poster presentations were made by researchers including col-

lege students and high school students, in addition to 22 poster presentations on world's top research projects.



Dr. Kazuhiro Kimura (right) shaking hands with Dr. Reona Esaki (left) in the ceremony.

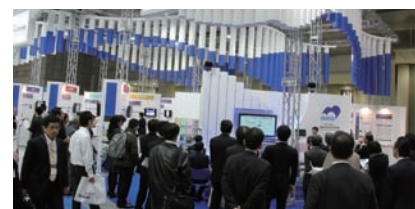
Dr. Yoshihisa Fujii receiving the award on behalf of Dr. Izumi Ichinose.

2 NIMS Researchers Receive Project Award at nano tech 2014

On January 29 to 31, nano tech 2014, the 13th International Nanotechnology Exhibition and Conference, was held at Tokyo Big Sight, and in this event, the presentation by Dr. Mitsuhiro Ebara, MANA Scientist of the Smart Biomaterials Group, Biomaterials Unit, titled "Development of Nanofiber Mesh Having Anti-Cancer Activity," won the nano tech 2014 Project Award (Life Technology Category). The nonwoven fabric Dr. Ebara presented in the exhibition is made of fiber equipped with the function of self-heating via external magnetic fields

and the function of releasing drugs when heated. Its availability as an effective treatment method capable of simultaneously realizing thermotherapy and chemotherapy of tumors was highly acclaimed, though it is still at the stage of basic experiment.

As for nano tech 2014, the event was organized under the same theme as the previous one, "Life & Green Nanotechnology" 10⁹ Innovation, and more than 48,000 people visited the exhibition. The NIMS booth received more than 1,500 visitors.



NIMS booth.

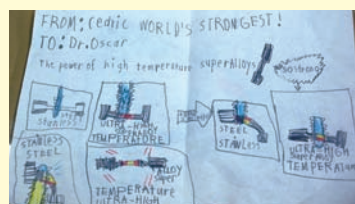


Dr. Ebara receiving the award from Dr. Tomoji Kawai, Chairman of the nano tech Executive Committee, in the ceremony (right).

Hello from NIMS

Dear NIMS NOW readers,

I fell in love with Japan when I first visited as a college student way back in 2001 and told myself that I will be back someday. Seven years later, with a Monbusho scholarship, I got into the University of Tsukuba



My son copied an illustration from the NIMS kids magazine.

and NIMS cooperative graduate school. Together with my young family, we are enjoying the rich culture, good food, and the four seasons of Japan.

To study/work and live in Tsukuba has been one of the best decisions in my life. It's the "Silicon Valley" of Japan where you meet great minds and at the same time you get to enjoy wonderful nature around you. I especially like biking on the sakura-lined bike lane from the University of Tsukuba to Doho Park on a beautiful spring day while pondering on my research questions.

It's been a privilege to be in NIMS as a grad student and now a post-doc. With its high-level research in all aspects of materials science coupled with state-of-the-art facilities,

it's the best atmosphere for a young scientist like me to be in. Even my 6-year-old son wants to be a scientist someday and work in NIMS. He also likes reading NIMS Now magazine.



Vallerie Ann Innis SAMSON
(Philippines)
2008 – Present
Post-doc



Visiting the Golden Pavilion in Kyoto.



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