

## INTERNATIONAL

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150th anniversary of the periodic table of chemical elements

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N9

Rb

Ca

Sr

Ra

# The periodic table is a treasure map

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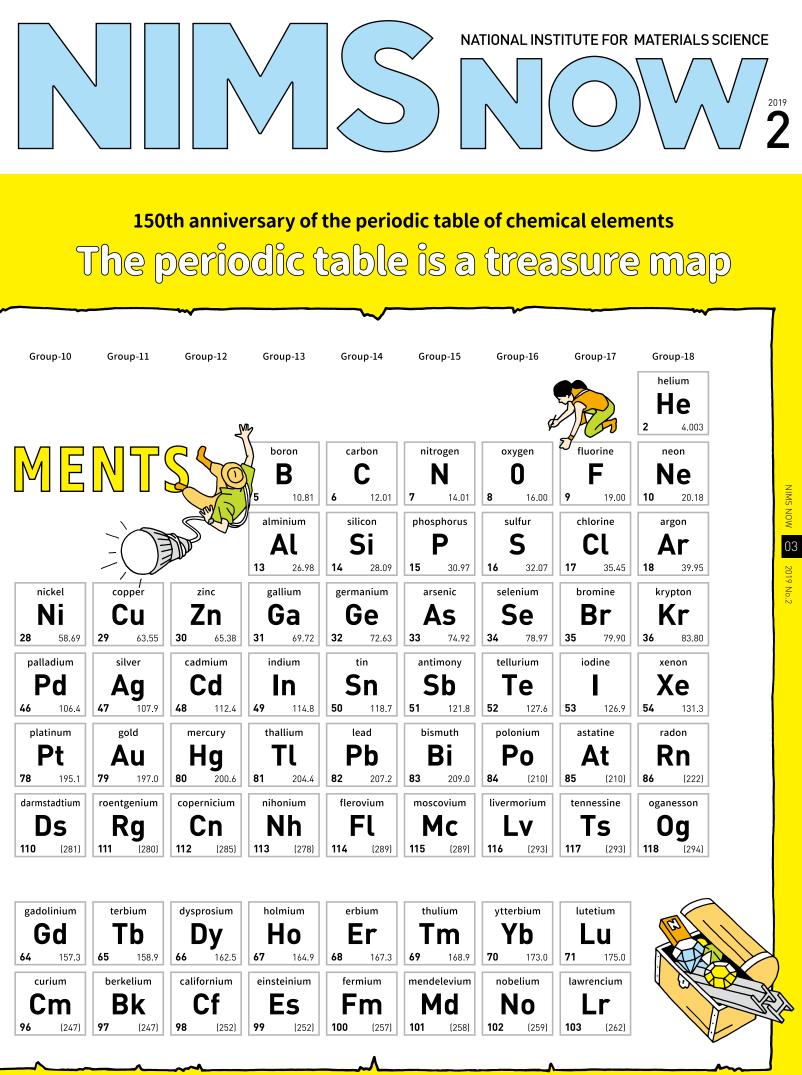
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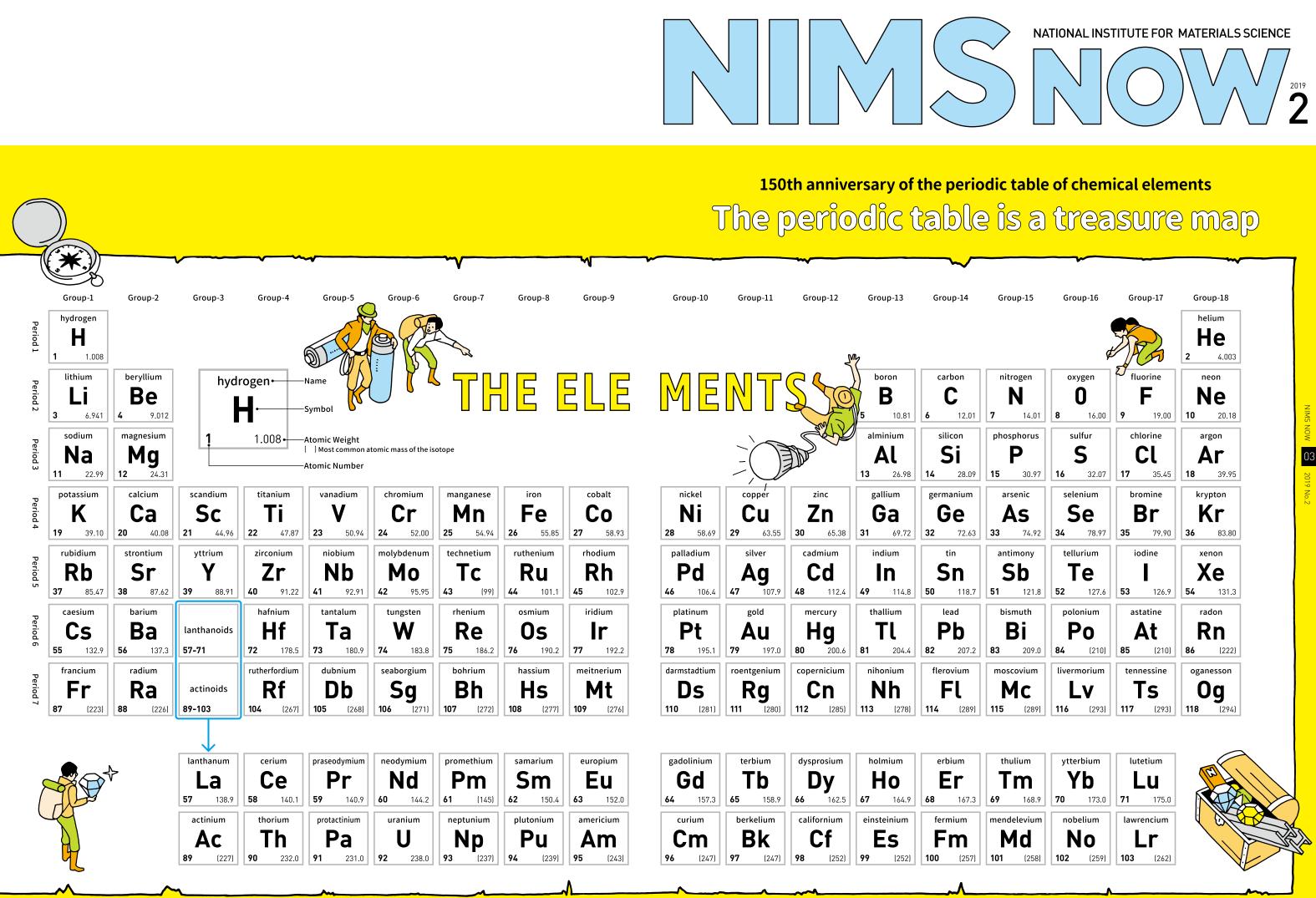
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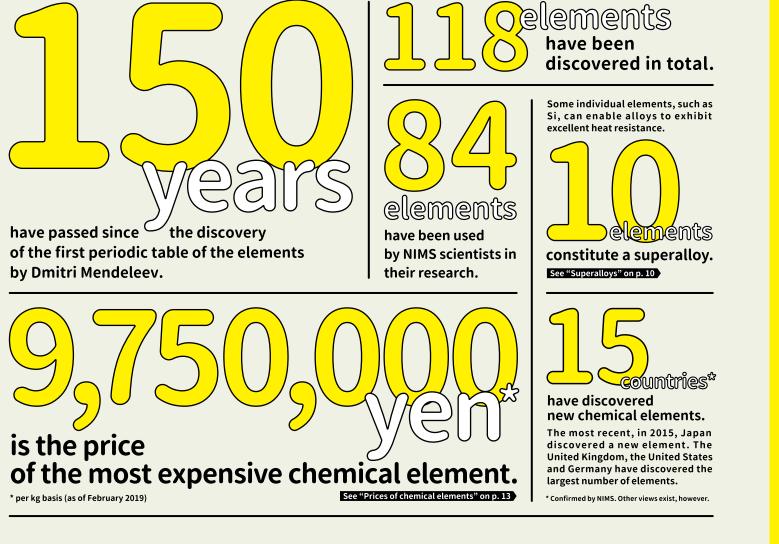
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# Figures surrounding the elements



The periodic table lists all of the chemical elements that compose all materials. Some may see the periodic table as dry and boring; something you were forced to memorize for tests in school.

Materials scientists, however, have a completely different view of the periodic table. They heavily rely on it in their search for the right elemental combinations that will enable materials to exhibit desirable properties.

A vast number of elemental combinations is possible due to the numerous options available in terms of the types and number of elements used, indicating the potential for the discovery of new materials. From this perspective, materials scientists are like explorers, boldly advancing into an untracked wilderness in search of answers.

For materials scientists, the periodic table

-a comprehensive representation of the elements, capable of offering insights into their natureis really a "treasure map," guiding the way to new discoveries.

Many materials are still waiting to be discovered. Intrepid materials scientists will continue their explorations, with their "map" to guide them.

# Let's take a look at the material scientist's treasure map!

Semiconductor materials **Catalytic materials Biomaterials Superconducting materials Superalloy materials Battery materials** GUEST! **Firèworks** 

# The adventure of discovery for novel materials

# My periodic table as a treasure map

Dr. Fumio KawamuraP.6
Dr. Hideki AbeP.7
Dr. Masanori KikuchiP.8
Dr. Masaaki IsobeP.9
Dr. Kyoko Kawagishi P.10
Dr. Akihiro Nomura P.11

Mr. Yoshio Yamazaki ..... P.12 (Yamazaki Fireworks MFG Co., Ltd)



Name

#### Dr. Fumio Kawamura

Target

### Semiconductor materials

I have been pursuing the development of semiconductors with superior performance through new combinations of chemical elements.

Li Be

Na Mg

Rb Sr

K Ca S

\* Valence: electric charge of an ion

Group12

valence of Ga.

Cs Ba lantha Hf Ta W Re Os Ir Pt

Fr Ra acti Rf Db Sg Bh Hs Mt Ds

\* Average valence: the average of valence value for an entire crystal structure



One of the most popular approaches to the development of new semiconductors is to use an existing semiconductor as a material and replace a chemical element in its crystalline structure with elements from groups adjacent to the original element on the periodic table. The elemental substitution without changing the crystal structure and average valence\* often improve its performance and extend the application fields.

N-containing semiconductors are generally

called "nitride semiconductors."

At Rn

Ts Oa

Group15

Al Si

Gallium nitride (GaN) is the initial semiconductor.

Ρ

Ja Zn Ga Ge As Se Br Kr

Ag Col-In-Sn Sb Te I Xe

S

#### Name

#### Dr. Hideki Abe

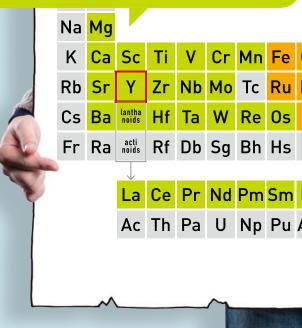
#### Target

### **Catalytic materials**

I have been researching catalysts—materials capable of expediting chemical reactions by closely interacting with atoms and molecules while remaining unchanged themselves.

## Elements susceptible to changes caused by chemical reactions

These elements assist and enhance catalysis. For example, they remove unwanted substances generated by catalytic reactions, maintaining an working environment to catalysis.



#### My research is...

The development of a new GaN-based semiconductor which is composed of Ga (group13) and N (group15) enabled the invention of blue LEDs—a revolutionary 21st-century lighting technology. The substitution of Ga into other group13 elements (Al or In) in GaN has created AlN or InN semiconductors, which have enabled us to realize the high-efficient LEDs emitting a variety of wavelength, resulting in the revolution of lighting devices. These light-emitting materials often have the potential to be used as light-absorbing materials. Because of these properties, GaN and InN semiconductors are expected for promising solar cell materials. However, Ga and In are minor metal, which inhibits the realization of a high-efficient solar cell.

Group14

The valence of Zn is usually two. By combining

Zn with Sn (group14) the average valence\* of the compound becomes three, matching the

The valence of these elements is usually four.

By combining one of them with Zn (group12) the average valence<sup>\*</sup> of the compound

becomes three, matching the valence of Ga.

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

I came up with a strategy to address this issue based on the concept of average valences\*: substitution of Ga (group13) in the GaN semiconductor with different elements listed in the groups on either side of Ga (i.e., group12 or 14) on the periodic table. Some of the group12 and 14 elements are non-toxic and earth-abundant, which is advantageous for reducing the production cost. Using these elements, I succeeded in synthesizing a high-quality ZnSnN<sub>2</sub> semiconductor by applying an extremely high pressure of 60,000 atm(atmospheric pressure). I am currently developing next-generation solar cells based on the concept of average valence.



The System enabling the synthesis of semiconductors under extremely high pressure

#### My research is...

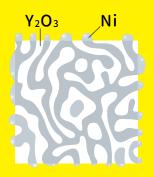
I have been engaged in various catalytic materials R&D, such as the development of materials used to purify automobile exhaust gases. My current focus is developing materials to facilitate hydrogen generation. Although hydrogen exists abundantly on the Earth, it exists largely in compounds rather than in a simple element. For this reason, hydrogen for use as a fuel for automobiles needs to be extracted from hydrogen compounds. The use of catalysts is vital in this process.

Methane (CH<sub>4</sub>), the main component in natural gas, is one of the major hydrogen compounds. Methane can be converted into hydrogen and carbon monoxide by allowing it to react with water vapor under high temperature using catalysts. Although catalysts for this purpose are already in practical use, I researched the creation of more efficient catalysts. As a result, I developed a catalyst with a novel structure called a "rooted catalyst," in which root-like Ni nanofibers penetrate an yttrium oxide ( $Y_2O_3$ ) support material. The catalyst was confirmed to function properly without performance degradation after 1,000 hours of continuous hydrogen production. I am currently pursuing industrial application of the catalyst, including larger scale synthesis of it.

 $\rightarrow$  For more details about this research, see p. 10 of the vol. 18, no. 5 NIMS NOW issue.

Catalysts are required to perform "tricky functions," such as increasing the rate at which a chemical reaction occurs without being altered itself. The basic approach to developing a catalytic material therefore involves selecting and combining two chemical elements—one susceptible and the other resistant to changes induced by chemical reactions.

	Elements resistant to changes induced by chemical reaction Metallic elements play a central role in catalytic functions. They ha ability to restore themselves after each catalytic reaction on the surfaces, thereby resisting changes in their properties.													
				Al	Si	Ρ	S	Cl	Ar		1			
Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe					
lr	Pt	Au	Hg	тι	Pb	Bi	Po	At	Rn					
Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og					
Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu						
Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr						
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"Rooted catalyst," in which root-like Ni nanofibers penetrate a carrier material Name

Name					_				1										
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	Li	Be		Sr—G	roup2	elemer	nts like	Ca—m	ау ехр	edite			В	С	Ν	0	F	Ne	Ser.
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			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
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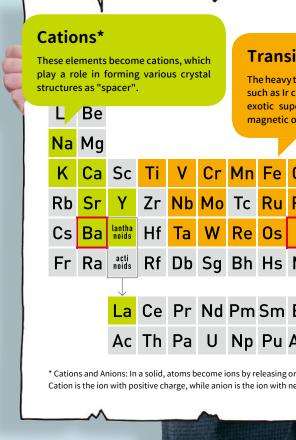
#### Name

#### Dr. Masaaki Isobe

#### Target

#### Superconducting materials

Superconductivity is a phenomenon in which the electrical resistivity becomes zero at low temperatures. My goal is to create new superconductors with a mechanism that can lead to breakthrough in properties.



#### My research is...

A variety of artificial bones have been being developed to achieve quick and complete bone healing. We succeeded in developing a novel artificial bone composed of hydroxyapatite and collagen (HAp/Col), enabling regenerate new bone into bone defects with the same speed as natural bone fracture healing. During this project, we developed a synthesis technique to recreate bone-like microstructure (composed of collagen fibers and nano-sized hydroxyapatite crystals aligned along the fibers). Patients' biological systems recognize the HAp/Col as genuine bones, and change them into new bones by natural bone metabolism. This property makes them suitable for use even in growing children. Moreover, unlike ceramic artificial bones, the HAp/Col has a viscoelastic nature to fit tightly to bone defects and to heal the defects effectively. They are already in use in orthopedics in Japan.

We plan to continue developing materials, such as an injectable artificial bone for minimally invasive surgery, antimicrobial artificial bones for preventing implant associated infections and coating materials that accelerate tight bonding (osseointegration) between metallic implants and bones.





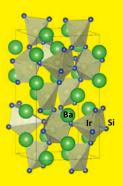
Viscoelastic artificial bone

#### My research is...

Superconductivity occurs when two electrons form a Cooper pairs (a pair of electrons bound together) at low temperatures. The stronger the attractive force (i.e., "glue") in a Cooper pair, the lower the likelihood that the superconductivity will break down. The attractive force had been originally thought to arise from thermal vibration of atoms (i.e., lattice vibration). However, the discovery of high-Tc (critical temperature) cuprate superconductors in 1986 revealed that the magnetic interaction between Cu atoms were associated with the forming Cooper pair. Since then, search for new superconductors originating from the magnetism has been actively promoted. I am also one of the researchers fascinated by the search for new superconductors. My earlier studies focused mainly on compounds containing Cu or its peripheral elements on the periodic table, but for the past several years, I have shifted my focus to the elements with large atomic numbers (i.e., heavy elements) such as Ir. There are two origins of magnetism in solid: electron "spin" and "orbital". In cuprates the magnetism is derived mainly from spin, while in iridium compounds both spin and orbital strongly influence the magnetism due to large relativistic interaction between a nuclear and electrons. I am searching for new type of superconductivity induced by the mechanism involving spin-orbit interaction. These efforts enabled me to succeed very recently in discovering a new superconductor BalrSi<sub>2</sub>.

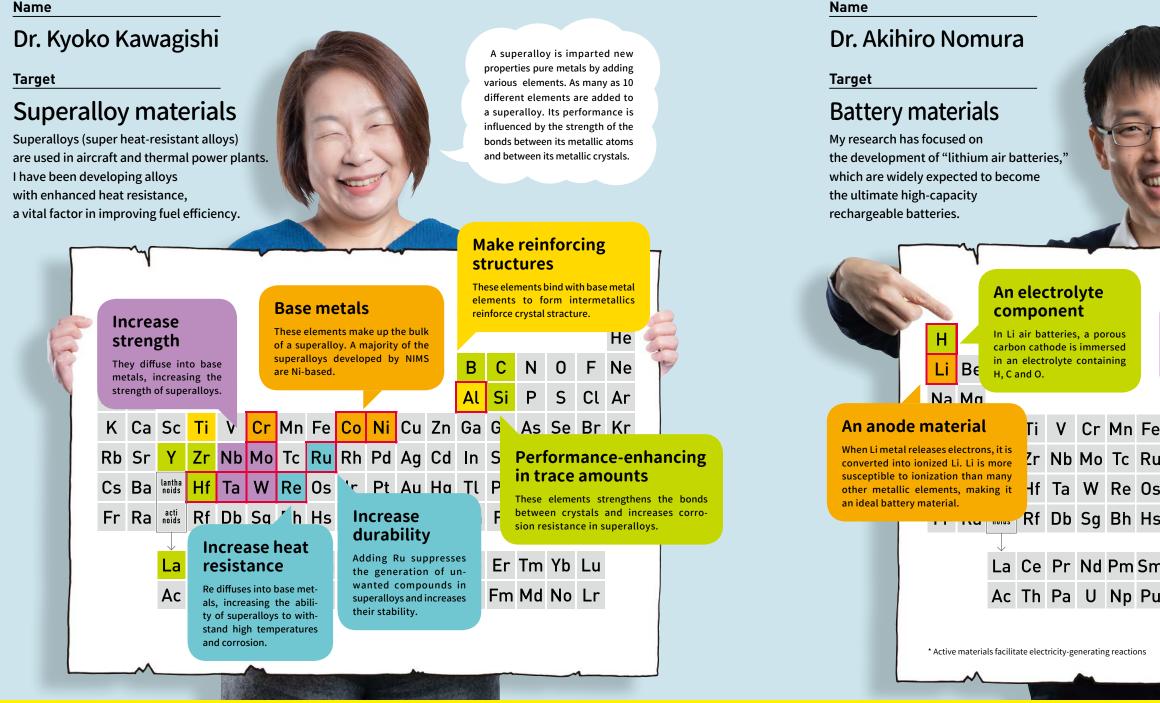
I am working on search for new type of superconductivity originating from "magnetism" in solid. The new superconductors are composed of transition metals (magnetic elements) and various other elements. The periodic table of elements is useful for design of the new materials. I divide the periodic table into three groups, and combine elements chosen from these groups.

transition-metal element He   can be a key player of the B C N O F Ne   B C N O F Ne   Al Si P S Cl Ar   Co Ni Cu Zn Ga Ge As Se Br Kr	r of the ith the		С	Ν	0		He	9	-
AlSiPSClAr			С	Ν				-	-1
		AL			U	F	Ne		
Co Ni Cu Zo Co Co Ac So Pr Kr			Si	Р	S	Cl	Ar		
CO INI CU ZII GA GE AS SE DI KI	Zn	Ga	Ge	As	Se	Br	Kr		
Rh Pd Ag Cd In S Sb Te I Xe	Cd	In	۶٦	Sb	Те	I	Хе		
Ir Pt Au Hg Anion-like* element	Hg	1	Anio	n-li	ke*	elen	nen	ts	
Mt Ds Rg Cn N These elements form covalent bond the transition-metal elements. It	Cn								
out a variety of magnetic states compound.		c	out a v	/ariety					-
Eu Gd Tb Dy H	Dy		Joinpot	inu.					
Am Cm Bk Cf Es Fm Md No Lr	Cf	Es	Fm	Md	No	Lr			
or attracting their electrons. Jegative charge.	trons.								



Crystal structure of the new BalrSi<sub>2</sub> superconducting material 5 NOW 0 2019 No.:

Name



#### My research is...

Aircraft engine and thermal power plant gas turbine combustor are extremely hot ( $\geq$  1,000°C). Superalloys are invaluable in these environments. Ni-based superalloys developed by NIMS have been used in turbine rotor blades in the engines of the Boeing 787. The ability of withstanding high temperatures enables the airliner to be more fuel efficient and significantly reduces its CO<sub>2</sub> emissions.

Each of the chemical elements added to superalloys has a specific role, and slight changes in the proportions of these elements may substantially alter the properties of the resulting superalloys. Superalloy design is complex because superalloys are expected to exhibit excellent performance across a variety of parameters, such as heat resistance, physical strength and corrosion resistance. Our team greatly appreciates the alloy design programs developed by NIMS, which enable me to predict the properties of superalloys We design. In 2012, We succeeded in developing a superalloy with the world's highest heat resistance -capable of withstanding a temperature of 1,120°C-by adding Re and Ru based on simulation results. I hope to develop alloys that can be produced relatively easily at low cost in order to promote wide use of superalloy products.



Turbine rotor blades for aircraft composed of superalloys

#### My research is...

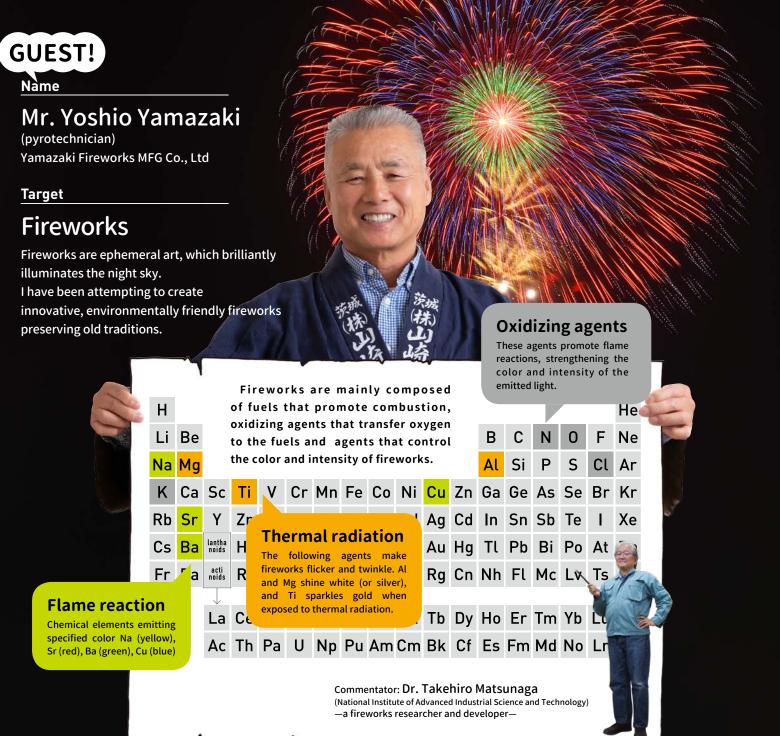
While the performance of Li ion battery is approaching the theoretical limit, the "Li air battery" is considered to be a promising higher capacity battery. Li ion and Li air batteries are similar in that they both store and generate electricity through the back-and-forth movement of Li ions between the anode and cathode. However, the Li air battery has greater potential to achieve weight reduction and capacity expansion Lithium air battery prototypes created by the research group (coin (left) and stacked (right) batteries) because it incorporates O<sub>2</sub> from ambient air as an active material. To enable Li air batteries to efficiently generate electricity, two requirements need to be met. First, large proportions of the externally obtained O<sub>2</sub> and Li ions must encounter each other and react in the cathode surface. Second, the accumulation of Li oxides—the product of reactions between O<sub>2</sub> and Li ions—must be controlled properly so that they do not inhibit the subsequent  $O_2$ -Li reaction. To meet these requirements, I used a porous carbon material with a large surface area as a cathode. For the Li air battery to store electricity, a reversal process needs to be achieved, whereby Li oxides are split into Li ions and O<sub>2</sub> and transferred to their original sources. I am striving to find electrolytes and additives that may facilitate this splitting reaction. Through these efforts, I hope to put Li air batteries into practical use as soon as possible.

Chemical elements used in high energy density batteries should be lightweight and capable of efficient electron transfer. Accordingly, chemical elements used in basic battery components are mostly those in Periods 1 and 2 on the periodic table.

#### A cathode active material\*

One way of reducing the weight of a battery is to utilize ambient O<sub>2</sub> into

	Ac	ath	ode					antly s					16
	ma	ateri	ial							He		0	
		ous C m l as cat			D	С	Ν	0	F	Ne	2		
					Al	Si	Ρ	S	Cl	Ar			
e	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
u	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Хе			
s	lr	Pt	Au	Hg	τι	Pb	Bi	Po	At	Rn			
s	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og			
			_					_	_				
η	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
u	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				



#### Message from Yamazaki

As many of you might know, the colors of fireworks are produced by the flame reaction. Only four coloring agents, i.e., Na (for yellow), Sr (for red), Ba (for green) and Cu (for blue), are currently used because of cost and safety reasons. Various types of colors and intensity of fireworks are created by changing the combination of these agents. Metallic particles, such as Mg, Al, and Ti, are used to produce visual effects. By using a mixture of these particles, attractive features are provided to the appearance of fireworks, such as moment sparkles and slowly scattering light, among others. My specialty is gintenmetsu (flickering silver) fireworks, the outermost light shown in the picture. It is difficult to make all the light disappear simultaneously. I selected No.10 shells, which produce large and radial fireworks, and meticulously examined

various combinations of Mg and Al as well as "star" (light emitting ball) production processes. These long processes of trial and error have paid off. The completed product won the Prime Minister's Award, the highest honor in the fireworks industry. I will continue to pursue ideal fireworks by modifying the traditional methods developed by my predecessors.

#### Message from Matsunaga

Cutting edge scientific research has been continuously developing fireworks technology. For example, rocket technology has been used to minimize the amount of unburned material falling to the ground after launch.

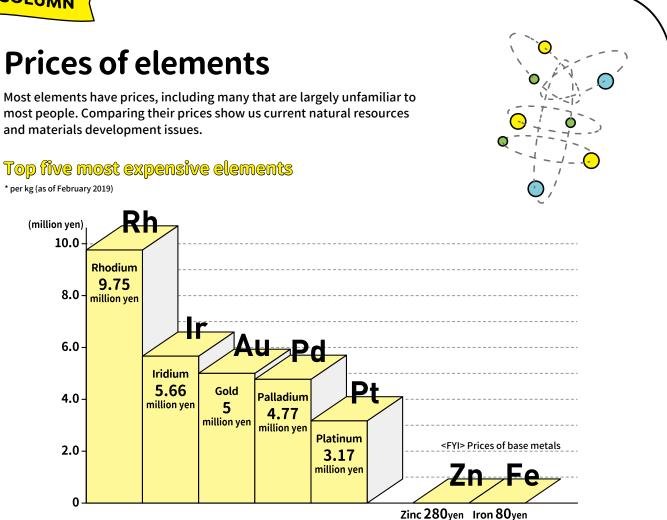
COLUMN

## **Prices of elements**

and materials development issues.

#### Top five most expensive elements

\* per kg (as of February 2019)



survey data from the Sustainability Design Institute

The prices of elements are generally determined by demand and supply. Accordingly, elements that are high in demand but scarce, costly to mine or difficult to extract and purify from compounds are expensive, and their prices increase as these supply issues intensify.

The top five elements (based on price per kg) are all metallic elements that are categorized as "noble metals" or "minor metals." Global demand for these

elements is increasing because they possess valuable properties that can be used to enhance industrial products. For example, adding trace amounts of these elements can dramatically increase the performance of materials produced. However, they tend to be pricey due to their rarity and because only a few countries produce/supply them. For instance, Rh is a vital catalytic material

used to clean automobile exhaust gases. Demand for Rh has steadily increased in parallel with the increasing automobile production despite the fact that 80% of Rh is supplied by a single nation: South Africa. These factors and the lack of substitutions to Rh have caused it to become very expensive.

To resolve these issues, materials researchers and developers are expediting efforts to replace minor metals



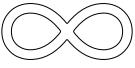
The price differences between the top five most expensive elements and other elements is huge. For example, the prices of the top five elements are three orders of magnitude higher than those of Zn and Fe, abundant base metal elements of great industrial value

> with inexpensive and easily accessible elements. For example, NIMS has succeeded in creating powerful magnets for electric vehicle motors without using the minor metal dysprosium (Dy). Strengthening research to explore the potential abilities of materials has become important to conserve limited natural resources and sustain social development.

													He
								в	С	Ν	0	F	Ne
								Al	Si	Ρ	S	Cl	Ar
۷	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Nb	Мо	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	T	Xe
Та	W	Re	0s	In	Pt	Au	Hg	тι	Pb	Bi	Po	At	Rn
Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Мc	Lv	Ts	Og
Pr	Nd	Pm	Sm	Eu	Gd	Тb	Dy	Ho	Er	Tm	Yb	Lu	
Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

minor metals and noble metals are indicated in blue and yellow, respectively. Although both groups represent scarce elements, their classification criteria are different. Noble metals are generally resistant to corrosion while minor metals have industrial importance. Therefore, some elements belong to both groups. In addition, rare metals belonging to Group 3 on the periodic table are called rare-earth elements (orange)

#### The possibilities of Material Science

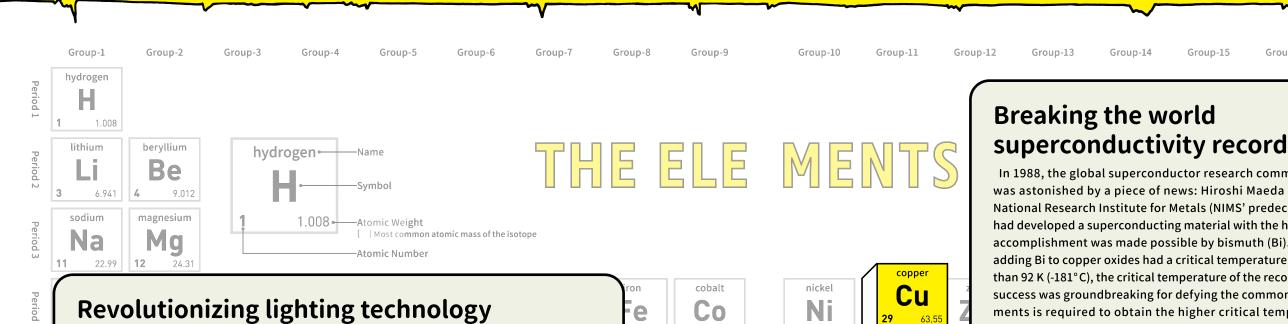






## **\** Elements that have changed the world **/**

**Elements have world-changing power.** Here are some stories about individual chemical elements that have driven amazing scientific discoveries.



When the first white LEDs (light-emitting diode) appeared on the market,

the light they generated had a bluish hue, noticeably differing from natural

white light. This blue shade was attributed to the use of blue LED chips cov-

ered with yellow phosphors to emit white light. Although a red light compo-

nent needed to be added for natural white light to be emitted, scientists had

been unable to create a red phosphor.

55.85

nium

U

ium

S

101.1

190.2

27

45

77

58.93

102.9

192.2

rhodium

Rh

iridium

Ir

28

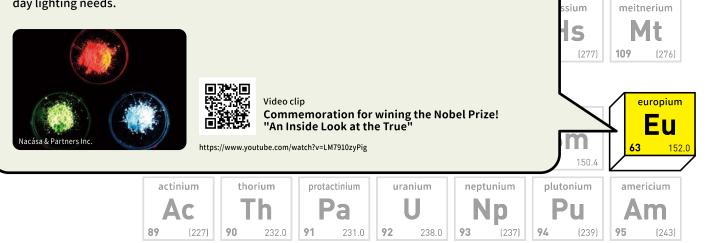
78

58.69

palladium

Pd

Europium (Eu) resulted in a breakthrough. Naoto Hirosaki at NIMS succeeded in producing a red light emitting phosphor by adding Eu to a SiAlON ceramic. Finally, LEDs capable of emitting warm white light were developed. Eu continues to be indispensable today in fulfilling our everyday lighting needs.



## Uncovering hidden properties of alminium (AI)

Al is a lightweight metal, but its low strength has limited its usage. However, by adding small amounts of other chemical elements, Al has been reinforced sufficiently to enable it to serve even as an aircraft fuselage material. The Al-based alloy known today as "duralumin" was discovered in Germany in 1906.

The addition of approximately 4% copper (Cu) most significantly changed the properties of Al. Duraluminwhich contains Cu and trace amounts of other chemical elements—is hugely light and practically as strong as steel. With these advantageous characteristics, duralumin has been used in a wide range of products.

Group-15

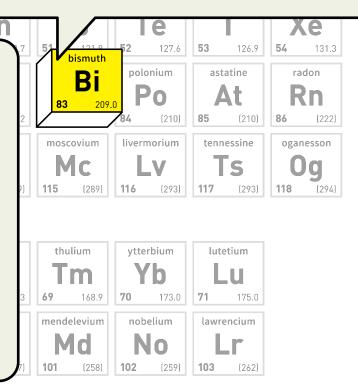
Group-16

Group-17

Group-18

In 1988, the global superconductor research community was astonished by a piece of news: Hiroshi Maeda of the National Research Institute for Metals (NIMS' predecessor)

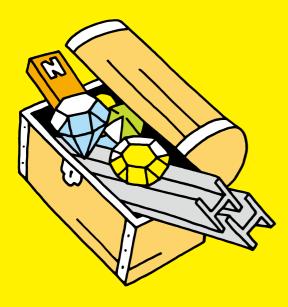
had developed a superconducting material with the highest ever critical temperature. This accomplishment was made possible by bismuth (Bi). The material Maeda synthesized by adding Bi to copper oxides had a critical temperature of 110 K (-163 °C), significantly higher than 92 K (-181°C), the critical temperature of the record holder at the time. In addition, this success was groundbreaking for defying the common belief that the use of rare earth elements is required to obtain the higher critical temperatures of superconductors. This superconducting material was later integrated into nuclear magnetic resonance (NMR) systems by NIMS researchers, resulting in the generation of extremely strong magnetic fields.













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