Impact Objectives

- Establish basic theory for mixed anion compounds
- Create new functionalities, discovering and developing the roots of chemical and physical functions that will meet the needs of future society
- Create new materials and develop material design concepts and methodologies that will lead to practical applications for the future

Advancing mixed anion compounds

An ambitious collaborative effort between 40 research groups across Japan is focused on understanding the complicated properties of mixed anion compounds and applying their data to new and refined technological applications

What is your background and how has that led to your role in this project?

I have a chemistry background, but in the early stages of my career, I was interested in the physical properties of transition metal oxides such as high temperature superconductivity and quantum phenomena in frustrated magnets. After that, I came to believe that what I really wanted to do was to explore new materials and I switched my research focus from condensed matter physics to solid state chemistry. Using a variety of techniques from conventional solid-state reactions to topochemical low-temperature reactions as well as high-pressure reactions, my group in Kyoto prepares various types of inorganic materials, some of which are mixed anion compounds. Luckily for me, several of the mixed anion compounds exhibit exotic chemical and physical properties such as low-temperature hydride (H^-) migration in titanium oxyhydrides and selective heavy metal capturing in titanium phosphide telluride. With these discoveries and those of other researchers, I became convinced that mixed anion compounds can be emerging materials with potential next-generation applications.

Can you give us a little background on this project and explain why we need more research in this area?

We have known about mixed anion compounds for many years and they are even found as minerals. Little attention has been paid to them in the last century. However, several landmark discoveries relating to them have been reported since 2000. These discoveries prompted us to consider that mixed anion compounds should be given more attention in a wide variety of research areas, ranging from chemistry to physics. Another reason is that the guiding principles for the study of mixed anions in terms of synthesis, analysis and function are still undiscovered and most of our knowledge of synthesis, analysis and function has been developed for oxide materials. In many cases, however, these cannot be applied to mixed anion compounds.

What are the key objectives of this project?

In this new area of research, we will create new materials and establish the basic theory of mixed anion compounds, developing material design concepts and methodologies that will lead to practical applications in the future, 10 to 30 years from now. In addition, we will create new functionality, discovering and developing the roots of chemical and physical functions that will meet the needs of society in the next 10 to 30 years. At present, we know only a little about mixed anion systems. There is much more to explore. Three years from now, in year five of the project, I hope that we will have established material design concepts and methodologies as well as new functions.

Have you had any particularly interesting or surprising findings in your investigations so far?

The introduction of H^- ions in barium titanate ($BaTiO_3$), the most well-known functional oxide, induces catalytic activity in terms of ammonia synthesis. Titanium has been regarded as a 'dead' element for ammonia synthesis since titanium nitride (Ti-N) bonding is too strong. It means that the H^- anion in oxides (oxyhydride) has the ability to break the triple bond in the N_2 molecule, the most difficult part of the process in NH_3 synthesis. In other words, the introduction of the H^- in oxides can break the so-called 'scaling rule'. Another important finding is the discovery of H^- size flexibility. Our x-ray diffraction measurement under high pressure revealed that the H^- anion is at least twice as flexible as the oxide anion (O^{2-}). Thus, the H^- anion can be compared to a 'balloon' while the other anions are the 'footballs'. We found that strontium vanadium oxide-hydride ($SrVO_2H$) exhibits novel insulator-to-metal transition under high pressure. ▶

New and sustainable technologies

> *Since my project launched, many researchers, including organic chemists and company workers in Japan, have come to understand what a 'mixed anion compound' is*

Sustainable technologies capable of changing the future of electronic devices, batteries and displays can now be created in the laboratory, thanks to the vast variety of mixed anion compounds available

Japan is a country rich in beauty but poor in natural resources. Unlike countries such as Venezuela, with an estimated £10.82 trillion worth of natural gas, petroleum and iron, Japan has virtually no natural energy resources and consequently is the world's largest importer of coal and liquefied natural gas. This has a huge impact on Japan's worldwide industrial competitiveness. As a result, Japanese researchers are working to develop new, high-performance materials that can be applied to future technologies. Professor Hiroshi Kageyama, a head researcher at the Graduate School of Engineering at Kyoto University, is the project coordinator for a collaboration of 40 leading Japanese research groups that seeks to investigate and develop mixed-anion compounds for new functionalities. Currently, inorganic compounds such as oxides and nitrides, typically binary compounds containing oxygen or nitrides, are base materials that support a wide variety of industry appliances, including electronic devices, batteries, displays and more. Although highly functional, single-oxide and single-nitride compounds are limited in their structural and chemical states because the building blocks (or coordination geometries around a metal) in these compounds are limited.

The group partners are working to expand Japanese industrial development by employing mixed anion compounds or compounds with multiple anions (negatively-charged ions) that expand beyond single-oxide or single-nitride compounds. Currently, scientists do not fully understand the guiding principles for the study of mixed anions and much of the scientific knowledge on their synthesis, analysis and function comes from single-oxide materials. In a five-year-long study, the group aims to create, observe and explore the functionalities of mixed anion compounds in order to expand this knowledge base. With a stronger foundation for the make-up and properties of mixed anion compounds, the team hopes to develop new and advanced materials that can be used in practical applications in the future.

BEYOND SINGLE ANION COMPOUNDS

Until the year 2000, many researchers were not paying much attention to mixed anion compounds. This is due to the fact that the Earth's atmosphere is far more conducive to simpler single-anion compounds such as metal oxides. For example, when elemental iron is heated in the air, iron oxide – or rust – is quickly created. Complex oxides can also be obtained by heating a mixture of binary oxides to high temperatures in a process known as a high-temperature solid-state reaction. The simplicity of this method has allowed a wide range of physicists to work with metal oxides and create a variety of new oxide structures and compositions. 'On the other hand,' Kageyama explains, 'mixed anion compounds cannot generally be prepared in such a facile method as air.' Inevitably, this makes controlling and creating mixed anion compounds far more difficult. However, the benefits that come from working with mixed anion compounds far outweigh the struggle of creating them. Unlike oxides and nitrides that only contain one type of 'building block', that is a singular anion, mixed anion compounds contain a diverse range of anions with different key features, such as valency, ionic radius, electronegativity and polarizability. Like a structure with different toy construction bricks, this variability allows for a wider range of compounds with distinct structures and dimensions.

In order to properly work with mixed anion compounds, Kageyama and his team have divided their study into three subgroups: group 1 for the creation of mixed anion compounds; group 2 for the observation of mixed anions and group 3 for the exploration of innovative functionalities. Group 1, led by Dr Hiraku Ogino from the National Institute of Advanced Industrial Science and Technology, is focused on establishing and synthesising mixed anion compounds using techniques such as high-pressure synthesis, topochemical reaction and solvothermal methods. Additionally, this group is also working to define the rules of anion arrangement through both experimental and theoretical analysis. Group 2, led by Professor Katsuro Hayashi of Kyushu University, is focused primarily on assessing light elements such as hydrogen as a means to deepen their understanding of mixed anion compounds. By combining x-rays and neutron diffraction methods, the team can evaluate the chemical state of hydrogen within the mixed anion compounds and, in doing so, paint a picture of the geometry within these complex compounds. Group 3, led by Professor Kazuhiko Maeda from the Tokyo Institute of Technology, is the final step in applying mixed anion compounds in the real world. The team's primary objective is to generate high-performance energy materials that can both produce and save energy. With these new developments, group 3 hopes to establish usable technologies that are far more diverse than single anion compounds and can sustain our future society.

DISCOVERING MIXED ANION PROPERTIES

A recent paper by Kuriki *et al.*, published in the *Journal of the American Chemical Society* (volume 140, page 6648-6655, 2018) showcases one successful example of extensive collaboration between 40 research groups. This work, involving the five PIs of this project (Associate Professor Kazuhiko Maeda, Dr Kengo Oka, Assistant Professor Kenta Hongo, Dr Ryo Maezono and Kageyama), describes the discovery of an oxyfluoride semiconductor known as pyrochlore ($Pb_2Ti_2O_{5.4}F_{1.2}$), that has an unprecedented small band gap of around 2.4 eV and the ability to act as a stable semiconductor photocatalyst, opening up new opportunities within materials research for heterogeneous photocatalysis with visible light. In February 2018, Kageyama, Hayashi and Maeda co-authored a review in *Nature Communications* (https://www.nature.com/articles/s41467-018-02838-4) outlining the opportunities that have been enabled by recent advances in mixed anion research. He found that the recent increase in interest in solid-based mixed anion compounds can very likely lead to significant contributions to the fields of energy conversion, electronic devices and catalysis.

These findings have come with their own set of challenges. 'One challenge,' describes Kageyama, 'is how to tune anion order/disorder and local coordination. In some cases, multiple anions are completely ordered. In other cases, they are complexly disorganised.' To address this, groups 1, 2 and 3 are working to develop new methods that can tackle this problem and deal with 'correlated disorder' within mixed anion compounds. Additionally, the synthesis of mixed anion compounds is a complicated affair. Thus, the team is focusing on using multiple tools and multistep processes that can provide a more diverse range of platforms on which to manipulate these compounds.

MAKING HEADWAY

The intriguing qualities of mixed anion compounds can be leveraged for a wide variety of applications. However, there is still much to discover about the principles and applications of these chemical structures. 'Most of the researchers are either not familiar with mixed anion materials or they are not aware of mixed anion compounds,' Kageyama states. 'Since my project launched, many researchers, including organic chemists and company workers in Japan, have come to understand what a 'mixed anion compound' is.'

This is key in future technological developments that are both efficient and sustainable. Specifically, in the fields of chemistry and materials science, understanding mixed anion compounds can mean establishing new design concepts and methodologies. This important study harnesses the expertise and collaborative efforts of over 100 researchers both in Japan and abroad and may prove to be the big step forward in uncovering the complicated, yet compelling properties of mixed anion compounds and applying them for future use.

Project Insights

FUNDING

The project was support by funding from the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research on Innovative Areas programme, grant numbers JP16H6438, JP16H6439, JP16H6440 and JP16H6441.

CONTACT

Professor Hiroshi Kageyama
Project Coordinator

T: +81 75383 2506
E: kage@scl.kyoto-u.ac.jp
W: https://www.mixed-anion.jp (the project website), http://www.ehcc.kyoto-u.ac.jp/eh10 (the Kageyama lab in Kyoto)

BIOS

Professor Hiroshi Kageyama graduated from Kyoto University in Japan with a BS in chemistry in 1993 and followed this up with an MS in chemistry in 1995 and PhD in 1998, both also from Kyoto University. He has been awarded a number of prestigious awards and prizes, including the CSJ Award for Creative Work in 2017 and the Japan Society for the Promotion of Science (JSPS) prize in 2014. Kageyama currently serves as Professor at the Graduate School of Engineering, Kyoto University, as well as Adjunct Professor at the Institute for Integrated Cell-Material Sciences at Kyoto University.

Mixed Anion

KYOTO UNIVERSITY FOUNDED 1897 KYOTO JAPAN