Interview with

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Bringing out the "Material Intelligence" with simulation technology - ICSD is capable of accelerating materials development

Mitsui Mining & Smelting Co., Ltd., a world leading company in nonferrous metals. Two members of the Materials Structure & Function Exploration Center were interviewed about how to utilize the ICSD for their research and development of various functional engineered materials.

Developing functional engineered materials with the world's top market-share under the slogan “Taking full advantage of Material Intelligence”

- JAICI: Please tell us about the business area of Mitsui Mining & Smelting Co., Ltd. and technical fields which you are good at.
- Dr. Tabira: Our company is one that has accumulated various technologies and experiences focusing on nonferrous metal materials, based on the mining and smelting business at Kamioka mine during the Meiji era. Under the slogan “Taking full advantage of Material Intelligence” we are developing functional engineered materials business, metal business, automotive parts & components business, and other related businesses.

  The functional engineered materials business is the largest business segment, in which battery materials, catalysts, engineered powders copper foils, thin film materials, ceramics, single crystals, and various functional engineered materials are handled. For example, by using mass-production of ultra-thin metal foils, which have been developed based on core technologies such as “electrolysis and plating” and “solution chemistry”, ultra-thin copper foils used as high-precision circuit boards are produced. This copper foil is an essential material for the miniaturization of mobile phones and occupies about 90% of the world market share. In addition, many of the world's top market-share products, such as catalysts for detoxifying exhaust gas from automobiles and motorcycles., copper powders for electronic equipment, and cerium oxide abrasives have been developed and produced.

Figure 1: A number of functional engineered materials from Mitsui Mining & Smelting Co., Ltd.

- JAICI: Please give an overview of the Materials Structure & Function Exploration Center.
- Dr. Tabira: Materials Structure & Function Exploration Center is a department of the Engineered Materials Sector R&D Center, however, it plays a role as a solution center not only for Engineered Materials Sector R&D Center, but also for solving company-wide issues. There are currently about 20 people engaged in analysis tasks required to respond to development and manufacturing issues. There may be cases where routine analysis are conducted with clear analysis objects, and there may be cases where they work together with the R&D department to study what should be analyzed under new materials development, etc. both of which work as two sides of the same coin and are essential to the development of the company.

Supporting material development through analysis of physical mechanism and responding to change of times and needs

- JAICI: Please tell us which areas the Materials Structure & Function Exploration Center is focusing on.
- Dr. Tabira: There are three areas on which our center is focusing: micro-structural analysis, chemical morphology analysis, and predictive analysis, so-called simulation. In order to produce cutting-edge materials, it is necessary to have technologies that enables us to characterize nano-scale small areas with high accuracy, and an analysis technology to connect the data to a solution.

  In the era when the smelting business was mainstream, the concentration measurement was mainly required for analysis, but with the expansion of the business of functional engineered materials, it became necessary to meet new needs such as structure analysis and morphology analysis. Being able to clearly explain the mechanism of physical properties etc. based on the analysis data also leads to securing customer trust.

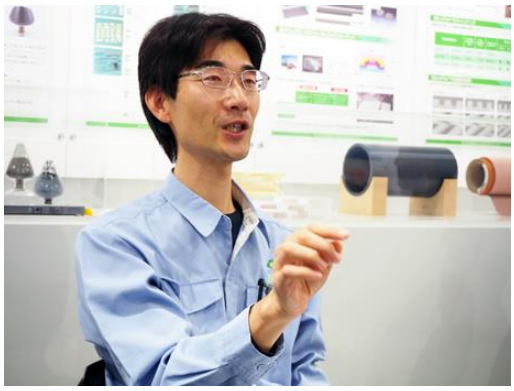
- JAICI: Please tell us how the current system of the center has been formed.
- Dr. Tabira: As an academic researcher at home and abroad, I studied crystal structure analysis, and I joined this company in 2001. At that time, the center's role was mainly identification of compounds by instrumental analysis using scanning electron microscope (SEM) or X-ray diffractometer (XRD), etc., and did not conduct structural analysis. However, after that, in order to meet the increase of the

variation in materials developed and the needs for diverse functional engineered materials, I believed that it was essential to have analysis technology that can explain physical mechanism. Therefore, I proposed to the company the introduction of a system necessary for crystal structure analysis, and decided to change the system to form an analysis center with new functions. It was not easy to get the understanding of the company, since it was necessary to increase technical staff and purchase expensive instruments. However, I was able to get assistance of the people having the same opinion in the material development department who recognized the need to improve analysis technology, so I was able to get the approval from the company. I think such an analysis center was still rare at the time for manufacturers of nonferrous metal materials. At that time, I introduced ICSD to set initial values for Rietveld analysis.

- Dr. Takahashi: I joined this company in 2000 after finishing my graduate university studies. I used to use ICSD since I was a student. But I had to search crystal structures from published materials before Dr. Tabira introduced ICSD, and I remember I was struggling to find the information I wanted. After introducing ICSD, it became possible to perform calculations immediately using the acquired CIF files, and that accelerated my work greatly.

  An opportunity that I started predictive analysis was a development project for cerium oxide abrasives. In our company, we offer various engineered powders by utilizing our abundant know-how accumulated through many years' development and manufacturing and powder control technology, and this cerium oxide abrasive can be used for polishing glass. In the development project, to investigate the chemical state of cerium there was a need for structure analysis by X-ray absorption near edge structure (XANES), and first-principles calculation was necessary for it. After that, the first-principles calculation can be used not only for XANES but also for simulations for material development, and as a result, works of the first-principles calculations have increased. Now simulation accounts for 80% of my work. ICSD is an essential tool for first-principles calculations. Since ICSD covers almost all crystal structures in published papers, it also helps to judge that it would be difficult to make the compound to be studied if it is not registered in ICSD.
- Dr. Tabira: With the progress of research all over the world, we guess that the completeness of the information registered in ICSD has also increased. However, competitors will see the same information, so it will be a key issue how quickly you find something valuable compared to others.

Dr. Tabira



Dr. Takahashi

ICSD is an essential tool for simulation to accelerate materials development

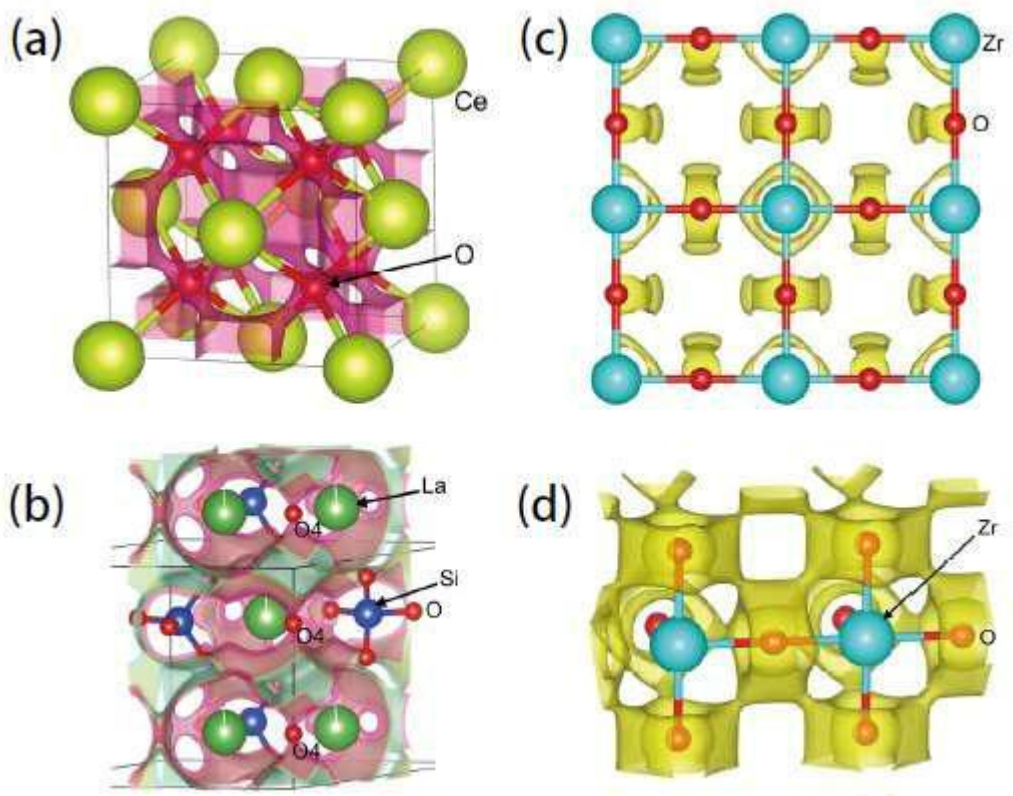
- JAICI: Specifically, in what situations is ICSD utilized?
- Dr. Tabira: ICSD is mainly used by myself and Takahashi. First of all, we use ICSD when we want to know more about analysis data. With respect to problems brought in from the whole company, we first analyze the compounds in order to understand the current situation, but in case where it is difficult to interpret the data thus obtained by the analysis, we use the crystal structure of the target compound in ICSD. For example, in case where properties that are far below the goal are obtained, we interpret the structure information obtained from ICSD in conjunction with the analytical data and find solutions to what and how to change it.

  The other use is simulation. By using crystal structure data obtained from ICSD, we calculate what kind of composition would give the desired physical properties and simulate it, and obtain the ideal state. After that, we search for a model that can explain the current compound state taking into consideration various defects, and then compare that model with the information in ICSD. It is also used to simply evaluate ionic crystals using bond valence sum (BVS) calculations. Bond valence sum is a classical and simple calculation which can predict more quickly than do first-principles calculation. It can give us the possible diffusion paths of oxide ions and lithium ions in crystal structures.
- Dr. Takahashi: Recently, ICSD is also used in the development of apatite-type lanthanum silicate electrolyte. At present, general solid electrolyte-type devices mainly use platinum electrode and yttria stabilized zirconia (YSZ) which is an oxide ion conductor. However, since the device using YSZ requires operating temperature of 600 degrees or more, a device that operates at lower temperature has been

required. Development of high-performance electrode materials and solid electrolytes and improvement of interface formation technology at the joints of these materials were necessary for that. Therefore, we created an oriented apatite solid electrolyte with high oxide ion conductivity using our proprietary manufacturing technology, and developed a solid electrolyte device that has advantage for operation at low and medium temperatures. The conductivity was as high as 10 times that of YSZ at 600 degrees, and 1000 times higher at 300 degrees.

In actual development procedure, we performed first-principles calculations using CIF file obtained from ICSD, and simulated to find which atoms in the crystal structure should be replaced to make diffusion of oxide ions more effective. Then an experimental team did repeated experiments to create trial compounds and evaluated them immediately, and we received their feedbacks on the simulation, and simulated again. By repeating this, we could develop the device efficiently. Finally, we have achieved lower operating temperature range by 200 degrees than the devices using current platinum electrodes and YSZ solid electrolytes.

- Dr. Tabira: The cerium oxide mentioned before by Takahashi is also used as a deoxidizer when packaging medicines and electronic parts, and ICSD was used to understand the mechanism of oxygen absorption. In order to absorb oxygen, a small amount of oxygen has to be removed from the crystal structure in advance, but during the fluorite type structure of cerium oxide is losing one-fourth of oxygen and becomes A-type rare earth structure (La_2O_3 type), structural changes such as an increase in lattice parameters and an ordered arrangement of oxygen vacancies occur depending on the amount of removed oxygen. By simulating in advance XRD patterns of the structures of each crystal phase using ICSD, it was possible to immediately grasp which phase it was or the rough amount of oxygen vacancy deficiency when the sample was actually measured. It helped discussions about reaction efficiency.



(Visualizer software: VESTA)

Figure 2: By importing ICSD CIF file and performing simulation, it is possible to discuss three-dimensional stability and diffusion paths of each ion.

(a) BVS map of oxide ion in cerium oxide,

(b) BVS map of oxide ions in lanthanum silicate,

(c), (d) Potential Energy Surface representing the stability of protons obtained from first principles calculations in $BaZrO_3$

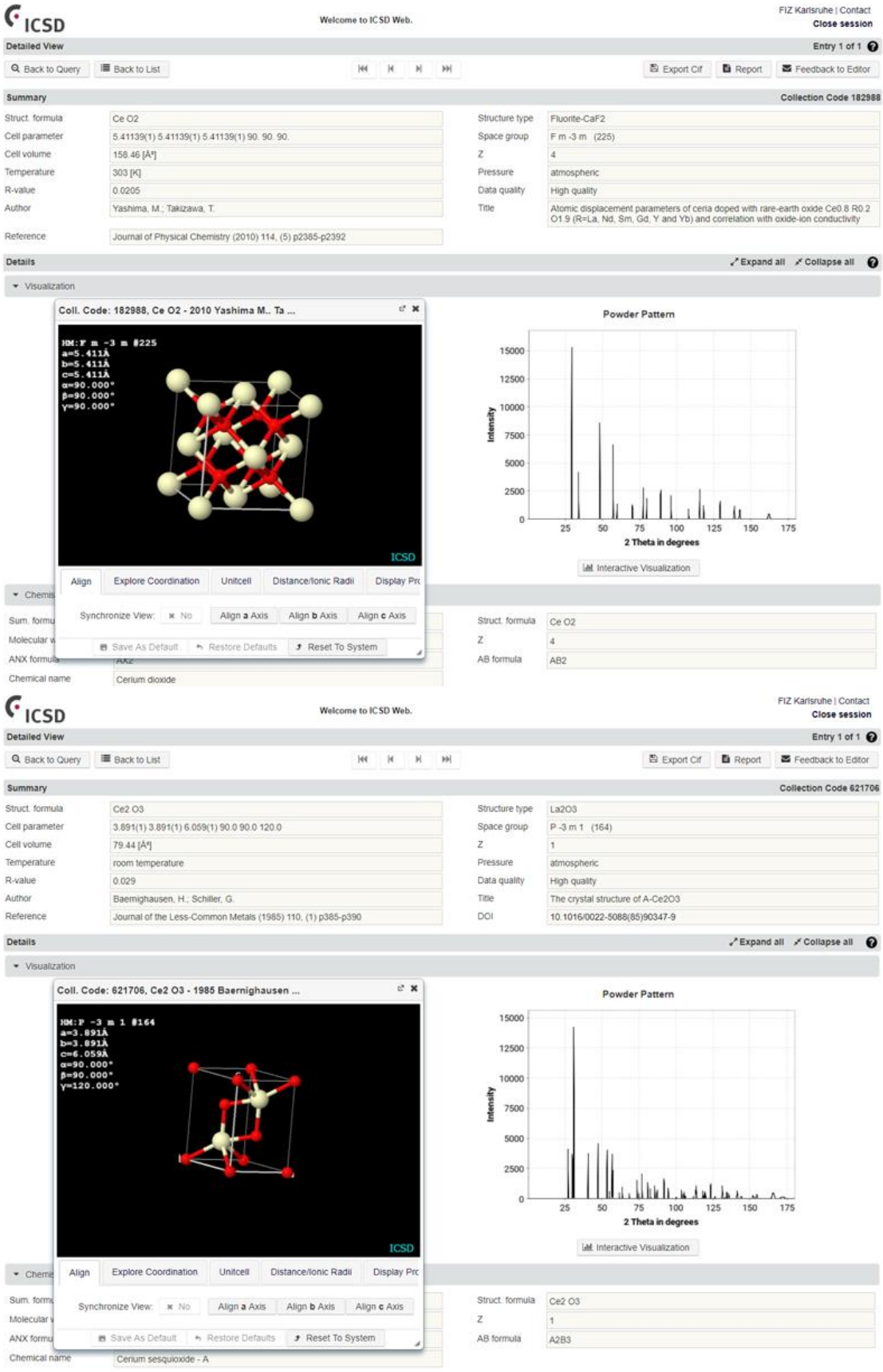


Figure 3: top: Record of CeO_2 (oxidized state); bottom: record of Ce_2O_3 (reduced state):

- JAICI: How do you feel about recent changes regarding analysis levels?
- Dr. Takahashi: When I started simulation, I often conducted calculations "in an exhaustive manner", but for the past five years, there appeared a calculation method using many structures data simultaneously, such as called materials informatics. I think that ICSD is what made it possible to accelerate a large number of simulations.
- Dr. Tabira: In the past, as for the choice of elements, development based on the people's many years' intuition, tips and experience was mainstream. However, simulation and advanced analysis have recently been carried out, and it has become possible to theoretically understand "why the element is good" and it has become possible to propose that "another element that works in the same way is also thus used". That is, modern or scientific intuition is created, and based on that, the experience value rises further. I think that it is related to our slogan "Taking full advantage of Material Intelligence", and it can be said that recent technological development has also evolved the way of utilizing "Intelligence".

- JAICI: Please tell us about your future aspirations.
- Dr. Tabira: Recently, as technology advances, the amount of processed information has increased, and we are now at a stage where many structures can be examined at once. On the other hand, I have concerned that high-speed materials development will be taken for granted. When considering competition all over the world, it will be necessary to enable to acquire integrated information in near future to accelerate the development. At present, we are evaluating structures one by one, and we hope that we will establish the system that can automatically extract points to be focused on by calculation to develop materials more quickly than ever. The points to be focused on are the differentiation point of the development capability of the company.
- Dr. Takahashi: Times are changing rapidly, so that speedup is certainly important. If preparation for calculations becomes easier, we can expect further improvement of the work efficiency.

- JAICI: Thank you for your time with this interview today.

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Established in 1950. Nonferrous metal manufacturer of Mitsui group with 12 major bases in Japan and 31 major bases in the world. Using “Taking full advantage of Material intelligence” as a research & development slogan, and developing functional engineered materials business, metals business, automotive parts & components business, engineering services of various industrial plants, production and sales of robot cable production, and IT systems, perlite related business. Ultra-thin copper foil, catalysts, copper powder, and cerium oxide abrasives have the top market share in the world (investigated by Mitsui Mining & Smelting, 2017).

Web site
https://www.mitsui-kinzoku.co.jp/