Academic Program [Oral A] | 07. Inorganic Chemistry：Oral A

Wed. Mar 26, 2025 1:00 PM - 3:40 PM JST | Wed. Mar 26, 2025 4:00 AM - 6:40 AM UTC
[C]C303(C303, Bldg. 2, Area 2 [3F])

[[C]C303-1pm] 07. Inorganic Chemistry

Chair: Ryota Shimizu, Naoki Tarutani

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[[C]C303-1pm-01]

The Effect of Halide Ions on the ^{211}At Flow Electrolytic Labeling Reaction

〇Akina Mitsukai[1], Yoshinobu Shirakami[2], Masashi Murakami[2], Kazuki Kajiyama[3], Atsushi Toyoshima[2] (1. Graduate school of Osaka Univ., 2. Institute for Radiation Sciences, 3. Osaka Univ.)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[[C]C303-1pm-02]

Solid-liquid extraction of group 2 elements with DGA-resin towards the chemical study of element 102, nobelium

〇Enni Khult[1,2], Masashi Kaneko[1], Hiroyuki Kazama[1], Ruilin Wang[1,2], Kyosuke Shibamoto[1,2], Miyu Konno[1,2], Yudai Itakura[1,2], Ryota Kikuchi[1], Kenta Mori[1], Kazushi Kawamoto[1], Hiromitsu Haba[2], Akihiro Nambu[2], Koichi Takamiya[3], Makoto Inagaki[3], Yoshitaka Kasamatsu[1,2] (1. Osaka University, 2. RIKEN, 3. KURNS)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[[C]C303-1pm-03]

Quantum chemical calculation on the electronic state dependence of the decay pass of Th-229m

〇Ryoutarou Masuda[1,2], Masashi Kaneko[1], Hiroyuki Kazama[1], Yuki Yasuda[1], Hashiba So[1,2], Yudai Shigekawa[2], Tomoya Naito[2,3], Yuki Miyamoto[4], Kouji Yoshimura[4], Atushi Shinohara[5], Yoshitaka Kasamatsu[1,2] (1. Osaka Univ, 2. RIKEN, 3. Tokyo Univ, 4. Okayama Univ, 5. Osaka Aoyama Univ)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[[C]C303-1pm-04]

The emergence of tetragonal structure and reentrant transition in tensile-strained $Bi_2(La_{1-x}Bi_x)O_4Cl$ solid solution

〇Daichi Kato[1], Artem Gabov[1], Takamasa Tsukamoto[2], Matsuzaki Yosuke [1], Naoji Kakudou[1], Akinori Saeki[3], Hajime Suzuki[1], Ryu Abe, Koji Fujita, Smagul Zh Karazhanov[4], Hiroshi Kageyama (1. Kyoto Univ., 2. The Univ. of Tokyo, 3. Osaka Univ., 4. Institute for Energy Technology)

Japanese
1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC
[[C]C303-1pm-05]

Chemical synthesis of $SnS_{0.9}Se_{0.1}$:Na,Ag nanoparticles and evaluation of thermoelectric properties of sintered pellets

○Itsuki Minowa[1], Simon Moore[1], Mari Takahashi[1], Shinya Maenosono[1] (1. JAIST)

1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC

Break

🏷 English

2:00 PM - 2:10 PM JST | 5:00 AM - 5:10 AM UTC

[[C]C303-1pm-06]

Polar functionalities based on ion conduction of a nonpolar metal cyanide complex

○Yuxin Shi[1], Ryo Ohtani[1], Masaaki Ohba[1] (1. Kyushu University)

🏷 Japanese

2:10 PM - 2:20 PM JST | 5:10 AM - 5:20 AM UTC

[[C]C303-1pm-07]

Novel electronic orbital states in ilmenite-type $CuVO_3$

○Hajime Yamamoto[1], Keigo Ochi[1], Takuya Aoyama[1,2], Kenya Ohgushi[1], Kenji Ishii[3], Daiju Matsumura[4], Takuya Tsuji[4], Tadashi Abukawa[1] (1. Tohoku University, 2. Hiroshima University, 3. QST, 4. JAEA)

🏷 English

2:20 PM - 2:30 PM JST | 5:20 AM - 5:30 AM UTC

[[C]C303-1pm-08]

Control of physical properties of $LaMnO_3$ thin films by hydrogen ion beam irradiation

○Shuhei Iwashita[1], Mitsuhiko Maesato[1], Susumu Hirata[1], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci. Kyoto Univ.)

🏷 Japanese

2:30 PM - 2:40 PM JST | 5:30 AM - 5:40 AM UTC

[[C]C303-1pm-09]

Electron-Phonon Coupling in Palladium Oxide

Yuta Nishikawa[1], Akihisa Ishikawa[1], ○Wataru Ota[1], Tohru Sato[1] (1. Kyoto Univ.)

🏷 English

2:40 PM - 2:50 PM JST | 5:40 AM - 5:50 AM UTC

[[C]C303-1pm-10]

Hydrogen doping into Sr_2IrO_4 under epitaxial strain

○Susumu Hirata[1], Mitsuhiko Maesato[1], Akira Chikamatsu[2], Hiroshi Kitagawa[1] (1. Grad. Sch. of Sci., Kyoto Univ., 2. Grad. Sch. of Sci., Ochanomizu Univ.)

2:50 PM - 3:00 PM JST | 5:50 AM - 6:00 AM UTC

Break

🏷 Japanese

3:00 PM - 3:10 PM JST | 6:00 AM - 6:10 AM UTC

[[C]C303-1pm-11]

Hydrogen doping of layered perovskite-type cuprates

○Masaki Wada[1], Mitsuhiko Maesato[2], Hiroshi Kitagawa[2], Susumu Hirata[2], Shuhei Iwashita[2] (1. Fac. of Sci. Kyoto Univ., 2. Grad. Sch. of Sci. Kyoto Univ.)

🏷 Japanese

3:10 PM - 3:20 PM JST | 6:10 AM - 6:20 AM UTC

[[C]C303-1pm-12]

Size-controlled direct preparation of granular titanosilicates with organic acids and evaluation of Sr adsorption performance

○Ryohei Tanimoto[1], Masatoshi Onuki[1], Naoki Asao[1] (1. Graduate School of Science and Technology, Shinshu University)

🏷 Japanese

3:20 PM - 3:30 PM JST | 6:20 AM - 6:30 AM UTC

[[C]C303-1pm-13]

Precise design of nano-porous $BaTiO_3$ thin films

○Norihiro Suzuki[1] (1. Tokyo Denki University)

🏷 Japanese

3:30 PM - 3:40 PM JST | 6:30 AM - 6:40 AM UTC

[[C]C303-1pm-14]

Pb substitution effect on electronic state and local structure of $Sr_{2.5}Bi_{0.5}NiO_5$

○Kenta Natsui[1], Hideyuki Kawasoko[1,2], Soichi Kikkawa[1], Kana Nishimura[3], Tomoteru Fukumura[3], Seiji Yamazoe[1] (1. Faculty of Science, Tokyo Metropolitan University, 2. JST-PRESTO, 3. Faculty of Science, Tohoku University)

^{211}At フロー電解標識反応におけるハロゲン化物イオンの影響

（阪大院理[1]・阪大機構[2]・阪大理[3]）○水飼 秋菜[1]・白神 宜史[2]・村上 昌史[2]・梶山 和希[3]・豊嶋 厚史[2]

Effect of Addition of Halide Ions on the ^{211}At Labeling by Flow Electrolytic method

([1]*Graduate School of Science, Osaka University*, [2]*Institute for Radiation Science, Osaka University,* [3]*School of Science, Osaka Unievrsity*) ○Akina Mitsukai[1], Yoshinobu Shirakami[2], Masashi Murakami[2], Kazuki Kajiyama[3], Atsushi Toyoshima[2]

^{211}At, with a half-life of 7.2 hours and alpha particle emission, attracts attention for its potential in Targeted Alpha Therapy (TAT) because of its high therapeutic effect against intractable advanced cancer. Molecularly targeted drugs are synthesized by labeling ^{211}At to low- and medium-molecular-weight compounds such as amino acids. However, there are still problems to be addressed such as long-term stability and limitations in liquid phase1). In this study, we focused on flow electrochemical method for labeling ^{211}At that proceeds at room temperature and avoid the use of harmful leaving groups or redox reagents.2)

To apply this method to pharmaceuticals, we employed an aqueous solution of 833 mM sodium bicarbonate as the electrolyte. Using the flow electrolysis, ^{211}At was electrolytically oxidized to reactive chemical species, which was then labeled to 3-iodo-L-tyrosine and 3-iodo-4-o-methyl-L-tyrosine by an exchange reaction between At and I. The results revealed that the labeling rate was enhanced by the addition of halide ions (Cl^-, Br^-, and I^-) coexisting with ^{211}At.

Keywords : Astatine; Electrochemistry; Iodotyrosine; Targeted Alpha Therapy; Molecular target drug

半減期 7.2 時間でアルファ線を放出する ^{211}At は、加速器での国内製造が可能であり、難治性進行がんに高い治療効果を示すことからアルファ線核医学治療薬の核種として注目を集めている。その一方で ^{211}At をアミノ酸などの低分子や中分子に標識して薬剤を合成する上では、前駆体の選択制や液性に制限があるなど課題が残されている1)。本研究では、常温で反応が進行し、有害な脱離基、酸化還元剤を使用せず多様な前駆体に適用可能な ^{211}At 標識法としてフロー電解標識法2)の開発を進めている。

薬剤への適用を目指し、弱塩基性である 833 mM 炭酸水素ナトリウム水溶液を電解質とし、フロー電解法により ^{211}At を電解酸化させて反応活性な化学種へと変化させ、At と I の交換反応によりヨードチロシン誘導体である 3-ヨード-L-チロシン及び 3-ヨード-4-o-メチル-L-チロシンの標識を行った。その結果、^{211}At と共存するハロゲン化物イオン（Cl^-, Br^-, I^-）によって標識率が向上することが分かった。

1) Synthesis of [^{211}At]4-astato-L-phenylalanine by dihydroxyboryl-astatine substitution reaction in aqueous solution has been reported. Y. Shirakami, T. Watabe, T. Toyoshima *et al*, *Sci. Chem.*, **2021**, *11*, 12982.

2) Oxidation of Element 102, Nobelium, with Flow Electrolytic Column Chromatography on an Atom-at-a-Time Scale has been reported. A. Toyoshima, Y. Kasamatsu, Y. Nagame *et al*, *J. Am. Chem.* **2009**, *131*, 9180

Solid-liquid extraction of group 2 elements with DGA-resin towards the chemical study of element 102, nobelium

([1]*Osaka University*, [2]*RIKEN,* [3]*KURNS*) ○Enni Khult[1,2], Masashi Kaneko[1], Hiroyuki Kazama[1], Ruilin Wang[1,2], Kyosuke Shibamoto[1,2], Miyu Konno[1,2], Yudai Itakura[1,2], Ryota Kikuchi[1], Kenta Mori[1], Kazushi Kawamoto[1], Hiromitsu Haba[2], Akihiro Nambu[2], Koichi Takamiya[3], Makoto Inagaki[3], Yoshitaka Kasamatsu[1,2]

Keywords: *nobelium, superheavy elements, DGA, solid-liquid extraction, DFT*

Elements with Z>100 are synthesized in nuclear fusion reactions, have short half-lives, and are available only as single atoms at a time. For this reason, rapid and automated chemical experiments utilizing partition methods are required. These studies, referred to as "online experiments", are conducted at accelerator facilities using the nuclear reaction products.

Nobelium (No), the element with *Z*=102, is an actinide with unique chemical properties. No exhibits a +2 oxidation state in aqueous solutions and its chemical behavior resembles that of group 2 elements, with an ionic radius intermediate between Ca^{2+} and Sr^{2+}. However, No^{2+} may have a softer acidic nature, contrasting with the hard acid characteristics of group 2 metal ions.[1] Further research is necessary to understand the chemical properties of No, which may be influenced by relativistic effects.

For a systematic chemical study of No, we propose extraction with diglycolamide (DGA) ligands, which allow for various structural modifications to tune extraction properties. In this work, we focused on studying the extraction of group 2 elements from nitric acid by TODGA-resin. The dependence of the weight distribution ratios K_d of Ca(II), Sr(II), and Ba(II) on the extraction system composition was studied to confirm the mechanism of the extraction. Experiments with Sr(II) and Ba(II) radiotracers were conducted to check the applicability of the extraction system to the online experiments with ^{255}No, which was then evaluated under the online experiment conditions. Finally, relativistic DFT calculations of the extracted M(II)-DGA complexes were performed to predict and explain the extraction behavior of No.

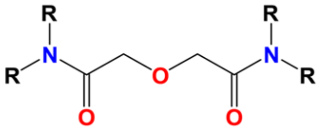


Figure 1. Diglycolamides (DGA). TODGA: R = n-octyl.

1) E. Watanabe, *PhD Diss., Osaka University* **2022**.

Th-229mの壊変機構の電子状態依存性に関する量子化学計算

（大阪大学[1]・理化学研究所[2]・東京大学[3]・岡山大学[4]・大阪青山大学[5]）○益田 遼太郎[1, 2]・金子 政志[1]・風間 裕之[1]・安田勇輝[1]・橋場奏[1,2]・重河優大[2]・内藤智也[2,3]・宮本祐樹[4]・吉村浩司[4]・篠原厚[5]・笠松良崇[1,2]

Quantum chemical calculation on the electronic state dependence of the decay pass of Th-229m

([1]*Osaka University*, [2]*RIKEN,* [3]*Tokyo University,* [4]*Okayama University,* [5]*Osaka Aoyama University*) Ryoutarou Masuda[1,2], Masashi Kaneko[1], Hiroyuki Kazama[1], Yuki Yasuda[1], So Hashiba[1,2], Yudai Shigekawa[2], Tomoya Naito[2,3], Yuki Miyamoto[4],Koji Yoshimura[4], Atsushi Shinohara[5], Yoshitaka Kasamatsu[1,2]

Th-229m is the first excited state of Th-229 with a reported excitation energy of 8.4 eV [1]. This energy is comparable to the binding energy of outermost electrons. Therefour, the half-life and decay pathways of Th-229m depends on its chemical state. The decay pathways of Th-229m are thought to involve competition between internal conversion, gamma-ray transition, and electronic bridge transitions. Gamma-ray transition has been observed; however, the reported values are not equivalent between each chemical state of Th-229m. The chemical state of Th in these studies remains unclear. We utilize quantum chemical calculations to analyze the electronic states of Th in various samples and evaluate the influence of changes in Th's electronic states on its decay properties. The calculations were performed using structural optimization via solid-state DFT calculations under periodic boundary conditions with Quantum ESPRESSO and single-point calculations considering spin-orbit interactions in isolated systems using ADF. As a result, the possibility of IC or EB was suggested for the samples in which a short half-life was observed.

Keywords：Nuclear; Nuclear Clock; Quantum Chemical Calculation; Decay Path; Th-229

Th-229mはTh-229の第一励起核であり、その励起エネルギーは8.4 eVと報告されている[1]。このエネルギーは最外殻電子の結合エネルギーと同程度であるため、化学状態によって壊変経路が変化する。Th-229mの壊変経路は内部転換（IC）とγ線遷移、電子架橋遷移（EB）が競合すると考えられている。γ線遷移は、イオントラップ法[2]や結晶へのTh-229mをドープ[1]によるThイオンを通じて観測された。これらの測定値は一致しておらず、その上Thの化学状態は明らかではない。そこで本研究では、量子化学計算を用いて各実験（イオントラップ法やCaF_2, MgF_2, $LiSrAlF_6$中にドープした場合）のThの電子状態を計算し、Thの電子状態の差異が壊変に与える影響を評価した。

計算はQuantum Espresso（QE）を用いた周期境界条件を考慮した固体のDFT計算による構造最適化とQEで得られた構造を基にADFを用いたスピン軌道相互作用を考慮した孤立系のDFT計算による一点計算を行った。

結果として、実際に短い半減期が観測された試料に対してはICやEBの可能性が示された。

[1] R. Elwell *et al*., Phys. Rev. Lett. **133**, 013201 (2024). [2] A. Yamaguchi *et al*., Nature **629**, 62 (2024).

$Bi_2(La_{1-x}Bi_x)O_4Cl$ 固溶体における正方晶構造の出現とリエントラント転移

（京大院工 [1]・東大 [2]・阪大 [3]・Institute for Energy Technology[4]）○加藤 大地 [1]、Artem Gabov[1]、塚本 孝政 [2]、松崎 洋介 [1]、覚道 直治 [1]、佐伯 昭紀 [3]、鈴木 肇 [1]、阿部 竜 [1]、藤田 晃司 [1]、Smagul Karazhanov[4]、陰山 洋 [1]

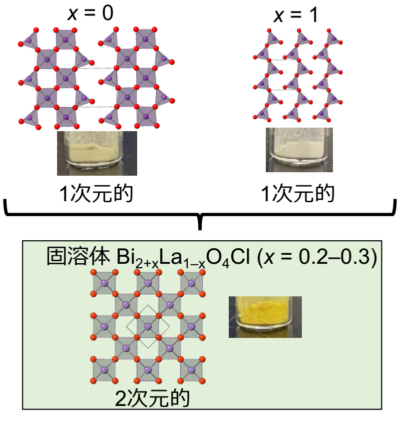
Tetragonal phase in $Bi_2(La_{1-x}Bi_x)O_4Cl$ solid solutionand its re-entrant phase transition

(Kyoto University[1], The University of Tokyo[2], Osaka University[3], Institute for Energy Technology[4]) ○Daichi Kato[1], Artem Gabov[1], Takamasa Tsukamoto[2], Yosuke Matsuzaki[1], Naoji Kakudo[1], Akinori Saeki[3], Hajime Suzuki[1], Ryu Abe[1], Koji Fujita[1], Smagul Karazhanov[4], Hiroshi Kageyama[1]

Manipulating chemical bonds in solids is key to achieving desirable properties. We recently found that replacing Y^{3+} in Bi_2MO_4Cl (with triple-fluorite slabs) with larger cations (La^{3+}, Bi^{3+}) induces tensile strain in the Bi-O square net, causing Bi-O bond cleavage to form double- and single-chain structures. Here, we synthesized a solid solution $Bi_2(La_{1-x}Bi_x)O_4Cl$ with nearly uniform tensile strain, revealing a high symmetry tetragonal (T) phase appear intermediate composition despite the end phase is low-symmetry monoclinic phase. The T phase exhibits a reentrant transition via the single-chain phase to a high-temperature T' phase. This study highlights tensile strain's role in phase competition and its potential for designing functional materials like photocatalysts.

Keywords : Mixed-anion compounds; Photocatalysts; Structural Chemistry; Solid state chemistry

固体内の化学結合の性質を理解しそれを制御することは、物性の制御において非常に重要である。本研究では、トリプル蛍石層を持つ酸ハロゲン化物の固溶体 $Bi_2(La_{1-x}Bi_x)O_4Cl$ を合成した [1)]。$x = 0, 1$ の組成が、Bi-O 結合の開裂により対称性の低い monoclinic 構造で 1 次元的な Bi-O ネットワークを有している一方、中間の組成（$0.15 \le x \le 0.35$）では対称性の高い tetragonal 相（T 相）を持つ二次元ネットワーク構造が出現するユニークな挙動を見出した。T 相は高い対称性に由来して、$x = 0, 1$ よりも小さいバンドギャップを有していた。また、T 相は昇温により monoclinic 相を介して再び高温で tetragonal（T'）相となるリエントラントな相転移を示した。Bi_2MO_4Cl は光触媒材料として注目されており、本研究は光触媒を含む蛍石相を含む物質の物性制御に新たな知見をもたらすと期待される。



1). Gabov, A.; Kato, D.; Tsukamoto, T.; Matsuzaki, Y.; Kakudou, N.; Saeki, A.; Suzuki, H.; Abe, R.; Fujita, K.; Karazhanov, S. Z.; Kageyama, H. Emergence of Tetragonal Phase and Reentrant Transition in Tensile-Strained $Bi_2(La_{1-x}Bi_x)O_4Cl$ Solid Solution. *Chem. Mater.* **2025**, 37 (1), 453-462.

Chemical synthesis of SnS$_{0.9}$Se$_{0.1}$:Na,Ag nanoparticles and evaluation of thermoelectric properties of sintered pellets

(*School of Materials Science, JAIST*) ○Itsuki Minowa, Simon Moore, Mari Takahashi, Shinya Maenosono

Keywords: Thermoelectric materials; Nanoparticles; Sulfide; Doping; Sustainable materials

Tin monosulfide (SnS) is attracting much attention as eco-friendly and low-cost thermoelectric materials due to nontoxic and abundant elements. Unfortunately, in general, dimensionless figure of merit ZT ($ZT = \sigma S^2 T/\kappa$; σ, S, κ, are the electrical conductivity, Seebeck coefficient and thermal conductivity, respectively) of SnS is quite low due to low carrier concentration. However, this can be improved by controlling the nanostructured defect and impurity doping, and we have succeeded in significantly enhancing the ZT value by sintering chemically-synthesized Ag and Se co-doped SnS nanoparticles (NPs).1) On the other hand, alkali metals are the most common p-type dopant for tin monochalcogenides. Zhou *et al.* fabricated Na-doped SnS pellets using a hot-melting method and reported an increase in carrier concentration from 8×10^{17} cm^{-3} to 2×10^{19} cm^{-3}.2)

In this presentation, we report the synthesis method of Ag, Na and Se co-doped SnS NPs and the evaluation of thermoelectric properties of their sintered pellets. SnS$_{0.9}$Se$_{0.1}$:Na,Ag NPs were synthesized by a hot injection method and sintered by hot press. **Fig. 1a** shows the TEM image of the as-synthesized NPs. As can be seen from the TEM image, the NPs are nearly spherical in shape, and the atomic concentrations of Sn, S, Se, Na, and Ag in the NPs were measured to be 51.8, 41.4, 5.2, 0.8, and 0.8 at%, respectively, by SEM-EDS. XRD patterns of NPs and pellet are shown in **Fig. 1b**. The XRD peaks of the NPs and pellet correspond well to the cubic and orthorhombic phases of SnS, respectively, indicating that a phase transition from the cubic to the orthorhombic phase occurs during sintering.

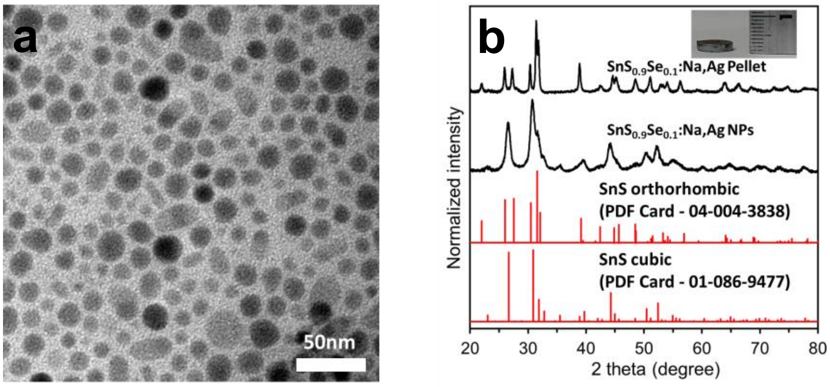


Fig. 1. (a) TEM image of SnS$_{0.9}$Se$_{0.1}$:Na, Ag NPs, (b) XRD patterns of NPs and pellet. Inset is a photo of the pellet.

1) Kobayashi, K. *et al*., *ACS Appl. Energy Mater*. (2024), **7**, 4484. 2) Zhou, B. *et al*., *ACS Appl. Mater. Interfaces* (2017), **9**, 34033.

Polar functionalities based on ion conduction of a nonpolar metal cyanide complex

([1] *Graduate School of Chemistry, Kyushu University*) ○Yuxin Shi[1], Benjamin Le Ouay[1], Ryo Ohtani[1], Masaaki Ohba[1]

Keywords: Ferroelectricity; Ionic Conductivity; Cyanide Metal Complexes; Polarity

Traditional ferroelectricity arises from spontaneous polarization due to symmetry breaking, limiting conventional ferroelectrics to 10 polar point groups. The polarization typically occurs within the lattice, resulting in relatively small and fixed values[1]. Our group previously discovered an exceptional ferroelectric proton conductor, $K_2MnN(CN)_4 \cdot H_2O$, composed of one-dimensional non-centrosymmetric chains that exhibit anomalously large polarization. This was attributed not only to its polar structure but also to proton-biased behavior[2]. Furthermore, it was suggested that long ion displacement in ionic conductors may lead to unconventional ferroelectric polarization[3].

In this study, we synthesized a non-polar ionic conductor, $Na_2MnN(CN)_4 \cdot 3H_2O$, composed of polar chain structures aligned in opposite directions. Thus, this compound crystalized at *C*2/*c* space group with non-polar nature. However, polarization-electric field（PE) measurements revealed a clear ferroelectric hysteresis loop, with a remnant polarization of up to 1850 $\mu C \cdot cm^{-2}$ at 323 K, 0.1 Hz, and 80% relative humidity. Electrochemical impedance spectroscopy (EIS) under direct current bias and positive-up-negative-down (PUND) tests over varied delay times demonstrated retained long-range proton migration. These findings suggest that achieving long-range proton displacement enables ferroelectricity even in non-polar materials, providing a novel mechanism for producing tunable and exceptionally large polarization.

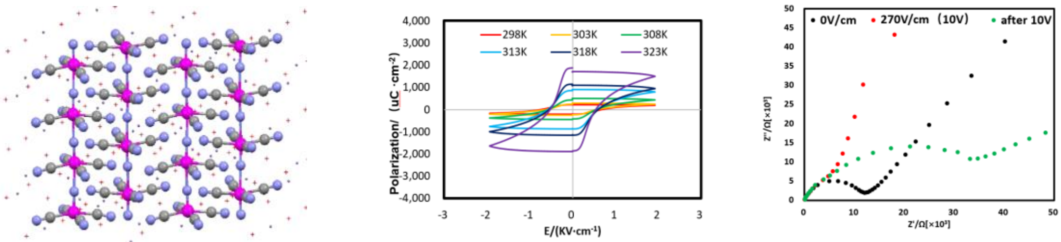


Figure. (Left) Crystal structure of $Na_2MnN(CN)_4 \cdot 3H_2O$.(Middle) *P*-*E* hysteresis loop at different temperature. (Right) Nyquist plots before, during, and after applying DC voltage.

1) Q.Pan,*Chem. Soc. Rev.*, **2024**,*53*, 5781. 2) J. Yanagisawa , *J. Am. Chem. Soc.* **2024** *146* (2), 1476-1483. 3)X.Wang, *J. Phys. Chem. Lett.* **2022**, *13*, 9552–9557

イルメナイト型 $CuVO_3$ の新奇な電子軌道状態

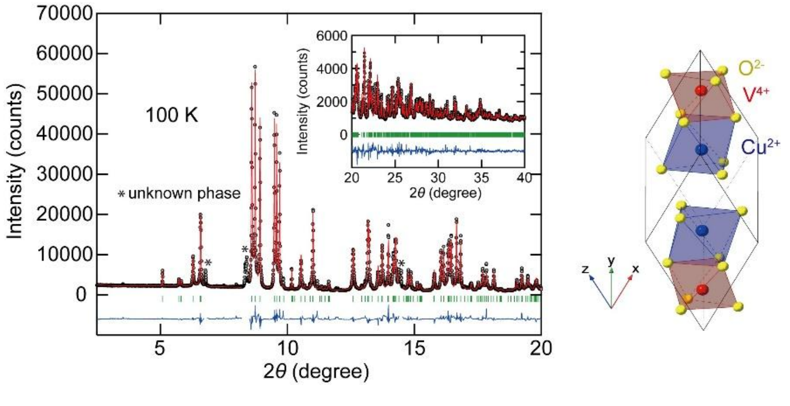
（東北大[1]・広島大[2]・QST[3]・JAEA[2]）○山本 孟[1]・越智 啓伍[1]、青山 拓也[2,1]、大串 研也[1]、石井 賢司[3]、松村 大樹[4]、辻 卓也[4]、虻川 匡司[1]

Novel electronic orbital states in ilmenite-type $CuVO_3$ ([1]*Tohoku University,* [2]*Hiroshima University,* [3]*QST,* [3]*JAEA*) ○Hajime Yamamoto,[1] Keigo Ochi,[1] Takuya Aoyama,[2,1] Kenya Ohgushi,[1] Kenji Ishii,[3] Daiju Matsumura,[4] Takuya Tsuji,[4] Tadashi Abukawa[4]

Most ilmenite-type vanadium oxides, $A^{2+}V^{4+}O_3$ (A = Mg, Mn, Co, Ni, and Zn), exhibit a V-V dimerization phenomenon below 400-550 K, which results from the formation of covalent bonds between the neighboring vanadium ions. Ilmenite-type $CuVO_3$ can also be synthesized under high-pressure (HP) and high-temperature conditions, however, the intrinsic physical properties and electronic states of $CuVO_3$ have not been revealed due to the difficulty in synthesizing high-quality samples caused by oxygen deficiency. In this study, we prepared the high-quality $CuVO_3$ sample using the HP synthesis method and conducted the crystal structure refinement (Figure) and various physical property evaluations. From the results, we discover the 3*d* orbital order and spin-liquid states of the Cu^{2+}, as well as the potential orbital (V-V dimer) liquid state of the V^{4+} in this compound.

Keywords : copper; vanadium; oxide; spin; orbital

多くのイルメナイト型バナジウム酸化物 $A^{2+}V^{4+}O_3$（A = Mg, Mn, Co, Ni, Zn）では、隣接する V イオン間に共有結合が形成されることで、およそ 400-550 K 以下の温度で V－V 二量体の形成が起こる1)。一方で $CuVO_3$ では、酸素欠損に起因した良質な試料の合成の困難さから、本質的な物性や電子状態を評価されていなかった2)。本研究では、超高圧合成法を用いて良質なイルメナイト型 $CuVO_3$ の作製を行い、結晶構造解析（図）と電子状態評価、各種の物性測定を行った。これらの実験から、Cu^{2+}の 3d 電子軌道秩序とスピン液体状態、V^{4+}の軌道液体状態の可能性を発見したので報告する。



1) Hajime Yamamoto, Sachiko Kamiyama, Ikuya Yamada and Hiroyuki Kimura, *Journal of the American Chemical Society*, 2022, 144, 3, 1082-1086.
2) B.L. Chamberland, *Journal of Solid State Chemistry*, 1970, 1, 2, 138-142.

$LaMnO_3$薄膜の水素イオン照射による物性制御

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Control of physical properties of $LaMnO_3$ thin films by hydrogen ion beam irradiation

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$LaMnO_3$ is known to exhibit colossal magnetoresistance (CMR) by hole doping, in which trivalent La^{3+} ions are partially substituted with divalent ions such as Sr^{2+} and Ca^{2+} [1, 2]. However, it is difficult to obtain electron-doped $LaMnO_3$ systems. We have focused on a doping method using hydrogen ion beam irradiation [3]. Hydrogen has the smallest atomic size and can be easily doped into various materials, and ion irradiation at low temperatures makes it possible to implant large amounts of hydrogen while suppressing its desorption. Indeed, high concentrations of hydrogen and electron doping have been achieved in several oxides by this technique [4, 5]. In this study, we report on hydrogen ion beam irradiation of $LaMnO_3$ thin films and its effects on electrical conductivity and magnetic properties.

Keywords : Hydrogen, $LaMnO_3$,

$LaMnO_3$はSrやCaなどの2価イオンをLaと一部置換するホールドープにより、超巨大磁気抵抗を示すことが知られている[1, 2]。しかし$LaMnO_3$系で、電子ドープ系を作製することは困難である。そこで、我々が注目したのが、水素イオンビーム照射によるドーピング手法である[3]。水素は原子サイズが最も小さく、様々な物質に容易にドーピングすることができ、低温でイオン照射を行うことにより、水素の脱離を抑えつつ大量に水素を注入することが可能である。この手法により、いくつかの酸化物において高濃度の水素と電子のドーピングが実現されている[4, 5]。今回我々は、$LaMnO_3$薄膜に対して水素イオンビーム照射を行い、電気伝導性や磁性などへの影響を調べたので報告する。

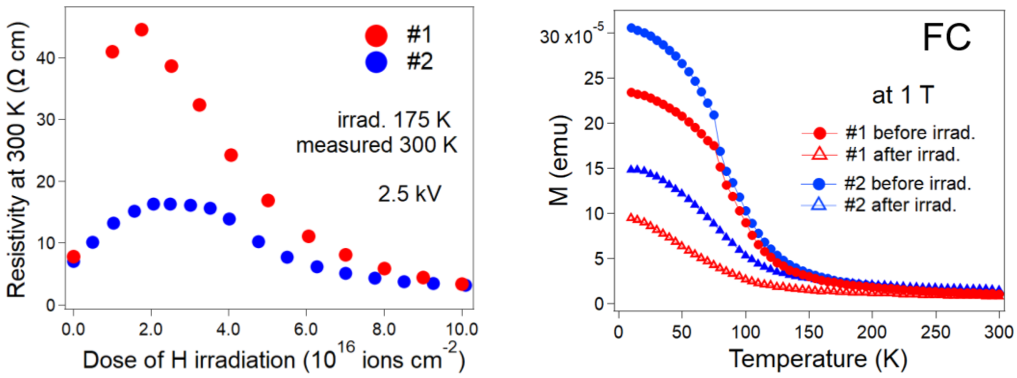

Fig. 1: Dose dependence of resistivity of $LaMnO_3$ thin films [#1: 55 nm thick, #2: 65 nm thick] (left) and magnetization before and after the hydrogen irradiation (right)

[1] A. Urushibara, *et al.*, *Phys. Rev. B* **51,** 14103 (1995).

[2] P. Schiffer, *et al.*, *Phys. Rev. Lett* **75**, 3336 (1995).

[3] R. Nakayama, *et al.*, *Rev. Sci. Instrum.* **88**, 123904 (2017).

[4] R. Nakayama, *et al.*, *Chem. Comm.* **54**, 12439 (2017).

[5] G. C. Lim *et al.*, *J. Am. Chem. Soc.* **146** (46), 32013 (2024).

酸化パラジウムにおける電子-フォノン相互作用

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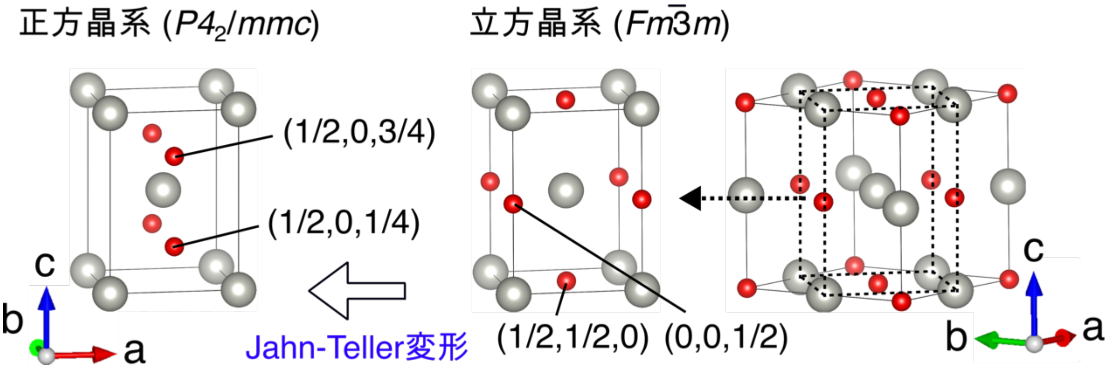
Electron-Phonon Coupling in Palladium Oxide ([1] *Fukui Institute for Fundamental Chemistry, Kyoto University*, [2]*Graduate School of Engineering, Kyoto University*) Yuta Nishikawa,[1,2] Akihisa Ishikawa,[1,2] ○Wataru Ota,[1,2] Tohru Sato,[1,2]

Palladium oxide, which has a tetragonal structure (space group: $P4_2/mmc$) at standard temperature and pressure, forms a cubic structure (space group: *Fm3m*) at high pressure or on a substrate. The symmetry lowering from *Fm3m* to $P4_2/mmc$ can be understood as a cooperative Jahn-Teller distortion induced by electron-phonon coupling. In this study, we investigated the vibronic structures responsible for the cooperative Jahn-Teller deformation.

Keywords : Vibronic coupling, Palladium oxide, Cooperative Jahn-Teller effect

酸化パラジウムは自動車触媒等の環境浄化触媒として利用されており、その基礎的な振電構造を理解することは重要である。酸化パラジウムは常温常圧下では正方晶系(空間群: *P42/mmc*)の構造を持つが、高圧条件下や基板上では立方晶系(空間群: *Fm3m*)の構造を持つ[1,2)]。*Fm3m*から*P42/mmc*への対称性低下は電子-フォノン相互作用を駆動力とする協働的ヤーン・テラー変形として理解できる。本研究では、酸化パラジウムの振電状態の第一原理計算を行い、協働的ヤーン・テラー変形を引き起こす振電構造について検討した。電子状態計算は密度汎関数理論(DFT)に基づいて行った。計算手法には、PBE+U法[3)]を用いた。PBE+UのU値は線形応答理論に基づいて第一原理的に決定した[4)]。DFT計算には、計算パッケージとして、Quantum ESPRESSOを用いた[5)]。



1) A. G. Christy *et al.*, Phys. Rev. B **1995**, *52*, 9259. 2) J. Kumer, *et al.*, J. Less. Common Metals **1989**, *147*, 59. 3) S. L. Dudarev *et al.,* Phys. Rev. B **1998**, *57*, 1505. 4) I. Timrov *et al.,* Comput. Phys. Commun. **2022**, *279*, 108455. 5) P. Giannozzi et al., *J. Phys.*: *Condens. Matter* **2009**, *21*, 395502.

Hydrogen doping into Sr_2IrO_4 under epitaxial strain

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Keywords: Hydrogen Ion Beam, Iridium Oxide, Transport Property, Epitaxial Strain

A layered perovskite compound Sr_2IrO_4 is an exotic $J_{\mathrm{eff}} = 1/2$ Mott insulator derived from spin-orbit interaction, and it is a candidate of novel superconductor due to its similarity to cuprate high-T_c superconductors. Theoretical studies have predicted the existence of superconducting phase[1], but it has not yet been observed. For observation of superconducting state, it is necessary to control carrier concentration by chemical doping or to control band structure by lattice distortion. However, it is difficult to decouple chemical doping and lattice distortion effects, because most conventional doping methods such as fluorine doping inevitably cause lattice distortion.

Hydrogen ion beam irradiation method is expected to avoid this problem because hydrogen is the smallest element and thus unlikely to cause lattice distortion. In addition, with our home-made apparatus, desorption of hydrogen is suppressed by a low-temperature irradiation, and a large amount of H doping can be realized[2]. In the previous research, it is already found that heavy carrier (electron) doping is possible in Sr_2IrO_4 by hydrogen ion beam irradiation with introducing small lattice distortion using $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate[3].

In this study, we report on an attempt of carrier doping into Sr_2IrO_4 thin films grown on $LaAlO_3$ substrate which impose compressive epitaxial strain using hydrogen ion beam irradiation and compare these results with the previous ones for Sr_2IrO_4 thin films grown on LSAT substrate. In addition, we discuss a remarkable thickness dependence on the change in conductivity by hydrogen ion beam irradiation, seen in thin film on $LaAlO_3$.

1) H. Watanabe *et al.*, *Phys. Rev. Lett.*, **2013**, *110*, 027002.
2) R. Nakayama *et al.*, *Rev. Sci. Instrum.*, **2017**, *88*, 123904.
3) Y. Yamashita *et al.*, *Phys. Rev. B*, **2021**, *104*, L041111.

層状ペロブスカイト銅酸化物への水素イオン注入

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Hydrogen doping of layered perovskite-type cuprates ([1]*Faculty of Science, Kyoto University*, [2]*Graduate School of Science, Kyoto University*) ○Masaki Wada,[1] Mitsuhiko Maesato,[2] Susumu Hirata,[2] Shuhei Iwashita,[2] Hiroshi Kitagawa[2]

$Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO) is known as the first cuprate superconductor showing n-type conduction.[1,2] The superconducting NCCO was discovered by replacing some of the trivalent Nd ions in the parent Nd_2CuO_4 with tetravalent Ce ions and annealing in a reducing atmosphere. In this study, we report an attempt to control the physical properties of Nd_2CuO_4 by a novel method of carrier doping using hydrogen ion beam irradiation.

Nd_2CuO_4 thin films were fabricated on $DyScO_3$ (110) substrates using a pulsed laser deposition (PLD) method at a substrate temperature of 750 °C and under 30 Pa oxygen pressure. The fabricated thin film was confirmed to be epitaxial (Fig. 1). Hydrogen ion beams were irradiated onto the fabricated thin film, and in situ transport measurements were performed using our home-made apparatus.[3]

Keywords : Cuprate superconductor; Hydrogen; Doping

$Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO)は n 型伝導を示す最初の銅酸化物超伝導体として知られている1,2)。NCCO の超伝導は、母物質である Nd_2CuO_4 の 3 価の Nd イオンを 4 価の Ce イオンに置換し、還元雰囲気下でアニールすることによって発見された。本研究では、従来とは異なる方法として、水素イオンビーム照射を用いたキャリアドープによる物性制御の試みについて報告する。

Nd_2CuO_4 薄膜は $DyScO_3$ (110) 基板上に PLD 法により基板温度 750 ℃、酸素分圧 30 Pa の条件下で成膜した。作製した薄膜がエピタキシャル薄膜であることを確認した(図 1)。自作の装置 3)を用いて、作製した薄膜に水素イオンビームを照射し、in situ 伝導度測定を行った。

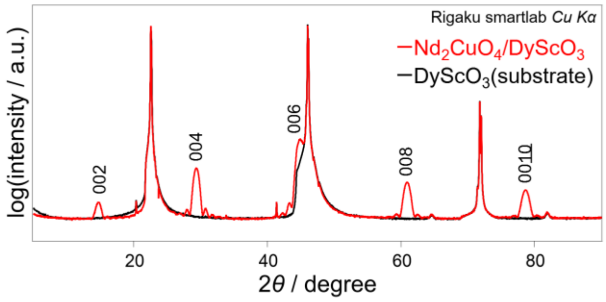

Fig. 1. Out-of-plane X-ray diffraction pattern of the Nd_2CuO_4 film

1) Y. Tokura, H. Takagi, S. Uchida, *Nature* **337**, 345 (1989).
2) H. Takagi, S. Uchida, Y. Tokura, *Phys. Rev. Lett*. **62**, 1197 (1989).
3) R. Nakayama *et al.*, *Rev. Sci. Instrum.*, **88**, 123904 (2017).

有機酸の活用を鍵とする粒状チタノシリケートの新規合成法の開発と Sr 吸着性能評価

（信州大院総理工）○谷本　龍平・小貫　雅敏・浅尾　直樹

Size-controlled direct preparation of granular titanosilicates with organic acids and evaluation of Sr adsorption performance（*Graduate School of Science and Technology, Shinshu University*） ○Ryohei Tanimoto, Masatoshi Onuki, Naoki Asao

Titanosilicates are known to behave as cation adsorbents and have been studied for removal of strontium ion from the radioactive contaminated water. Decontamination is normally conducted under fixed-bed column conditions, which generally requires granulation of adsorbents. Here, we report a direct fabrication method of granular titanosilicates using organic acids (Fig. 1). This approach enables control of the adsorbent particle size by selecting the structure of the organic acid. For example, the average sizes were 0.67 mm and 0.37 mm when trimellitic acid and 2,5-dihydroxyterephthalic acid were used, respectively. The resulting materials capture Sr selectively even in artificial seawater conditions, having competing cations such as calcium and magnesium. Furthermore, the materials can be reused repeatedly without significant degradation of the adsorption performance (Fig. 2).

Keywords : Titanosilicate, Adsorption, Strontium, Granular adsorbent, Organic acid

チタノシリケートは、ストロンチウムに対して高い吸着性能を有することが知られているが、汚染水を通水条件で除染するためには、粉末状の吸着材料を造粒化する必要がある。今回我々は、有機酸を活用することにより、チタノシリケートを粒状物として直接合成する手法を開発した（Fig.1）。本手法は、用いる有機酸の種類によって吸着材の粒径を制御することが可能であり、特にトリメリット酸を用いた時に平均粒径は0.67㎜になり、2,5-ジヒドロキシテレフタル酸を用いた時に0.37㎜に変化するという結果が得られた。本材料は、カルシウムやマグネシウムなど競合イオンが高濃度で存在する人工海水中においてストロンチウイオンを選択的に除去することが可能であり、さらに吸着性能を損なうことなく再利用が可能であった(Fig.2)。

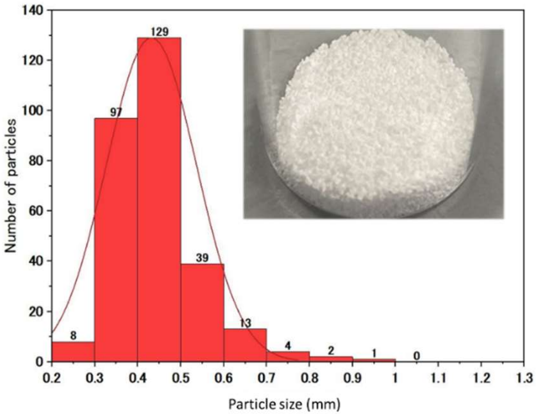

Figure1. Particle size distribution and photographic image of granular titanosilicate.

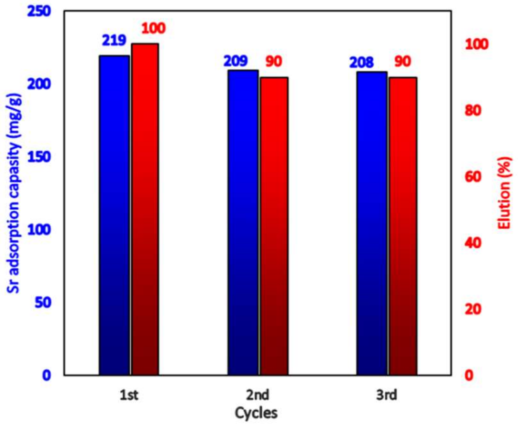

Figure2. Recycling experiments for strontium adsorption.

ナノ多孔性 $BaTiO_3$ 薄膜における精密設計

（東京電機大）○鈴木 孝宗

Precise Design of Nano-porous $BaTiO_3$ Thin Films (*Tokyo Denki University*)

○Norihiro Suzuki

Although barium titanate ($BaTiO_3$: BTO) is an old ferroelectric material, which was discovered in 1940s, it is still commonly used due to its environmentally-benign (i.e., lead-free) character as well as well-balanced properties among ferroelectricity, piezoelectricity, and dielectric constant. BTO has an anisotropic ferroelectricity and its Curie temperature (i.e., the temperature at which ferroelectricity disappears due to a phase transition) enhances by lattice distortion induced by nano-porosity1), 2). In this study, to maximize the ferroelectricity of a nano-porous BTO thin film, control of both a crystal lattice plane and a nano-porous structure was attempted.

By combining a sol-gel method, in which surfactant micelles are used as templates of nano-pores, and a liquid phase epitaxial growth, a nano-porous BTO thin film with a controlled crystal lattice plane was successfully obtained. In addition, an ordered nano-porous structure was achieved by calcining the template consists of closely packed polystyrene nanoparticles after filling the precursor solution into the gaps.

Keywords : Nano-porous Materials, Organic Templates, Sol-gel Method, Liquid Phase Epitaxial Growth, Barium Titanate

チタン酸バリウム($BaTiO_3$: BTO)は1940年代に発見された古い強誘電体であるが、強誘電性・圧電特性・比誘電率のバランスが良く、鉛フリーの環境に優しい材料でもあるため、現在でも有用な強誘電体である。BTOの強誘電性は異方性があり、また、先行研究によりナノ細孔がもたらす結晶格子歪みにより、Curie温度（相転移により強誘電性を失う温度）が上昇することを見いだしている1), 2)。そこで本研究では、ナノ多孔性BTO薄膜の強誘電性を最大限に引き出せるよう、結晶格子面とナノ細孔構造の制御を試みた。

界面活性剤ミセルをナノ細孔の鋳型に用いたsol-gel法と液相エピタキシャル成長を組み合わせることで、結晶格子面が制御されたナノ多孔性BTO薄膜の合成に成功した。また、ポリスチレンナノ粒子を最密充填させた鋳型を準備し、隙間を前駆溶液で満たした後に鋳型除去を施すことで、規則的なナノ細孔構造を実現した。

1) Chemical Preparation of Ferroelectric Mesoporous Barium Titanate Thin Films: Drastic Enhancement of Curie Temperature Induced by Mesopore-Derived Strain, N. Suzuki *et al.*, *Chem. Eur. J* **2014**, *20*, 11283.

2) Origin of thermally stable ferroelectricity in a porous barium titanate thin film synthesized through block copolymer templating, N. Suzuki *et al.*, *APL Mater.* **2017**, *5*, 076111.

$Sr_{2.5}Bi_{0.5}NiO_5$の電子状態と局所構造におけるPb置換効果

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Pb substitution effect on electronic state and local structure of $Sr_{2.5}Bi_{0.5}NiO_5$ ([1]*Faculty of Science, Tokyo Metropolitan University,* [2]*JST-PRESTO*, [3]*Faculty of Science, Tohoku University*) Kenta Natsui[1], Hideyuki Kawasoko[1,2], Soichi Kikkawa[1], Kana Nishimura[3], Tomoteru Fukumura[3], Seiji Yamazoe[1]

In $Sr_{2.5}Bi_{0.5}NiO_5$ (SBNO), composed of rock-salt $Sr_{1.5}Bi_{0.5}O_2$ and perovskite $SrNiO_3$ layers, the change of the Sr/Bi arrangement in the $Sr_{1.5}Bi_{0.5}O_2$ layers from a disordered to an ordered state results in 1/100-fold reduction of the electrical resistivity [1]. Also, in the Pb-substituted ordered $Sr_{2.5}(Bi_{1-x}Pb_x)_{0.5}NiO_5$ (Pb:SBNO), decreased degree of the Sr/Bi ordering leads to an increase in electrical resistivity [2]. However, the origin of the correlation between the Sr/Bi ordering and electrical resistivity remains unclear.

In this study, we evaluated the electronic states and local structures of these SBNO and Pb:SBNO using X-ray absorption fine structure (XAFS) analysis to elucidate the origin of the electrical resistivity change. In both the ordered and disordered SBNO, Ni was trivalent regardless of the Sr/Bi arrangement. The stronger pre-edge peak intensity at the Ni-K edge of the ordered SBNO suggests that the Sr/Bi ordering enhances the hybridization between Ni 3d and O 2p orbitals, resulting in the large decrease in electrical resistivity. In Pb:SBNO, Pb was tetravalent, and the valence state of Ni reduced with increasing the Pb amount. Thus, the electrical resistivity increase in Pb:SBNO can be attributed to not only the lower degree of Sr/Bi ordering but also smaller amount of hole carriers. On the presentation, we will discuss the results of local structural analysis using EXAFS.

Keywords：Layered Nickelate, Local atomic arrangement, X-ray Absorption Fine Structure

$Sr_{1.5}Bi_{0.5}O_2$岩塩層と$SrNiO_3$ペロブスカイト層からなる$Sr_{2.5}Bi_{0.5}NiO_5$ (SBNO)では、$Sr_{1.5}Bi_{0.5}O_2$層の Sr/Bi 配列が無秩序状態から秩序状態に変化することで、電気抵抗率が 1/100 程度に減少する [1]。また、Pb 置換した秩序相$Sr_{2.5}(Bi_{1-x}Pb_x)_{0.5}NiO_5$ (Pb:SBNO)では、Sr/Bi 配列の秩序度が低下し、電気抵抗率が増大する [2]。しかし、これらの Sr/Bi 配列の秩序度合いが電気抵抗率と相関する起源は明らかになっていない。

そこで本研究では、SBNO と Pb:SBNO について、X 線吸収微細構造解析により電子状態と局所構造を評価し、電気抵抗率の変調の起源を考察した。秩序相と無秩序相の SBNO では、Sr/Bi 配列によらず、Ni は 3 価であった。さらに、秩序相の方が、Ni K 端のプリエッジピークの強度が大きく、Sr/Bi 配列の秩序化により Ni 3d 軌道と O 2p 軌道が強く混成した結果、電気抵抗率の大幅な減少につながったと考えらえる。また Pb:SBNO では、Pb は 4 価であり、Pb 置換量の増大に伴い、Ni の価数が低減した。したがって、Pb:SBNO の電気抵抗率の増大は、Sr/Bi 配列の秩序度の低下に加え、Ni の価数減少よる伝導を担う正孔キャリアの減少に由来すると考えられる。当日は、EXAFS を用いた局所構造解析の結果も含めて議論する予定である。

[1] K. Matsumoto *et al*., *Adv. Sci.* **2023**, 10, 2304978. [2] 西村 花奈 他, 第 84 回応用物理学会秋季学術講演会 (2023).