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

Mon. Mar 18, 2024 1:00 PM - 3:10 PM JST | Mon. Mar 18, 2024 4:00 AM - 6:10 AM UTC
A1444(1444, Bldg. 14 [4F])

[A1444-1pm] 07. Inorganic Chemistry

Chair: Norihiro Suzuki, Satoshi Muratsugu

Japanese
1:00 PM - 1:10 PM JST | 4:00 AM - 4:10 AM UTC
[A1444-1pm-01]

Development of synthesis method for λ-Ti_3O_5 using titanium chloride as a starting material and evaluation of its heat-storage properties

○Riku Seiki[1], Tomoko Kubota[1], Akito Fujisawa[1], Akhmad Fadel Fadilla[1], Jia Fangda[2], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. The Univ. of Tsukuba , 2. The Univ. of Tokyo)

English
1:10 PM - 1:20 PM JST | 4:10 AM - 4:20 AM UTC
[A1444-1pm-02]

Terbium single-molecule magnets embedded in an inorganic coordination framework showing self-thermometry using luminescence

○Junhao Wang[1], Jakub J. Zakrzewski[2], Mikolaj Zychowicz[2], Yue Xin[3], Hiroko Tokoro[1], Shin-ichi Ohkoshi[3], Szymon Chorazy[2] (1. University of Tsukuba, 2. Jagiellonian University, 3. The University of Tokyo)

Japanese
1:20 PM - 1:30 PM JST | 4:20 AM - 4:30 AM UTC
[A1444-1pm-03]

Epitaxial growth of metal–organic framework on α-Al_2O_3(0001) substrate

○Shunta Iwamoto[1], Ryo Nakayama[2], Seoungmin Chon[1], Ryota Shimizu[2], Taro Hitosugi[1,2] (1. Tokyo Tech, 2. The Univ. of Tokyo)

Japanese
1:30 PM - 1:40 PM JST | 4:30 AM - 4:40 AM UTC
[A1444-1pm-04]

Luminescence mechanism in Sn-doped zinc phosphate glass

○Yuiho Kouno[1,2], Naoki Haruta[1,2], Hirokazu Masai[3], Tohru Sato[1,2] (1. FIFC, Kyoto Univ., 2. Grad. Sch. Eng., Kyoto Univ., 3. AIST)

1:40 PM - 1:50 PM JST | 4:40 AM - 4:50 AM UTC

Break

Japanese
1:50 PM - 2:00 PM JST | 4:50 AM - 5:00 AM UTC
[A1444-1pm-05]

Spin relaxation properties of molecular qubit candidates using $Cr^{V}N$ complexes with $S = 1/2$

○Naoya Yamamoto[1], Mizue Asada[2], Benjamin Le Ouay[1], Ryo Ohtani[1], Toshikazu Nakamura[2], Masaaki Ohba[1] (1. Kyushu university, 2. Institute for Molecular Science)

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

[A1444-1pm-06]

Synthesis of nickel oxide nanocrystals by supercritical hydrothermal method and their thin film formation

○Tomoki Kawase[1], Tomoya Oshikiri[1,2], Takaaki Tomai[1,3], Hiromasa Niinomi[1], Masaru Nakagawa[1] (1. IMRAM, Tohoku Univ., 2. RIES, Hokkaido Univ., 3. FRIS, Tohoku Univ.)

🏷 English

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

[A1444-1pm-07]

Electron doping into Sr_2IrO_4 under epitaxial strain using hydrogen ion beam method

○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.)

🏷 Japanese

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

[A1444-1pm-08]

Preparation and structural characterization of new ruthenium phosphide

○Mai Nakanishi[1], Takumi Moriyama[1], Satoshi Muratsugu[1], Mizuki Tada[1,2] (1. Dept. Chem. Nagoya Univ., 2. RCMS, Nagoya Univ.)

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

Break

🏷 Japanese

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

[A1444-1pm-09]

Appearance of ferromagnetism in nanoporous $EuTiO_3$ thin film

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

🏷 Japanese

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

[A1444-1pm-10]

Fabrication of porous iron oxide films by a casting with nanocolloidal solution

○Sakiko Miyamoto[1], Hiroaki Uchiyama[1], Yasushi Obora[1] (1. Fac. Chem. Matl. & Bioeng., Kansai Univ.)

🏷 Japanese

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

[A1444-1pm-11]

Structural control of organically bridged siloxane oligomers obtained by hydrolysis and condensation of bis(triethoxysilyl)benzene

○Mayu Suzuki[1], Miharu Kikuchi[1], Taiki Hayashi[1], Takamichi Matsuno[1,2], Atsushi Shimojima[1,2] (1. School of Advanced Science and Engineering, Waseda University, 2. Kagami Memorial Research Institute for Materials Science and Technology, Waseda University)

Development of synthesis method for λ-Ti_3O_5 using titanium chloride as a starting material and evaluation of its heat-storage properties

([1]Dep. of Materials Sciences, Faculty of Pure and Applied Sciences, Univ. of Tsukuba, [2]Dep. of Chemistry, School of Science, Univ. of Tokyo) ○Riku Seiki,[1] Tomoko Kubota,[1] Akito Fujisawa,[1] Akhmad Fadel Fadilla,[1] Jia Fangda,[2] Shin-ichi Ohkoshi,[2] Hiroko Tokoro[2]

Keywords: *Titanium oxide; Heat-storage material; Pressure-induced phase transition*

[Introduction] The lambda-phase trititanium pentoxide (λ-Ti_3O_5) was reported as a pressure-responsive heat-storage material that enable to preserve thermal energy in the long-term.[1], [2] In this study, we developed a synthesis method to obtain λ-Ti_3O_5 simply by using titanium chloride as a starting material.

[Experiment] A mixed solution of H_2O, $TiCl_4$, and NH_3 was prepared in a round bottle flask. The solution was stirred at 50 °C for 20 hours in an oil bath. The precipitation was extracted from the solution by centrifugation, washed with ethanol, and heated at 60 °C for 24 hours to obtain a precursor. Then the precursor was sintered at 1100 °C for 20 hours under a hydrogen flow rate of 0.5 dm^3 min^{-1}, obtained a black powder sample.

[Results] XRF measurement indicated that the composition formula was $Ti_{3.00(3)}O_{5.00(3)}$ (Calculated: Ti 64.22, O 35.78 wt%; Found: Ti 64.53, O 35.47 wt%). Powder X-ray diffraction (PXRD) pattern and Rietveld analysis indicated that the obtained black powder was a single phase of λ-Ti_3O_5 (monoclinic, *C*2/m; a = 9.8332(2), b =3,78568(7), c = 9.9688(2), β = 91.259(2) °) and the crystalline size was estimated 57 ± 3 nm. Pressure threshold (P_{th}) for converting 50 % of λ-Ti_3O_5 to β-Ti_3O_5 was approximately 300 MPa. The transition enthalpy (ΔH_{trans}) of the temperature-induced phase transition from pressure-produced β-Ti_3O_5 to λ-Ti_3O_5 was 7.78 ± 0.26 kJ mol^{-1} at 462 K. Next, we investigate the influence of the crystalline size on the P_{th} and the ΔH_{trans}. The examination of the relationship between crystalline size and the P_{th} and the ΔH_{trans} demonstrated that a reduction in crystalline size and an increase in the proportion of surface atoms intensify the influence of surface energy on the Gibbs free energy. This decreases the ΔH_{trans} and consequently increases the P_{th}. Understanding the relationship between the crystalline size and heat storage properties is essential for developing effective heat storage materials.

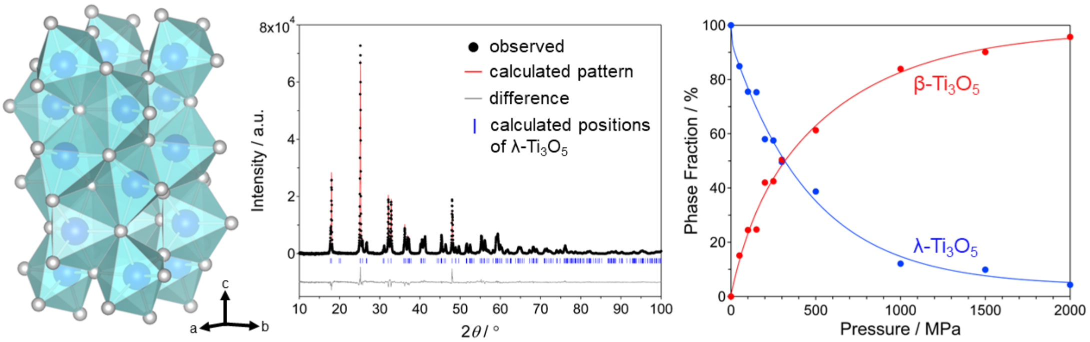


Fig. 1: Crystal structure of λ-Ti_3O_5 (left), PXRD pattern with Rietveld analysis of the obtained black powder sample (middle), and the phase fraction of λ-Ti_3O_5 and β-Ti_3O_5 (right).

1) S. Ohkoshi, et al. *Nature Chem.*, 2010, **2**, 539. 2) H. Tokoro, et al., *Nature Commun.*, 2015, **6**, 7037.

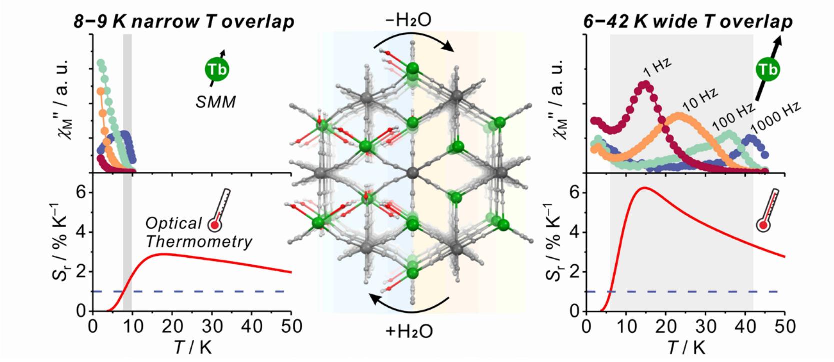
Terbium single-molecule magnets embedded in an inorganic coordination framework showing self-thermometry using luminescence

([1]*Institute of Pure and Applied Sciences, University of Tsukuba*, [2]*Faculty of Chemistry Jagiellonian University,* [3]*School of Science, The University of Tokyo*)
○Junhao Wang,[1] Jakub J. Zakrzewski,[2] Mikolaj Zychowicz,[2] Yue Xin,[3] Hiroko Tokoro,[1] Shin-ichi Ohkoshi,[3] Szymon Chorazy[2]

Keywords: Single-Molecule Magnet, Luminescence Thermometry, Emission

Research on combining magnetic and optical properties within a single-phase material unveils novel cross-effects, facilitating the development of advanced magneto-optical functional devices. Lanthanide(III) complexes are such materials, which can accommodate both luminescent functionalities and single-molecule magnet (SMM) property, promising for high-density information storage devices with optical features.

In this work, we constructed a three-dimensional cyanido-bridged coordination framework, $[Tb^{III}(H_2O)_2][Co^{III}(CN)_6]\cdot 2.7H_2O$ (**1**), and its thermally desolvated phase, $Tb^{III}[Co^{III}(CN)_6]$ (**2**), and investigated the conjunction of Tb(III)-centered SMM and luminescent functional properties in them. Upon topotactic transformation between two phases, the terbium complexes underwent a geometry change between an 8-coordinated square antiprism (in **1**) and a 6-coordinated trigonal prism (in **2**), which led to switching of both SMM and luminescent properties. Tb(III) in **1** revealed a moderate magnetic anisotropy with SMM character detectable up to 8.5 K. Upon dehydration, a much larger magnetic anisotropy energy barrier of 594(18) cm^{-1} was detectable up to 42 K. Characteristic luminescence observed from Tb(III) exhibited a hue switching of in the emission color. Additionally, their emissions as a function of temperature made both **1** and **2** luminescent ratiometric thermometers, working in the cryogenic temperature regime as low as ca. 6 K, showcasing SMMs with self-temperature monitorable features by optical means.



1) Y. Xin, et al., *J. Am. Chem. Soc.* **2019**, *141*, 18211. 2) J. Wang, et al., *J. Am. Chem. Soc.* **2020**, *142*, 3970. 3) J. Wang, et al., *Angew. Chem., Int. Ed.* **2023**, *62*, e202306372.

α-Al$_2$O$_3$(0001)基板上での金属有機構造体のエピタキシャル成長

（東工大物質理工[1]・東大院理[2]）○岩本 俊太[1]・中山 亮[2]・CHON Seoungmin[1]・清水 亮太[2]・一杉 太郎[1,2]

Epitaxial growth of metal–organic framework on α-Al$_2$O$_3$(0001) substrate ([1]*School of Materials and Chemical Technology, Tokyo Institute of Technology*, [2]*Graduate School of Science, the University of Tokyo*) ○Shunta Iwamoto,[1] Ryo Nakayama,[2] Seoungmin Chon,[1] Ryota Shimizu,[2] Taro Hitosugi[1,2]

Epitaxial growth of metal–organic frameworks (MOFs), in which crystals are grown on a substrate with a well-defined orientation, is important for utilization of anisotropic properties and interface research. Recently, epitaxial growth between MOFs and other materials has been reported[1)] and has attracted much attention. However, epitaxial growth of MOFs on metal oxides without surface modification is difficult and there is no report. In this study, we report the epitaxial growth of UiO-66-(OH)$_2$ (111) on an α-Al$_2$O$_3$ (0001) substrate. H$_4$dobdc and Zr(acac)$_4$ thin films were deposited by vacuum deposition. The thin film was annealed with 5 μL of 75vol% aqueous acetic acid solution. X-ray diffraction φ-scans of Al$_2$O$_3$ 104 and UiO-66-(OH)$_2$ 200 (Fig. 1) exhibit peaks at the same in-plane angle, confirming epitaxial growth.

Keywords : Metal–Organic Framework, Epitaxial growth, Physical Vapor Deposition

金属有機構造体(MOF)は金属イオンと有機配位子からなる多孔性材料である。MOFの異方的な特性の活用や界面研究のためには、種結晶となる基板上に結晶方位を規定して結晶が成長する、エピタキシャル成長が重要である。近年、MOF と異種材料との間でのエピタキシャル成長が報告され[1)]、注目を集めている。しかし、表面修飾のない金属酸化物上でのエピタキシャル成長は難しく、報告例はない。本研究では、Zr(IV)系 MOF の UiO-66-(OH)$_2$ ([Zr$_6$(OH)$_4$O$_4$(H$_2$dobdc)], dobdc = 2,5-dioxidiobenzene-1,4-dicarboxylate) の α-Al$_2$O$_3$(0001)基板上でのエピタキシャル成長に成功した。なお、これまでの MOF のエピタキシャル成長は Cu(II)系 MOF の報告のみであり、安定性の高い Zr(IV)系 MOF のエピタキシャル成長は本研究が初である。

UiO-66-(OH)$_2$ 薄膜を、真空蒸着と溶媒蒸気加熱の二段階で合成した。前駆体として、膜厚 80 nm の H$_4$dobdc と膜厚 250 nm の Zr(acac)$_4$ (zirconium(IV) acetylacetonate) を、室温で α-Al$_2$O$_3$(0001)基板上に順に堆積した。堆積後、薄膜と濃度 75vol%の酢酸水溶液 5 μL を、大気中でセルに封止し、200 °C で 12 時間加熱した。

面直 X 線回折より、UiO-66-(OH)$_2$ の(111)面直配向を確認した。また、Al$_2$O$_3$ の 104 回折と UiO-66-(OH)$_2$ の 200 回折について ϕ スキャンを行うと、同一の面内角にピークが得られ(図 1)、エピタキシャル成長していることがわかった。

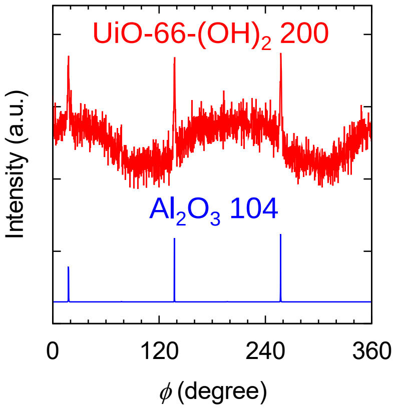


図 1 X 線回折非対称面 ϕ スキャン

1) Falcano et al., *Nat. Mater.* **2017**, 16, 342–348.

Sn ドープ亜鉛リン酸塩ガラスの発光機構に関する理論的研究

(京大福井セ [1], 京大院工 [2], 産総研 [3])
○河野由帆 [1,2]・春田直毅 [1,2]・正井博和 [3]・佐藤徹 [1,2]

Theoretical study on luminescence mechanism in Sn-doped zinc phosphate glass

([1]*Fukui Institute for Fundamental Chemistry, Kyoto University,* [2]*Graduate School of Engineering, Kyoto University,* [3]*National Institute of Advanced Industrial Science and Technology*)
○ Yuiho Kouno[1,2], Naoki Haruta[1,2], Hirokazu Masai[3], Tohru Sato[1,2]

The quantum mechanics/molecular mechanics (QM/MM) model of luminescent Sn-doped ZnO-P_2O_5 glass is constructed based on the non-doped glass structure estimated by the reverse Monte Carlo method. Time-dependent density functional theory calculations reveal that the experimentally observed absorption peak at about 5.0 eV is mainly ascribed to the $S_0 \rightarrow S_{175}$ of the present model, which is the electronic transition between delocalized molecular orbitals around a 4-coordinate Sn^{2+}, including the $s \rightarrow p$ transition.

Keywords : QM/MM; Density functional theory; Reverse Monte Carlo

Sn ドープ ZnO-P_2O_5（SZP）ガラスは高効率な青色発光を生じることから [1)]、希土類フリー発光ガラス材料として注目を集めている。ガラス中で Sn は 2 価であり [2)]、発光は Sn^{2+}の $s \rightarrow p$ 遷移に由来すると予想されている。しかしそのガラス構造は特定されておらず、高効率発光に寄与する局所構造及び発光メカニズムは未解明であった。本研究では、SZP ガラスの吸収/発光スペクトルを再現する量子力学/分子力学（QM/MM）モデルを構築し、その発光メカニズムを解明することを目的とする。

$[SnO_m]^{-2(m-1)}$錯体に対する密度汎関数理論（DFT）計算によれば、三角錐型 3 配位や四角錐型 4 配位の Sn^{2+}で HOMO 準位が低くなり、2 価が安定となる。そこで、逆モンテカルロ法により推定された Sn ドープ前のガラス構造 [3)]において、三角錐型 3 配位の Zn^{2+}を Sn^{2+}に置換した QM/MM モデルを構築した（Fig. 1）。時間依存 DFT 計算を行ったところ、吸収スペクトルのメインピークは Sn^{2+}の $s \rightarrow p$ 遷移由来の $S_0 \rightarrow S_{175}$ となり、実験で観測されるピーク位置を概ね再現することが分かった（Fig. 2）。

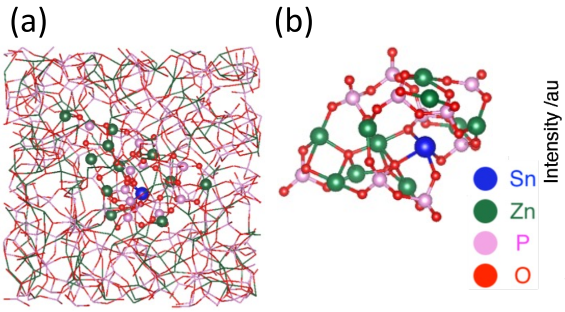


Fig. 1: (a) The optimized ONIOM model and (b) its QM region.

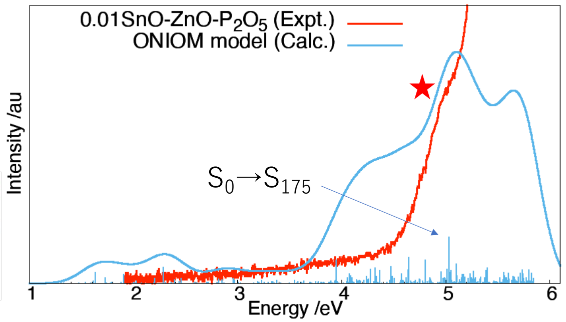


Fig. 2: The experimental absorption spectrum[4)] and the theoretical one with the linewidth of 1300 cm^{-1}.

1) H. Masai *et al.*, *Opt. Express*. **2012**, 20, 27319. 2) A. Torimoto *et al.*, *J. Ceram. Soc. Jpn*. **2016**, 124, 554. 3) H. Masai *et al.*, *Phys. Status Solidi B*. **2020**, 257, 2000186. 4) H. Masai, unpublished result.

スピン 1/2 系クロム(V) 錯体を用いた分子量子ビットのスピン 緩和特性

（九大院理 [1]・分子科学研究所 [2]）○山本 直也 [1]・浅田 瑞枝 [2]・ルウェ バンジャマン [1]
大谷 亮 [1]・中村 敏和 [2]・大場 正昭 [1]

Spin Relaxation Properties of Molecular Qubits Based on a Spin-1/2 Cr^VN Complexes

([1] *Department of Chemistry, Grad. School of Science, Kyushu Univ.*, [2]*Institute for Molecular Science*) ○Naoya Yamamoto,[1] Asada Mizue,[2] Le Ouay Benjamin,[1] Ryo Ohtani,[1] Toshikazu Nakamura,[2] Masaaki Ohba[1]

A mononuclear complex [Cr^VN(salen)] (salen = *N,N'*-Bis(salicylidene)ethylenediamine) having S = 1/2 spin was prepared as a molecular qubit candidate. In order to weaken intermolecular interaction between paramagnetic Cr(V) centers in the lattice, solid solutions [$Cr_xMn_{(1-x)}N$(salen)] were prepared by diluting with diamagnetic isomorph [Mn^VN(salen)]. Frequency dependence of AC susceptibility of the solid solutions clearly exhibited magnetic relaxation behavior and the relaxation time increased with decreasing content of Cr(V). Inversion recovery and Hahn-echo experiments by pulse EPR spectra demonstrated spin relaxation behavior at room temperature.

Keywords : Spin qubit; Spin relaxation; Pulse EPR; Magnetic relaxation; Chromium(V)

量子ビット（Qubit）は 2 つの独立な量子状態から構成される二準位系であり、スピン量子数 S = 1/2 の状態はゼーマン効果により S = ±1/2 の二準位系を形成するため、Qubit として利用できる。Qubit の性能はスピン緩和時間により評価される。スピン緩和過程には分子構造の堅さや対称性、スピンと周辺環境の相互作用が影響する。設計性の高い金属錯体では、分子構造や周辺環境を制御できるため、S = 1/2 の常磁性金属錯体は分子 Qubit として有望な候補である。本研究では、S = 1/2 の Cr (V) を中心金属に、構造的に強固であり修飾しやすい H_2salen を用いた [Cr^VN(salen)]$^{1)}$ (Fig. 1)、および反磁性の [Mn^VN(salen)] で希釈した固溶体 [$Cr_xMn_{(1-x)}N$(salen)] のスピン緩和特性について、SQUID およびパルス EPR 測定より検討した。SQUID による交流磁気測定によって、固溶体のクロム濃度の減少に伴って緩和時間が長くなることが確認された。更に、パルス EPR 測定において、[$Cr_{0.01}Mn_{0.99}N$(salen)] を合成し、極低温から室温までの温度領域で反転回復実験を行った結果、室温でスピン緩和挙動が観測され、緩和時間は 4.15 μs と見積もられた(Fig. 2)。

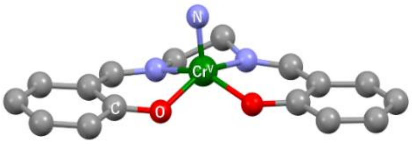


Fig. 1 Structure of [CrN(salen)]

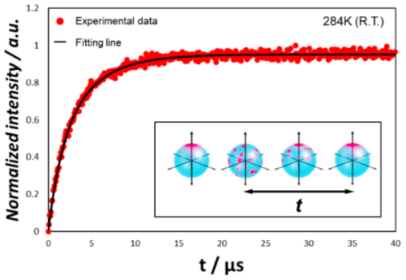


Fig. 2 Inversion recovery experiment and sequence at 284K (R.T.)

1) N.Azuma, Y.Imori, *et al, Inorganica Chimica Acta,* **1997**, 266, 29

超臨界水熱法による酸化ニッケルナノ結晶の合成と薄膜形成法の検討

（東北大多元研 [1]・北大電子研 [2]・東北大学際研 [3]）○川瀬 智暉 [1]・押切 友也 [1,2]・笘居 高明 [1,3]・新家 寛正 [1]・中川 勝 [1]

Synthesis of nickel oxide nanocrystals by supercritical hydrothermal method and their thin film formation

([1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*, [2]*Research Institute for Electronic Science, Hokkaido University,* [3]*Frontier Research Institute for Interdisciplinary Sciences, Tohoku University*) ○Tomoki Kawase,[1] Tomoya Oshikiri,[1,2] Takaaki Tomai,[1,3] Hiromasa Niinomi,[1] Masaru Nakagawa[1]

Nickel oxide (NiO) has a high refractive index and wide bandgap, which is promising for a positive-type (p-type) semiconductor layer with hole transport abilities. We have attempted to fabricate NiO thin films by pulsed laser deposition and sol-gel methods. [1,2] In this study, a thin film was fabricated using NiO nanocrystals with high crystallinity synthesized by a supercritical hydrothermal method. The method effect of film fabrication on photoelectrochemical properties was investigated. NiO nanocrystal dispersion was prepared using nickel nitrate, oleic acid, and octane under supercritical conditions. Then, we fabricated NiO thin films by two methods. One is the Langmuir-Schaefer method. Another is molding the dispersion on the substrate with a polydimethylsiloxane (PDMS) flat mold. As a result, the reduction reaction proceeded under UV light irradiation on a photocathode of the NiO nanocrystal thin film fabricated with the PDMS flat mold. This might be due to the smaller voids between nanocrystals caused by molding process.

Keywords : nickel oxide; p-type semiconductor; supercritical hydrothermal synthesis; nanocrystals; thin film formation

酸化ニッケル(NiO)は高い屈折率と広いバンドギャップを有し、ホール輸送が可能なポジティブ(p)型半導体層の構成材料として有用である。我々はこれまでにパルスレーザー堆積法やゾルゲル法での NiO 薄膜の作製を試みてきた [1,2]。本研究では超臨界水熱法にて合成した高い結晶性を有する NiO ナノ結晶を用いて p 型半導体薄膜を形成し、その形成法が光電気化学特性に与える影響について検討した。前駆体として硝酸ニッケル水溶液、有機修飾剤としてオレイン酸、分散媒としてオクタンを高温高圧の超臨界条件下で反応させ、平均粒径約 20 nm の NiO ナノ結晶分散液を調製した。極性溶媒上で NiO ナノ結晶分散液を展開、分散媒を揮発させることで形成された自己組織化膜を基板に転写する Langmuir-Schaefer 法、および有機溶媒を吸収する特性を有するポリジメチルシロキサン(PDMS)平板モールドで基板上に滴下した分散液を押印成形する方法で NiO 薄膜を形成した。その結果、PDMS 平板モールドで作製した NiO ナノ結晶薄膜を光陰極として用いた場合に紫外光照射下での還元反応が進行した。これは、押印によりナノ結晶間の空隙が小さくなったためであると考えられる。

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2) 押切 友也, 手塚 隆博, 荒木 魁, 新家 寛正, 松尾 保孝, 三澤 弘明, 中川 勝, 第 70 回応用物理学会春季学術講演会, 18p-A305-4(2023).

Electron doping into Sr_2IrO_4 under epitaxial strain using hydrogen ion beam method

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

Hydrogen (H) takes various charge states in solids, from −1 (hydride, H^-) to +1 (proton, H^+), and can drastically change the physical properties of solids as a dopant. The H doping also has an advantage that it is unlikely to cause a large lattice distortion. However, the conventional H doping methods such as exposure to hydrogen gas and electrolytic charging are applicable to limited materials, and the amount of doped H is generally small. Hydrogen ion beam irradiation is an excellent H doping method applicable to all materials. In addition, with our home-made apparatus, desorption of H is suppressed by a low-temperature irradiation, and a large amount of H doping can be realized[1].

A layered perovskite compound Sr_2IrO_4 is an exotic $J_{\mathrm{eff}} = 1/2$ Mott insulator derived from spin-orbit coupling and on-site Coulomb 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[2,3], 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 of conventional doping methods such as fluorine doping[4] inevitably cause lattice distortion. Hydrogen ion beam irradiation method is expected to avoid this problem because it is unlikely to cause lattice distortion. In the previous research, it is already found that heavy carrier (electron) doping is possible in Sr_2IrO_4 by hydrogen ion beam irradiation without introducing the lattice distortion using $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate[5]. Therefore, lattice distortion and carrier concentration can be freely controlled by the combination of epitaxial strain and hydrogen ion beam irradiation. In this study, we report on an attempt of electron doping into Sr_2IrO_4 thin films grown on $LaAlO_3$ substrate which impose compressive epitaxial strain using hydrogen ion beam irradiation, and compare with the previous results for Sr_2IrO_4 thin films grown on LSAT substrate.

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2) H. Watanabe *et al.*, *Phys. Rev. Lett.*, **2013**, *110*, 027002.
3) Z. Y. Meng *et al.*, *Phys. Rev. Lett.*, **2014**, *113*, 177003.
4) T. Maruyama *et al.*, *J. Mater. Chem. C,* **2020**, *8*, 8268-8274.
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新規ルテニウムリン化物の調製と構造解析

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Preparation and structural characterization of new ruthenium phosphide

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○Mai Nakanishi,[1] Takumi Moriyama,[1] Satoshi Muratsugu,[1] Mizuki Tada[1, 2]

Metal phosphides are expected to be applied as catalysts, and ruthenium phosphide (Ru_2P) is reported to be highly active for the deoxygenation reaction of sulfoxides and hydrogen evolution reaction due to its tolerance to sulfur poisoning. We prepared new metal phosphides with the incorporation of another transition metal species to Ru_2P in order to develop new properties of metal phosphides, and Pt was incorporated into the Ru phosphides. New multi component ruthenium phosphide (denoted as **compound 1**) was prepared, and its XRD pattern suggested that its crystalline structure was similar to that of Rh_2P (a CaF_2-type structure). Detailed structural characterizations of **compound 1** through TEM, HAADF-STEM, XPS and XAFS are investigated.

Keywords：*Metal phosphide, Ruthenium, Alloy*

金属リン化物は触媒材料としての展開が期待される無機化合物群の一つであり、その中でもルテニウムリン化物 (Ru_2P, RuP_2) は、硫黄種に対する高被毒耐性に由来するスルホキシドの脱酸素化[1]や水素発生反応 (HER)[2]において高い触媒特性を示すことが近年報告されている。金属リン化物の更なる高機能化・新規触媒機能の開拓を志向し、本研究では、Ru_2P に対し第三の遷移金属元素を複合させた、新規ルテニウム-遷移金属複合リン化物の調製を目指した。第三の遷移金属元素として、酸素発生反応 (ORR) にも高い活性を示す白金 (Pt) を選択し、硫黄種に対する高被毒耐性を兼ね備えた HER/ORR 触媒の開発を目指した。

新規 Ru-Pt 複合リン化物の調製は、Ru_2P の調製法を基にして、Ru 塩前駆体に加えて Pt 塩前駆体も混合することで行った。調製条件を最適化して得られた固体粉末試料 (**compound 1** と略記) の XRD では、明瞭な回折パターンが観測された。この回折パターンは Ru_2P のそれとは一致せず、白金リン化物 (例 : PtP_2) とも異なる回折パターンであった (**図 1**)。既存の粉末結晶データーベースとの比較により、**compound 1** はロジウムリン化物 (Rh_2P) と同じ空間群 (*Fm*-3*m* (225))である CaF_2 型構造をもつことであることが推察された。**compound 1** の ICP-OES より、Pt/Ru/P がモル比 1/1/1 と求まり、組成比を考慮した粉末XRDのシミュレーションにより、CaF_2 型構造であることを確認した。**compound 1** の構造について、TEM, HAADF-STEM による格子像、面間隔解析、XPS, XAFS による構成する元素の価数、局所配位構造解析を行ったので、併せて報告する。

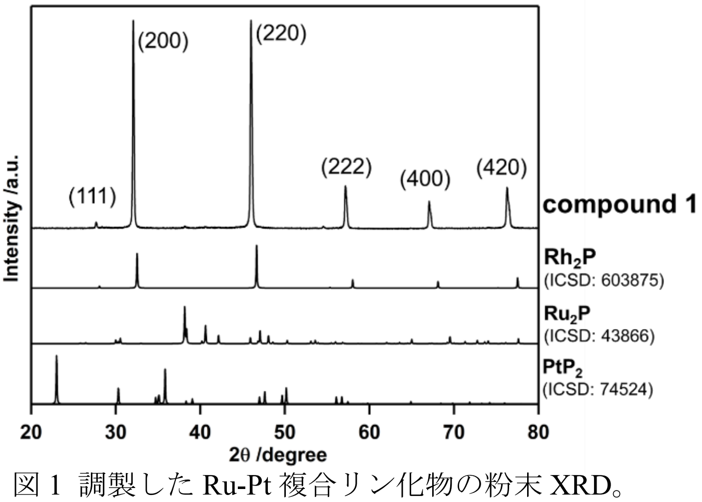

図 1 調製した Ru-Pt 複合リン化物の粉末 XRD。

[1] H. Ishikawa et al., *JACS Au*, **2022**, *2*, 419−427.
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ナノ多孔性 $EuTiO_3$ 薄膜における強磁性発現

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Appearance of ferromagnetism in nanoporous $EuTiO_3$ thin film

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Although bulk $EuTiO_3$ is antiferromagnetic, it is known to exhibit ferromagnetism with its crystal lattice is distorted. In this study, the appearance of ferromagnetism in $EuTiO_3$ was attempted by facilely introduced crystal lattice distortion via chemically-synthesized nanopores.1) Analysis of high-magnified TEM images around nanopores revealed that a biaxial strain sufficient to induce ferromagnetism was created inside the crystallized framework. When magnetism of synthesized nanoporous $EuTiO_3$ thin film was measured, the film showed ferromagnetism as expected. High-magnified TEM also revealed that the surface of the framework was amorphous, forming the core-shell structure. Because a previous study reported that amorphous $EuTiO_3$ had ferromagnetism,2) the amorphous shell may also contribute to the appearance of ferromagnetism of synthesized nanoporous $EuTiO_3$ thin film.3)

Keywords : Porous Materials; Nano-materials, Ferromagnetism, Crystal Lattice Distortion, Ceramics

$EuTiO_3$ はバルクでは反強磁性体であるが、結晶格子が歪むと強磁性体になる事が知られている。本研究では、化学的手法により作製したナノ細孔を用い、結晶格子歪みを簡易的に導入することで $EuTiO_3$ の強磁性発現を試みた 1)。ナノ細孔周辺の高倍率 TEM 画像を解析したところ、結晶化した細孔骨格内に強磁性発現に十分な結晶格子歪みがもたらされていることが明らかとなった。そこで、作製したナノ多孔性 $EuTiO_3$ 薄膜の磁性を測定したところ、狙い通り強磁性を示した。また、高倍率 TEM 画像から、細孔骨格表面はアモルファスであり、コアーシェル構造を形成していることも明らかとなった。先行研究よりアモルファス $EuTiO_3$ が強磁性をもたらす 2)ことが報告されていることから、アモルファス層の存在が、作製したナノ多孔性 $EuTiO_3$ 薄膜における強磁性の発現に寄与している可能性も考えられる 3)。

1) Synthesis of porous $EuTiO_3$ thin film and an attempt to achieve multiferroic properties, N. Suzuki *et al.*, The 101st CSJ Annual Meeting (2021)［多孔性 $EuTiO_3$ 薄膜の作製とマルチフェロイック化への試み 日本化学会第 101 春季年会（2021）］

2) Ferromagnetism induce by lattice volume expansion and amorphization in $EuTiO_3$ thin films, K. Tanaka *et al.*, *J. Mater. Res.* **2013**, 28, 1031-1041.

3) Chemical synthesis of nanoporous $EuTiO_3$ thin film and induced ferromagnetism, N. Suzuki *et al.*, *Appl. Surf. Sci.* **2023**, 615, 156421.

ナノコロイドをコーティング液に用いたキャスト法による酸化鉄多孔質膜の作製

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Fabrication of porous iron oxide films by a casting with nanocolloidal solution

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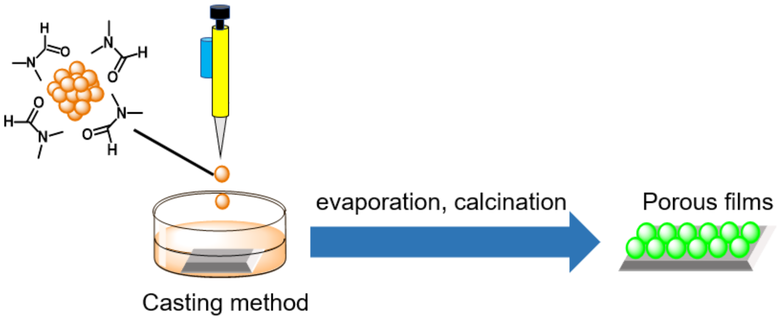
Coating of metal colloids is an effective method to fabricate porous films with applications in areas such as photocatalysis and photoelectrochemistry.[1]

We have reported a one-step synthesis of metallic nanoparticles using *N,N*-dimethylformamide (DMF) as a solvent, reductant and stabilizer.[2, 3] These nanocolloids have high catalytic activities for various organic transformations. In this presentation, we fabricated coating films by a casting method using DMF-stabilized iron oxide nanocolloids. The surface of the coating films was characterized by a FE-SEM. As a result, we have confirmed that nano-sized porous films are produced with uniformity and density.

Keywords : Porous films; Nanocolloid; Casting; Iron oxide

金属コロイドを用いたコーティングは多孔質膜を作製する有効な手法であり，多孔質膜は光触媒作用や光電気化学などの分野に応用されている 1).

当研究室では *N,N*-ジメチルホルムアミド(DMF)を溶媒，還元剤，保護剤として用いる簡易な合成法により安定な微小金属コロイドを合成し，それらを用いた触媒反応の開発を行ってきた 2,3). 本研究では DMF 保護酸化鉄ナノ粒子をキャスト法により基板上にコーティングを行った．得られたコーティング膜を FE-SEM で解析した結果，ナノサイズの粒子が均一かつ緻密に基板上に成膜されている多孔質膜を確認した．



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ビス(トリエトキシシリル)ベンゼンの加水分解・縮合により得られる有機架橋型シロキサンオリゴマーの構造制御

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Structural Control of Organically Bridged Siloxane Oligomers Obtained by Hydrolysis and Condensation of Bis(triethoxysilyl)benzene ([1]*School of Advanced Science and Engineering, Waseda University*, [2]*Kagami Memorial Research Institute for Materials Science and Technology, Waseda University*) ○ Mayu Suzuki,[1] Miharu Kikuchi,[1] Taiki Hayashi,[1] Takamichi Matsuno,[1,2] Atsushi Shimojima[1,2]

Organosiloxane-based materials have various applications because they exhibit high thermal stability and diverse properties depending on the structures and the types of organic groups. For precise structural control, it is important to prepare well-defined organosiloxane oligomers as building blocks. In this study, hydrolysis and condensation of 1,3-bis(triethoxysilyl)benzene in the presence of quaternary ammonium hydroxide was conducted to form well-defined organically bridged siloxane oligomers.

Keywords : Organosiloxanes; Organo-bridged alkoxysilane; Siloxane oligomer; Hydrolysis and condensation

[緒言]有機シロキサン材料は高い熱安定性を有し、構造や有機基の種類により多様な性質や機能を示す。フェニレン基などの有機基で架橋されたアルコキシシランの加水分解・重縮合反応により様々な多孔質材料が作製されており、特異な吸着能等の発現が報告されている 1,2)。本研究では、有機シロキサン骨格を分子レベルから精密に組み上げるためのビルディングブロック 3)として、構造が規定された有機架橋型シロキサンオリゴマーの合成について検討した。1,3-ビス(トリエトキシシリル)ベンゼン(*m*-BTEB)の加水分解・縮合反応を第四級アンモニウムイオン存在下で行うことで、フェニレン架橋型シロキサンオリゴマーの構造制御に成功したので報告する。

[実験]水酸化テトラメチルアンモニウムの存在下で、*m*-BTEB の加水分解・縮合を行った。$\mathrm{SiO^-}$/SiOH 基をトリメチルシリル化し、再結晶操作により精製することで生成物の詳細な分析を行った。

[結果]*m*-BTEB の加水分解溶液の ^{29}Si NMR スペクトルにおいて、主に $\mathrm{T^1}$ と $\mathrm{T^2}$ (T^n: $-\mathrm{C_6H_4}\boldsymbol{Si}(\mathrm{OSi})_n(\mathrm{OH\ or\ O^-})_{3-n}$)環境の 2 本のシグナルを観測したことから、構造が規定されたオリゴマーの形成が示唆された。シリル化後の生成物の ^{29}Si NMR スペクトルより、$\mathrm{M^1}$($(\mathrm{SiO})\boldsymbol{Si}\mathrm{Me_3}$)および $\mathrm{T^3}$ 環境のシグナルを観測し、その積分強度比は 1.0:1.0 であった。MALDI-TOF MS 分析より $\mathrm{Si_8O_8(C_6H_4)_4(OSiMe_3)_8}$ に帰属されるピークを観測した。以上の結果から、8 つの頂点に$-\mathrm{OSiMe_3}$ 基が修飾されたかご型 4 量体の形成が示唆された。

1) M. P. Kapoor and S. Inagaki, *Bull. Chem. Soc. Jpn*. **2006**, *79*, 1463; 2) R. Millini and G. Bellussi, *Catal. Sci. Technol.* **2016**, *6*, 2502; 3) H. Kuge *et al.*, *Chem. Asian J.* **2008**, *3*, 600.