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

Thu. Mar 27, 2025 3:55 PM - 5:15 PM JST | Thu. Mar 27, 2025 6:55 AM - 8:15 AM UTC
[C]C304(C304, Bldg. 2, Area 2 [3F])

[[C]C304-2vn] 07. Inorganic Chemistry

Chair: Hideyuki Kawasoko, Tatsuya Moriai

Japanese
3:55 PM - 4:15 PM JST | 6:55 AM - 7:15 AM UTC
[[C]C304-2vn-01]

Flux Growth and Exfoliation Applications of Chalcogenide Compounds Single Crystals

〇Fumitaka Hayashi[1], Yuto Yokotsuka[1], Chokradjaroen Chayanaphat[1], Kudo Ryota[1], Tetsuya Yamada[1], Katsuya Teshima[1] (1. Shinshu University)

English
4:15 PM - 4:35 PM JST | 7:15 AM - 7:35 AM UTC
[[C]C304-2vn-02]

Evaluation of heat-storage properties of lambda-type trititanium pentoxide and synthesis of metal-substituted lambda-type trititanium pentoxide

〇Riku Seiki[1], Akito Fujisawa[1], Akhmad Fadel Fadilla[1], Tomoko Kubota[1], Shin-ichi Ohkoshi[2], Hiroko Tokoro[1] (1. The Univ. of Tsukuba, 2. The Univ. of Tokyo)

English
4:35 PM - 4:55 PM JST | 7:35 AM - 7:55 AM UTC
[[C]C304-2vn-03]

Quantitative Analysis of Electronic Structure–Property Relationship in Multi-Element Alloy Catalysts with X-ray Spectroscopy and *Ab Initio* Calculation

〇Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Hiroyuki Hayashi[3], Takaaki Toriyama[4], Tomokazu Yamamoto[4], Yasukazu Murakami[4,5], Shogo Kawaguchi[6], Toshiaki Ina[6], Yoshiki Kubota[7], Toyonari Yaji[8], Kazuo Kojima[8], Isao Tanaka[3], Hiroshi Kitagawa[1] (1. Grad. Sch. Sci., Kyoto Univ., 2. Hakubi Center, Kyoto Univ., 3. Grad. Sch. Eng., Kyoto Univ., 4. URC, Kyushu Univ., 5. Grad. Sch. Eng., Kyushu Univ., 6. JASRI/SPring-8, 7. Grad. Sch. Sci., Osaka Metro. Univ., 8. SRC, Ritsumeikan Univ.)

English
4:55 PM - 5:15 PM JST | 7:55 AM - 8:15 AM UTC
[[C]C304-2vn-04]

Mild, Facile Synthesis of Perovskite Oxynitride Nanoparticles Towards High-entropy Thermoelectric Materials

〇Simon David Moore[1], Mari Takahashi[1], Shinya Maenosono[1] (1. School of Materials Science, Japan Advanced Institute of Science and Technology)

フラックス法による層状カルコゲナイド化合物の単結晶育成と剥離応用

（信州大）○林 文隆・横塚 雄斗・Chokradjaroen Chayanaphat・工藤 諒大・山田 哲也・手嶋 勝弥

Flux Growth and Exfoliation Applications of Chalcogenide Compounds Single Crystals

(*Shinshu University*) ○Fumitaka Hayashi, Yuto Yokotsuka, Chayanaphat Chokradjaroen, Ryota Kudo, Tetsuya Yamada, Katsuya Teshima

Transition metal dichalcogenides (TMD) have been attractive for their semiconducting character. TMD materials are represented by the chemical formula MX_2, M refers to a transition metal atom (*e.g.*, Mo, W) and X is a chalcogen atom (*e.g.*, S, Se). TMD can be produced in an atomic-scale thickness with direct band gap and suitable spin-orbit coupling through chemical vapor deposition and exfoliation, which make it favorable for especially electronics applications. In general, it is challenging to grow large, high-quality parent MX_2 crystals, and achieving scalable crystal growth is highly desirable. Herein, we report the flux growth of MoX_2 (X = S, Se, Te) single crystals from chloride and molybdate-based fluxes for the first time. When examining the holding temperature using NaCl flux, large MoS_2 crystals exceeding 50 µm were obtained, although size variation was observed at 1100 °C. In contrast, using K_2MoO_4 flux resulted in relatively uniform MoS_2 crystal particles with an approximate size of 20 µm. The grown MoX_2 crystals were exfoliated using a hexane-butyllithium solution.

Keywords : Transition metal dichalcogenides; Nanosheet; Exfoliation; Two-dimensional materials

遷移金属カルコゲナイド（TMD）は化学式 MX_2 で表され，M は遷移金属原子（Mo, W 等）を，X はカルコゲン原子（S, Se 等）を指す。TMD は化学気相成長（CVD）や剥離によって原子スケールの厚みで作製可能である。単層 TMD は直接遷移型のバンドギャップと適切なスピン軌道結合をもち，半導体特性に優れた材料である。大型 MoX_2 単結晶の液相育成はほとんど例がなく，大規模スケールで高品質な結晶育成が望まれる。本研究では，塩化物やモリブデン酸塩フラックスからの MoX_2 単結晶（X=S, Se, Te）育成を報告する。MoX_2 結晶の育成に，フラックスとして NaCl や K_2MoO_4 等を用い，溶質として金属 Mo と S を用いた。これらの原料を石英封緘し，所定温度で 24 時間加熱した。NaCl フラックスを用いて保持温度を検討すると，1100 °C にて，サイズにばらつきが見られるものの，50 µm を超える大型 MoS_2 結晶粒子を得た。K_2MoO_4 フラックスを用いると，比較的均一サイズで，20 µm 程度の MoS_2 結晶粒子を得た。当日は，MoX_2 結晶の成長様式や化学剥離の結果についても議論する。

謝辞：本研究の一部は，内閣府 SIP 事業（JPJ012307）および科研費基盤研究 B（24K01234）の援助のもとに遂行された。記して謝意を表する。

Evaluation of heat-storage properties of lambda-type trititanium pentoxide and synthesis of metal-substituted lambda-type trititanium pentoxide

([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] Akito Fujisawa,[1] Akhmad Fadel Fadilla,[1] Tomoko Kubota,[1] Shin-ichi Ohkoshi,[2] Hiroko Tokoro[1] **Keywords**: *titanium oxides, heat-storage properties, pressure-induced phase transition, metal substitution*

[Introduction] The lambda-type trititanium pentoxide (λ-Ti_3O_5, Fig. 1) was reported as a pressure-responsive heat-storage material to preserve thermal energy in the long-term [1, 2]. In this study, we developed a synthesis method for λ-Ti_3O_5 simply by preparing a precursor using titanium chloride as a starting material and evaluated the heat-storage properties [3]. Additionally, using the developed method, we synthesized manganese-substituted λ-$Mn_xTi_{3-x}O_5$ and investigated the effect of Mn substitution for the heat-storage property.

[Experiment] Sample **1**: A mixed solution of H_2O, NH_3, and $TiCl_4$ was prepared and stirred in a round bottle flask. The precipitation was extracted from the solution by centrifugation. Then the obtained precursor was sintered under a hydrogen flow of 0.5 $dm^3\,min^{-1}$ at 1100 °C for 5 h. Samples **2**, **3**, **4**, **5**: A mixed solution of H_2O, NH_3, and $TiCl_4$, $MnCl_2 \cdot 4H_2O$ was prepared and stirred. The molar ratios of Mn to Ti were 3 % (**2**), 5 % (**3**), 7 % (**4**), and 10 % (**5**), respectively. The precipitation was extracted, washed with ethanol, and heated. The obtained precursors were sintered under a hydrogen flow.

[Result] X-ray fluorescence (XRF) measurement indicated that the composition formula of **1** was $Ti_{3.00(5)}O_{5.00(5)}$ (Calc.: Ti 64.22, O 35.78 wt%; Found: Ti 64.53, O 35.47 wt%). XRD pattern with Rietveld analysis indicated that the obtained **1** was a single phase of λ-Ti_3O_5 (monoclinic, $C2/m$; $a = 9.8332(2)$ Å, $b = 3.78568(7)$ Å, $c = 9.9688(2)$ Å, $\beta = 91.259(2)$ °) and the crystallite size was estimated 57 ± 3 nm. The heat-storage properties of **1**, the pressure threshold (P_{th}) was ca. 300 MPa and the transition enthalpy (ΔH_{trans}) was 7.78 kJ mol^{-1} at 462 K. The relationship between the crystallite size and the heat-storage properties demonstrated that a reduction in crystallite size and an increase in ratio of surface atoms intensify the influence of surface energy on the Gibbs free energy and consequently it decreased the ΔH_{trans}. The relationship between Mn-substituted ratio to Ti atoms and lattice constants (a, b, c) of **2**, **3**, **4**, **5** were shown in Fig. **2**. These lattice constants were changed depending on the Mn substitution ratio. The heat-storage property of **2**, **3**, **4**, **5** will be presented in the oral presentation.

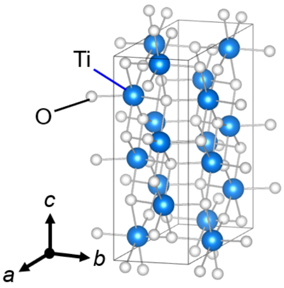

Fig. 1: Crystal structure of λ-Ti_3O_5.

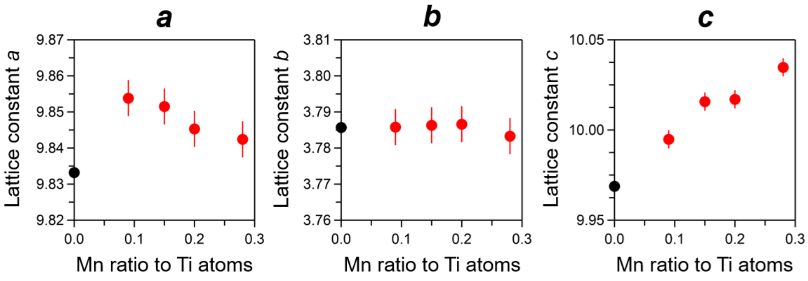

Fig. 2: Three lattice constants versus Mn substitution ratio to Ti atoms plots (left: a, center: b, right: c). Black plots are **1** and red plots are **2**, **3**, **4**, **5**.

References

[1] S. Ohkoshi, et. al., *Nature Chem.* **2010**, *2*, 539. [2] H. Tokoro, et. al., *Nature Commun.* **2015**, *6*, 7037. [3] T. Kubota, R. Seiki, et. al., *Materials Advances*, **2024**, *5*, 3832.

Quantitative Analysis of Electronic Structure–Property Relationship in Multi-Element Alloy Catalysts with X-ray Spectroscopy and *Ab Initio* Calculation

([1]*Grad. Sch. Sci., Kyoto Univ.*, [2]*Hakubi Center, Kyoto Univ.*, [3]*Grad. Sch. Eng., Kyoto Univ.*, [4]*URC, Kyushu Univ.*, [5]*Grad. Sch. Eng., Kyushu Univ.*, [6]*JASRI/SPring-8*, [7]*Grad. Sch. Sci., Osaka Metro. Univ.*, [8]*SRC, Ritsumeikan Univ.*) ○Masashi Nakamura[1], Dongshuang Wu[1], Megumi Mukoyoshi[1], Kohei Kusada[1,2], Hiroyuki Hayashi[3], Takaaki Toriyama[4], Tomokazu Yamamoto[4], Yasukazu Murakami[4,5], Shogo Kawaguchi[6], Toshiaki Ina[6], Yoshiki Kubota[7], Toyonari Yaji[8], Kazuo Kojima[8], Isao Tanaka[3] and Hiroshi Kitagawa[1]

Keywords: Multi-Element Alloy, Catalyst, XANES, DFT, Structure–Property Relationship

Although alloying is a powerful strategy to develop catalysts with desired properties, it is not self-evident how the inter-element interactions in alloys affect their catalytic properties. The recent prosperity of multi-element alloy (MEA) catalysts makes the problem more challenging[1]. Limited investigations into individual alloys are not enough to break through the situation. To discuss the interactions among different combinations of elements in a single framework, we propose that the quantitative analyses of element-selective electronic structures by X-ray spectroscopy[2] and *ab initio* calculation are prospective.

We synthesized a 5-element MEA of platinum-group metals (PGMs; Ru, Rh, Pd, Ir and Pt) and 6-element MEAs with an additional base metal (BM; Fe, Co, Ni, Ga, In or Sn), and investigated their performance in CO_2 hydrogenation. As a result, their CO selectivities ranged from 30 to 100%. The electronic structures of PGMs were quantified in two different approaches; XANES spectra were measured on the MEA catalysts to precisely evaluate the complicated real samples while *ab initio* calculations were performed on binary alloys to resolve the individual contributions of elemental interactions. Then, the correlations among the electronegativities of constituents, the quantities characterizing electronic structures (charges estimated by calculation or characteristic values of XANES spectra) and CO selectivity were examined. The results indicated that alloying PGMs with BM induced electron transfer following electronegativities, and the consequent modulation of the PGM valence led to the change in adsorption energies of intermediates and the selectivities (**Fig.**).

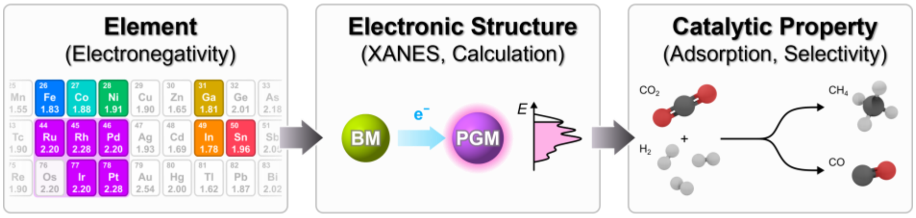

Fig. Schematics of element–electronic structure–property relationship in the MEA catalysts.

1) Y. Yao *et al.*, *Science*, **2022**, *376*, eabn3103., 2) J. Chen, *et al.*, *J. Phys. Chem. C*, **2022**, *125*, 2327.

Mild, Facile Synthesis of Perovskite Oxynitride Nanoparticles Towards High-entropy Thermoelectric Materials

(*School of Materials Science, Japan Advanced Institute of Science and Technology*)
○Simon David Moore, Mari Takahashi, Shinya Maenosono

Keywords: Chemical synthesis; Strontium Titanate; Nitridation; Sustainable; High entropy nanoparticles

Currently commercially available thermoelectric (TE) materials – which can convert directly from a temperature difference to an electric current – have high conversion efficiency (represented by the *ZT* value), but make use of toxic or rare elements. In contrast, oxides, including perovskites, are known to be non-toxic and stable to high temperatures.[1] However, their *ZT* values are low due to poor electrical conductivity, large band gap[2] and high thermal conductivity. Increasing *ZT* generally involves the introduction of dopant elements such as La, Bi or Pb, which harms the sustainability of such materials.[3] In this research, we focus on the synthesis of highly sustainable perovskite nanoparticles for future application as TE materials.

$SrTiO_3$ nanoparticles (NPs) (Fig. 1) were synthesized using a mild, facile gel-sol method, followed by characterization by XRD, TEM, EDS, XPS, and UV-vis. Synthesis also included the introduction of different alloying elements, such as Ca and Mn, to the Sr and Ti sites. The introduction of multiple alloying elements is known to increase the configurational entropy, leading to benefits such as significantly reduced thermal conductivity. Following the synthesis of alloyed $SrTiO_3$ NPs a nitridation step was performed by mixing with urea at mild temperatures to substitute a portion of the O atoms with N and thus reduce the optical band gap.[4] The produced oxynitride NPs had a measured indirect optical band gap of 2.2 eV, significantly reduced from the 3.1 eV of the $SrTiO_3$ NPs.

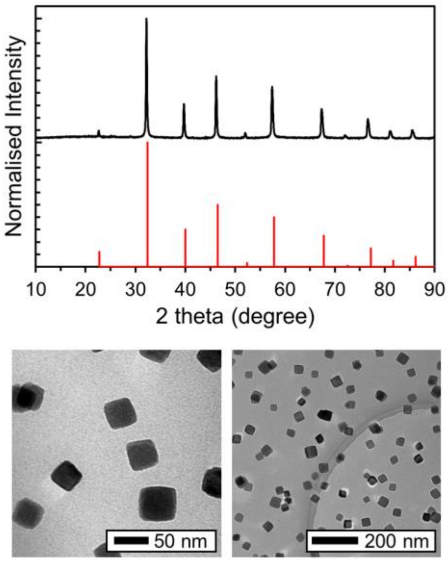

Figure 1: XRD pattern and TEM images of as-synthesised $SrTiO_3$ NPs. Red is the reference pattern for cubic $SrTiO_3$ (PDF: 00-005-0634)

References

[1] Shi, X. L. et al. *Nano Energy* **2020**, *78*, 105195. [2] Cardona, M. *Phys. Rev.* **1965**, *140*, 2A, A651-655. [3] Ma, J. et al. *J. Energy Storage* **2024**, *90*, 111890. [4] Atkinson, I. et al. *J. Photochem. Photobiol. A: Chem.* **2019**, *368*, 41-51.