

Low-temperature Ammonothermal Synthesis of LaTaON₂

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Pure perovskite-type LaTaON₂ crystal powders with high crystallinity were synthesized in supercritical ammonia using sodium amide as a flux. The synthesis temperature for this new method is 873 K, approximately 300 K lower than that for previous methods. The obtained powders have a pseudocubic lattice with a lattice constant of $a = 0.4049$ nm, which is in good agreement with the reported value.

Transition-metal oxynitrides have received much attention owing to various applications in electronic devices because of their unusual dielectric and optical properties and ionic conductivity as well as their catalytic activity and show particular potential as photocatalysts for the splitting of water. They have a number of other intriguing properties as well. For example, Jansen et al. reported that the perovskite Ca_(1-x)La_xTaO_(2-x)N_x ranges in color from yellow to red and, thus, might prove useful as a pigment to replace cadmium-containing materials.¹ Particularly intriguing are the recent findings that some Ta-based oxynitrides can serve as visible-light-driven photocatalysts because of their narrow band gaps. For example, Domen et al. reported recently that Ta-based oxynitrides such as TaON,² Y₂Ta₂O₅N₂,³ and LaTaON₂⁴ show high activity for water reduction and oxidation in aqueous solutions containing sacrificial reagents under visible-light irradiation.

Despite these promising findings, transition-metal oxynitrides have been much less investigated in terms of syntheses, properties, and applications than have the corresponding oxides. For example, transition-metal oxynitrides are still generally synthesized by the conventional but rather difficult routes of calcining oxide or reactive oxide precursors with flowing ammonia at high temperatures.⁵ However, the products so obtained rarely exhibit the expected properties but rather tend to exhibit low crystallinity,⁶ slow reaction rates, and significant structural defects because of the long duration and high temperature of calcination.

Among the new methods for synthesizing oxynitrides, the use of supercritical ammonia shows promise. Important advantages of this method compared with the conventional methods are that it gives well-crystallized nitrides such as GaN,⁷ CaAlSiN₃⁸⁻¹⁰ at relatively low temperatures and that it suppresses defect formation because the reaction scheme is not so much a solid-state reaction as it is a liquid-state reaction. However, there are no reports about the synthesis of transition-metal oxynitrides in supercritical ammonia. Thus, in the present study, our goal is to demonstrate the synthesis of well-crystallized perovskite LaTaON₂ by reacting metal precursors in ammonia under supercritical conditions.

For preparation of LaTa alloy powder precursor, La (>99.9%, High Purity Chemical) and Ta (>99.9%, High Purity

Chemical) metals were arc-melted, then quenched rapidly in an argon atmosphere. The formed precursor was ground and crushed to a powder with a sample mill in a nitrogen atmosphere.

For ammonothermal treatment, precursor alloy (<50 μm) was mixed with sodium amide (>90%, Wako, Japan) at a molar ratio of La/Na = 5 and placed in a bottom-sealed nickel tube in a nitrogen-filled glovebox. The tube was transformed into a vertically positioned superalloy pressure vessel, which was then filled with anhydrous liquid ammonia (99.9%, Showa Denko, Japan) via condensation. The pressure vessel was heated to the appropriate treatment temperature (773–1073 K) at a rate of 5 K min⁻¹ and an ammonia pressure of 100 MPa for 15–75 h. The obtained sample was washed several times with ethanol and HCl (pH 2) to remove sodium amide and La(OH)₃ and then dried at 343 K for 6 h in air. All of the samples after treatment contained some amount of La(OH)₃, which was easily removed by washing with 0.01 M aqueous HCl solution.

The treated samples were characterized as follows: Structures were determined by powder X-ray diffraction (XRD; RINT-2000, Rigaku, Japan) with Cu Kα radiation ($\lambda = 1.54178$); data were collected in the range $2\theta = 5-70^\circ$ (scan speed = 2° min^{-1} , step width = 0.02°); absorption spectra were determined by UV-vis diffuse reflectance spectrometry (Lambda 35, Perkin-Elmer, U.S.A.). Average La and Ta contents were quantified by energy-dispersive X-ray spectroscopy (EDX; S-4500, Hitachi, Tokyo, Japan) at 15 kV. Particle size and morphology were determined by scanning electron microscopy (SEM; SEMS-4500, Hitachi, Tokyo, Japan). Spectra were analyzed using the Quantex software program. Crystal quality was determined by transmission electron microscopy (TEM; JEM-3100FEF, JEOL, Tokyo, Japan).

Figure 1 shows XRD patterns of the samples after ammonothermal treatment. The final product at 873 K and 100 MPa is well-crystallized LaTaON₂, with all detected peaks assignable to the perovskite LaTaON₂ phase. The peaks correspond to a pseudocubic lattice constant of $a = 0.4049$ nm, in agreement with the reported value. The sample color is orange-yellow.

Figure 2 shows UV-vis diffuse reflectance spectra of the samples after ammonothermal treatment. The absorption edge is at 670 nm.

The samples after ammonothermal treatment vary according to the treatment temperature. Treatment at <773 K transforms the black precursor alloy into white La(OH)₃. Treatment at >873 K transforms it into red LaTaON₂. The shape, size, and lattice constant of LaTaON₂ crystals synthesized in 100 MPa of supercritical ammonia do not depend significantly on either reaction time (15–45 h) or reaction temperature (873–1073 K).

Addition of sodium amide as a mineralizer proved necessary for the formation of LaTaON₂ from the precursor alloy in

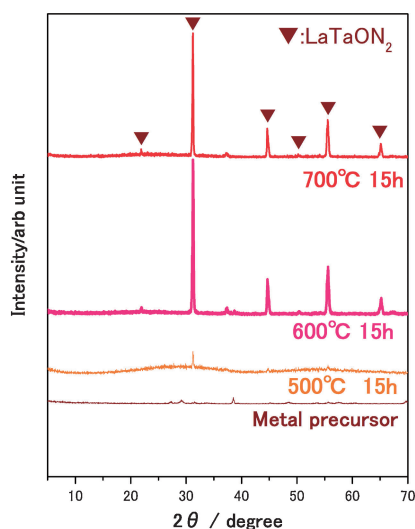


Figure 1. XRD patterns of synthesized LaTaON_2 at various temperature by ammonothermal treatments.

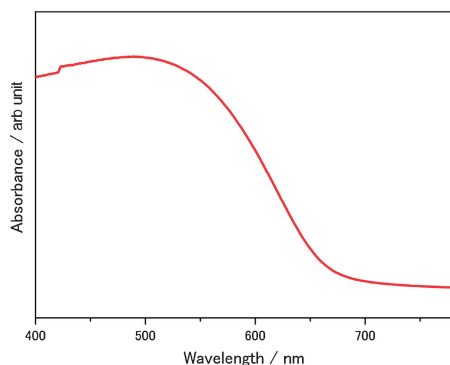


Figure 2. UV-vis diffuse reflectance spectra of the LaTaON_2 synthesized at 973 K for 15 h.

supercritical ammonia. Without this addition, no apparent reaction between alloy and ammonia occurs until 1073 K. The reason for this behavior is that ammonia is a poorer solvent for ionic substances than water; sodium amide increases the reaction rate by increasing the amount of anions in the supercritical ammonia solution. Addition of oxygen species is unnecessary, because moisture as an impurity from air, sodium amide, or water, supplies ample amount of oxygen. Addition of sodium hydroxide or more sodium amide causes the products to contain large amounts of $\text{La}(\text{OH})_3$.

Figure 3 shows SEM and TEM images of samples treated at 973 K and 100 MPa. The synthesized LaTaON_2 powder consists of cubic particles with an average size in the approximate range of 500 nm–1 μm . The La/Ta ratio is about 1, as confirmed by elemental analysis, and no sodium is present in the bulk product after washing with HCl. The bright images and corresponding selected area electron diffraction (SAED) patterns show that the LaTaON_2 particles are small, cubic, and well-crystallized. In

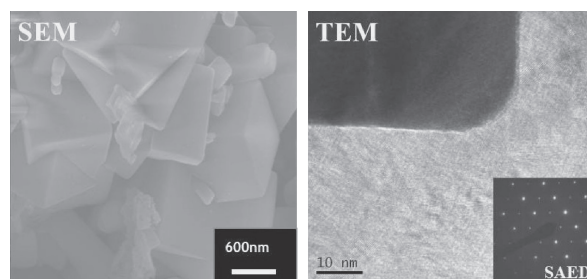


Figure 3. SEM and TEM images of the LaTaON_2 synthesized at 973 K for 15 h.

contrast, the precursor alloy consists of particles generally about one micrometer in size but occasionally irregularly shaped and up to dozens of micrometers in size. We speculate that reaction proceeds in NH_3 – NaNH_2 supercritical fluid solvent solution and that LaTaON_2 forms as a result of the decomposition of any intermediate.

In conclusion, we have succeeded in preparing phase-pure LaTaON_2 perovskite with good crystallinity in supercritical ammonia using sodium amide as a mineralizer. Preparation proceeds with a synthesis temperature of above 773 K, which is approximately 300 K lower than that for previous methods. The obtained product has a pseudocubic lattice constant of $a = 0.4049$ nm, in good agreement with the reported value. Particle size and morphology change drastically during reaction, prompting us to speculate that reaction proceeds in NH_3 – NaNH_2 supercritical fluid solvent solution. We are expanding upon this work by measuring photocatalytic activity and dielectric properties and preparing another transition-metal oxynitride, with the hope of extending this method to the synthesis of other oxynitrides.

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