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Formation and morphological change of BaTaO₂N perovskite from BaCN₂/Ta₂O₅ mixture

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Abstract

Metal oxynitrides are generally synthesized by heating their component oxides in a flow of ammonia for longer than 20 h. In the present study, pure BaTaO₂N oxynitride perovskite powder was obtained by heating a mixture of tetragonal BaCN₂ and Ta₂O₅ in a flow of nitrogen. The BaTaO₂N powder synthesized at slightly below the melting point of tetragonal BaCN₂ (910 °C) was found to consist of coarse aggregates of 300 nm-sized particles based on scanning electron microscopy observations. In contrast, BaTaO₂N powder obtained above the melting point of tetragonal BaCN₂ contained highly-dispersed particles after washing with acid. This difference is attributed to the dissolution and precipitation of the surfaces of the BaTaO₂N grains in the BaCN₂ melt to generate grain boundary layers soluble in acid. This work represents the first report of the synthesis of a metal oxynitride using a metal carbodiimide as both the metal and nitrogen source.

Keywords; perovskite-type oxynitride; metal carbodiimide; thermal analysis

1. Introduction

Perovskite-type oxynitrides such as SrTaO_2N and BaTaO_2N have attracted considerable attention as relaxor-type ferroelectric materials [1-7] and visible light-driven photocatalysts [8-10]. These materials are typically synthesized in powder form by heating their respective oxide precursors under a flow of ammonia (hereafter referred to as “ammonolysis”) at 900 – 1000 °C for several days [11-13]. However more recently, novel synthetic routes have been reported by many groups. Clarke et al. demonstrated the formation of oxynitride perovskites based on reactions between alkaline earth metal monoxides and TaON at approximately 1500 °C [14]. Phase-pure oxynitrides were obtained, but their color was brown, which indicates the presence of numerous anion defects due to the partial decomposition of the oxynitride perovskites at high temperatures [14]. Reactions between alkaline earth metal carbonates and tantalum nitride (Ta_3N_5) have been found to generate pure SrTaO_2N and nearly-single phase BaTaO_2N powders under a nitrogen flow at 1100 and 850 °C, respectively [15,16]. In both cases gaseous CO_2 was emitted by the decarboxylations of SrCO_3 or BaCO_3 on an alumina boat, following which CO was generated during the reaction between CO_2 and Ta_3N_5 to form TaON as a reaction intermediate. The corresponding oxynitride perovskites were subsequently formed by the reactions between the alkaline earth metal

monoxides and this TaON intermediate [15,16]. In each case, a SrTaO₂N or BaTaO₂N powder having a uniform particle size of approximately 300 nm was obtained reflecting the particle sizes of the starting materials [15,16]. Another synthetic route to SrTaO₂N based on the use of C₃N₄ as a reducing agent and a nitrogen source has also been developed [17]. Phase-pure SrTaO₂N was obtained by the reaction between a Sr₂Ta₂O₇ precursor and C₃N₄ at 800 °C, accompanied by the evolution of gaseous C₂N₂. The particle sizes of SrTaO₂N prepared via this route were very small (< 100 nm) because of the low reaction temperature compared to that applied during conventional ammonolysis (1000 °C), which forms micron-scaled aggregates of submicron particles [17]. Ta-based perovskite-type oxynitrides have also been prepared using urea as a nitrogen source in reactions having short durations [18,19]. However, the resulting materials have been shown to contain impurity phases.

Oxynitride perovskites are unstable at high temperature even under a nitrogen atmosphere, and both SrTaO₂N and BaTaO₂N release a portion of their nitrogen above 900 °C [2,20]. Thus, it can be helpful to employ starting materials that are nitrogen rich so as to intermittently supply nitrogen to the reaction system to avoid the partial nitrogen loss from the oxynitride products during the synthesis. Our group has previously examined liquid phase sintering and crystal growth of the perovskite-type

BaTaO₂N and Sr_{1-x}Ba_xTaO₂N using tetragonal barium carbodiimide (*t*-BaCN₂) with a melting point of 910 °C, as a flux to dissolve the oxynitrides. Cubic microcrystals and polycrystalline ceramics with a maximum relative density of 84.1% were obtained in molten BaCN₂ from the powders of BaTaO₂N and SrTaO₂N, respectively [6,21,22]. The surfaces of the as-grown BaTaO₂N crystals were surrounded by Ba-rich compounds, including residual BaCN₂ and the Ruddlesden-Popper type layered oxynitride perovskite Ba₂TaO₃N [6]. Clear ferroelectric polar phase alternation signals in piezoresponse force microscope (PFM) were observed on the BaTaO₂N crystals after washing with acid to remove the surface Ba-rich layer [6].

Alkaline earth metal carbodiimides are ionic crystals comprising metal cations and symmetric [N=C=N]²⁻ anions, which are different from asymmetric cyanamide anions ([N-C≡N]²⁻). These compounds act as fluxes for the synthesis of oxynitrides and are also promising nitrogen sources because they contain a high percentage of nitrogen. The number of the reports using metal carbodiimides or cyanamides for nitridation reaction is very limited. As an example, the ternary metal nitrides CaAlSiN₃:Eu²⁺ and Ca₁₆Si₁₇N₃₄ were synthesized by using CaCN₂ as both the calcium and nitrogen source at lower temperature than those required for solid-state reactions with nitrogen [23,24]. In the present study, *t*-BaCN₂ and Ta₂O₅ were employed as the starting materials for the

preparation of oxynitrides and their reaction temperature was investigated with thermogravimetry (TG). The microstructures of the BaTaO₂N products were also studied and their formation processes are discussed.

2. Experimental

Tetragonal BaCN₂ powder (*t*-BaCN₂) was synthesized by heating approximately 300 mg of BaCO₃ powder (99.9%, FUJIFILM Wako Pure Chemical) on an alumina boat under a 50 mL/min flow of ammonia (99.9%, Sumitomo Seika) at 900 °C for 10 h, as in our previous work [25]. TG - differential thermal analysis - mass spectrometry (TG-DTA-MS, STA2500-QMS403 Aeolos, Netzsch) assessments were conducted using approximately 10 mg mixtures of *t*-BaCN₂ and Ta₂O₅ powder (99.9%, FUJIFILM Wako Pure Chemical) containing equimolar amounts of barium and tantalum, so as to investigate the reaction temperature. The mixed powder sample was transferred into an alumina crucible and the sample chamber was evacuated to below 3 Pa prior to introducing helium gas. The sample was subsequently heated in a 200 mL/min flow of helium at a heating rate of 10 °C/min up to 1000 °C.

BaTaO₂N powders were synthesized from the reaction of dry mixture of *t*-BaCN₂ and Ta₂O₅ powders. The Ba:Ta molar ratios in the initial mixture were changed

in a range from 1.0 to 1.5. Each powder mixture was placed in an alumina boat and then heated in an alumina tube furnace under a 30 mL/min flow of nitrogen (99.99%) at various temperatures (700 – 910 °C) and for varying durations (5 min – 5 h). Both the heating and cooling rates were 200 °C/h. The original white powder changed in color to red or reddish black upon the heating. The initial material also transformed to an aggregated solid after heating at 910 °C because of the melting and solidification of unreacted BaCN₂ [6,21,26]. This product adhered to the surface of the alumina boat and was removed by washing with 1 M nitric acid followed by distilled water. The powder products were obtained by filtration using a filter paper with pore diameters smaller than 5 μm (Toyo Roshi K. K.).

Powder X-ray diffraction (XRD, Ultima IV, RIGAKU) using Cu K α radiation was employed for crystalline phase identification. XRD profiles were obtained over the 2θ range of 10 – 90° with a scanning speed and step size of 10°/min and 0.02°, respectively. Crystalline phase ratios were estimated using the Rietveld method in conjunction with the RIETAN-FP program [27]. The chemical compositions of the powder products were evaluated using X-ray fluorescence spectroscopy (XRF, SEA 6000, Hitachi) for the molar ratios of barium and tantalum in combination with a combustion oxygen/nitrogen analyzer (EMGA-620W, Horiba) for the anion contents

with Si_3N_4 and Gd_2O_3 as references. The nitrogen content in the Si_3N_4 (JCRM-R004, The Ceramic Society of Japan) was certificated to be 38.5 wt%. Commercially available Gd_2O_3 (99.9%, FUJIFILM Wako Pure Chemical) was used after calcination at 1000 °C. Preliminary CHN combustion analyses (CE440, Exeter Analytical Inc.) were conducted to quantify the amount of residual carbon in the powder products. The conventional ammonolysis method was employed using a powder mixture of BaCO_3 and Ta_2O_5 with a Ba:Ta molar ratio of 1.03:1 to obtain a reference BaTaO_2N powder. In this synthesis, the powder mixture was heated on an alumina boat under a flow of ammonia at 930 °C for 30 h. Preparation from a barium-rich starting mixture is effective to avoid the formation of Ta_3N_5 as an impurity probably due to a loss of barium via the reaction of BaO with the alumina boat [2]. The microstructures of the powders were studied with a scanning electron microscopy (SEM, JSM-6390LVS, JEOL). The optical properties of the BaTaO_2N powder products were studied using a UV-Vis spectrometer (V-550, JASCO) in the wavelength range from 400 to 800 nm. Alpha-alumina powder (99%, Kojundo Chemical Laboratory Co., Ltd.) was employed as a reference of reflectance. The specific surface area of each specimen was determined via the Brunauer-Emmett-Teller (BET) method using a surface area analyzer (BELSORP-mini, Microtrac-BEL). The surface conditions of the BaTaO_2N particles were characterized by

X-ray photoelectron spectroscopy (XPS, JPS-9200, JEOL) using Al K α X-rays.

3. Results and discussion

3.1 Reaction between *t*-BaCN₂ and Ta₂O₅

The result of TG-DTA-MS analysis of a powder mixture of *t*-BaCN₂ and Ta₂O₅ is depicted in Fig. 1. **Caution: a small amount of HCN can be released during the heating of BaCN₂, and so this procedure should be conducted in a fume hood.**

A slow weight loss beginning at 620 °C continued to approximately 750 °C. A subsequent rapid weight loss and a large exothermic event begin simultaneously at 750 °C. This exothermic event may originate from the heat of BaTaO₂N formation.

Molecular weights of gas species were detected with the MS. Large amount of the gases with $m/z = 28$ (CO, N₂, or both) and 44 (probably CO₂) as well as a small amount of the gas with $m/z = 27$ (HCN) were observed during the rapid weight loss. The HCN may have been formed by the reaction between *t*-BaCN₂ and adsorbed ammonia or water.

The original white powder was found to change to a reddish black powder after the TG measurement. This material contained the nitrogen-deficient cubic oxynitride perovskite BaTaO₂N_{1- δ} (lattice parameter $a = 0.4106(1)$ nm) as its main crystalline phase, along with a trace amount of δ -TaN (see Fig. S1 in Supporting Information). The BaTaO₂N_{1- δ}

and δ -TaN were formed via the partial decomposition of BaTaO₂N causing a slight weight loss above 950 °C, as was also previously observed in a TG study of BaTaO₂N [2].

3.2 Syntheses of BaTaO₂N powders

Powder mixtures of *t*-BaCN₂ and Ta₂O₅ containing equimolar amounts of barium and tantalum were annealed under a flow of nitrogen and the XRD patterns of the powder products are presented in Figs. 2(a) – (d). Perovskite-type BaTaO₂N was not formed in the sample heated at 700 °C for 10 min as shown in Fig. 2(a), but appeared as the main phase in the product heated at 700 °C for 5 h (Fig. 2(b)). Crystalline BaTaO₂N was generated up to 800 °C while unreacted *t*-BaCN₂ and Ta₂O₅ as well as Ba₅Ta₄O₁₅ and BaTa₂O₆ were contained in the powder products prepared at temperatures up to 800 °C (Figs. 2(b) and 2(c)). Nearly or completely pure phase BaTaO₂N powders were obtained by heating at 880 – 910 °C for 5 h (Figs. 2(d) – (f)). Samples in a powder form were obtained by heating up to 880 °C, which is slightly below the melting point of *t*-BaCN₂ (910 °C) [21,26]. The product obtained by heating a starting mixture with equimolar amounts of Ba and Ta at 910 °C for 5 h (Fig. 2(d)) partially transformed to a solidified lump due to the solidification of the molten BaCN₂. It also had a black

coloration, probably due to the partial reduction of Ta^{5+} caused by the partial decomposition of the reddish BaTaO_2N . The sample adhered to the alumina boat and a black powder was obtained as a filtrate after washing with nitric acid. This powder contained a cubic perovskite oxynitride as its main phase, as shown in Fig. 2(d), but was also contaminated by a trace amount of $\delta\text{-TaN}$. This was presumably due to a slight loss of barium via reaction with the alumina boat and some degree of vaporization of BaCN_2 at high temperatures [6,21,26]. Fig. S2 demonstrates that the perovskite-phase purity was 93.5 wt%, together with 6.5 wt% $\delta\text{-TaN}$ as an impurity. The chemical composition of the acid-washed product did not match with the expected stoichiometric composition because of its shortage of barium and nitrogen amounts (first line of Table 1).

In another trial, an excess $t\text{-BaCN}_2$ was mixed with Ta_2O_5 to obtain a Ba:Ta molar ratio of 1.5:1 so as to supply efficient amounts of barium and nitrogen. A reddish powder and a solidified lump were obtained upon heating this mixture at 880 and 910 °C for 5 h, respectively. Soluble impurities were removed by washing with nitric acid and the resulting filtrates were found to comprise a single phase of BaTaO_2N , as shown in Figs. 2(e) and (f). The lattice parameter for cubic BaTaO_2N obtained by heating at 910 °C for 5 h (Fig. 2(f)) was $a = 0.4111(1)$ nm, which was comparable to the value for the reference BaTaO_2N powder prepared by the ammonolysis route ($a =$

0.4112(1) nm) and the literature value ($a = 0.41128(1)$ nm) [12]. The chemical composition of this material agreed with the stoichiometric value (second line of Table 1). Crystallinity of the BaTaO₂N obtained from the *t*-BaCN₂ and Ta₂O₅ mixture was significantly higher than that of the reference BaTaO₂N as represented in XRD patterns (Fig. S3). Carbon contamination in the washed product was negligible according to the CHN combustion analysis, for which the detection limit is below 0.7 wt%. The preparation of BaTaO₂N from *t*-BaCN₂ and Ta₂O₅ required only 5 h at 880 – 910 °C in the present work, while the conventional ammonolysis requires a dwell time of more than 20 h at 900 – 1000 °C [1,2,12,13]. This difference can likely be ascribed to the high reactivity of BaCN₂, as has also been reported for the SrCN₂ reaction intermediate generated during the reaction between Sr₂Ta₂O₇ and C₃N₄ to synthesize SrTaO₂N [17].

3.3 Morphological changes in BaTaO₂N particles depending on the synthetic route

The microstructures were compared by SEM observations on single phase powders of BaTaO₂N. The particle size distributions of phase-pure BaTaO₂N specimens were investigated by examining more than 200 grains in the SEM images (a part of the SEM images are shown in Fig. 3). Figs. 3(a) and (b) show the BaTaO₂N samples synthesized by the reaction between *t*-BaCN₂ and Ta₂O₅ using a Ba:Ta molar ratio of

1.5:1 with heating slightly below and above the melting point of *t*-BaCN₂, respectively. The particle sizes of these materials ranged from 100 to 850 nm, while those of the sample prepared via the ammonolysis of a BaCO₃/Ta₂O₅ mixture were smaller than 300 nm (Fig. 3(c)). The average grain sizes of the BaTaO₂N samples in Figs. 3(a), (b) and (c) were 320, 330 and 170 nm, respectively. The particle sizes of the products obtained from *t*-BaCN₂/Ta₂O₅ mixtures were larger than those of the ammonolysis products, likely because the former process involved significant diffusion caused by the reaction between BaCN₂ and Ta₂O₅. The former material was also observed to have a smaller BET surface area of 2.8 m²/g as compared to 5.2 m²/g for the ammonolysis product.

The BaTaO₂N sample obtained at 880 °C (below the melting point of *t*-BaCN₂, Fig. 3(a-1)) was synthesized by a solid state reaction. In this material, the 300 nm particles were found to generate coarse aggregates, similar to the ammonolysis product (Fig. 3(c-1)) [2,12]. In addition, the BaTaO₂N synthesized in conjunction with a BaCN₂ melt crystallized in a polygonal form, as shown in Fig. 3(b-1). Cubic or cuboid grains reflecting the euhedral form of the perovskite-type structure (as also seen in our previous studies on BaTaO₂N and Sr_{1-x}Ba_xTaO₂N [6,21]) were not observed. This likely occurred because a large part of the BaCN₂ melt was consumed by the reaction with Ta₂O₅ such that an equilibrium between solid and liquid phases was not attained. This

sample contained highly-dispersed particles, as shown in Fig. 3(b-1). The BaTaO₂N was partially dissolved in the molten BaCN₂ and so precipitated on the grain surfaces, while the surfaces were surrounded by acid-soluble Ruddlesden-Popper type oxynitrides such as Ba₂TaO₃N and unreacted BaCN₂, as in the case of BaTaO₂N ceramics sintered with BaCN₂ as an additive [6]. These layers were removed by the acid wash process to produce dispersed BaTaO₂N particles.

Diffuse-reflectance spectra were obtained from the BaTaO₂N powders, as shown in Fig. 4. The absorption edge of the BaTaO₂N prepared from molten BaCN₂ and Ta₂O₅ (1.93 eV, Figs. 2(f) and 3(b)) was almost the same as that of the reference BaTaO₂N (1.87 eV, the ammonolysis product), but the reflectance value for the former was slightly lower than that for the latter. This difference can possibly be ascribed to the presence of small amount of various electrically conductive materials, including nitrogen-deficient oxynitride perovskites or impurities such as TaN. The Ta 4f XPS spectrum (Fig. S4) exhibited a shoulder peak at approximately 22.9 eV for the BaTaO₂N obtained from a mixture of *t*-BaCN₂ and Ta₂O₅, indicating the presence of TaN as a minor phase on the grain surface. [28].

4. Conclusion

In conclusion, the formation of a BaTaO₂N phase from a *t*-BaCN₂/Ta₂O₅ mixture was found to begin between 700 and 800 °C. A single phase of BaTaO₂N powder was obtained after heating a mixture containing an excess of BaCN₂ at approximately 900 °C for 5 h under a nitrogen flow followed by acid washing. Heating the starting materials above the melting point of *t*-BaCN₂ yielded highly-dispersed BaTaO₂N particles. This outcome is attributed to the partial dissolution and precipitation of BaTaO₂N to molten BaCN₂, thus forming grain boundary layers that were soluble in acid. The technique used to tune the particle morphology herein may present an effective approach to synthesizing oxynitride powders for the full-densification of ceramics as well as visible light-driven photocatalysts with controlled particle morphologies.

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Table 1 Elemental compositions of the BaTaO₂N powders.

Preparation condition	Ba /wt%	Ta /wt%	O /wt%	N /wt%
Washed black product from <i>t</i> -BaCN ₂ /Ta ₂ O ₅ with Ba : Ta = 1 : 1* (910 °C-5 h)	32.9(3)*	54.8(5)*	9.2(1)*	3.1(1)*
Washed red product from <i>t</i> -BaCN ₂ /Ta ₂ O ₅ with Ba : Ta = 1.5 : 1 (910 °C-5 h)	37.6(4)	50.0(4)	8.7(1)	3.7(1)
Ammonolysis product from BaCO ₃ /Ta ₂ O ₅ (930 °C-60 h)	38.9(2)	48.6(3)	8.9(1)	3.6(1)
Theoretical values of stoichiometric BaTaO ₂ N	37.7	49.7	8.8	3.8

*Contaminated by a small amount of δ -TaN.

Figure captions

Fig. 1 TG-DTA-MS data obtained from a powder mixture of *t*-BaCN₂ and Ta₂O₅ with an equimolar Ba:Ta ratio under a flow of helium. Here, $m/z = 28$ indicates N₂ and CO, $m/z = 44$ is CO₂ and $m/z = 27$ is HCN.

Fig. 2 Powder XRD patterns of the products prepared from *t*-BaCN₂ and Ta₂O₅. The starting materials used to synthesize (a) – (d) contained equimolar amounts of barium and tantalum. The annealing temperatures and the duration times were (a) 700 °C for 10 min, (b) 700 °C for 5 h, (c) 800 °C for 5 h, and (d) 910 °C for 5 h (note that this product was washed with nitric acid). Patterns (e) and (f) correspond to the acid-washed products obtained by firing mixtures for which Ba:Ta molar ratio was 1.5:1 at (e) 880 and (f) 910 °C for 5 h. Where \diamond : BaTaO₂N (ICSD 202763), \circ : Ba₅Ta₄O₁₅ (JCPDS 18-193), \square : BaTa₂O₆ (ICSD 27082), \dagger : Ta₂O₅ (JCPDS 25-922), \downarrow : tetragonal BaCN₂ [23], $*$: δ -TaN (ICSD 76456), $?$: unknown phases. The inset shows a photographic image of the BaTaO₂N powder that generated pattern (f).

Fig. 3 SEM images and particle size distributions of single phase BaTaO₂N powders obtained by (a-1, 2) the reaction between *t*-BaCN₂ and Ta₂O₅ (with a 1.5:1 Ba:Ta molar ratio) at 880 °C (for which the XRD pattern is provided in Fig. 2(e)), (b-1, 2) the reaction of the same starting mixture at 910 °C (XRD pattern in Fig. 2(f)), and (c-1, 2) the conventional ammonolysis of a BaCO₃ and Ta₂O₅ mixture at 930 °C. The average grain sizes of samples (a), (b) and (c) were 320, 330 and 170 nm, respectively.

Fig. 4 Diffuse-reflectance spectra of BaTaO₂N powders generated by (a) conventional ammonolysis and (b) the reaction between *t*-BaCN₂ and Ta₂O₅. Sample (b) was prepared using the same conditions as used to form the materials for which data are provided in Figs. 2(f) and 3(b) (that is, heating of a starting *t*-BaCN₂/Ta₂O₅ mixture having a 1.5:1 Ba:Ta molar ratio at 910 °C for 5 h and subsequent washing with nitric acid).

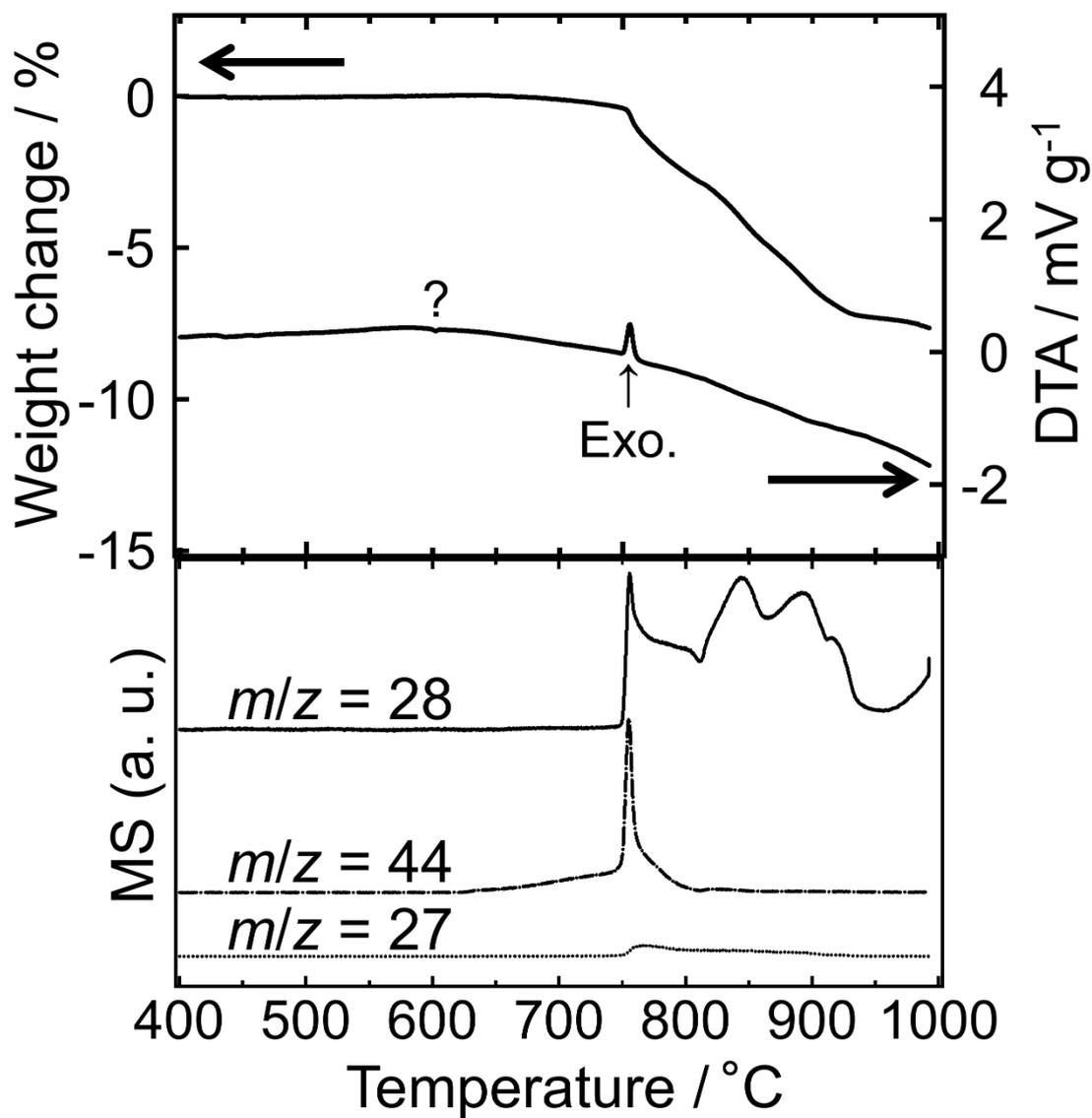


Fig. 1 TG-DTA-MS data obtained from a powder mixture of t -BaCN₂ and Ta₂O₅ with an equimolar Ba:Ta ratio under a flow of helium. Here, $m/z = 28$ indicates N₂ and CO, $m/z = 44$ is CO₂ and $m/z = 27$ is HCN.

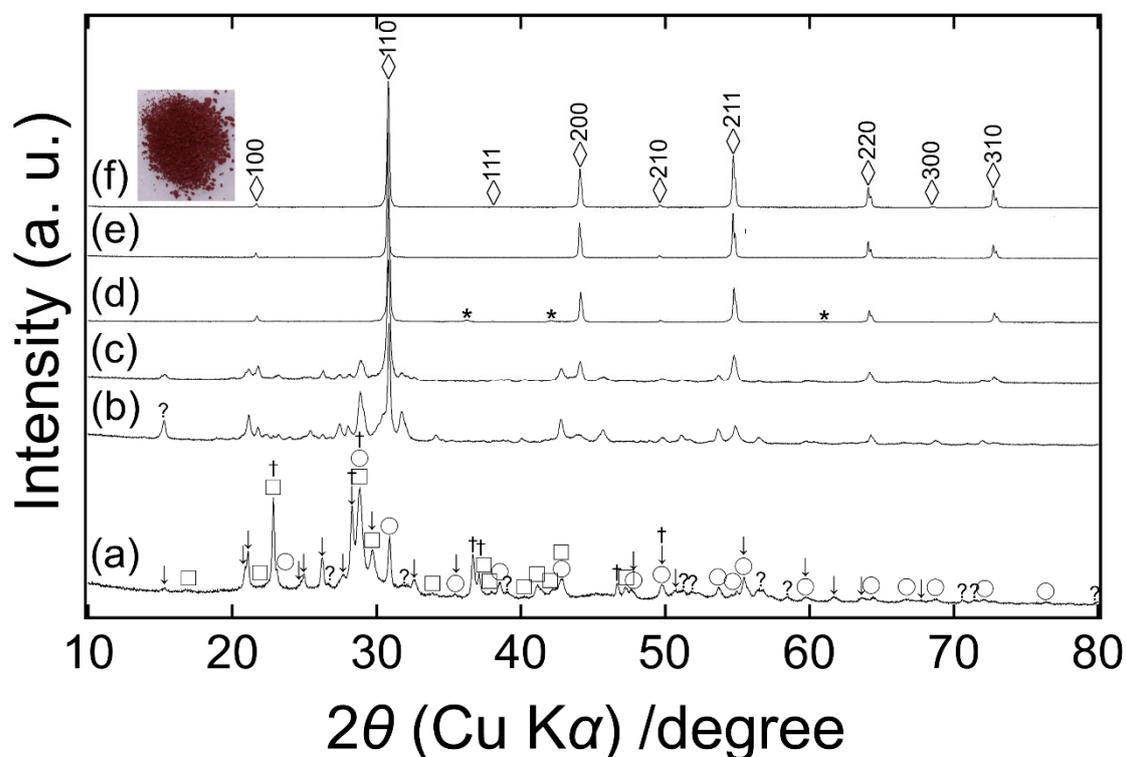


Fig. 2 Powder XRD patterns of the products prepared from t - $BaCN_2$ and Ta_2O_5 . The starting materials used to synthesize (a) – (d) contained equimolar amounts of barium and tantalum. The annealing temperatures and the duration times were (a) 700 °C for 10 min, (b) 700 °C for 5 h, (c) 800 °C for 5 h, and (d) 910 °C for 5 h (note that this product was washed with nitric acid). Patterns (e) and (f) correspond to the acid-washed products obtained by firing mixtures for which Ba:Ta molar ratio was 1.5:1 at (e) 880 and (f) 910 °C for 5 h. Where \diamond : $BaTaO_2N$ (ICSD 202763), \circ : $Ba_5Ta_4O_{15}$ (JCPDS 18-193), \square : $BaTa_2O_6$ (ICSD 27082), \dagger : Ta_2O_5 (JCPDS 25-922), \downarrow : tetragonal $BaCN_2$ [23], $*$: δ - TaN (ICSD 76456), $?$: unknown phases. The inset shows a photographic image of the $BaTaO_2N$ powder that generated pattern (f).

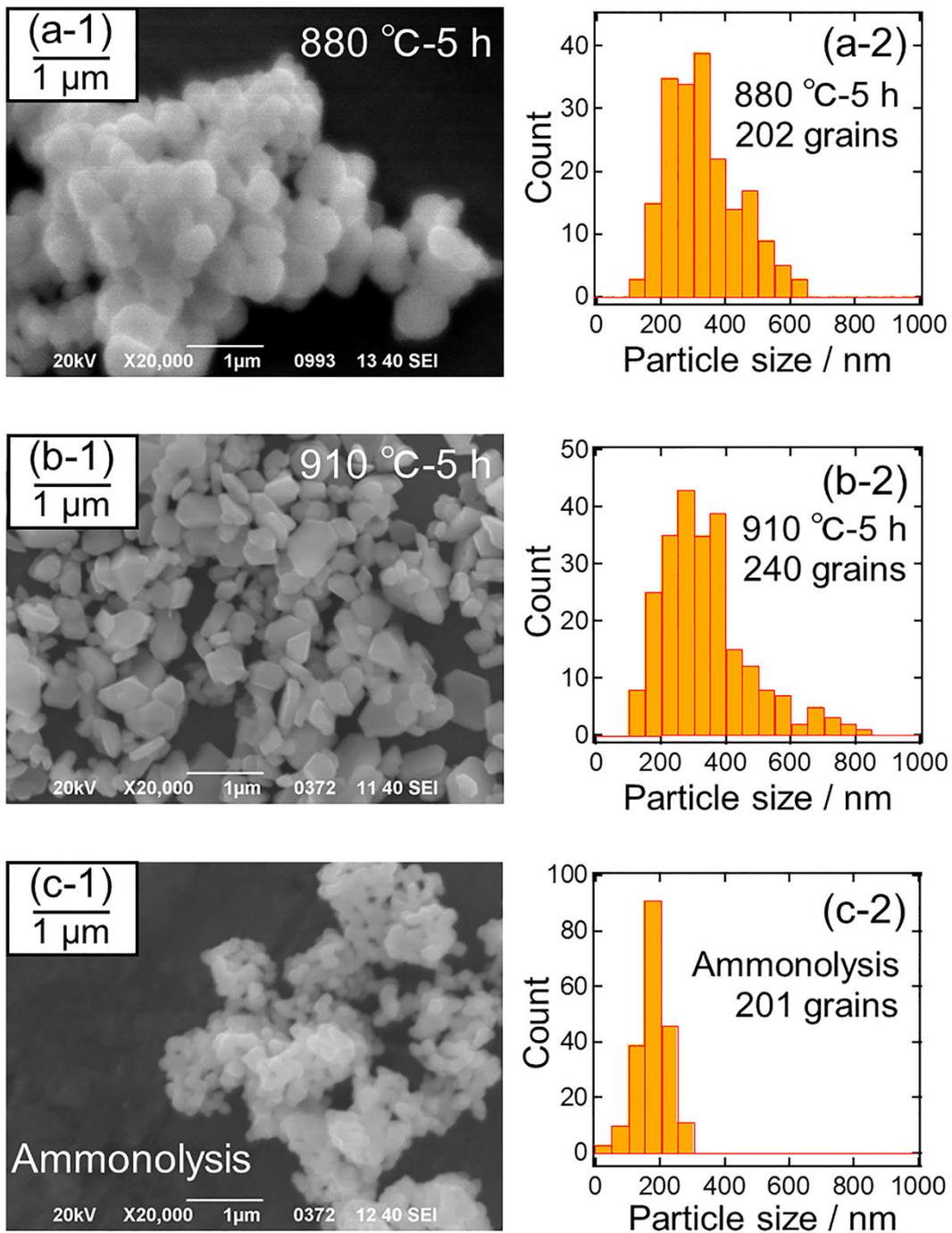


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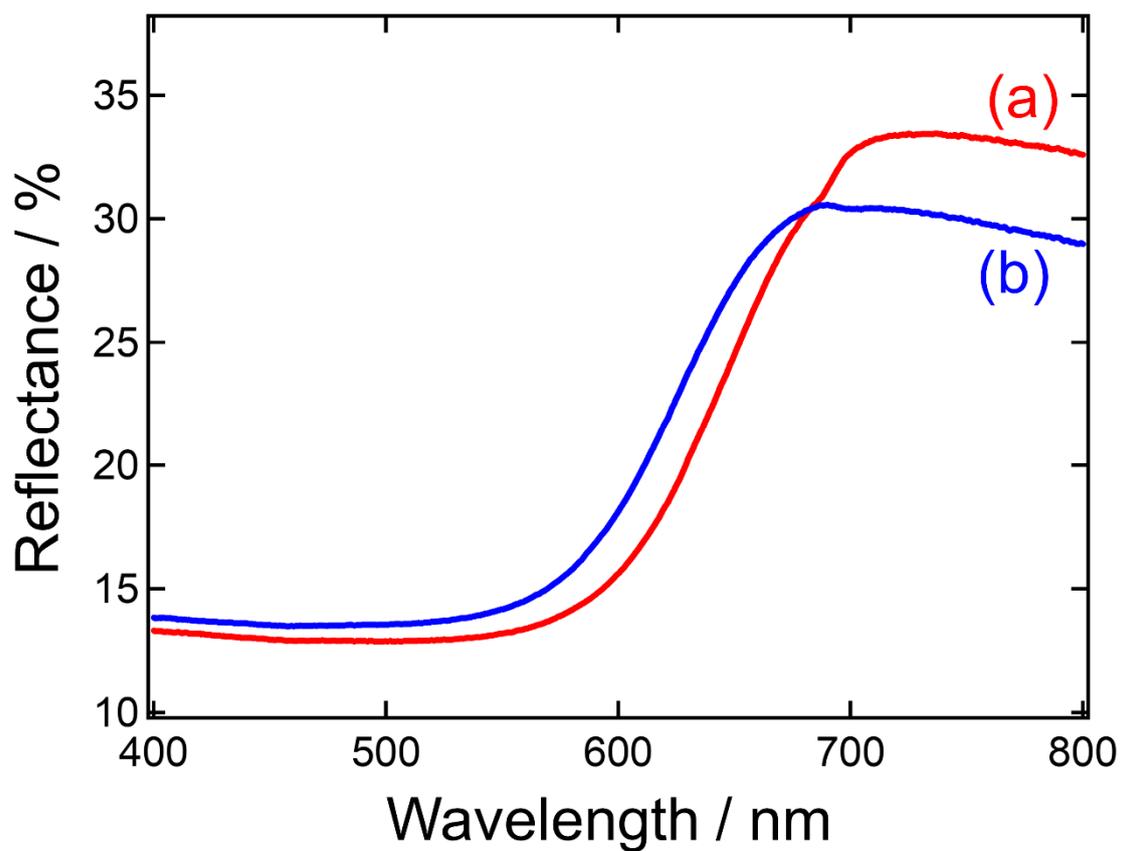


Fig. 4 Diffuse-reflectance spectra of BaTaO₂N powders generated by (a) conventional ammonolysis and (b) the reaction between *t*-BaCN₂ and Ta₂O₅. Sample (b) was prepared using the same conditions as used to form the materials for which data are provided in Figs. 2(f) and 3(b) (that is, heating of a starting *t*-BaCN₂/Ta₂O₅ mixture having a 1.5:1 Ba:Ta molar ratio at 910 °C for 5 h and subsequent washing with nitric acid).