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# Synthesis of perovskite-type oxynitrides $\text{SrNb}(\text{O},\text{N})_3$ and $\text{CaTa}(\text{O},\text{N})_3$ using carbon nitride

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## Abstract

The synthesis of oxynitride perovskites based on the use of gaseous ammonia as the nitrogen source requires high reaction temperatures and long durations. In the present work, reduction and nitridation reactions using carbon nitride ( $\text{C}_3\text{N}_4$ ) were employed to prepare  $\text{SrNbO}_2\text{N}$  and  $\text{CaTaO}_2\text{N}$  from their oxide precursors, without the use of ammonia. The phase evolution behaviors and the reaction mechanisms were investigated by acquiring thermogravimetric and X-ray diffraction data. The formation of metal cyanamide as an

intermediate was found to be vital to realizing low-temperature synthesis of these compounds. Scanning electron microscopy observations also indicated that the particle sizes of the oxynitrides prepared using  $C_3N_4$  were smaller than those obtained by ammonolysis reactions, due to the low formation temperature of 800 °C associated with the present  $C_3N_4$  process.

Key words: perovskite; oxynitrides; carbon nitride; powder processing

## **Introduction**

Perovskite oxynitrides having the general formulae  $ABO_2N$  and  $ABON_2$  are useful functional materials with a wide range of applications. The majority of known perovskite-type oxynitrides have potential applications as dielectric materials [1], photocatalysts [2, 3] and nontoxic pigments [4]. The conventional preparation route for oxynitrides is the thermal ammonolysis of oxides under a flow of gaseous ammonia. However, a high reaction temperature and long duration are required for the ammonolysis reaction due to the limited diffusion rate of nitrogen [1, 5]. In order to overcome these extreme aspect of processing, several novel synthesis approaches that do not use ammonia have been investigated. Sun et al. developed a direct synthesis approach for the oxynitride  $SrTaO_2N$  from  $SrCO_3$  and  $Ta_3N_5$  in a nitrogen atmosphere [6]. Clark et al. reported that  $ATaO_2N$  ( $A=Ca, Ba, Sr$ ) could be synthesized through a high-temperature solid-state reaction between  $AO$  and  $TaON$  at 1500 °C for 3 h under  $N_2$  [7]. However, prior to this heat-

treatment, the  $Ta_3N_5$  and TaON must be produced by heating  $Ta_2O_5$  under a flow of ammonia at 950 and 850 °C, respectively. The utilization of ammonia is thus not avoided in these processing routes. In our own previous work, we successfully synthesized SrTaO<sub>2</sub>N using carbon nitride ( $C_3N_4$ ) [8]. In this process, the  $C_3N_4$  reacts with the Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> precursor to form SrCN<sub>2</sub> and Ta<sub>3</sub>N<sub>5</sub> intermediates on residual Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>. These intermediates then react with the oxide residue to form SrTaO<sub>2</sub>N at 800 °C, which is 200 °C lower than the temperature required for ammonolysis. Recently, the formation of metal cyanamide ( $M-CN_2$ ) intermediates, such as La<sub>2</sub>O<sub>2</sub>CN<sub>2</sub> and ZnCN<sub>2</sub> has also been suggested as an ammonia-free synthesis of the oxynitrides LaTiO<sub>2</sub>N and GaN:ZnO, respectively [9, 10]. It is evident that intermediates play an important role in the formation of oxynitrides in these systems, although the reactivity of  $C_3N_4$  with other oxide precursors to form perovskite-type oxynitrides has not yet been examined. Metal cyanamides can be obtained from many alkaline and alkaline earth metals and, in the present work, we used Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> or Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> as precursors for nitridation reactions with  $C_3N_4$  to synthesize SrNbO<sub>2</sub>N and CaTaO<sub>2</sub>N, respectively. The reactivity of  $C_3N_4$  with the precursors to form oxynitride perovskites was investigated by comparing the formation of intermediate phases.

### **Experimental procedure**

The oxide precursors were prepared from the raw materials CaCO<sub>3</sub> (purity 99.9%, Fujifilm Wako Pure Chemical Co.), SrCO<sub>3</sub> (purity 99.9%, Fujifilm Wako Pure Chemical

Co.), Ta<sub>2</sub>O<sub>5</sub> (purity 99.9%, Fujifilm Wako Pure Chemical Co.) and Nb<sub>2</sub>O<sub>5</sub> (purity 99.9%, Fujifilm Wako Pure Chemical Co.). Stoichiometric mixtures of the carbonates and oxides were calcined at 1200 °C for 10 h in air to prepare the Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> precursors. The mixtures were ground and calcined twice to obtain phase-pure oxide precursors. C<sub>3</sub>N<sub>4</sub> was synthesized via the calcination of melamine (purity 99.0%, Fujifilm Wako Pure Chemical Co.) at 550 °C for 6 h in air. A small amount of hydrogen remained in the calcined product and the chemical composition of the product was estimated to be C<sub>3</sub>N<sub>4.5</sub>H<sub>1.5</sub> based on CHN analysis, although the compound is still referred to herein as C<sub>3</sub>N<sub>4</sub>. The oxide precursors were mixed with the C<sub>3</sub>N<sub>4</sub> by ball milling using zirconia balls and ethanol, employing a Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> or (Ca<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>):C<sub>3</sub>N<sub>4</sub> molar ratio of 1:1.5. Each mixture was subsequently pressed into a pellet and then loaded into an alumina boat, after which it was heated at various temperatures for 6 h in a N<sub>2</sub> flow (50 ml/min, 99.99%) in a silica tube furnace.

The crystalline phases of the products were determined by powder X-ray diffraction (XRD; Ultima IV, Rigaku), collecting data at 0.02° steps over the 2θ range of 15° to 60°. Thermogravimetric differential thermal analysis (TG-TGA) data were acquired using a thermogravimetric analyzer (STA 2500, NETZSCH) in a nitrogen flow of 100 ml/min. The sample chamber was evacuated to 10 Pa prior to the measurements. The morphology of each product was observed by field-emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL).

## Results and discussion

The thermal behavior of a  $\text{Sr}_2\text{Nb}_2\text{O}_7/\text{C}_3\text{N}_4$  mixture was examined using TGA under a flow of nitrogen. The resulting TGA plot (Figure 1) exhibits three stages. The first significant mass loss of 21.5% started at 380 °C and finished at approximately 700 °C, while the second loss of 2.1% occurred around 800 °C. The TGA curve was almost constant above 1000 °C after the third mass loss. XRD patterns were obtained at each final temperature associated with a mass loss and are shown in Figure 2. Only diffraction peaks attributed to  $\text{Sr}_2\text{Nb}_2\text{O}_7$  present in the pattern for the starting mixture (Figure 2(a)) because of the amorphous nature of the  $\text{C}_3\text{N}_4$ . At 700 °C, a small amount of  $\text{SrCN}_2$  and a niobium-based rock salt phase can be observed together with residual  $\text{Sr}_2\text{Nb}_2\text{O}_7$ . A  $\text{Sr}_4\text{Nb}_2\text{O}_9$  impurity was formed along with the perovskite phase and the rock salt phase at 1100 °C. The oxygen and nitrogen concentrations in the perovskite phase could not be accurately determined because of the presence of the minor impurity phases. Hence, hereafter, the chemical formula the perovskite phase is denoted as  $\text{SrNb}(\text{O},\text{N})_3$ . The TGA and XRD results suggest that the first and largest mass loss was caused by the decomposition of  $\text{C}_3\text{N}_4$  as shown in Figure S1 in Supporting Information (SI) together with the formation of  $\text{SrCN}_2$  and rock salt type  $\text{Nb}(\text{O},\text{N})$ . The generation of the perovskite phase from  $\text{SrCN}_2$ ,  $\text{Nb}(\text{O},\text{N})$  and unreacted  $\text{Sr}_2\text{Nb}_2\text{O}_7$  caused the second mass loss, similar to results obtained during  $\text{SrTaO}_2\text{N}$  formation from  $\text{Sr}_2\text{Ta}_2\text{O}_7$  and  $\text{C}_3\text{N}_4$  [8]. The third mass loss is ascribed to the decomposition of the perovskite phase, in which the  $\text{SrNb}(\text{O},\text{N})_3$  decomposed to  $\text{Sr}_4\text{Nb}_2\text{O}_9$  and a rock salt phase. The thermal decomposition of the  $\text{SrNbO}_2\text{N}$  was

investigated in an Ar flow and this material was determined to degrade to give a mixture of  $\text{Sr}_4\text{Nb}_2\text{O}_9$  and the rock salt-like compound  $\text{Nb}_4\text{N}_3$  together with significant  $\text{N}_2$  release above  $950\text{ }^\circ\text{C}$  [11].

The mixture of  $\text{Sr}_2\text{Nb}_2\text{O}_7/\text{C}_3\text{N}_4$  was also heated at temperatures from  $600$  to  $800\text{ }^\circ\text{C}$  for  $6$  h in the tube furnace under a flow of  $\text{N}_2$ , and the XRD patterns obtained from the products are shown in Figure S2 in the SI. At  $600\text{ }^\circ\text{C}$ , a small amount of  $\text{SrCN}_2$  and a rock salt phase were observed together with  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , in agreement with the TGA results. At  $700\text{ }^\circ\text{C}$ , the perovskite phase appeared along with  $\text{SrCN}_2$  and rock salt phase intermediates, although a portion of the  $\text{Sr}_2\text{Nb}_2\text{O}_7$  still remained. A nearly pure  $\text{SrNb}(\text{O},\text{N})_3$  perovskite phase with only a small quantity of a minor phase was obtained at  $800\text{ }^\circ\text{C}$ . The formation of the  $\text{SrNb}(\text{O},\text{N})_3$  perovskite could therefore be achieved at temperatures as low as  $800\text{ }^\circ\text{C}$  in a flow of  $\text{N}_2$ , rather than at the temperature of  $950\text{ }^\circ\text{C}$  required for  $\text{NH}_3$ -based nitridation [12]. The products appeared black, suggesting the presence of an electrically conductive impurity such as a rock salt-type niobium phase as shown in Fig. S3 in the SI. The lattice parameters for the product were determined to be  $a = 5.70756(3)\text{ \AA}$ ,  $c = 8.09421(1)\text{ \AA}$  and  $c/\sqrt{2}a = 1.00278\text{ \AA}$ , all of which are smaller than the literature values ( $a = 5.71068(3)\text{ \AA}$ ,  $c = 8.10400(7)\text{ \AA}$ ,  $c/\sqrt{2}a$  value =  $1.0034\text{ \AA}$ ) [12]. The smaller lattice parameters and  $c/\sqrt{2}a$  value are attributed to partial nitrogen loss from the perovskite-type oxynitride, as has also been reported in the case of the nitrogen deficient compound  $\text{SrTaO}_2\text{N}_{0.7}$  [13]. This partial nitrogen loss indicates that the perovskite phase was electrically conductive due to the reduction of Nb. The black color can also be ascribed

to the presence of an electrically conductive perovskite phase. In comparison, calcination reactions of mixtures with the  $\text{Sr}_2\text{Nb}_2\text{O}_7:\text{C}_3\text{N}_4$  molar ratios of 1:1 and 1:2 were conducted at the same heating conditions. Insufficient and over-reduction reactions were observed at molar ratios of 1:1 and 1:2, respectively as shown in Fig. S4 in the SI.

The TGA results obtained from the  $\text{Ca}_2\text{Ta}_2\text{O}_7/\text{C}_3\text{N}_4$  mixture are presented in Figure 3. A significant mass loss of 16.2% occurred between 380 and 750 °C, after which a second mass loss of 2.6% is evident. The XRD patterns for the TGA samples at the temperatures associated with each mass loss are shown in Figure 4. At 750 °C, the diffraction pattern did not change from that for the oxide precursor and, even at 1100 °C, the oxide precursor still remained together with the perovskite-type  $\text{CaTa}(\text{O},\text{N})_3$  phase. Characteristic diffraction lines for  $\text{CaCN}_2$  were not observed at any point.

The XRD pattern for the material obtained from the nitridation of  $\text{Ca}_2\text{Ta}_2\text{O}_7$  at 800 °C in the tube furnace for 6 h is shown in Figure S5 in the SI. A part of the original  $\text{Ca}_2\text{Ta}_2\text{O}_7$  remained in the specimen produced after heating at 800 °C, together with the  $\text{CaTa}(\text{O},\text{N})_3$  perovskite, and so the product was mixed with  $\text{C}_3\text{N}_4$  again to conduct a second heat treatment. The residual  $\text{Ca}_2\text{Ta}_2\text{O}_7$  disappeared after the second heating, while  $\text{Ta}_3\text{N}_5$  and  $\text{TaN}$  were formed. The product had a dark green coloration as shown in Fig. S6 in the SI, implying that over-reduction had been caused by the additional  $\text{C}_3\text{N}_4$ . We also conducted a calcination of a mixture of  $\text{Ca}_2\text{Ta}_2\text{O}_7:\text{C}_3\text{N}_4$  with a molar ratio of 1:3. XRD pattern of the product is shown in Fig. S7. By increasing the molar ratio of  $\text{C}_3\text{N}_4$ , large amount of  $\text{Ca}_2\text{Ta}_2\text{O}_7$  remained and an impurity phase of  $\text{Ta}_3\text{N}_5$  appeared. Compared with this result,

a second heat treatment with additional  $C_3N_4$  is an efficient way to enhance the phase purity of  $CaTa(O,N)_3$ . In previous work,  $SrTaO_2N$  was obtained from the reaction between the intermediates  $SrCN_2$  and  $Ta_3N_5$  and residual  $Sr_2Ta_2O_7$  in an one-step process [8]. The lack of formation of  $CaCN_2$  during this process might therefore necessitate a two-step heat treatment to consume the starting  $Ca_2Ta_2O_7$  and to obtain  $CaTa(O,N)_3$ .

The  $SrCN_2$  intermediate was detected as an intermediate following the reaction between  $Sr_2Nb_2O_7$  and  $C_3N_4$ , and reacted with the rock salt phase and the residual oxide precursor to produce  $SrNb(O,N)_3$ , similar to the case of  $SrTaO_2N$  [8]. In contrast, the absence of  $CaCN_2$  indicates that the reaction mechanism associated with a  $Ca_2Ta_2O_7/C_3N_4$  mixture is different from that for a  $Sr_2Nb_2O_7/C_3N_4$  mixture. In some studies,  $SrCN_2$  has been obtained from  $SrCO_3$  by heating in a flow of gaseous ammonia at 700 °C. However, the synthesis of phase-pure  $CaCN_2$  from  $CaCO_3$  under ammonia is challenging, suggesting that the formation of  $CaCN_2$  is more difficult than that of  $SrCN_2$  [14-16]. Because of the presence of  $SrCN_2$  as an intermediate, the perovskite phase could be obtained at 800 °C when synthesizing  $SrTaO_2N$  [8] and  $SrNb(O,N)_3$ . Conversely, in the case of  $CaTa(O,N)_3$ , the absence of  $CaCN_2$  required the addition of  $C_3N_4$  to achieve the nitridation of the residual  $Ca_2Ta_2O_7$ .

The morphologies of these specimens were examined using FE-SEM, as shown in Figure 5. The particle size of approximately 100 nm was smaller than that for material produced via the ammonolysis method. These smaller particles resulted from the lower formation temperature, and would be suitable for photocatalysis applications and as precursors for

sintering.

## **Conclusion**

Nearly pure single phases of  $\text{SrNb}(\text{O},\text{N})_3$  and  $\text{CaTa}(\text{O},\text{N})_3$  were obtained from  $\text{Sr}_2\text{Nb}_2\text{O}_7/\text{C}_3\text{N}_4$  and  $\text{Ca}_2\text{Ta}_2\text{O}_7/\text{C}_3\text{N}_4$  mixtures, respectively. Reactions between intermediates and the unreacted oxide precursor formed the perovskite phase  $\text{SrNb}(\text{O},\text{N})_3$  at a lower reaction temperature and in a shorter reaction time as compared to the ammonia nitridation method. It was determined that the lack of formation of  $\text{CaCN}_2$  during the reaction between  $\text{Ca}_2\text{Ta}_2\text{O}_7$  and  $\text{C}_3\text{N}_4$  requires a two-step heat treatment to obtain  $\text{CaTa}(\text{O},\text{N})_3$ . The particle sizes of the samples prepared using  $\text{C}_3\text{N}_4$  were significantly smaller than those derived from the ammonolysis reaction.

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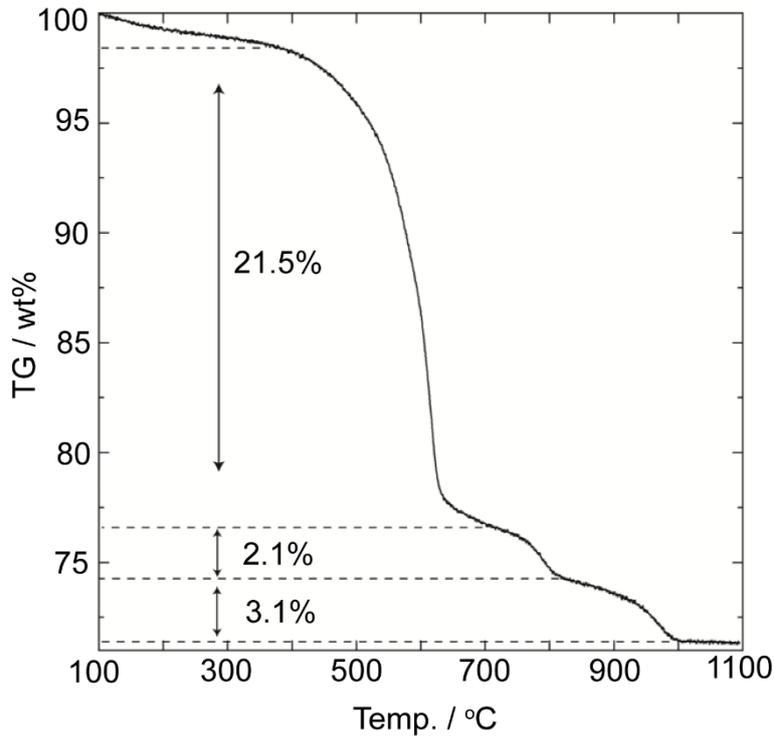
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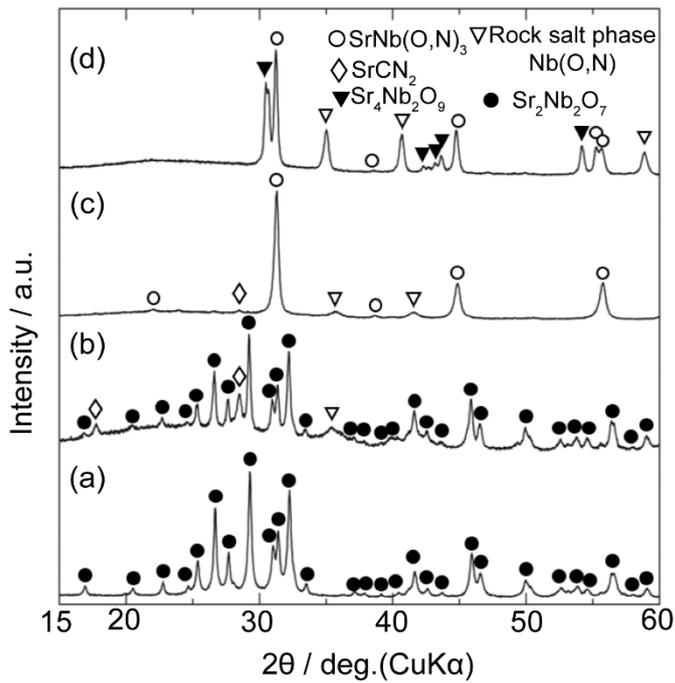
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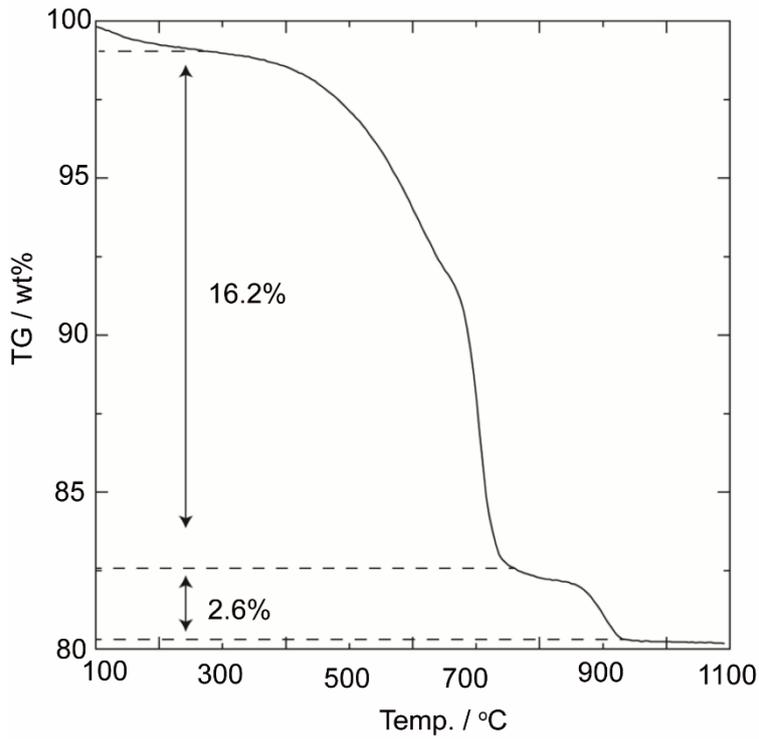
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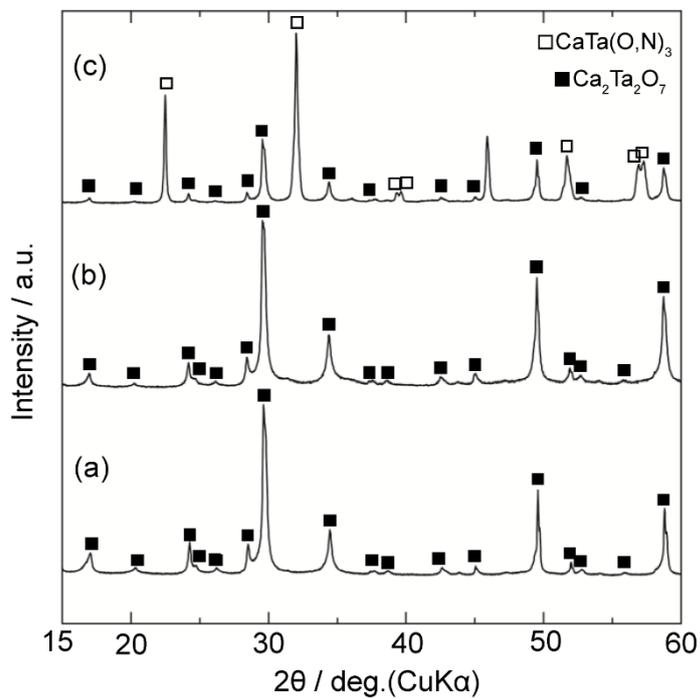
**Figure 1.** TGA curve obtained from a  $\text{Sr}_2\text{Nb}_2\text{O}_7/\text{C}_3\text{N}_4$  mixture in a nitrogen flow.



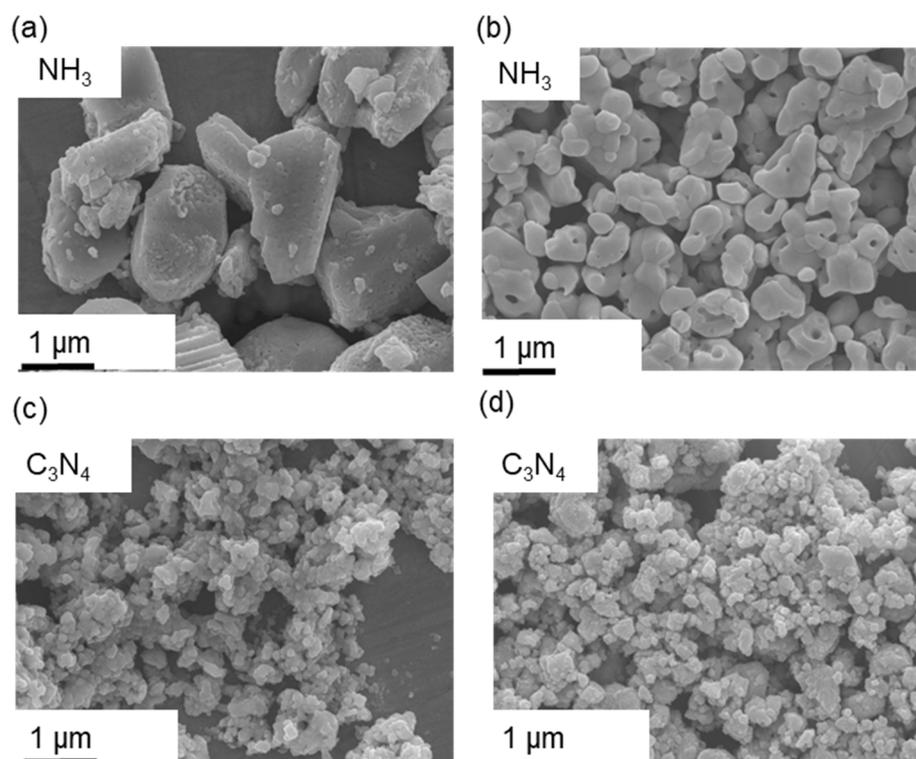
**Figure 2.** XRD patterns for (a) the starting oxide  $\text{Sr}_2\text{Nb}_2\text{O}_7$  and the products after TGA trials with heating to (b) 700 °C, (c) 800 °C and (d) 1100 °C.



**Figure 3.** TGA curve obtained from  $\text{Ca}_2\text{Ta}_2\text{O}_7/\text{C}_3\text{N}_4$  mixture under a nitrogen flow.



**Figure 4.** XRD patterns for (a) the starting oxide  $\text{Ca}_2\text{Ta}_2\text{O}_7$  and the products after TGA trials with heating to (b) 750 °C and (c) 1100 °C.



**Figure 5.** FE-SEM images of the oxynitrides (a and c) SrNb(O,N)<sub>3</sub> and (b and d) CaTa(O,N)<sub>3</sub> prepared using (a and b) ammonia (c and d) C<sub>3</sub>N<sub>4</sub>.