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Short Communication

Direct synthesis of $SrTaO_2N$ from $SrCO_3/Ta_3N_5$ involving CO evolution

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Abstract

$SrTaO_2N$ powder was prepared by a novel reaction between Ta_3N_5 and $SrCO_3$, instead of the traditional nitridation of $SrTaO_{3.5}$. The phase evolution and reaction mechanism during the reaction were investigated. The mixed gas evolution of CO, CO_2 and N_2 were observed in the heat-treatment of $Ta_3N_5/SrCO_3$. The $SrTaO_2N$ product possessed an average particle size of 330 nm in a narrow distribution with the stoichiometric oxygen and nitrogen content. Its ceramics with various relative density were also fabricated by pressureless sintering of the as-prepared $SrTaO_2N$ powder, showing a high sinterability. The fully-annealed $SrTaO_2N$ bulks with a RD = 82.8% showed a relatively large dielectric constant and an improved dielectric loss.

Keywords: $SrTaO_2N$; Perovskite oxynitrides; Powder synthesis; Reaction mechanism; Dielectric properties

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1. Introduction

Perovskite $SrTaO_2N$ has received considerable attention due to its promising applications in dielectrics and harmless pigments.[1,2] $SrTaO_2N$ powder is generally synthesized at 1000 °C by ammonolysis of $SrTaO_{3.5}$ precursors, which are prepared by the traditional solid state reaction (SSR). The nitridation in NH_3 generally requires a relatively high temperature and a long duration to complete the diffusion of nitrogen.[3,4] Additionally, gas exchange by the flow of NH_3 is necessary in the gas–solid reactions. Sometimes only surface can be nitrided on the product.[4] To achieve a full ammonolysis of $SrTaO_{3.5}$, a total duration of 80 h with intermediate grindings performed in every 20 h was needed in our previous work.[5,6]

Various methods have been developed for the preparation of oxynitride compounds to enhance the reaction efficiency. Mineralizers (e.g. KCl or $CaCl_2$) were often mixed with the oxide precursors to lower the reaction temperature during the nitridation in NH_3.[7] Nevertheless, it was reported that the oxynitrides ($CaTaO_2N$, $SrTaO_2N$, and $LaTaON_2$) from this method inevitably contained a potassium contamination (in about 0.5 at% relative to Ta), which was confirmed by the lower nitrogen contents compared to the samples from SSR.[8] On the other hand, soft chemistry methods (SCMs) have been widely used to prepare the amorphous precursors in recent year.[9–11] Lower nitridation temperature and/or shorter reaction time were realized by starting from the amorphous oxide precursors than that from the oxides in SSR.[6] For the nitridation of the amorphous oxide precursors, the formation of orange $SrTaO_2N$ could be completed at 1000 °C for only 12 h in flowing NH_3.[12]

Recently, a new route was explored to synthesize $SrTaO_2N$ by Clarke et al., called *high-temperature synthesis*,[13] where $SrTaO_2N$ powder was obtained through the direct reaction between SrO and TaON at 1500 °C for 3 h under N_2 atmosphere instead of NH_3. While the product was phase pure, the obtained oxynitride was brownish, suggesting the presence of anionic deficiencies rather than the stoichiometric composition in the orange $SrTaO_2N$ from SSR or SCM. In addition, it was reported that nitrogen in $SrTaO_2N$ was easily lost in the heat-treating at above 1000 °C under Ar or N_2 atmosphere, where the apparent color of the product changed into brown from original orange and showed a lower nitrogen content than the stoichiometry of $SrTaO_2N$.[6,14]

On the other hand, we note that the thermochemical dissociation of CO_2 in the presence of some reduced oxides (e.g.

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$CeO_{2-\delta}$, FeO) has been investigated, yielding mixtures of carbon monoxide (CO) and the oxides in high oxidation state (CeO_2, Fe_3O_4).[15–17] In comparison with metal oxides, there are very few reports on the system of metal nitrides/CO_2, mainly because of the irreversible conversion of the nitrides. The corresponding oxynitrides and oxides are expected to be formed successively, resulting from a series conversion of the metal nitrides.[18]

Accordingly, in the present work we design a novel method to synthesize $SrTaO_2N$ powder, starting from Ta_3N_5 and $SrCO_3$. $SrCO_3$ will decompose into a mixture of SrO and CO_2. The reaction between CO_2 and Ta_3N_5 is likely to generate TaON, which subsequently reacts with SrO to produce $SrTaO_2N$ in an absence of NH_3. Benefitting from the high reactivity of the in situ formed intermediates, the reactions can be completed under a mild condition to obtain $SrTaO_2N$ powder with stoichiometric composition. Moreover, attempts are made to sinter the as-received $SrTaO_2N$ powder to investigate the sinterability as well as the dielectric properties.

2. Experimental

Ta_3N_5 (the mean particle size: 300 nm, particle size <410 nm for 90%) was prepared by the nitridation of Ta_2O_5 (purity 99.9%, Wako Pure Chemicals Co. Ltd., Osaka, Japan) at 950 °C for 12 h in flowing NH_3 of 50 ml/min. The phase purity of Ta_3N_5 was confirmed (see Fig. S1 in Supporting Information). It was mixed with $SrCO_3$ (purity 99.9%, Wako Pure Chemicals Co. Ltd., Osaka, Japan) in acetone with a molar ration of 1:3 in ambient air. The slurry was dried overnight and then fired at a rate of 5 °C/min in an Al_2O_3 crucible in flowing N_2 of 100 ml/min under various conditions. Characterization of the powder product was conducted after cooling down to room temperature. On the other hand, $SrTaO_2N$ powder was also prepared by the conventional solid state reaction route (SSR), as described in our previous work[6] and also the Supporting Information.

The thermal reaction of the mixture $SrCO_3/Ta_3N_5$ was studied by thermogravimetry (TG; TG8120GH, Rigaku Co. Ltd., Tokyo, Japan) connected to a chromatography (Micro-GC 3000, INFICON, Overland Park, USA). The measurement was carried out in the range of 25–1200 °C (holding at 1200 °C for 0.5 h) with a heating rate of 10 °C/min in the flow of Ar (40 ml/min). The additional thermal analysis of Ta_3N_5 was also carried out in flowing 10% CO_2 and Ar in the TG-GC, using the same method as mentioned above. CO_2 concentration in the flowing gas was controlled utilizing mass-flow controllers (CO_2: SLA5850S, Brooks Instruments, Hatfield, USA; Ar: Kofloc CR-700, Kojima Instrum., Kyoto, Japan). The total flowing rate of CO_2/Ar for GC was set as 50 ml/min.

The as-received powders after heat-treated at different conditions were investigated by X-ray diffraction (XRD; Ultima IV, Rigaku Co. Ltd., Japan). An oxygen/nitrogen analyzer (EMGA-620W, Horiba STEC Co. Ltd., Kyoto, Japan) was applied for the chemical composition analysis of the pure product after heating $SrCO_3/Ta_3N_5$ at 950 °C for 10 h. Scanning electron microscopy (SEM; JSM-6500F, JEOL Co. Ltd., Tokyo, Japan) was used to observe the powder morphology. The average size and size distribution of particles were estimated by observing at least 400 particles from the SEM images, including volume median diameter (d_{v50}) and the 10% and 90% diameters (d_{v10} and d_{v90}).

Partial loss of Sr had been observed during the sintering of additive-free $SrTaO_2N$ ceramics, with an impurity of the tantalum compound.[6,12] Thus, $SrCO_3$ additive in 2.5 and 5 wt% was mixed with the present $SrTaO_2N$ powder prepared from Ta_3N_5 and $SrCO_3$. The mixture was uniaxially pressed at 10 MPa, cold isostatically pressed at 150 MPa, and then pressurelessly sintered at 1350–1400 °C in a graphite furnace (High Multi 500, Fuji Dempa Kogyo Co. Ltd., Osaka, Japan) under 0.2 MPa N_2 pressure. The heating rate was maintained at 20 °C/min below 1200 °C, and then 10 °C/min at higher temperatures. After dwelling at the desired peak temperatures, the furnace was naturally cooled to room temperature.

Polishing was performed with 4000-grit sandpaper (particle size: 3 μm) to obtain parallel and flat surfaces on the two sides of the sintered bodies. The as-sintered ceramics after polishing were annealed at 1000 °C for 12 h in flowing NH_3 (100 ml/min) to recover the stoichiometric composition and the insulating behavior. Polished surface of the sintered ceramics was analyzed by XRD. The relative density of the as-prepared ceramics was determined using a water vacuum penetration technique in combination with Archimedes method. This method employed in this work was similar to that described by American Society for Testing and Materials (ASTM) C373-88.[19] Electrical properties were measured on the post-annealed $SrTaO_2N$ ceramics with Ag paste (4922N, DuPont, Wilmington, USA) as electrodes in the frequency range from 10^2 to 10^6 Hz at room temperature, using LCR meters (4274A and 4285A, Hewlett Packard Co. Ltd., Palo Alto, USA).

3. Results and discussion

Fig. 1 presents the X-ray diffraction (XRD) patterns for the products heat-treated at various temperatures with no holding

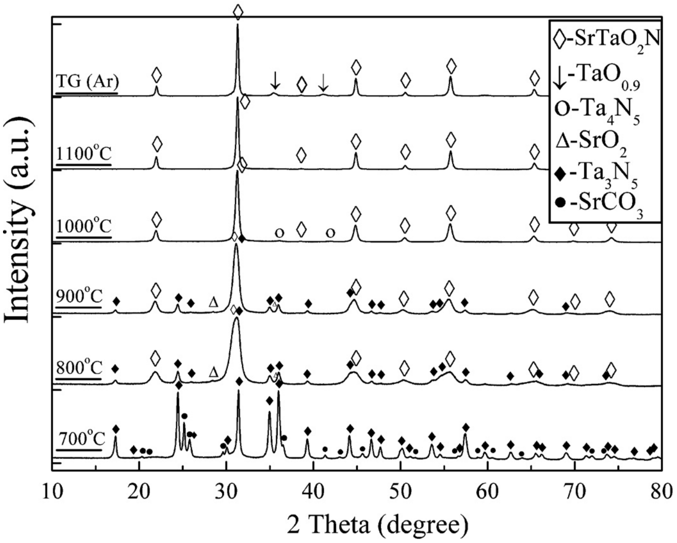

Fig. 1. XRD patterns of the products after heating $Ta_3N_5/SrCO_3$ mixture in flowing N_2 to different temperatures with no holding and after TG-GC measurement (1200 °C for 0.5 h in flowing Ar).