B₂O₃ as a new sintering additive for perovskite-type SrTaO₂N oxynitride ceramics

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ABSTRACT

The development of new sintering processes for ferroelectric perovskite-type oxynitrides is a crucial aspect of realizing practical applications of these materials. The present study examined the sintering of SrTaO₂N with B₂O₃, a new additive. The addition of B₂O₃ was found to significantly lower the sintering temperature. In addition, observations by transmission electron microscopy showed that the B₂O₃ combined with SrO to form an amorphous structure that enhances the diffusion of elements during high-temperature sintering.

1. Introduction

Perovskite-type oxynitrides have attracted much attention as lead-free dielectric materials [1–3]. The ferroelectric response of BaTaO₂N microcrystals obtained from BaCN₂ melt have been reported [4]. This response is attributed to the formation of polar nano-regions made of local cis-type ordering of nitrogen atoms in TaO₂N₃ octahedra. Piezoresponse force microscopy has also been used to examine thin surface layers of dense SrTaO₂N and BaTaO₂N ceramics [5,6]. In addition, cis-type anion ordering in such materials has been confirmed by neutron diffraction structural analysis and density functional theory calculations [7–9].

Sintering of the perovskite-type oxynitrides SrTaO₂N and BaTaO₂N has been examined as a means of obtaining dense bulk ceramic specimens so as to investigate the electrical properties and potential applications of these materials [2,3,10]. However, it is difficult to obtain bulk ceramics comprising perovskite-type oxynitrides because SrTaO₂N and BaTaO₂N tend to release a portion of nitrogen above 950 and 900°C, respectively. This process occurred even during heating under a N₂ atmosphere, and generates nitrogen-deficient perovskites having n-type semiconducting properties [10,11]. In prior work, a single phase nitrogen-deficient SrTaO₂N ceramic was obtained after high-temperature sintering above 1400°C in conjunction with SrCO₃ as an additive to compensate for the loss of SrO during the sintering process [3]. Thus, post ammonolysis is crucial for recovering the nitrogen content and electrical insulating properties of the sintered ceramics [2,3,10]. Fully recovered sintered SrTaO₂N and BaTaO₂N ceramics have been produced with relative densities (RDs) below 90%. SrTaO₂N ceramics with an RD value of 83% were found to have a dielectric constant, εᵣ, in the range of 350–600 with a dielectric loss, tanδ, of less than 0.1 [3]. BaTaO₂N ceramics having an RD value of 73% showed εᵣ values ranging from 320 to 620 at 10⁴ Hz and 10⁵ Hz, respectively [10]. However, the interior of sintered ceramics with RD values higher than 90% have been found not to be nitrided, and also to have inhomogeneous microstructures. It appears that dense structures are obtained at the outer surfaces while the interiors are poorly sintered [6]. In prior studies, the high-temperature sintering was performed in boron nitride (BN) crucibles, and so it is possible that certain boron-containing compounds affected the microstructure of the outer surfaces of the ceramics. In preliminary experiments by our own group, SrTaO₂N heated in alumina crucibles did not exhibit a suitable degree of sintering even at 1400°C, indicating that boron originating from the BN crucible might indeed have a significant effect on the sintering of oxynitride perovskites. B₂O₃ has been widely studied as a low temperature sintering additive, which has the melting point of approximately 450°C [12–15]. Ternary boron oxides were also reported to form a liquid phase during the sintering process and enhance a sintering behavior of oxide ceramics [16–18]. Formation of a SrO-B₂O₃ liquid phase has been expected to improve the sintering of SrTaO₂N oxynitride with B₂O₃ additive.

Recently, sintering of BaTaO₂N below its nitrogen release temperature using spark plasma sintering (SPS) in conjunction with a BaCN₂ melt was demonstrated, with the aim of preventing the loss of nitrogen. In this prior work, the sintering temperature of 900°C was slightly higher than the melting point of BaCN₂, and sintering durations as short as 5 min were employed. The RD of the resulting BaTaO₂N ceramic was 84%, and
the desired chemical composition and electrical insulating properties were retained [19]. An RD above 90% was achieved by prolonging the sintering time to 60 min, but the insulating properties were deteriorated because of the release of a portion of the nitrogen from the oxynitride.

Based on the above, new sintering techniques providing microstructures that are both dense and homogeneous are still required for the preparation of perovskite-type oxynitrdes. In the work reported herein, the perovskite-type oxynitride, SrTaO$_2$N was sintered with B$_2$O$_3$, as a new sintering additive, together with SrCO$_3$. The crystalline phases and microstructures of the sintered products were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM), while the sintering mechanism associated with the addition of B$_2$O$_3$ was investigated using transmission electron microscopy (TEM). The electrical properties of specimens subjected to post-annealing in an NH$_3$ flow were also assessed.

2. Experimental

SrTaO$_2$N powder was obtained from the ammonolysis of Sr$_2$Ta$_2$O$_7$ as a precursor under a 100 mL/min flow of NH$_3$ (99.9%, Sumitomo Seika), similar to our previously reported method [2]. The Sr$_2$Ta$_2$O$_7$ precursor was obtained from the solid-state reaction between SrCO$_3$ and Ta$_2$O$_5$ (99.9%, FUJIFILM Wako Pure Chemicals). A portion of the SrTaO$_2$N was mixed with 2.5 wt% SrCO$_3$ and 0–1.0 wt% B$_2$O$_3$ (99.9%, FUJIFILM Wako Pure Chemicals) using an agate mortar and pestle with anhydrous ethanol as a suspension medium. Particle sizes of the additives were approximately 500 nm and 1 μm, respectively. The resulting mixture was uniaxially pressed into pellets and then cold isostatic pressed at 150 MPa to form compacts. These powder compacts were subsequently sintered at temperatures in the range of 1200 to 1600°C for 1 to 10 h under a 0.2 MPa N$_2$ atmosphere in alumina crucibles. The sintered ceramics were post-annealed in an NH$_3$ flow at 1000°C for 15 h to recover any lost nitrogen.

The crystalline phases of the sintered ceramics were characterized using powder XRD (Ultima-IV, Rigaku) with Cu-Kα radiation, operating at 40 kV and 40 mA. XRD patterns were collected over the 2θ range of 15–80° with a step size of 0.02°. The Sr and Ta concentrations in the samples were determined using X-ray fluorescence spectroscopy (XRF; SEA6000VX-SII, Hitachi), while the microstructures of the fracture surfaces of the sintered ceramics were observed by SEM (JEM-6390LV, Jeol). Thin slices of a sintered ceramic with an RD of 93% were fabricated by focused ion beam microscopy (FIB; JIB-4600 F, Jeol) in preparation for the TEM observations (Titan G2 60–300, FEI Co.). Energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were performed in conjunction with the TEM observations. The dielectric properties of these materials were investigated using an LCR meter (4274A, Hewlett Packard) over the frequency range of 10$^2$ to 10$^5$ Hz at room temperature. Prior to analysis, Pt electrodes were sputter deposited on both surfaces of the post-annealed ceramics.

3. Results and discussion

Figure 1 shows the microstructures of the sintered ceramics heated at 1400°C for 3 h. The particle size in the product sintered with 2.5 wt% SrCO$_3$ without B$_2$O$_3$ was approximately 200 to 300 nm, and so was similar to that in the original SrTaO$_2$N precursor powder (Figure 1a). The extent of sintering between the round particles in this specimen to form a porous structure was very poor and the RD value for the product was only 45.0%. Using both 2.5 wt% SrCO$_3$ and 1.0 wt% B$_2$O$_3$ as additives significantly improved the grain growth and sintering of the SrTaO$_2$N particles, as shown in Figure 1b. The particle size in the sintered product was close to 1 μm and the RD

![Figure 1. SEM images of fracture surface of SrTaO$_2$N ceramics sintered at 1400°C for 3 h with (a) solely SrCO$_3$ and (b) SrCO$_3$ and B$_2$O$_3$ as additives. The SrCO$_3$ and B$_2$O$_3$ contents in these samples were 2.5 and 1.0 wt% relative to the mass of SrTaO$_2$N, respectively.](image-url)
value was increased to 95.4%. Densification was homogeneously throughout the ceramic and similar microstructures were observed in both the inner and outer parts of the specimen.

The RD values are plotted as function of sintering temperature in Figure 2. The ceramic sintered with 2.5 wt% SrCO$_3$ and 1.0 wt% B$_2$O$_3$ at 1200°C for 3 h had an RD value below 50% and its color changed to light brown from the orange of the original SrTaO$_2$N powder. The RD value increased to 95% upon increasing the sintering temperature above 1400°C and the product was black in color, indicating that an electrically conductive ceramic was obtained at this high temperature. Lower RD values were observed in the case of ceramics sintered at 1600°C, as compared with the samples heated at 1400 and 1500°C. This possibly occurred because the rapid grain growth at higher temperatures did not exclude small pores from the product during the sintering process. The sample color was found to change from brown at 1200°C to black at 1400°C. The ceramic sintered with SrCO$_3$ and without B$_2$O$_3$ showed a 53.4% RD even after heating at 1600°C, and the sintered products without B$_2$O$_3$ additive were orange and brown at 1400 and 1600°C, respectively. Thus, the use of B$_2$O$_3$ as an additive enhanced the sintering of the SrTaO$_2$N and allowed the sintering temperature to be significantly reduced, by at least several hundred degrees relative to that required for sintering without B$_2$O$_3$. The highest RD value was obtained at 1400°C after 3 h using both B$_2$O$_3$ and SrCO$_3$. The sintering temperature was therefore fixed at 1400°C during subsequent investigations of the effect of the B$_2$O$_3$ content on the crystalline phases.

The crystalline phases of the sintered ceramics obtained with 2.5 wt% SrCO$_3$ and different B$_2$O$_3$ amounts were investigated by powder XRD, with the results shown in Figure 3. A small amount of a TaO$_{2.9}$ impurity phase was observed in the XRD pattern obtained from the ceramic sintered with 2.5 wt% SrCO$_3$ and 1.0 wt% B$_2$O$_3$. This phase was attributed to the loss of SrO from the SrTaO$_2$N during high-temperature sintering, as was also observed in our previous research [3]. The Sr/Ta ratio for the ceramic was approximately 1.04, suggesting that a portion of the SrO from the SrTaO$_2$N reacted with the B$_2$O$_3$ remaining as an amorphous Sr-B-O phase. Without the B$_2$O$_3$ additive, the sintered product comprised a single phase having a perovskite-type structure. Incorporating the B$_2$O$_3$ evidently promoted the formation of a TaO$_{2.9}$ impurity phase based on the reaction of excess B$_2$O$_3$ with SrO in the SrTaO$_2$N. Consequently, decreasing the B$_2$O$_3$ concentration reduced the amount of the impurity phases so that a nitrogen-deficient, single phase perovskite-type SrTaO$_2$N ceramic was obtained using 0.15 wt% B$_2$O$_3$ together with 2.5 wt% SrCO$_3$.

The sintered product obtained at 1400°C for 1 h with 2.5 wt% SrCO$_3$ and 0.15 wt% B$_2$O$_3$ had an RD of 82.8%, and this value was increased to 93.3% by extending the sintering duration to 10 h. In addition, the porous structure observed after 1 h of sintering became dense and the particle size increased to the micrometer scale after 10 h (Figure 4). Interestingly, the single phase perovskite-type structure was retained after the longer sintering duration. These data confirm that the use of B$_2$O$_3$ as an additive with SrCO$_3$
improved the sintering of the SrTaO\textsubscript{2}N. Using the optimal additive amounts and sintering conditions, a nitrogen-deficient, single phase perovskite-type SrTaO\textsubscript{2}N ceramic with an RD value of 93.3% was obtained.

The effect of adding B\textsubscript{2}O\textsubscript{3} and SrCO\textsubscript{3} during sintering of SrTaO\textsubscript{2}N on the microstructure of the ceramic was analyzed by TEM. A triple point surrounded by three grains in the SrTaO\textsubscript{2}N ceramic sintered at 1400°C for 10 h with both 2.5 wt% SrCO\textsubscript{3} and 0.15 wt% B\textsubscript{2}O\textsubscript{3}, which had an RD value of 93.3% is shown in Figure 5. This TEM image shows an amorphous nature of the triple point surrounded by grains with lattice fringes. The lattice fringes associated with the bottom left grain in Figure 5b have a 0.288 nm spacing and are attributed to the (200) lattice planes in tetragonal SrTaO\textsubscript{2}N [7,8]. Electron diffraction pattern observed from the triple point shown in inset of Figure 5b represents a halo ring pattern indicating the triple point was amorphous. The EDS mapping images acquired from another triple point are presented in Figure 6 together with a high-angle annular dark field scanning TEM (HAADF-STEM) image. Only Sr, B and O signals are observed at the triple point, and the presence of the light elements B, N and O was also confirmed using EELS. The EELS spectrum obtained from the triple point and the surrounding grain are shown in Figure 7. Both B and O K-edges were observed in the spectrum.

**Figure 4.** SEM images of fracture surfaces of SrTaO\textsubscript{2}N ceramics sintered with 2.5 wt% SrCO\textsubscript{3} and 0.15 wt% B\textsubscript{2}O\textsubscript{3} at 1400°C for (a) 1, (b) 3 and (c) 10 h.

**Figure 5.** (a) Bright field TEM bright field image of SrTaO\textsubscript{2}N ceramic specimen with RD = 93.3% and (b) magnified image of the region indicated by the white square in (a). The inset in (b) represents the electron diffraction pattern observed from the triple point.
obtained from the triple point, while a N K-edge was found only in the oxynitride grain structure, along with an O K-edge. Note that the C signal is attributed to contaminants from the vacuum pump. Based on these observations, the triple point in the SrTaO₂N sintered ceramic was confirmed to be an amorphous phase consisting of Sr, B and O. Quantitative analysis of the triple point could not be performed because of electron beam damage to the specimen during electron irradiation. The SrO(SrCO₃)ₓB₂O₃ molar ratio was estimated to be 89:11 based on the initial additive amounts, and a glass phase has been reported to form in binary SrO-B₂O₃ systems in the case of 0.2 < x < 0.47 in xSrO+(1-x)B₂O₃ [20]. This represents a higher B₂O₃ content than that estimated from the nominal additive concentrations (that is, 2.5 wt% SrCO₃ and 0.15 wt% B₂O₃). However, SrO loss from SrTaO₂N during high-temperature sintering was demonstrated in our previous studies [2,3]. This SrO loss would be expected to shift the chemical composition of the SrCO₃/B₂O₃ mixture to generate a B₂O₃-rich glass. The additives would form a liquid phase during sintering at 1400°C because the highest melting temperature of the glass-forming region in the binary SrO-B₂O₃ system is 1158°C [21]. This liquid phase would cause increased diffusion of various elements in the SrTaO₂N and thus promote sintering of the SrTaO₂N grains.

SrTaO₂N sintered above 1000°C releases a portion of its nitrogen and changes to an electrically conductive ceramic with a black color. The nitrogen content of this ceramic can be restored by post-annealing in an NH₃ flow below 1000°C, so that an orange SrTaO₂N ceramic is obtained. To recover the nitrogen content in the interior part of a bulk ceramic specimens, an RD of less than 90% is necessary. In the present work, nitrogen-deficient SrTaO₂N ceramics that were black in color with an RD of 82.8% were generated upon heating at 1400°C for 1 h with

Figure 6. (a) HAADF-STEM image of SrTaO₂N ceramic specimen with RD = 93.3% and EDS mapping images for (b) Sr, (c) Ta, (d) O, (e) N, and (f) B in the same area.

Figure 7. TEM-EELS spectra of (a) triple point and (b) grain shown in Figure 6a. The arrows indicate the energy positions corresponding to the B, C, N and O K-edges.
4. Conclusions

The effects of adding B$_2$O$_3$ during sintering of the perovskite-type oxynitride SrTaO$_2$N were investigated, and this oxide was found to significantly enhanced the sintering of SrTaO$_2$N when used together with SrCO$_3$. The SrCO$_3$ and B$_2$O$_3$ additives formed a liquid phase during high-temperature sintering and remained as an amorphous phase that promoted diffusion between the oxynitride grains. The use of B$_2$O$_3$ allowed the sintering temperature to be lowered to 1400°C while still obtaining homogeneous sintered ceramics.

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Disclosure statement

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