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Spark Plasma Sintering of Dielectric BaTaO₂N close to the Melting Point of the BaCN₂ Additive

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Abstract

The perovskite-type oxynitride BaTaO₂N is a promising lead-free relaxor ferroelectric material. However, this material releases a part of its nitrogen during its sintering above 1350 °C. Subsequent annealing of the resulting sintered BaTaO₂N_{0.85} ceramics under an ammonia flow is necessary to recover an insulating, stoichiometric BaTaO₂N ceramics. Very recently, molten BaCN₂ was reported to be a useful flux for the preparation of BaTaO₂N microcrystals without the loss of nitrogen. In the present work, BaTaO₂N powder was sintered with a BaCN₂ additive under mechanical pressure, using a spark plasma sintering system. Nitrogen loss from the BaTaO₂N ceramic was avoided during liquid phase sintering at approximately 900 °C. The stoichiometric BaTaO₂N ceramic product with a relative density of 79.8% was an electrically insulator and it showed its relative dielectric constants, ϵ_r , in the range from 320 to 650 and a loss $\tan\delta$ values from 0.04 to 0.19 at room temperature.

Keywords: oxynitride, perovskite, metal carbodiimide, spark plasma sintering

1. Introduction

Oxynitride materials with perovskite-type structure, in particular BaTaO₂N, have attracted considerable attention as promising lead-free relaxor ferroelectric materials.[1-3] Based on powder neutron diffraction data, the average crystal structure of BaTaO₂N is reported to be centrosymmetric cubic ($a = 0.41128$ nm) with the space group $Pm\bar{3}m$. [4] The formation of one-dimensional polar nanoregions (PNRs) is also suggested by neutron pair distribution functions and electron diffraction data, and displacive disorder has been proposed to explain the large dielectric constant for this compound.[5,6] The formation of a *cis*-type anisotropic anion configuration in TaO₄N₂ octahedra has also been confirmed by neutron diffraction studies on oxynitride perovskites.[7,8] Density functional theory (DFT) calculations based on these structural studies have suggested the presence of polar linkages consisting of two types of helical Ta-N-Ta-N chains in various directions and with various lengths.[3] The relaxor-like ferroelectricity of *cis*-TaO₄N₂ is considered to be induced by the PNRs formed by polar chains in BaTaO₂N and SrTaO₂N without chemical inhomogeneity.

Thermochemical analyses of BaTaO₂N have demonstrated the release of approximately 15% of its nitrogen above 900 °C. The resulting nitrogen-deficient perovskite BaTaO₂N_{0.85} is stable even at 1550 °C in a nitrogen atmosphere, but

completely decomposes to a mixture of its component oxides and nitrides in helium.[1]

A reddish, insulating BaTaO₂N powder compact was sintered above 1350 °C in a nitrogen atmosphere following the above thermochemical study to obtain a black BaTaO₂N_{0.85} ceramics. Subsequent annealing of this material in a flow of ammonia was necessary to compensate for the partial nitrogen loss from the perovskite lattice so as to recover insulating behavior from the semiconductive BaTaO₂N_{0.85}. The annealed BaTaO₂N ceramic, having a relative density (RD) of 73.0%, was found to have a relative dielectric constant, ϵ_r , ranging from 290 to 620 that was moderately affected by temperature between 30 and 150 °C.[1] These dielectric constants are smaller than the values of several thousand previously reported for powder compacts heated in ammonia at 1050 °C, presumably as a result of the transfer of electrons resulting from the conductive nature of this material.[2] In the case of dense BaTaO₂N_{0.85} ceramics with RD values above 90%, only an outermost surface layer with a thickness of several micrometers returns to the reddish BaTaO₂N, because the microstructure is so dense that gaseous ammonia cannot penetrate any further into the interior.[1,9] A clear piezoresponse was obtained from a thin specimen removed from the dense ceramic surface, similar to results obtained with SrTaO₂N.[9,10] However, despite the stoichiometric composition of BaTaO₂N ceramic specimen, its *P-E* response curve was not saturated due to the electrical leakage occurring

because of the poor insulating properties. Sintering at a temperature lower than that associated with partial decomposition is therefore important to obtain fully dielectric materials.

Very recently, tetragonal BaCN_2 with a melting point of approximately $910\text{ }^\circ\text{C}$ was found to be useful for the preparation of microcrystals of oxynitride perovskites including $\text{Sr}_{1-x}\text{Ba}_x\text{TaO}_2\text{N}$ ($x = 0.04 - 0.17$)[11,12] and BaTaO_2N . [13] Reddish and cubic oxynitride crystals having sizes of several micrometers were produced by heating powdered mixtures of BaCN_2 and various oxynitrides. The BaTaO_2N crystals obtained from a BaCN_2 melt were also found to have excellent insulating properties and saturation of polarization at applied voltages greater than 60 V at $120\text{ }^\circ\text{C}$. [13] Ferroelectric polar phase alternation associated with a PNR mechanism was subsequently observed using piezoresponse force microscopy (PFM), by self-standing BaTaO_2N crystals synthesized via this technique. [13] Therefore, a BaCN_2 melt may represent a useful means of fabricating polycrystalline BaTaO_2N ceramics without nitrogen loss during sintering. In this process, the BaTaO_2N powder surface is wetted to assist in the diffusion of the solute through the BaCN_2 solvent, similar to liquid phase sintering. [14] Spark plasma sintering (SPS) could also be helpful as an approach to rapid sintering under pressure so as to avoid the thermal decomposition of BaTaO_2N . [15-17]

In the present work, BaTaO₂N powder was sintered with BaCN₂ as an additive while applying uniaxial mechanical pressure employing an SPS apparatus. The crystalline phases, microstructure and electrical properties of the resulting ceramic products were studied. The aim of this work was to establish the feasibility of obtaining ferroelectric BaTaO₂N ceramics without the partial loss of nitrogen from the perovskite crystalline lattice.

2. Experimental

BaTaO₂N and BaCN₂ powders were prepared by the ammonolysis of either a mixture of powdered BaCO₃ and Ta₂O₅ (99.9%, FUJIFILM Wako Pure Chemical) or pure BaCO₃, with heating at approximately 900 – 950 °C, respectively, using previously reported procedures.[1,11,18] **Caution: toxic gases such as dicyan can be generated by the decomposition of BaCN₂, so the following procedure should be conducted in a fume hood.** The prepared BaTaO₂N powder with a quantity of about 0.8 g was then mixed with 0 – 20 wt% BaCN₂ in a planetary ball milling system using zirconia balls (5 mm in diameter) with 5 mL hexane (> 95%, FUJIFILM Wako Pure Chemical) as the dispersion medium in a 45 mL zirconia pot. Mixing was performed at a rotation rate of 570 rpm for 10 min, under a nitrogen atmosphere to avoid oxidation or hydrolysis of the BaCN₂. [11]

The milled powder mixture was sintered to produce a 1 mm-thick disc having a diameter of 1 cm using the SPS apparatus (LABOX-1575, SinterLand Inc.). A schematic diagram summarizing the sintering procedure is presented in **Fig. S1** in **Supporting Information**.

In this process, approximately 500 mg of a BaTaO₂N/BaCN₂ powder mixture was sandwiched between two 150 mg portions of additive-free BaTaO₂N powder. These materials were positioned between two carbon punches and a die, using graphite sheeting to avoid BaCN₂ contamination. The sample chamber was evacuated, after which nitrogen gas (> 99.999%) was introduced to a pressure of 0.08 MPa prior to heating. A uniaxial mechanical pressure up to 100 MPa was applied to the sample and the chamber was heated to approximately 900 °C at a rate of 200 °C/min, then held at that temperature for a time span of 1 – 10 min. Mechanical pressure was maintained throughout the entire SPS process. First of all, the temperature of the sample chamber was investigated. The temperature of sample chamber slightly exceeded the melting point of BaCN₂ (910 °C)[11,12] with a temperature setting of 900 °C. When only BaCN₂ powder was heated with the same temperature setting, the BaCN₂ powder completely melted even in a short keeping time of a few minutes, confirming the presence of BaCN₂ melt for liquid phase sintering during heating. The sintering conditions and properties of the ceramic products are summarized in **Table S1** in **Supporting Information**.

Characterization of the ceramic products

The sintered ceramics were polished with 1000 grit sandpaper having SiC particles with sizes of 2 – 3 μm to remove excess BaTaO₂N powder adhering to the ceramic surface. Their bulk densities were calculated using the geometric method and RD values were obtained assuming that the products comprised pure BaTaO₂N (theoretical density = 8.69 g cm⁻³). [4] The amount of BaCN₂ in the ceramic products cannot be quantified because of a partial loss of molten BaCN₂ by its vaporization and partial decomposition at high temperature as reported in our previous publications. [11-13] Moreover, some of molten BaCN₂ reacts with the surface of BaTaO₂N grains to form Ba-rich Ruddlesden-Popper type oxynitride perovskites. The Archimedes method was not applicable in the present case because ceramics in the present work contain a number of open pores, which makes it impossible to obtain the precise density values. Crystalline phases of the polished ceramic surfaces were identified using X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu K α radiation over the 2θ range of 20 – 80° at a scan rate of 10°/min with a step size 0.02°. XRD profile fitting and calculations of the phase proportions were conducted using a Rietveld software package (RIETAN-FP). [19]

Chemical compositions of the ceramic products were determined from X-ray fluorescence data (XRF, SEA6000VX-SII, Hitachi) so as to ascertain the molar

proportions of Ba and Ta. Combustion analysis (EMG-620W, Horiba) was employed to quantify the oxygen and nitrogen contents in the materials, using Si_3N_4 (Ceramic Society of Japan) and Gd_2O_3 (99.9%, FUJIFILM Wako Pure Chemical) as references. The latter reference was calcined at 1000 °C to remove adsorbates. The carbon contents were less than the detection limit of the CHN combustion analyzer (< 0.3 wt%, MICROCODER JM10, J-Science Lab.).

A thin slice of the ceramic product with RD = 80.7% indicated as sample (b) in **Table S1**, which was sintered with 5 wt% of BaCN_2 at 70 MPa keeping at 900 °C for 1 min was prepared for transmission electron microscopy (TEM) observations. Sample thinning was performed using a focused ion beam (SMI 3050SE, Hitachi High-Technologies). The microstructure and composition of the resulting specimen, less than 100 nm in thickness, were assessed from TEM images (Titan3 G2 60-300, FEI) with a Cs-spherical aberration corrector, in conjunction with energy-dispersive X-ray spectroscopy (EDS). The fracture surfaces of the ceramic products were examined using field-emission scanning electron microscopy (FE-SEM, JSM-6500F, JEOL).

The electrical properties of sample (e) with RD = 79.8% in **Table S1** were assessed using an impedance analyzer (4294A, Agilent Technologies, Inc.) after depositing Pt electrodes at least 100-nm thick by sputtering (JFC-1100E, JEOL) on flat

surfaces. Measurements were conducted at room temperature over the frequency range of $10^2 - 10^6$ Hz.

3. Results and discussion

The effects of added BaCN₂ and of applied mechanical pressure

Preliminary SPS processing was applied to the BaTaO₂N powder with or without added BaCN₂ to elucidate the effect of BaCN₂ on densification. All samples were heated at approximately 900 °C, which corresponds to the melting point of BaCN₂. [11-13] No densification was observed in the case of the additive-free BaTaO₂N powder, while the powder mixtures containing some amount of BaCN₂ rapidly densified to RD values greater than 66.5%. These values are plotted against the amount of added BaCN₂ for the products treated using SPS for 5 min or shorter in **Fig. 1(a)**. From these data, it is evident that the BaCN₂ additive had a significant effect on the degree of densification. Interestingly, an excess of BaCN₂ (20 wt%, sample (o) in **Table S1**) resulted in a ceramic product that readily fractured into small particles. A BaCN₂ content of less than 10 wt% was found to maintain the disk shape of the products. The initial BaTaO₂N powder evidently partially dissolved in the molten BaCN₂ and then precipitated again, similar to a crystal growth process. [13] This dissolution and precipitation of some proportion of the

BaCN₂ enhanced the densification by far faster than the previous high temperature sintering. [1]

As for **Fig. 1**, samples sintered with a large amount of BaCN₂ (7 wt%) tend to show lower RD values. This may be because BaTaO₂N solid particles are sometimes separated by molten BaCN₂, which disturbs the densification of BaTaO₂N in the case of 7 wt% of BaCN₂. As for the case of the addition of 5 wt% BaCN₂, the distance between solid particles is appropriate due to the absence of too much amount of molten BaCN₂, to make the ceramic products a little denser. However, the reason why the 10 wt% samples became slightly denser than 7 wt% ceramics still remains unclear. Some penetration of molten BaCN₂ into the BaTaO₂N powder beds was detected by analyzing Ba/Ta molar ratios of the powder beds using XRF. Excess amount of Ba (by more than 5 mol%) compared with Ta was contained. This, evacuation of BaCN₂ out of the main BaTaO₂N/BaCN₂ mixture, was significant when large amount of BaCN₂ additive of 7 wt% or more was mixed before heating and high pressure was applied. So, the effect of BaCN₂ amount in the initial mixtures on RD values cannot be compared quantitatively because a rich amount of molten BaCN₂ was not utilized for densification effectively.

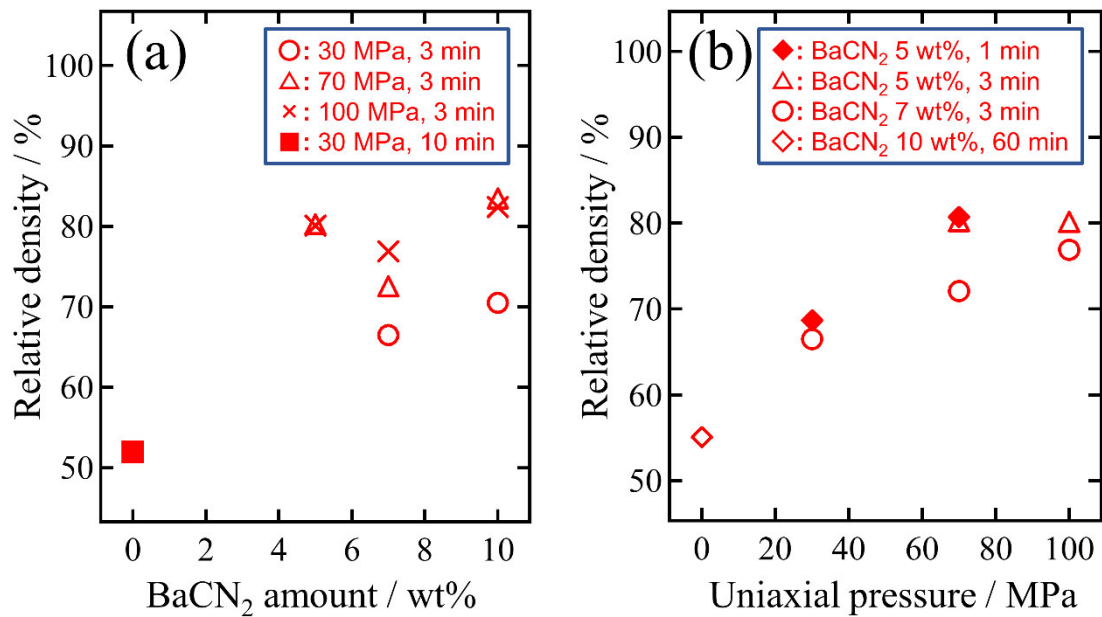


Fig. 1 Relative densities of BaTaO₂N ceramics as functions of **(a)** the amount of BaCN₂ additive and **(b)** the applied uniaxial pressure. The plotted data are for samples with stoichiometric nitrogen contents. The errors are smaller than the legends and so are not provided.

The effect of the applied mechanical pressure is summarized in **Fig. 1(b)**. The combination of BaTaO₂N and 10 wt% BaCN₂ did not exhibit any densification upon heating at 900 °C for 1 h in the absence of pressure, while the RD values increased to greater than 70% when applying pressures of 30 MPa. The molten BaCN₂ was evidently able to infiltrate between the BaTaO₂N particles to wet the particle surfaces when mechanical pressure was applied. Above 70 MPa, no further increases in RD were obtained. It is possible that the molten BaCN₂, which seemed to assist the diffusion of BaTaO₂N during crystal growth, was squeezed out from the main BaTaO₂N/BaCN₂

sample body to the upper and lower BaTaO₂N powder beds at pressures higher than 70 MPa.

Samples of BaTaO₂N powder were densified with 5 wt% of BaCN₂ for various heating times at approximately 900 °C. Photographic images of the ceramics sintered for 3 min (sample (e) in **Table S1**) and 60 min (sample (q)) are presented in **Fig. 2**. Red, electrically insulating materials (**Fig. 2(a)**) were obtained for duration shorter than 5 min, while heating for longer than 5 min resulted in black semiconductors (**Fig. 2(b)**). Thus, a portion of the nitrogen in the original material was lost from the oxynitride perovskite during treatment in a reducing atmosphere in the presence of graphite sheets, die and punches. These data indicate that a maximum heating duration of 5 min appears to be optimal when the aim is to obtain BaTaO₂N dielectric ceramics. The maximum RD value observed for a stoichiometric BaTaO₂N ceramic in these trials was 84.1% in the case of sample (k).

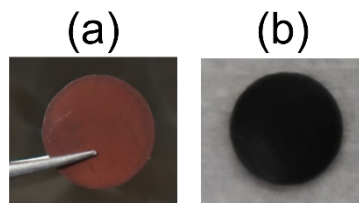


Fig. 2 Photographic images of BaTaO₂N ceramics (e) and (q) (**Table S1**), sintered with 5 wt% BaCN₂ as an additive at 900 °C for **(a)** 3 min and **(b)** 60 min.

Sintering mechanism for BaTaO₂N with BaCN₂

The XRD pattern obtained from the polished surface of the BaTaO₂N ceramic produced by sintering with 5 wt% BaCN₂ at 70 MPa and 900 °C for 3 min (sample (k)) is presented in **Fig. 3**. The main crystalline phase was determined to be perovskite-type BaTaO₂N with lattice parameter $a = 0.411009(11)$ nm, in good agreement with the literature value ($a = 0.41128$ nm).[4] Ba-rich Ruddlesden-Popper-type Ba₂TaO₃N also appeared as a secondary phase, at a concentration of 5.8 wt%. Detailed Rietveld fitting data is summarized in **Fig. S2**. A similar Ba₂TaO₃N impurity was observed in a study of the crystal growth of BaTaO₂N during the reaction between BaTaO₂N and BaCN₂. [13] The excess oxygen in this Ba₂TaO₃N phase is believed to have been supplied from adsorbed oxygen and/or moisture on the surfaces of the BaTaO₂N/BaCN₂ mixture and/or the interior of the SPS equipment. The presence of this Ba₂TaO₃N impurity suggests that the present densification of BaTaO₂N does not proceed by simple liquid phase sintering. That is, the material diffusion process during the densification is likely to be assisted by chemical reactions in which the perovskite dissolves and recrystallizes in the molten BaCN₂. This process occurs between the BaTaO₂N main phase and the BaO intermediate formed during the partial oxidation of the BaCN₂. Similar insertions of rock-salt layers of alkaline-earth metal oxide between oxynitride perovskite lattices were previously

reported for $\text{Sr}_2\text{NbO}_3\text{N-SrNbO}_2\text{N}$ and $\text{Sr}_2\text{TaO}_3\text{N-SrTaO}_2\text{N}$ systems.[20,21] Crystalline phase of BaCN_2 was not detected in the XRD profile probably because of its phase transition to amorphous and crystalline polymorphs, the amount of each one is too small to be clearly detected in XRD measurements. The phase transformation of BaCN_2 during its cooling from melting point is discussed in our previous publication [11,12] and more detail is now under our further investigations.

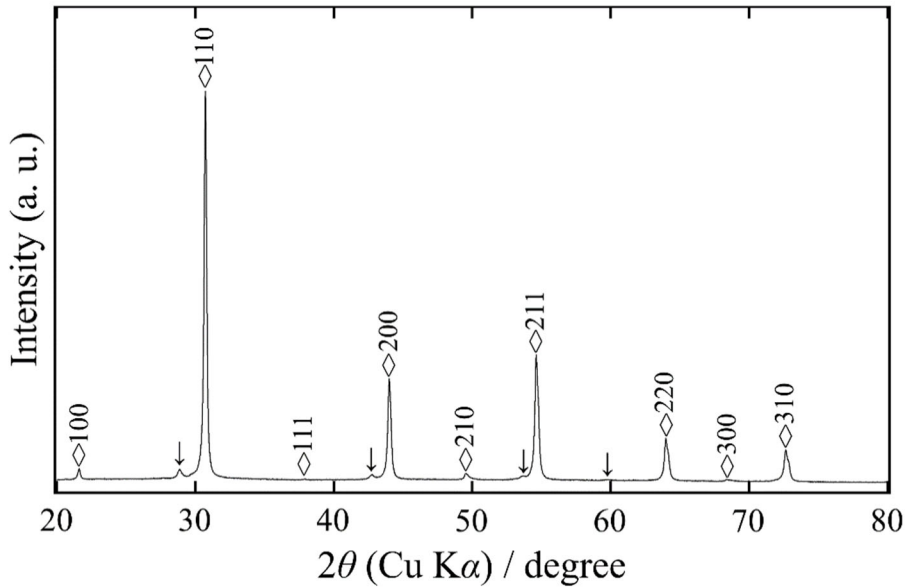


Fig. 3 XRD pattern of the polished ceramic surface of the specimen sintered with 5 wt% BaCN_2 at 70 MPa and 900 °C for 3 min (sample (k) in **Table S1**), having an RD of 84.1%. Diamonds and arrows indicate peaks attributed to BaTaO_2N (ICSD 202763) and $\text{Ba}_2\text{TaO}_3\text{N}$ (JCPDS 47-1388), respectively.

TEM bright field images were acquired from a thin specimen of the sample (b) ceramic having an RD of 80.7%, and are provided in **Fig. 4(a)**. It is apparent that the grains in the ceramics were connected via thin boundaries and that voids were present in the

microstructure. Compared with the primary particle size of as-prepared BaTaO₂N powder shown in **Fig. S3**, a slight grain growth seems to have occurred during SPS processes, although it is not significant very much. The presence of large voids approximately equal in size to the grains can likely be ascribed to insufficient packing of the original powders. Thus, higher RD values could be obtained by increasing the packing of the initial BaTaO₂N powder contacts through modifying the particle sizes. EDS compositional analyses were conducted on several parts across a grain boundary in conjunction with high-magnification high-angle annular dark field scanning TEM (HAADF-STEM). A typical image is presented in **Fig. 4(b)**. The Ba/Ta molar ratios were determined at the various measurement points indicated on this figure, and the resulting values were normalized relative to the ratio at **point 1** (in the interior of a BaTaO₂N grain). The proportion of Ba was found to gradually increase on going from the grain interior to the exterior, with the maximum value at the triple point (**point 4** in **Fig. 4(c)**). The molten BaCN₂ is believed to have spread out into the narrow grain boundary area as a result of the application of mechanical pressure, so as to wet the surfaces of the BaTaO₂N grains. The BaCN₂ flux was also likely to have been concentrated at triple points in the solidified BaTaO₂N grains. Based on the above data, the sintering process in the present study is summarized diagrammatically in **Fig. 5**. In

this mechanism, the BaTaO_2N grain surfaces are wetted by molten BaCN_2 to fill the boundaries, as shown in **Fig. 5(a)**. The BaTaO_2N grains subsequently dissolve in the molten BaCN_2 and then precipitate to form Ba-rich side phases such as $\text{Ba}_2\text{TaO}_3\text{N}$ on the surfaces of the grains. This step is accompanied by slight grain growth to connect BaTaO_2N particles, as in **Fig. 5(b)**. Finally, each BaTaO_2N grain is connected via thin boundaries of the BaTaO_2N itself. These boundaries contain small amounts of Ba-rich components (primarily residual BaCN_2 and $\text{Ba}_2\text{TaO}_3\text{N}$). Intermittently, these Ba-rich constituents are concentrated at the triple points of the BaTaO_2N grains, as depicted in **Fig. 5(c)**.

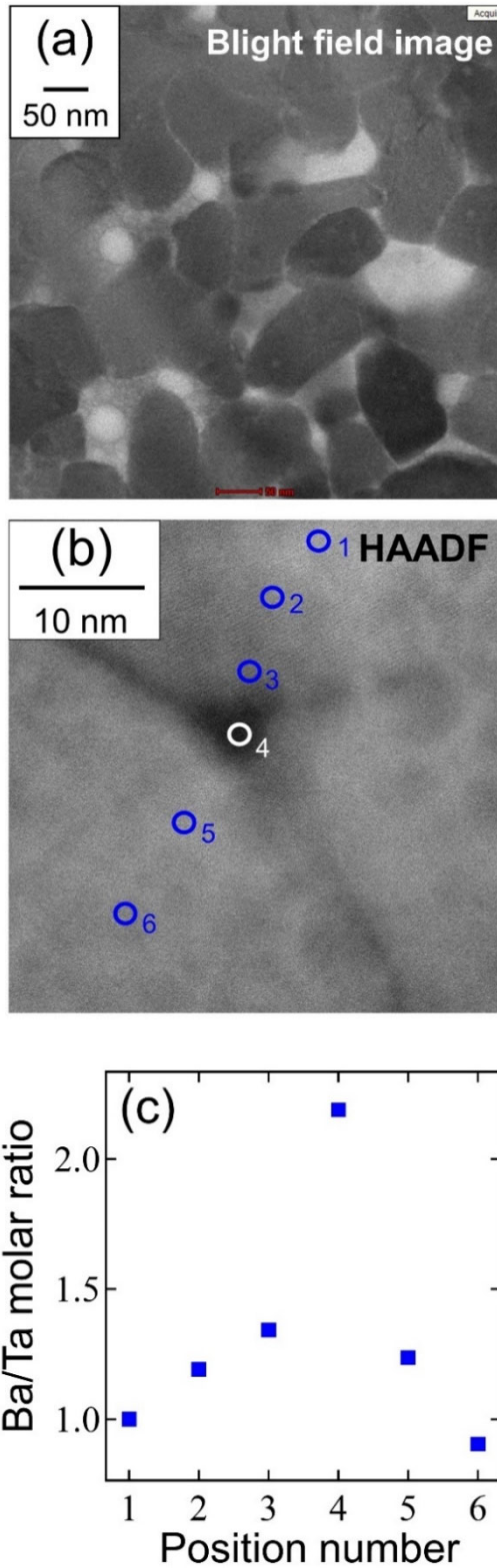


Fig. 4 (a) TEM bright field and (b) HAADF-STEM images of a BaTaO₂N ceramic specimen with RD = 80.7% (sample (b)). (c) The Ba/Ta molar ratios determined using EDS at the points marked in (b).

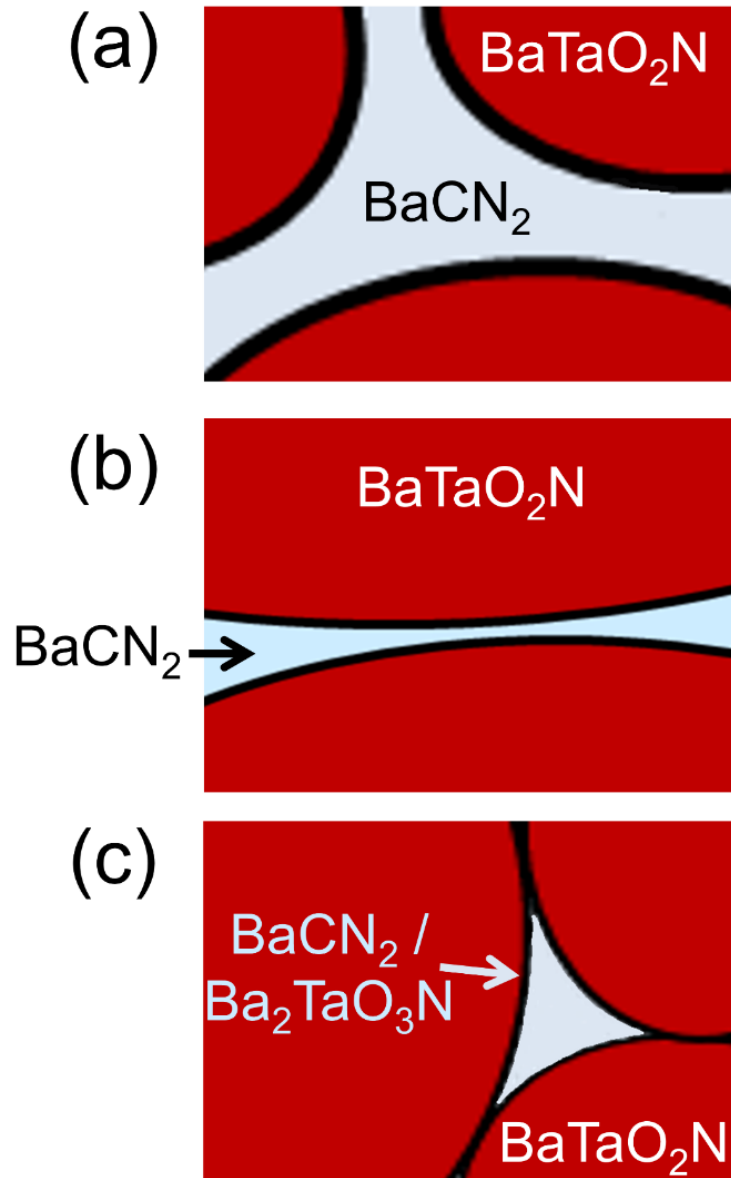


Fig. 5 Schematic diagrams summarizing the sintering of BaTaO₂N with molten BaCN₂. **(a)** Wetting of the surfaces of BaTaO₂N grains, **(b)** grain growth associated with the dissolution and precipitation of BaTaO₂N in the molten BaCN₂ flux, and **(c)** the formation of a triple point after sintering.

SEM micrographs were acquired to assess the as-prepared BaTaO₂N powder and the fracture surfaces of a sintered BaTaO₂N ceramic (sample (k)). These images showed that the grains were well connected with one another in the ceramic. Neither significant necking between grains nor apparent grain growth were observed, despite the high RD of 84.1% for this material (**Fig. 6**). All the grains that had been compacted were bonded at the boundaries formed through the action of the molten BaCN₂. Grain growth during the short duration of the SPS process is typically minimal, as reviewed for SPS processes on inorganic oxides.[16]

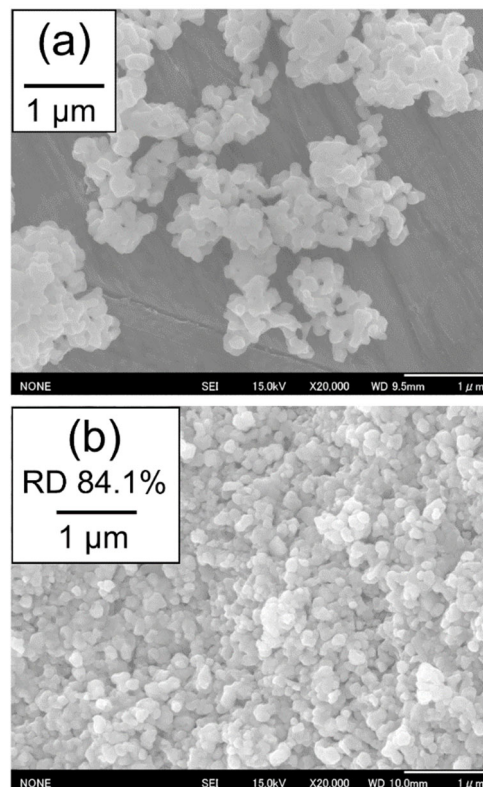


Fig. 6 SEM micrographs of (a) the as-prepared BaTaO₂N powder and (b) the fracture

surface of a BaTaO₂N ceramic with RD = 84.1% prepared by sintering with 5 wt% BaCN₂, 70 MPa mechanical pressure and 5 min hold at 900 °C (sample (k)).

Electrical properties of BaTaO₂N ceramics

The electrical properties of a BaTaO₂N ceramic (sample (e)) were assessed at room temperature over the frequency range of 10² – 10⁶ Hz. This sample was relatively dense (RD = 79.8%) among the products in the present work. The complex impedance plot obtained from this material is shown in **Fig. 7(a)**. This plot exhibits only a small part of a large arc, suggesting that this ceramic behaved as an insulator, even without the subsequent post-annealing in ammonia required in previous studies.[1,9] **Fig. 7(b)** demonstrates values for the relative dielectric constants, ϵ_r , of 320 – 650 and for the dielectric loss $\tan\delta$ of 0.04 – 0.19. These values are comparable to the highest yet reported for post-annealed ceramics with RD = 73.0% sintered at high temperatures ($\epsilon_r = 290 – 620$ and $\tan \delta = 0.04 – 0.4$).[1] The present as-sintered BaTaO₂N ceramics thus exhibited comparable dielectric performance to materials synthesized in the previous works even they are not post-annealed. These results can presumably be due to the elimination of the partial loss of nitrogen by sintering at 900 °C. This temperature is below that at which nitrogen is lost from BaTaO₂N and close to the melting point of BaCN₂. In summary, the fabrication of BaTaO₂N ceramics maintaining their original nitrogen content and

electrically insulating properties was achieved in conjunction with low temperature sintering at 900 °C. The post-ammonolysis process typically applied after the previously reported high temperature sintering[1] is not required.

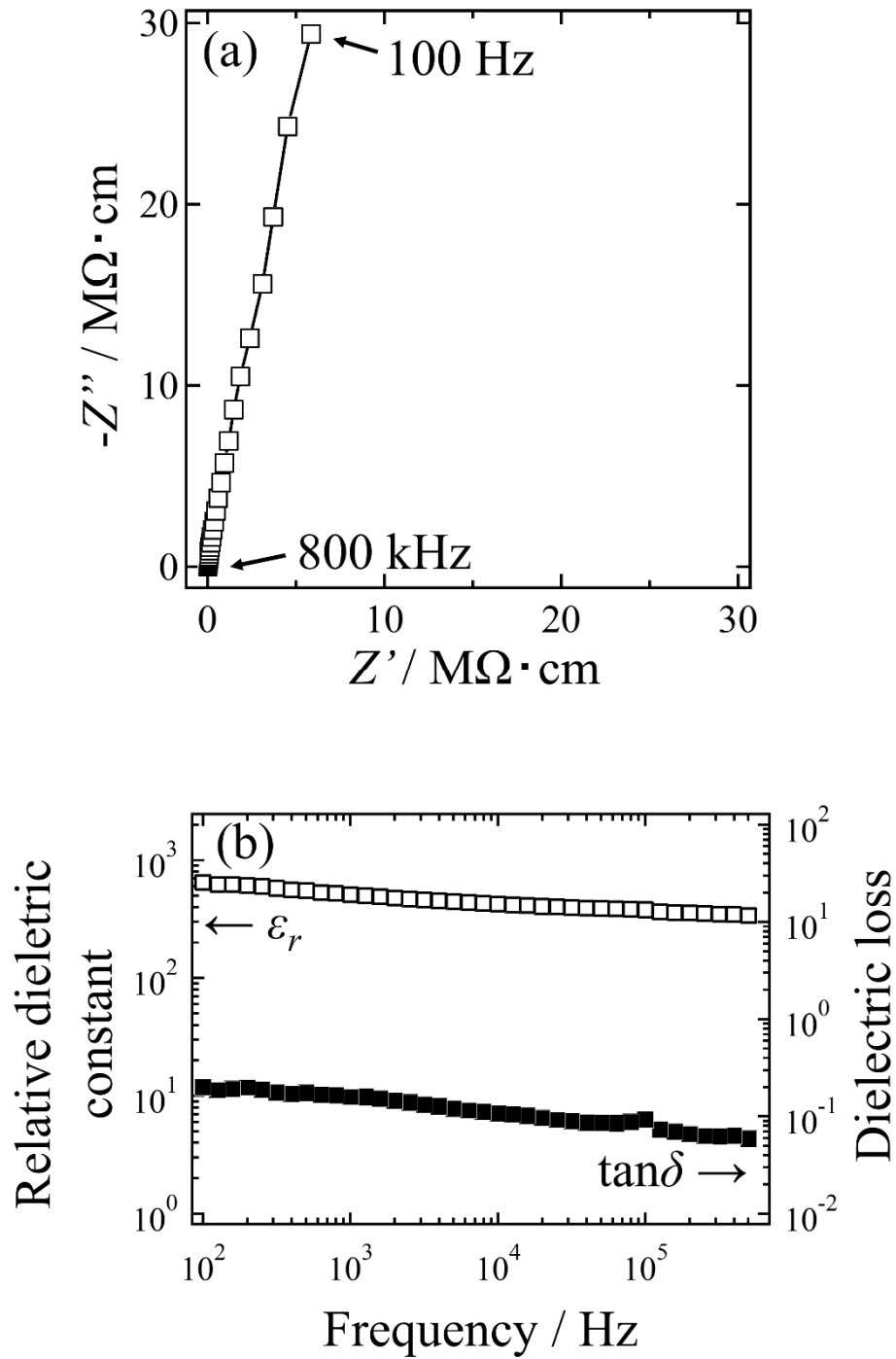


Fig. 7 (a) A Cole-Cole complex impedance plot and **(b)** dielectric properties as functions of frequency for a BaTaO₂N ceramic (sample (e)) at room temperature. The errors are smaller than the legends, so are not provided.

4. Conclusion

BaTaO₂N powder was sintered at approximately 900 °C (relatively low compared to other sintering studies) together with added BaCN₂ under mechanical pressure in an SPS apparatus, as a means of avoiding partial nitrogen loss. BaTaO₂N grains were found to be bonded through dissolution and precipitation at their surfaces in the BaCN₂ melt. A minor reaction product comprising a Ba-rich compound (possibly the Ruddlesden-Popper type compound Ba₂TaO₃N) was identified at the grain boundaries and triple points of the resulting ceramics. Rapid heating and cooling in the SPS furnace effectively avoided partial nitrogen loss from the BaTaO₂N, and the low melting point of BaCN₂ allowed reduced temperature processing. A maximum relative density of 84.1% was obtained among the BaTaO₂N ceramics, which also maintained their original nitrogen content. Both the relative dielectric constants of 320 – 650 and losses of 0.04 – 0.19 for the present ceramics having an RD of 79.8% are comparable to values previously reported for post-ammonolysis products with RD = 73.0% sintered at high temperatures ($\epsilon_r = 290 - 620$, $\tan\delta = 0.04 - 0.4$). The present SPS at approximately the melting point of the BaCN₂ additive is expected to allow the fabrication of commercially-viable relaxor-type ferroelectric ceramics based on the BaTaO₂N oxynitride.

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