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Short communication

Hot isostatic press sintering and dielectric properties of $SrTaO_2N$ ceramics

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Abstract

$SrTaO_2N$ prepared by a citrate route was capsule hot isostatic press sintered at 196 MPa for 3 h at 1200, 1400 and 1600 °C. Densification over 80% was attained for all the sintered bodies with partial reduction, which was observed as a change of color from brown to dark gray. Exaggerated grain growth was observed with some amount of open pore for the product sintered at 1400 °C. The sample was successfully returned to the brown insulator color after annealing in ammonia flow at 1000 °C. The resultant $SrTaO_2N$ ceramics exhibited a considerably high relative dielectric permittivity of 7.8×10^3 at 10^2 Hz.

Keywords: Oxynitride; Hot isostatic pressing; Perovskite; Dielectric

1. Introduction

The dielectric response of oxynitride materials was first deduced from infrared reflection spectra and the value was not significantly high [1]. Perovskite type oxynitrides have recently attracted substantial renewed attention after Kim et al. [2] reported ATaO$_2$N (A = Sr, Ba) ceramics with excellent dielectric response comparable to that of the conventional Pb(Zr,Ti)O_3 (PZT) dielectric [3]. The $SrTaO_2N$ bulk sintered in flowing NH_3 has considerable porosity of approximately 45% [2], although impedance spectroscopy indicated a bulk relative permittivity of approximately 3000, despite the relatively low density, and the permittivity remained almost constant within the temperature range of 180–300 K [2]. Structure refinement using neutron diffraction revealed the presence of local polarity induced by the tilted connection of *cis*-TaO_4N_2 octahedra along the *c*-axis [4]. Densification of the $SrTaO_2N$ was recently improved to greater than 90% by reaction sintering using $SrCO_3$ or La_2O_3 sintering additives in a 0.2 Pa nitrogen atmosphere [5,6]. The process required post annealing to compensate for the nitrogen loss during sintering. This procedure was successful to prepare insulating samples when $SrCO_3$ was used as the additive, and the dielectric constant was greater than 10^4. Further improvement of densification without compositional change is required to obtain highly densified products with controlled electrical properties.

Hot isostatic press (HIP) sintering has been widely used to densify covalent materials that exhibit low self-diffusivity and tend to decompose at higher sintering temperatures [7,8]. Both Si_3N_4 and AlN ceramics with high density close to the theoretical value have been obtained by HIP sintering, which has resulted in improved mechanical and electrical properties [9,10]. In addition, fully dense SiAlON ceramics have been prepared by additive-assisted HIP sintering [11]. Therefore, it is expected that HIP sintering would also be effective for the densification of $SrTaO_2N$ ceramics.

In the present study, the HIP sintering process, microstructure and dielectric properties of $SrTaO_2N$ ceramics were investigated in the sintering temperature range from 1200 to 1600 °C. To the best of our knowledge, this is the first report on the characterization of HIP sintered $SrTaO_2N$ ceramics.

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2. Experimental

$SrTaO_2N$ powder was synthesized by ammonolysis of precursors obtained from a stoichiometric mixture of $SrCO_3$ (Wako Pure Chemicals, 99.9%) and $TaCl_5$ (Sigma-Aldrich, 99.99%) powders dissolved in anhydrous ethanol through a citrate route, as described in our previous report [4–6]. The amount of citric acid was equimolar to that of the Ta ions. The solution was heated and stirred at 150 °C and then pre-fired at 350 °C for 1 h. The ammonolysis reaction was carried out in flowing ammonia at 1000 °C with a heating rate of 5 °C/min, and then held for 12 h before cooling to room temperature.

Sintering was performed by HIP using argon gas as the pressure-transmitting medium. Before HIP sintering, the $SrTaO_2N$ powders were uniaxially pressed at 98 MPa into 6 mm diameter discs using a rigid steel die, followed by cold isostatic pressing at a pressure of 245 MPa. The green compacts were encased within Pt sheets (50 μm thick) and covered with BN powder in cylindrical shape. The resultant cylinders were vacuum sealed in Pyrex^{TM} glass capsules under a reduced pressure of 1.3×10^{-1} Pa. Bulk consolidation was conducted using HIP equipment (Kobe Steel Co. Ltd., System 5X O2-HIP) at 1200, 1400 and 1600 °C under 196 MPa with a soaking time of 3 h. The heating and cooling rates were fixed at 600 and 300 °C/h, respectively. The sintered bulks were then annealed at 1000 °C for 12 h in flowing ammonia. This post-annealing procedure was necessary to obtain highly resistive bulks for reliable dielectric property measurements.

The $SrTaO_2N$ products were characterized by X-ray diffraction (XRD) with Cu Kα radiation (Rigaku, Ultima IV). Data were collected over the angular range of 20–80° with a step size of 0.02° and counting times of 2.0 s/step. The bulk density was measured using both the geometric and Archimedes methods. Scanning electron microscopy (Jeol, JSM-6390LA) was used to observe the microstructure of the ceramics. The post-annealed samples were polished to obtain parallel surfaces and then coated with silver paste (DuPont, 4922 N) as electrodes. The dielectric properties were measured using impedance analyzers (Yokogawa–Hewlett-Packard, 4274 A; Hewlett-Packard, 4285 A) in the frequency range from 10^2 to 10^6 Hz at room temperature. Impedance plots were fitted and extrapolated using the Cole-Cole empirical relation.

3. Results and discussion

The starting powder was pure $SrTaO_2N$ in XRD crystallized in the tetragonal $I4/mcm$ space group [4]. Crystallinity was improved with HIP sintering temperatures higher than the preparation temperature of 1000 °C. No secondary phase was evident after HIP sintering at 1200 °C, as shown in Fig. 1(b). HIP sintering in an evacuated glass capsule was effective to suppress the Sr loss observed in the conventional sintering [5]. A trace amount of impurities, which might be related to TaC, ζ-$TaC_{0.47}$ and/or ζ-$TaC_{0.6}$ (JCPDS 19-1292, 1293,1294), were found in $SrTaO_2N$ HIP sintered at 1400 °C (see Fig. 1(c)). It may suggest the contamination of amorphous carbon in the starting powder. The impurity then disappeared after post-annealing, as depicted in Fig. 1(c). The formation of TaC related impurities was also observed with conventional sintering in the reaction with the residual carbon produced through the citrate route [5,6]. $Sr_2Ta_2O_7$ and $Ta_{1.1}O_{1.05}$ impurities were evident in the product obtained after sintering at 1600 °C, probably due to the enhanced reactivity of residual oxygen in the HIP sintered capsule, and these impurity phases remained even after post-annealing.

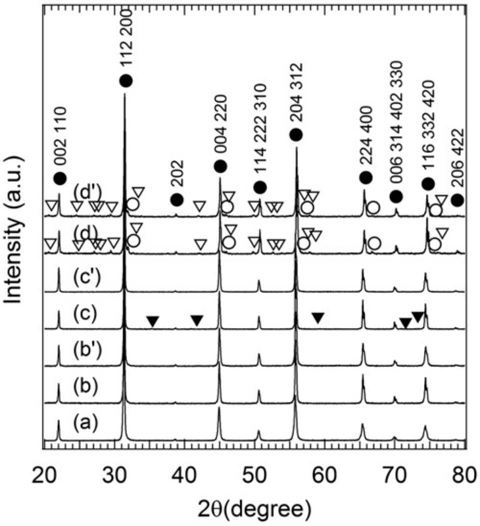

Fig. 1. XRD patterns of (a) $SrTaO_2N$ powder, $SrTaO_2N$ bulks HIP sintered at (b) 1200, (c) 1400, and (d) 1600 °C, and (b′–d′) their respective post-annealed products. Filled circles, filled triangles, open triangles and open circles represent the diffraction lines for $SrTaO_2N$, TaC, $Sr_2Ta_2O_7$ and $Ta_{1.1}O_{1.05}$, respectively.

All the bulk samples changed color from brown to dark gray after HIP sintering, which was closely related to the anion deficiency in the crystal lattice caused by the reductive atmosphere inside the glass capsule. Annealing in ammonia returned the color of the sample sintered at 1400 °C to brown, probably because the anion deficiency was supplemented. This result is similar to that reported previously, in which $SrTaO_2N$ bulks were sintered in nitrogen with $SrCO_3$ sintering aid [5,6]. However, the post-annealing treatment was unsuccessful for the samples sintered at 1200 and 1600 °C and the sample color remained dark gray after annealing. This was attributed to the dense microstructure with compacted grains of the as-sintered ceramics, as described later. The relative densities of $SrTaO_2N$ bulks HIP sintered at 1200, 1400 and 1600 °C were 90, 82 and 86%, respectively. A slight decrease in density was observed for all samples after annealing, for example, the bulk density of the sample sintered at 1400 °C decreased from 82% to 80%. Compared with the density (ca. 55%) reported by Kim et al. [2], densification was significantly enhanced when changing from conventional sintering to HIP sintering.

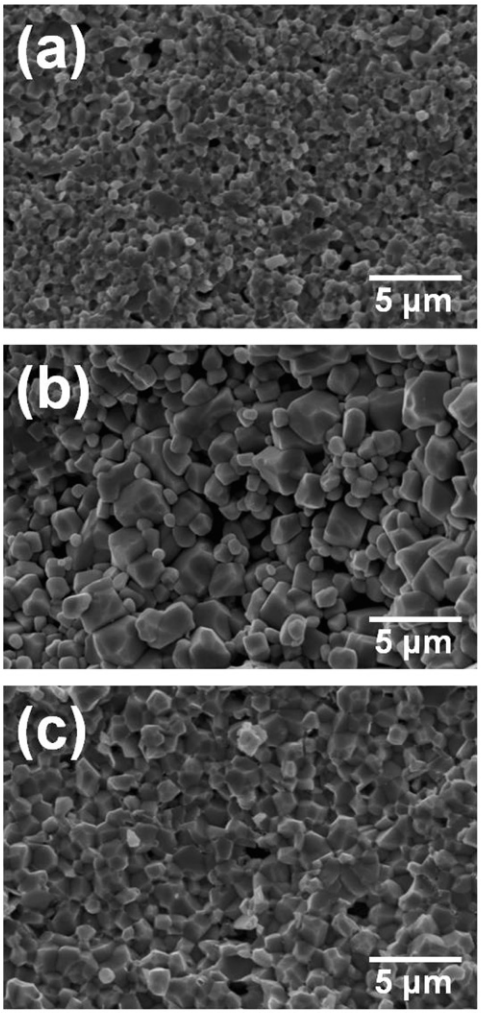

Fig. 2. Fracture surfaces of $SrTaO_2N$ sintered at (a) 1200, (b) 1400 and (c) 1600 °C.

Densification of the $SrTaO_2N$ ceramics sintered at different temperatures was confirmed by observation of the microstructure. The $SrTaO_2N$ sample sintered at 1200 °C was dense with a well-developed microstructure comprised of submicron grain sizes, as shown in Fig. 2. Grain growth was promoted as the sintering temperature was raised to 1600 °C, and the resultant bulk had uniform microstructure with evident grain boundaries and an average grain size of 1.1 ± 0.2 µm. In contrast, the microstructure of the $SrTaO_2N$ bulk sintered at 1400 °C was inhomogeneous with small grains located at the boundaries of larger grains (ca. 2 µm). Many pores were also evident near the grain boundaries, which indicated a relatively high porosity and low bulk density. The grain growth and densification behavior of the sample HIP sintered at 1400 °C was quite different from those sintered at 1200 and 1600 °C. It is considered that prior to sintering, some residual $SrCO_3$ formed in citrate route remained in the $SrTaO_2N$ powder [5]. The $SrCO_3$ then began to decompose at around 1400 °C and released CO_2 causing the relatively low density, while the densification of $SrTaO_2N$ occurred simultaneously. Useful role of $SrCO_3$ has been reported in conventional sintering of $SrTaO_2N$ [5]. At the lower sintering temperature of 1200 °C, the decomposition of $SrCO_3$ did not occur, so that densification was not hindered, which resulted in lower bulk porosity. In contrast, when sintering at 1600 °C, the $SrCO_3$ had already completely decomposed, and developed the sintering at grain boundary enclosing CO_2 gas in its closed pore. It reduced the relative density to 86% at 1600 °C from the value of 90% at 1200 °C. Dense microstructures with closely-compacted grains were obtained for the $SrTaO_2N$ bulks sintered at 1200 and 1600 °C; therefore, the post annealing process was unsuccessful. During the annealing process, the uptake of oxygen/nitrogen (especially nitrogen) leads to a slight expansion of the crystal lattice [5] and also the bulk volume. Sometimes, cracks and even complete fragmentation of the ceramic bodies was induced for HIP sintered $SrTaO_2N$ with densities higher than 85% of the theoretical value. In contrast, a certain number of open pores in the sample sintered at 1400 °C provided the space for volume expansion and facilitated the annealing process to be back to brown color.

The $SrTaO_2N$ ceramic sintered at 1400 °C had a dielectric constant (ε_r) in the order of 7.8×10^3 at 10^2 Hz, as depicted in Fig. 3. This is much higher than that previously reported by Kim et al. [2], and is comparable with our previously reported values on the conventional sintered body with sintering aid [5,6]. It is also comparable with the permittivity obtained for the typical $BaTiO_3$ dielectric at its Curie temperature [12]. Therefore, it is considered that enhanced densification is beneficial to improve the dielectric properties. In comparison to the conventionally sintered $SrTaO_2N$ [2], the dielectric loss (tan δ) of the HIP sintered bulk also decreased, but was still rather high, at ca. 0.3 at 10^6 Hz. It has been suggested that for well-densified $SrTaO_2N$ ceramics with a relative density above 90%, a high dissipation factor is obtained due to the difficulty in the removal of anion deficiencies [5,6]. In the present study, some porosity (ca. 20%) still remained in the ceramic although the bulk density of HIP sintered $SrTaO_2N$ increased. The high tan δ could be attributed to the larger grains in HIP sintered $SrTaO_2N$, as evident in

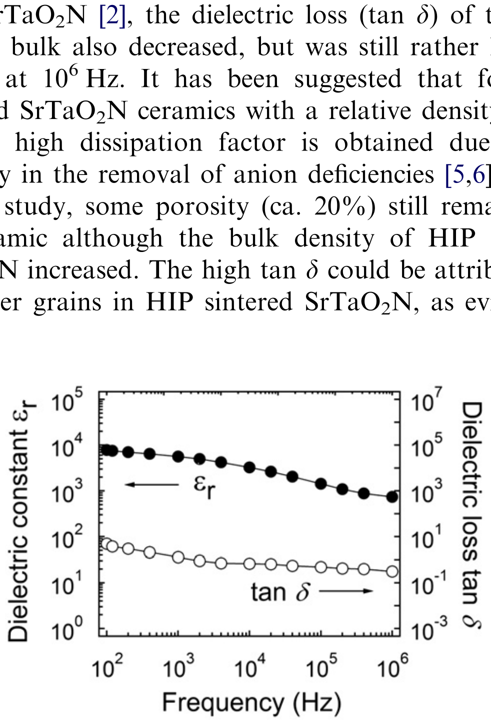

Fig. 3. Relative dielectric constant (ε_r) and dielectric loss (tan δ) for $SrTaO_2N$ bulk HIP sintered at 1400 °C.

Fig. 3(b). During the annealing process, oxygen and nitrogen species diffused faster at grain boundaries than into grains; therefore, a decrease of grain boundaries due to exaggerated grain growth hindered the elimination of anion vacancies and led to an increase of space charges.

A complex impedance plot of the $SrTaO_2N$ bulk sintered at 1400 °C was fitted using a nonlinear curve with a corresponding equivalent circuit model. The bulk resistance R_b value, assigned as the intercept of the Z'-axis in the Cole–Cole plot, is approximately $3.3 \times 10^5\ \Omega$, which is much higher than that for $SrTaO_2N$ conventionally sintered in NH_3 [2], and indicates a relatively lower dielectric loss.

4. Conclusion

In conclusion, capsule HIP sintered $SrTaO_2N$ at 1400 °C had relative density of 82% with exaggerated grain growth and some amount of open pore. It was successfully annealed in NH_3 and the resultant $SrTaO_2N$ product with a bulk density of 80% had a considerably high relative dielectric permittivity of 7.8×10^3 at 10^2 Hz.

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