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Dielectric anisotropy and sinterability improvement of $Ba_4Nd_{9.33}Ti_{18}O_{54}$ textured ceramics

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Abstract

The ⟨0 0 1⟩-textured $Ba_4Nd_{9.33}Ti_{18}O_{54}$ (BNdT) ceramics were fabricated by templated grain growth process. Acicular particles prepared using K_2SO_4 molten salt were used as template and aligned by tape casting in the equiaxed BNdT powder. Crystalline phases of sintered specimen exhibited $\{h\,k\,0\}$ and $\{0\,0\,1\}$ development in the plane of parallel and perpendicular to the casting direction, respectively. The formation of a slight amount of secondary phase in the template particles and the compositional deviation inhibited the densification and texture development for BNdT. To improve the sinterability, the composition shifted from BNdT to $Ba_2Ti_9O_{20}$ (B2T9) rich side slightly in $BaO{-}Nd_2O_3{-}TiO_2$ ternary system, which enables to promote a liquid phase during the sintering, was examined as a matrix phase. Resultant ceramics including B2T9-rich matrix phase displayed high density and large dielectric anisotropy. Temperature dependence of dielectric constant showed negative and positive behavior between the direction of parallel and perpendicular to the ⟨0 0 1⟩-textured BNdT. Near-zero temperature coefficient of resonant frequency (τ_f) in TE_{011} mode was obtained in the textured ceramics with the degree of $\{0\,0\,1\}$ orientation of approximately 0.37 on the disk plane. The exceptional temperature behavior of BNdT made it possible to control the τ_f over the wide range by the combination of dielectric anisotropy.

Keywords: Dielectric properties; Grain growth; Sintering; $BaTiO_3$ and titanates; Anisotropy

1. Introduction

Development of microwave dielectric materials has contributed considerably to progress of wireless communication technology. A number of materials have been found as low loss dielectrics at microwave frequency. $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R: rare earth) solid solutions (BRT-ss) are well known as one of the important material with high dielectric constant (ε_r) and low dielectric loss (high $Q{\cdot}f$).[1] It is also known that dielectric properties of BRT-ss strongly depend on the composition x and the rare earth element. Therefore, much attention has been attracted to BRT-ss from the view point of not only industrial application but also of academic interest. The mechanism of the dielectric properties has been discussed based on the crystal chemistry.

BRT-ss has a tungsten bronze type structure with an orthorhombic unit cell lattice parameters $a = 12.2$ (Å), $b = 22.4$ (Å) and $c = 7.7$ (Å). Framework of corner-sharing TiO_6 octahedra in the *ab*-basal plane link along the *c*-axis with zigzag tilting. As a result of the anisometric crystal structure, BRT-ss tend to show anisotropic development of elongated grains in the microstructure. Because of the inhomogeneity, the processing route of ceramics preparation for BRT-ss sensitively affects the sinterability and the dielectric properties. Negas and Davies[1] have investigated the influence of processing routes on the dielectric properties of $Ba_{6-3x}R_{8+2x-y}Bi_yTi_{18}O_{54}$. They reported the effect of preferred (0 0 1) alignment on the dielectric properties. Hoffman and Waser[2] have also reported effect of hot forging on the sinterability and properties of BRT-ss. The dielectric anisotropy based on the structural data of BRT-ss had been described by Valant et al.[3] Thus foregoing it is evident that large anisotropy exists in the properties in BRT-ss. However, despite many investigations concerned with BRT-ss, there are few reports on the anisotropic properties. Moreover, abnormal behavior in properties BRT-ss have been reported by Belous et at.[4] Further investigations are required to understand more about the correlation between the crystal structure and the dielectric properties.

Recently, templated grain growth (TGG)[5] and related techniques are recognized as one of the most important processing route to obtain textured electroceramics with the improved

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properties. In this process, a small amount of anisotropic grains, which are designated as "template", is mixed and aligned in a fine-grained matrix powder. Initial anisotropic grains act as seeds for preferential growth of matrix grains during the sintering process. Finally, highly grain-oriented ceramics are obtained. We have previously reported[6] the textured ceramics of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BSmT) [R = Sm and $x = 2/3$] by using TGG technique. However a decrease of density was observed with increase of template particles. On the other hand, in the conventional preparation of BSmT, it has been reported[7] that the shifting of the composition slightly from BSmT to $Ba_2Ti_9O_{20}$ rich side in $BaO–Sm_2O_3–TiO_2$ ternary system promoted liquid phase during the sintering without affecting the dielectric properties. In this study, the dielectric anisotropy in BNdT [R = Nd and $x = 2/3$ of BRT-ss] prepared by the templated grain growth process are investigated. The $Ba_2Ti_9O_{20}$ rich BNdT composition was used as a matrix phase in order to improve the sinterability of the textured ceramics. The sinterability and the dielectric anisotropy of textured BNdT in undoped and $Ba_2Ti_9O_{20}$-rich matrixes are compared to those prepared by conventional method.

2. Experimental procedure

BNdT template particles and matrix powder were prepared separately in the beginning. High-purity $BaCO_3$, Nd_2O_3 and TiO_2 were mixed according to the BNdT composition with an equal weight of K_2SO_4 in a ball mill for 24 h. The mixture was heat-treated at 1300 °C for 12 h and washed several times to remove residual K_2SO_4. On the other hand, matrix phases based on the composition of the BNdT and with 4 mol% $Ba_2Ti_9O_{20}$ (B2T9-rich BNdT) were prepared by solid-state synthesis, respectively. Raw materials described above were calcined at 1000 °C for 2 h. The slurries prepared from the template particles, the matrix powder, polyethylene glycol and poly(vinyl butyral) were formed into a green sheet by tape casting. After drying, the sheets were cut and stacked into a green block. The binder was burned off by heating at 600 °C for 2 h. The blocks were then cold isostatically pressed at 200 MPa and sintered at 1460 °C for 2 h. The sintered ceramic blocks were cut and machined into two types of disk shapes, in one with the plane is parallel and in the other it is perpendicular to the casting plane (abbreviated as BNdT(//) and BNdT(⊥), respectively.)

The densities of the sample were measured by the Archimedes' method. The microstructures were observed by scanning electron microscopy (SEM; JSM-5200, JEOL). The crystalline phases and texture development in the samples were identified by X-ray diffraction method (XRD; X'Pert MPD, Philips) using Cu Kα radiation. The degree of orientation was calculated using the Lotgering's equations.[8] Microwave dielectric properties (dielectric constant ε_r, quality factor $Q{\cdot}f$, temperature coefficient of resonant frequency (τ_f) were measured by Hakki and Colemans' method[9] in the $TE_{01\delta}$ mode using a network analyzer (HP-8757, Hewlett Packard). The τ_f was measured in the temperature range between 20 and 80 °C. An impedance analyzer (HP-4294A, Agilent) was used for measuring the temperature dependence of ε_r at 1 MHz. Silver electrode was made on both side of the disk specimen prior to the measurement of the temperature dependence.

3. Results and discussion

Fig. 1a and b show the SEM micrograph and the XRD pattern respectively of particles obtained by K_2SO_4 molten salt at 1300 °C for 12 h. The presence of acicular particles are evident in Fig. 1a. The diffraction peaks were identified as BNdT although a small difference in the intensity is observed which is due to the particle anisotropy. A small amount of secondary phase was detected, as shown in Fig. 1b. This secondary phase remained even after prolonged heating. Formation of the secondary phase implies a deviation from the composition of the template particles. Katayama et al.[10] have reported the preparation of $BaNd_2Ti_4O_{12}$ ($x = 1/2$) by NaCl–KCl molten-salt synthesis. Although they have succeeded in synthesizing a single-phase with fine particle size at 1000 °C, the powder has very small particle size. In TGG process, template particle is required having a certain size and large aspect ratio to achieve alignment of template during formation easily. NaCl–KCl molten salt led to form single phase, columnar shape and more homogeneous particles in case of $Ba_4Sm_{9.33}Ti_{18}O_{54}$.[11] However, in the case of BNdT, the salts could not be acceptable. Therefore the powder obtained with K_2SO_4 at 1300 °C for 12 h was used as template in this study.

Fig. 2 shows apparent density of BNdT and B2T9-rich BNdT ceramics as a function of template concentration. The inhomogeneity in the BNdT template particles inhibited the sinterability.

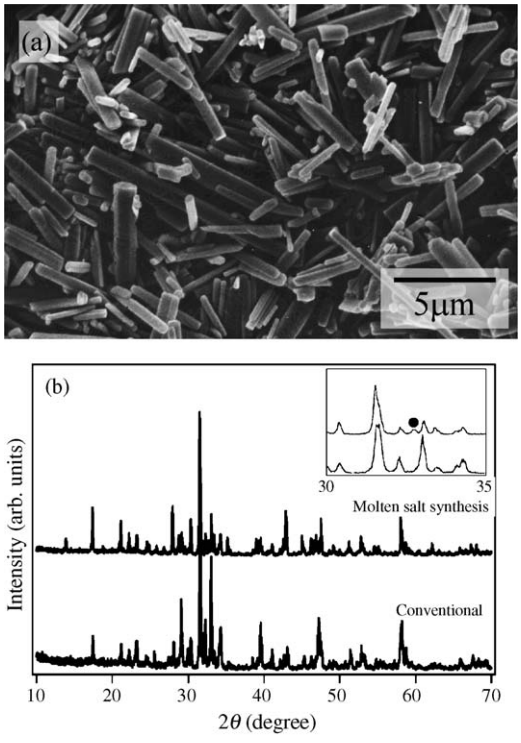

Fig. 1. (a) SEM photograph of BNdT particles. (b) XRD patterns of solid-state and molten-salt synthesized BNdT. The inset in (b) displays the magnification of $2\theta = 35–40°$. Black circle exhibits unknown phase.

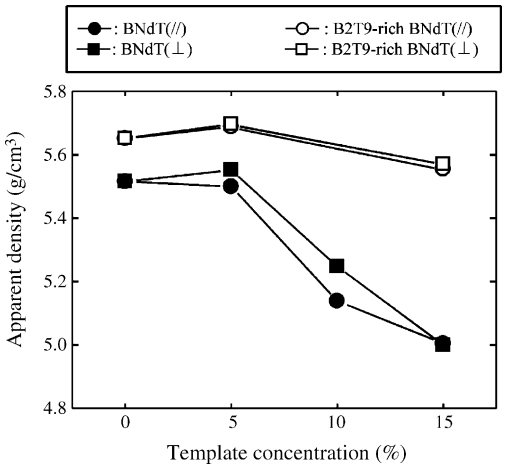

Fig. 2. Apparent density of BNdT and B2T9-rich BNdT ceramics as a function of template concentration.

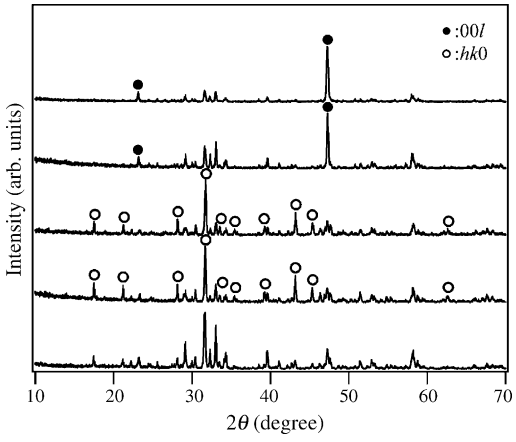

Fig. 3. XRD patterns of (a) non-textured BNdT without template, (b) BNdT(//), (c) B2T9-rich BNdT(//), (d) BNdT(⊥) and (e) B2T9-rich BNdT(⊥) with template concentration of 15 wt%.

On the other hand, use of B2T9-rich matrix is effective in improving the density significantly. The XRD patterns recorded from the polished surface of various BNdT ceramics are shown in Fig. 3. The sample with B2T9-rich matrix showed higher texture development compared with the sample with ordinary BNdT matrix.

Table 1 summarized apparent density, degree of orientation, and microwave dielectric properties for non-texutred and textured BNdT ceramics with template concentration of 15 wt%. The ε_r decreased significantly when ordinary BNdT was used as

Table 1
Microwave dielectric properties for non-textured and textured BNdT ceramics with template concentration of 15 wt%

	ρ (g/cm^3)	F	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
Non-textured BNdT	5.52	0	83.0	9300	59.2
BNdT(//)	5.00	0.50 {$hk0$}	71.8	8900	109.2
BNdT(⊥)	5.01	0.19 {0 0 1}	65.4	9400	35.2
B2T9-rich BNdT(//)	5.58	0.54 {$hk0$}	88.5	8700	109.7
B2T9-rich BNdT(⊥)	5.57	0.37 {0 0 1}	79.8	9500	0

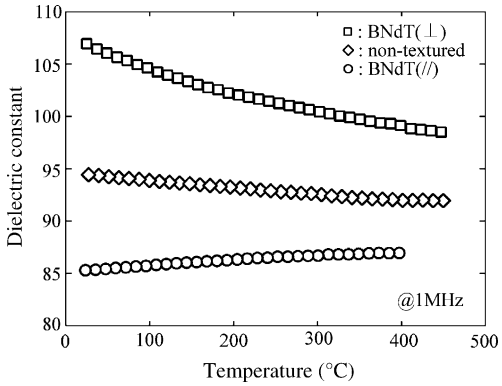

Fig. 4. Temperature and crystallographic direction dependence of the dielectric constant for non-textured BNdT and textured B2T9-rich BNdT with template concentration of 15 wt%.

matrix phase because of the low density. In contrast, as a result of high density and the anisotropy, BNdT(//) with B2T9-rich matrix exhibited higher ε_r than BNdT(⊥) with B2T9-rich matrix. On the other hand, decrease of the density did not affect to the $Q{\cdot}f$ value. Although the $Q{\cdot}f$ of BNdT(//) is lower than BNdT(⊥) and the reasons for it is not clear. Large difference is observed in the τ_f between BNdT(//) with B2T9-rich matrix and BNdT(⊥) with B2T9-rich matrix. Fig. 4 shows the temperature dependence of dielectric constant at 1 MHz for non-textured and textured BNdT prepared with B2T9-rich matrix and 15 wt% template particles. Remarkable difference in temperature behavior results from the anisotropy. BNdT(⊥) always showed negative temperature behavior and the higher dielectric constant at room temperature. In contrast, BNdT(//) showed positive temperature behavior with a lower dielectric constant. Non-textured ceramics exhibited an averaged value of dielectric constant.

The reason of large difference in τ_f is explained as follows. It is known that τ_f is related to the temperature coefficient of dielectric constant (τ_ε) and linear thermal expansion coefficient of the material (α_l) by the equation of $\tau_f = -\tau_\varepsilon/2 - \alpha_l$. In general α_l in electroceramics is approximately +10 ppm/°C. Thus the τ_f mainly depends on τ_ε if the material has a large τ_f. In addition, τ_f is opposite sign to τ_ε by the equation as described above. The electric field in the measurement of the dielectric constant at 1 MHz is perpendicular to the transverse plane. On the other hand, the TE modes have field component in the transverse plane. In BNdT(//) sample, ⟨0 0 1⟩-elongated grain mainly distributed to parallel to the transverse plane. The increase of c-axis component in the transverse plane led to the decrease of τ_ε and the increase in τ_f. In contrast, ⟨0 0 1⟩-elongated grain distributed to perpendicular to the transverse plane in BNdT (⊥) sample. The increase of ab-axes component in the transverse plane of BNdT(//) resulted in the opposite results. The present results on this work showed good agreement with earlier reports.[1,2,6]

Fig. 5 shows the variation of τ_f as a function of degree of {$hk0$} orientation for BNdT(//) and {0 0 1} orientation for BNdT(⊥) with various template concentrations, respectively. It was found that the τ_f linearly varies almost proportional to the orientation degree. In summary, near-zero τ_f obtained in BNdT(⊥) is explained as a result of compensation of the dielectric anisotropy between ab-axes and c-axis components. Further

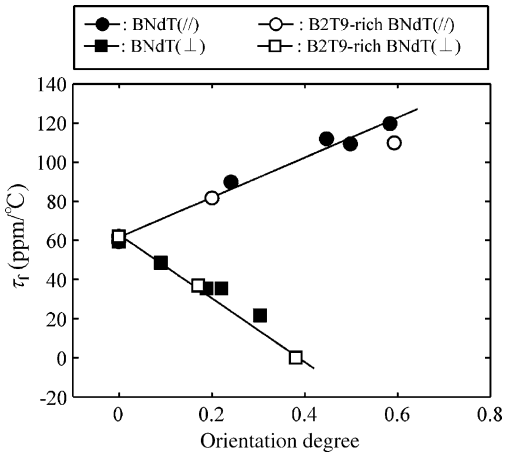

Fig. 5. Variation of τ_f as a function of orientation degree.

studies on the anisotropy in BRT-ss are in progress. More highly textured BRT-ss may exhibit previously unidentified properties.

4. Conclusion

⟨0 0 1⟩-textured BNdT ceramics were prepared using templated grain growth technique with acicular BNdT particles as templates. The density of BNdT ceramics decreased with the amounts of templated particles because of the deviation of composition and presence of secondary phase within the template particles. Use of $Ba_2Ti_9O_{20}$ rich matrix powder improved the sinterability significantly. Textured BNdT ceramics showed a large dielectric anisotropy. An opposite temperature behavior was observed in ε_r between the direction of parallel and perpendicular to ⟨0 0 1⟩-textured BNdT. Near-zero τ_f was obtained when a degree of {0 0 1} orientation for the disk plane was about 0.37. The temperature dependence could be controlled to a desired value including near-zero ppm/°C by adjusting the orientation of grains in the BNdT ceramics. The importance of grain-orientation to control the dielectric properties is demonstrated by using dielectric anisotropy.

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