Control of temperature coefficient of resonant frequency in Ba$_4$Sm$_{9.33}$Ti$_{18}$O$_{54}$ ceramics by templated grain growth

Kensuke Wada*, Ken-ichi Kakimoto, Hitoshi Ohsato

Department of Materials and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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Abstract

A novel tuning method of temperature dependence of dielectric properties in Ba$_4$Sm$_{9.33}$Ti$_{18}$O$_{54}$ (BSmT) microwave material was demonstrated by texture engineering. Two kinds of grain-oriented BSmT ceramics were obtained using a templated grain growth technique. Highly fiber-textured ceramics were fabricated by tape casting of slurry with a mixture of (001)-elongated BSmT template particles and fine-grained BSmT powder. On the other hand, partially grain-oriented ceramics were also obtained from the uniaxially pressed mixture of the template particles and the fine-grained powder. Orientation degree of sintered BSmT ceramics increased with a content of template particles. As compared with the specimen prepared by normal sintering technique, the textured ceramics displayed a large anisotropy in the dielectric properties, especially in the temperature coefficient of resonant frequency ($\tau_f$). Consequently, near-zero $\tau_f$ was obtained in the textured ceramics with (hk0)-orientation degree of approximately 0.10 in the surface of the disk specimen. In addition, the $\tau_f$ could be controlled to a desired value from ranging $-90$ to $+25$ ppm/°C by adjusting the grain orientation in the specimen. Measurement of the temperature dependence of dielectric constant, which correlates with $\tau_f$, revealed positive and negative behaviors for (hk0) and (001) textured BSmT ceramics, respectively. The tuning of $\tau_f$ was explained as a rule of mixture of dielectric anisotropy in BSmT.

Keywords: Templated grain growth; Microwave dielectric properties; Dielectric anisotropy; Tungsten bronze type-like structure

1. Introduction

With the development of high-frequency communication technology, microwave dielectric materials with excellent temperature stability of the resonant frequency (near-zero $\tau_f$) and lower dielectric loss (higher $Q\cdot f$ value) have been required for resonator applications with high performance. Despite a number of investigations for microwave dielectrics, materials with both near-zero $\tau_f$ and high $Q\cdot f$ are limited to specific compositions such as Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ [1], (Zr, Sn)TiO$_4$ [2] or Ba$_2$Ti$_9$O$_{20}$ [3]. Therefore, investigations for the improvement of $\tau_f$ have mainly focused on the modification of base material using chemical methods including the formation of solid solution [4] or the doping of other chemicals with opposite $\tau_f$ for the base material [5]. For the formation of solid solution, the matching in ionic radius and electric charge with substituted constituent is required. On the other hand, less reactivity with the main phase is strongly required for the doping modification. As another example, laminated ceramics consisting of several different layers have also been prepared with the combination of different materials having positive and negative $\tau_f$ [6]. In the most cases, however, a large change in $\tau_f$ causes serious influence in the dielectric constant ($\varepsilon_r$) and/or the $Q\cdot f$ value, compared with the original properties.

Recently, there has been much interest in texture engineering because it can allow emphasizing anisotropy of various physical properties. The application to electroceramics is one of the most attractive subject to obtain extraordinary properties compared with polycrystalline ceramics [7,8]. In microwave dielectric materials, there is little information in the literature with regard to textured ceramics. It is empirically known that microwave dielectric
properties of Ba$_{6-3x}$R$_8$+$_2$Ti$_{18}$O$_{54}$ ($R$: rare earth) solid solutions, which are the compounds showing both high $\varepsilon_r$ and $Q\cdot f$ [9], depend on their processing route sensitively. Negas and Davies [10] and Hoffman and Waser [11] have reported the engineering of preferred grain orientation by applying various processing routes such as uniaxial hard die and extrusion [10] or hot-forging [11]. They have reported some of prefered orientation and anisotropy in the dielectric properties. The crystal structure of Ba$_{6-3x}$R$_8$+$_2$Ti$_{18}$O$_{54}$ solid solution is orthorhombic tungsten bronzetype like unit cell. Corner-sharing [TiO$_6$]$_8$ octahedra form a network with pentagonal, rhombic and triangular sites in $ab$-basal plane while the octahedra with tilt align in the direction of the $c$-axis in the crystal structure. This anisometric crystal cell is considered to be origin of dielectric anisotropy.

In this study, textured Ba$_3$Sm$_{3x}$Ti$_{19}$O$_{54}$ ($R = $Sm and $x = 2/3$, abbreviated as BSmT) ceramics were fabricated by templated grain growth (TGG) technique. Recently, TGG [12] and related techniques [13] are recognized as one of the most important processing route to obtain textured ceramics with enhanced dielectric properties [14,15]. In this method, a small amount of anisometric grains, which are designated as ‘template’, is mixed and aligned in a fine-grained matrix powder. Initial anisometric grains act as seeds for preferential growth of matrix grains during the sintering process. As a result, highly grain-oriented ceramics are obtained. In the present experiment, two kinds of processing by TGG were performed for sample preparation to reveal the possibility of texture engineering for microwave dielectric materials. One is the fabrication of the sample using a mixture of template particles and fine-grained powders by conventional processing of uniaxial pressing (Process I). The other is the fabrication of sample using stacked tape-cast sheets (Process II). Since the tape casting technique enables unidirectional alignment of template particles within the green sheet, the resulting ceramics can be obtained with enhanced crystallographic texture. We discussed the correlation among dielectric properties, grain orientation and distribution of electric field in the dielectrics.

2. Experimental procedure

2.1. Powder synthesis

The initial step in this study was the preparation of BSmT matrix powder and template particles by solid-state reaction and molten salt synthesis, respectively. Reagent grade BaCO$_3$, Sm$_2$O$_3$ and TiO$_2$ were ball-milled for 24 h in ethanol. The ball-milled powder after drying was calcined at 1000 °C for 2 h and used as matrix powder. On the other hand, the template particles were prepared by molten salt synthesis. The same resource powder of BSmT was ball-milled for 24 h with an equal weight of equimolar NaCl–KCl salts. The powder mixture was placed in a covered alumina crucible. Heat treatments were carried out at temperature in the range from 1000 to 1250 °C. The cooled reactants were washed with deionized water several times to remove residual salts.

2.2. Process I

The BSmT powder and template particles were ball-milled for 6 h in template content from 0 to 15 mass%. After drying, the powder mixture was uniaxially pressed into cylindrical compacts of 12 mm in diameter. These green compacts were sintered at 1460 °C for 2 h with heating and cooling rate of 5 °C/min.

2.3. Process II

Slurries including BSmT template particles, the matrix powder, polyethylene glycol and poly(vinyl butyral) were formed into a green sheet by tape casting. Template concentration was varied from 0 to 15 mass%. After drying, the sheets were cut and stacked into a green block. The green block was heated at 600 °C for 2 h to burn organic binders. Then the blocks were cold isostatic pressed at 200 MPa and sintered at 1460 °C for 2 h. The sintered ceramic blocks were cut and machined to two types of disk shapes, whose plane is parallel (BSmT($//$)) or perpendicular (BSmT($\perp$)) to the casting plane, as shown in Fig. 1(a) and (b).

2.4. Characterization

Microstructural observations were conducted using a scanning electron microscopy (SEM, JSM-5200, JEOL). The particles size distribution was measured using a laser diffraction method (Microtrac Model 7995, Nikkiso) with the dispersion of powders in distilled water by ultrasonic vibration. The X-ray diffraction (XRD, X'Pert MPD, Philips) using Cu K$_\alpha$ radiation was performed for phase identification and determination of orientation degree of textured ceramics. The density of the sintered ceramics was evaluated using Archimedes’ method. Microwave dielectric properties were measured using the modified method of Hakki and Coleman [16] and Kobayashi [17] in the TE$_{011}$ mode (HP-8757, Hewlett Packard). Fig. 1(c) indicates the vector field distribution of TE$_{011}$ mode. The temperature coefficient of resonant frequencies was measured in
the temperature range between 20 and 80 °C. An impedance analyzer (HP-4294A, Agilent) was used for measurement of the temperature dependence of dielectric constant at 1 MHz. Prior to the measurement of the temperature dependence, silver electrode was formed on both side of disk specimen.

3. Results and discussion

3.1. Characterization of BSmT template particles

Fig. 2 shows XRD patterns of powders obtained by molten salt synthesis at various reaction temperatures for 12 h. At 1000 °C, the product was identified as Na$_{0.5}$Sm$_{0.5}$TiO$_3$. It is considered that unreacted Ba$^{2+}$ was removed with Cl$^-$ during washing because Na$_{0.5}$Sm$_{0.5}$TiO$_3$ was formed preferentially prior to formation of BSmT at low temperature. Upon heating, BSmT was formed while Na$_{0.5}$Sm$_{0.5}$TiO$_3$ decomposes. As the reaction proceeds, single-phase BSmT was obtained above 1200 °C. The particles size distribution of powder prepared at 1100 and 1200 °C for 12 h is shown in Fig. 3. At 1100 °C,
the distribution was broad due to presence of aggregate particles. In contrast, the powder obtained at 1200 °C has a sharp distribution than that obtained at 1100 °C. Fig. 4 shows the particle morphologies of BSmT powders prepared by molten salt synthesis. The molten-salt synthesis led to the formation of particles with anisometric shape. In heating at 1100 °C for 12 h, rod-like shape particles with the length of about 10 μm are observed together with fine-equiaxed and aggregated particles (Fig. 4(a)). In heating at higher temperature, the powder consisted of only rod-like particles (Fig. 4(b)). These results including Figs. 2 and 3 exhibit that the fine-equiaxed and aggregate particles observed in Fig. 4(a) is Na0.5Sm0.5TiO3. At higher heat-treatment temperature, rod-like particles had less angular in shape and small aspect ratio (Fig. 4(c)). Template particles are required having large aspect ratio to enable the alignment easily during the processing. Therefore the condition to obtain single phase and particles with large aspect ratio was selected like Fig. 4(d).

3.2. Templated grain growth of BSmT ceramics

Fig. 5 shows typical microstructures on the natural surface of BSmT ceramics prepared by various processing routes at 1460 °C for 2 h. In the sample prepared by normal sintering of calcined powder, randomly oriented grains with small size are observed in Fig. 5(a). In the sample prepared by ‘Process I’ with template concentration of 5 mass% (abbreviated as BSmT-5S), some of anisometric grains exist as shown in Fig. 5(b). During uniaxial pressing in Process I, it is considered that longitudinal direction of template particles tends to distribute perpendicular to pressing direction in the sample. In addition, BSmT(∥) and BSmT(⊥) prepared by ‘Process II’ with template concentration of 15 mass% (abbreviated as BSmT(∥)-15T and BSmT(⊥)-15T, respectively) exhibited a strongly textured microstructure. Rod-shape grains aligned one-directionally parallel to casting direction can be observed in Fig. 5(c) and (d).

The XRD patterns on the polished surface of various BSmT ceramics are shown in Fig. 6. For comparison, a XRD pattern of polycrystalline powder prepared by normal sintering of calcined powder is also indicated as randomly oriented pattern in Fig. 6(a). In BSmT-5S, slight difference of peak intensity compared with Fig. 6(a) is observed (Fig. 6(b)). In BSmT(∥)-15T and BSmT(⊥)-15T, strongly preferred (hk0) and (001) orientation can be seen, respectively (Fig. 6(c) and (d)). These XRD patterns indicate that template particles have acted as seeds to develop c-axis oriented texture along the longitudinal direction of rod-like particles. The orientation degree, F, was quantified by Lotgering’s method [18] using following equation, $F = (P - P_0)/(1 - P_0)$, where $P = \sum I/\sum I_{hk0}$, $P_0 = \sum I_0/\sum I_{0hk0}$. In Figs. 7 and 8, the degree of (hk0) and (001) orientation is shown as a function of template concentration. The degree of (hk0) orientation was calculated for the sample prepared by Process I and Process II BSmT(∥), respectively. The degree of (001) orientation was also calculated for BSmT(⊥) in Process II. It is found that orientation degree for both Process I and II was proportional to template concentration. This indicates that adjusting of

![Fig. 5. SEM micrographs of (a) BSmT ceramics prepared by conventional process, (b) BSmT-5S, (c) BSmT(∥)-15T and (d) BSmT(⊥)-15T.](image-url)
template concentration enable to control grain orientation in the BSmT ceramics.

### 3.3. Microwave dielectric properties

Table 1 summarized density, orientation degree, and microwave dielectric data for various types of BSmT ceramics. All types of samples exhibited high $Q \cdot f$ value of more than 9000 GHz. Although BSmT(∥) type samples tended to show higher $Q \cdot f$ value than others, the reason is not yet clear. BSmT-5S had slight lower $\varepsilon_r$ than randomly oriented ceramics due to the low density. On the other hand, in spite of equivalent densities to randomly oriented BSmT ceramics, there is difference in $\varepsilon_r$ between BSmT(⊥)-15T and BSmT(∥)-15T. The difference during processing between BSmT(∥)-15T and BSmT(⊥)-15T is only the direction of stacking and machining. Hence, it is clear that an anisotropy of BSmT leads to the change in $\varepsilon_r$. While the difference between randomly oriented ceramics and textured ceramics in $\varepsilon_r$ and $Q \cdot f$ value was not large, a noteworthy dielectric anisotropy was observed in $\tau_f$. Whereas BSmT(⊥)-15T exhibited large negative value of $-90$ ppm/°C, BSmT(∥)-15T exhibited positive value of $+25$ ppm/°C. In particular near-zero $\tau_f$ was achieved successfully in BSmT-5S ceramics.

To reveal the effect of grain orientation in $\tau_f$, the relationship between $\tau_f$ and orientation degree was examined. Fig. 8 shows the variation of $\tau_f$ as a function of degree of (hk0) and (001) orientation for all textured samples.

### Table 1

| Orientation degree, density and microwave dielectric data for various BSmT ceramics |
|-----------------|-----|-------|-----|-----|-------|
| Orientation degree (%) | $\rho$ (g/cm$^3$) | $F$ (%) | $\varepsilon_r$ | $Q \cdot f$ (GHz) | $\tau_f$ (ppm/°C) |
|-----------------|-----|-------|-----|-----|-------|
| Non-textured 5T | 5.68 | 0 | 77.61 | 9322 | -13.4 |
| Process I BSmT-5S | 5.51 | 10.9 | 76.28 | 9396 | 1.8 |
| BSmT(∥)-15T | 5.69 | 90.3 | 83.60 | 10,227 | 24.9 |
| Process II BSmT(⊥) | 5.69 | 66.1 | 74.52 | 9122 | -90.2 |

Fig. 7. Degree of (hk0) orientation for BSmT ceramics prepared by ‘Process I’ and BSmT(∥), and degree of (001) orientation for BSmT(⊥) as a function of template concentration.

Fig. 8. Variation of $\tau_f$ for (hk0) and (001) textured BSmT ceramics as a function of orientation degree.
It was found that the $\tau_f$ varies almost proportional to the orientation degree. In this work, despite the significant change occurred in $\tau_r$, the $\varepsilon_r$ and $Q\cdot f$ value remained suitable corresponding to those observed in randomly oriented ceramics. This result leads to conclude that grain-orientation control for microwave dielectric materials is one of the effective methods to improve the $\tau_f$ significantly without serious influence in the $\varepsilon_r$ or $Q\cdot f$ values if the material has a large dielectric anisotropy.

Generally, it is known that $\tau_f$ is related to the temperature coefficient of dielectric constant ($\tau_r$) and linear thermal expansion coefficient of the material ($\alpha_t$) by the equation of $\tau_f = -\frac{\tau_r}{2 - \alpha_t}$. Because $\alpha_t$ in ceramics usually exhibits approximately $+10$ ppm/°C, $\tau_f$ mainly correlates with $\tau_r$ when the material has a large temperature dependence in dielectric constant. Fig. 9 shows the temperature dependence of dielectric constant at $1$ MHz for BSmT(//)-15T, BSmT(⊥)-15T and randomly oriented BSmT. It is clearly observed that BSmT(//)-15T has lower $\varepsilon_r$ than randomly oriented ceramics and positive trend, whereas BSmT(⊥)-15T has higher $\varepsilon_r$ and negative trend. In the measurement of temperature dependence, the electric field is thickness direction of the disk. Note that electric field is difference between the measurement at the frequency of $1$ MHz and the measurement at microwave frequency (Fig. 1(c)). In addition, $\tau_f$ is opposite sign to $\tau_r$ by the equation as described above. In BSmT, development of (hk0) texture on the disk plane such as BSmT(//)-15T means the increase of the c-axis component in the transverse direction of the disk. Similarly, development of (001) texture on the disk plane such as BSmT(⊥)-15T means the increase of the $ab$-axes components in the transverse direction of the disk. Hence, in the measurement at microwave frequency, BSmT(//)-15T exhibited larger $\varepsilon_r$ and $\tau_f$ than randomly oriented BSmT, while BSmT(⊥)-15T exhibited smaller $\varepsilon_r$ and $\tau_f$. The present results on this work showed good agreement with combination of reported results [9,10] more clearly. Near-zero $\tau_f$ obtained in BSmT-5S was concluded as the compensation of dielectric anisotropy between $ab$-axes components and c-axis component. The tuning of $\tau_f$ in this study is explained as a rule of mixture of dielectric anisotropy. Relationship between dielectric anisotropy and crystal structure of Ba$_6$Fe$_{3}$Ru$_2$Ti$_{18}$O$_{54}$ solid solution is considered as important subject of research to understand the origin of dielectric properties.

### 4. Conclusion

Textured and dense BSmT ceramics were fabricated by templated grain growth technique. The microstructures and microwave dielectric properties were compared with conventional ceramics prepared from solid-state reaction. In the preparation of template particles, reaction at high temperature and long duration of heating period yielded almost single phase of (001)-elongated BSmT grains without aggregation. Highly fiber-textured ceramics were fabricated by tape casting of slurry with fine-grained powder and the template particles. On the other hand, partially grain-oriented ceramics were also obtained from the uniaxially pressed mixture of the template particles and calcined powder. During the sintering, anisotropic grain growth occurred from the templated particles in the green compact. The orientation degree of templated BSmT ceramics increased with the template concentration. Textured ceramics showed a large anisotropy in $\tau_r$, while those demonstrated nearly equivalent dielectric constant and quality factor to the specimen prepared by normal sintering of calcined powder. BSmT ceramics with near zero $\tau_f$ were obtained when a degree of (hk0) orientation for the disk plane achieved to approximately $0.10$. A opposite temperature behavior was observed in $\varepsilon_r$ between (hk0) textured BSmT and (001) textured BSmT. The $\tau_f$ could be controlled to a desired value from $-90$ to $+25$ ppm/°C by adjusting the orientation in the ceramics. The superiority of grain-orientation control was demonstrated using a dielectric anisotropy.

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