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Microstructure and microwave dielectric properties of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ ceramics containing columnar crystals

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Abstract

The tungstenbronze-type-like $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ [$x=2/3$, $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BST)] is known as an excellent microwave dielectric material. In this study, $Ba_4Sm_{9.33}Ti_{18}O_{54}$ powder having needle-like or columnar shapes were prepared by NaCl–KCl molten salt route at 1100 °C. By this method. The derived BST columnar crystals were then added to calcined BST powder to form oriented ceramics. The columnar crystals acted as seeds for anisotropic grain growth within the specimens. For up to 10 wt.% seed crystals, the specimens demonstrated nearly equivalent ε_r and $Q{\cdot}f$ values to the specimens prepared without seed particles. In contrast, τ_f increased monotonously with an increasing amount of seed crystals. It is noteworthy that $\tau_f=0$ ppm/°C was expected in BST specimens prepared with 5 wt.% of columnar crystals. The relationship between microstructure development and dielectric properties is discussed.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Grain growth; Molten salt synthesis; Sintering

1. Introduction

The $BaO–R_2O_3–TiO_2$ (R: rare earth) ternary system has been much investigated in the research field of microwave dielectric materials.[1,2] In this system, $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions showing high dielectric constant were discovered on the tie line joining $BaTiO_3$ and R_2TiO_5 composition.[3] The $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solution shows a tungustenbronze-type-like structure with the following crystal structure data: orthorhombic, $a\approx12.2$ (Å), $b\approx22.3$ (Å), $c\approx7.7$ (Å), $Z=2$. The fundamental structural formula of this compound is $[R_{8+2x}Ba_{2-3x}V_x]_{A1}[Ba_4]_{A2}[V_4]_CTi_{18}O_{54}$, where V is a vacancy, the $A1$-site is rhombic forming 2×2 perovskite blocks, while the $A2$-site and C-site are pentagonal and trigonal, respectively. At $x=2/3$ composition, the R and Ba cations separately occupy $A1$- and $A2$-sites which leads to the highest $Q{\cdot}f$ value. Under the special condition of $R=$Sm and $x=2/3$, the composition $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BST) exhibits the high dielectric constant $\varepsilon_r\approx80$ and the highest $Q{\cdot}f$ value of 10,000 GHz within the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions. However, the temperature coefficient of resonant frequency (τ_f) for BST remains under −10 ppm/°C. In order to achieve $\tau_f=0$ ppm/°C, the partial substitution of cation sites has been explored.[4]

Solid-state synthesis has generally been used for the preparation of microwave dielectric ceramics, and equiaxed particles are used as starting materials. Therefore, the control of grain shape and orientation in the sintered body is difficult. On the other hand, the molten salt synthesis route, that is the flux method, is known as an excellent technique for controlling the shape of powder particles.[5] However, only a few studies have applied the molten salt synthesis route for preparation of microwave dielectric materials.[6,7] In most cases, these studies concentrated on the synthesis of materials at lower temperature than solid-state synthesis rather than the control of particle morphology.

In the present study, we prepare BST anisotropic crystals by molten salt synthesis. These crystals were mixed with equiaxed calcined BST powder in order to examine the sintering behavior of the mixture and control the microwave dielectric properties.

2. Experimental procedure

$Ba_4Sm_{9.33}Ti_{18}O_{54}$ (BST) anisotropic crystals were synthesized by the molten salt method. Stoichiometric

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amounts of $BaCO_3$ (99.7%), Sm_2O_3 (99.9%) and TiO_2 (99.8%) were weighted and then mixed by ball-milling in ethanol for 24 h prior to addition of the salt. Equal weight of equimolar NaCl–KCl salts were added to the BST mixture and mixed for 30 min in an agate mortar by a pestle. Heat treatment was carried out at temperature between 900 and 1100 °C. The residual salt was removed by washing with hot deionized water several times.

On the other hand, equiaxed BST particles were prepared by solid-state reaction for the starting mixture. The mixture was ballmilled in ethanol for 24 h and calcined at 1000 °C for 2 h. The calcined powder was mixed with the particles obtained by the molten salt method for seed crystals as a template. In the mixture, the fraction of the anisotropic particles was varied from 0 to 15 wt.%. The mixtures were ballmilled for 6 h. The dried mixtures were uniaxially pressed at 98 MPa to form pellets 12 mm diameter after adding 1 wt.% of PVA. The pellets were sintered at 1460 °C for 2 h.

Linear shrinkage during sintering was measured and the apparent density of sintered samples estimated by the Archimedes method. The crystalline phase was identified by powder X-ray diffraction (XRD) using CuK_α radiation (X'pert-MPD; Philips). The microstructure was observed by scanning electron microscopy (SEM; JSM-5200, JEOL). Some of SEM specimens were prepared by chemical etching. Microwave dielectric properties of miror-polished pellets were measured by the Hakki and Colesman method.[8]

3. Results and discussion

3.1. Preparation and characterization of columnar crystals

Fig. 1 shows powder XRD patterns of the reaction products synthesized by the molten salt method at temperatures between 900 and 1100 °C for 2 h. $Ba_4Ti_{13}O_{30}$, $BaTiO_3$ and $Sm_2Ti_2O_7$ phases were the main phases identified in the samples prepared at 900 and 1000 °C. However, these phases were not detected in the sample prepared at 1100 °C, instead many peaks attributed to the tungstenbronze-type-like solid solution appeared. This indicates that the preparation of BST particles was possible by NaCl–KCl flux at temperatures as low as 1100 °C.

Morphology change in the reaction products at 1100 °C is shown in Fig. 2 as a function of the reaction time for the molten salt method. Two types of the reaction products, columnar crystals and small particles, were

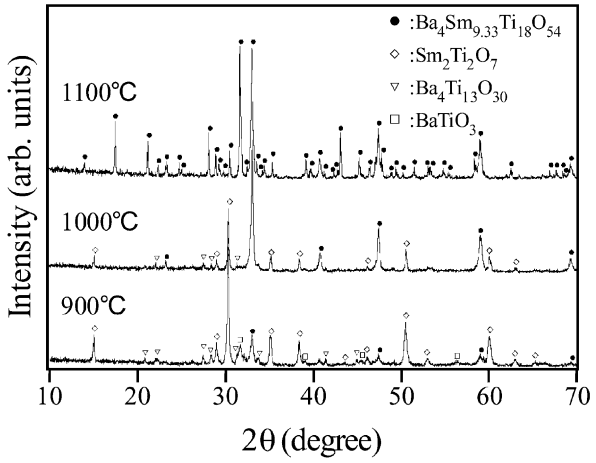

Fig. 1. XRD patterns of powders subjected to heat treatment at various temperature for 2 h.

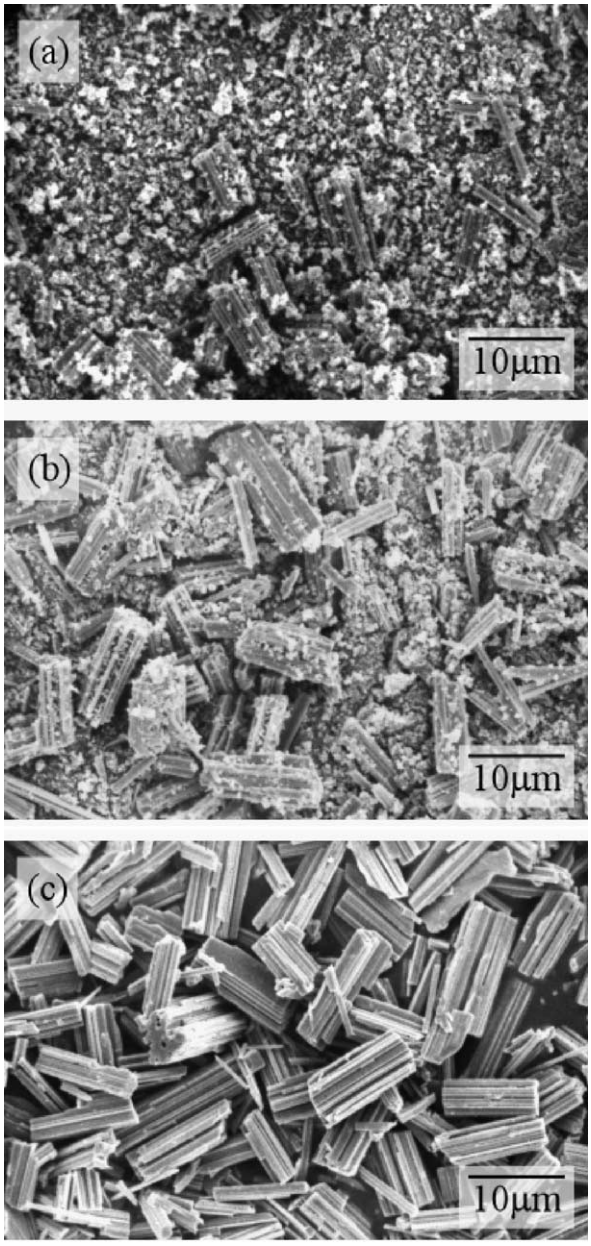

Fig. 2. SEM micrographs of powders obtained after heat treatment at 1100 °C for (a) 2 h, (b) 12 h and (c) 24 h.

observed in the specimen with a reaction time of 2 h [Fig. 2(a)]. Both of the reaction products exhibit the same crystal structure as tungstenbronze-type-like solid solutions, but are substantially different in shape. The small particles distribute with aggregation. It is obvious that the volume of small particles decreased with the increase of heating period. The reaction product heat-treated for 24 h consists of columnar grains only. The anisotropic grains are 5–15 μm in length and 1–3 μm in diameter.

Fig. 3 shows the XRD patterns of the reaction products obtained after heat treatment at 1100 °C for different periods. A tungstenbronze-type-like BST structure is observed in the specimen heat treated for 1 h. It should be noted that some specific peak intensities differ between the specimens. The peak intensity of BST 004 in the vicinity of $2\theta = 47°$, weakens with increased holding time at 1100 °C. This seems to be due to the development of preferential orientation within the sample. Finally, the 004 peak disappeared in the sample heated for 24 h. The mechanism of BST crystal growth is considered to be as follows. The aggregated BST equiaxed small particles were formed in the initial period of molten salt reaction by multiple nucleation growth in the flux. Subsequent heating caused a change of the shape of primary reaction products from fine particles to columnar crystals. In the case of heat treatment at 1100 °C, a soaking time for 24 h is necessary to transform them competely from small BST particles to columnar crystals. It was confirmed that these grains were single crystals by polarization microscopy.

3.2. Sintering of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ including columnar crystals

In the BST ceramics seeded with columnar crystals sintered at 1460 °C, anisotropic grains are well developed. SEM photographs of the surface of the specimens are shown in Fig. 4. For the reference sample, prepared without columnar crystals, most grains are small in size, and small amounts of elongated grains are also observed [Fig. 4(a)]. On the other hand, anisotropic elongated grains are well developed in the specimen prepared with columnar crystals (Fig. 4(b)). Fig. 5 shows SEM images taken from chemically etched polished samples. For the polished surfaces, anisotropic grain growth was observed in Fig. 5(b). Preferred orientation of the BST sintered samples was observed in XRD patterns obtained from the sample surface, as shown in Fig. 6. All the patterns for samples prepared with different amounts of columnar crystal additions demonstrate a structure typical of the solid solutions. However, specific preferred orientation is observed depending on the amount of the addition. The *hk*0 peaks such as 140 and 2 10 0 appear with increasingly stronger intensity with increasing amount of columnar crystals. In contrast, the peak intensity corresponding to 004 becomes weaker. These facts show *hk*0 preferred orientation, which was produced by acicular anisotropic growth in BST ceramics including columnar crystals. Fig. 7 demonstrates the relationship between the content of columnar crystals and the shrinkage behaviour

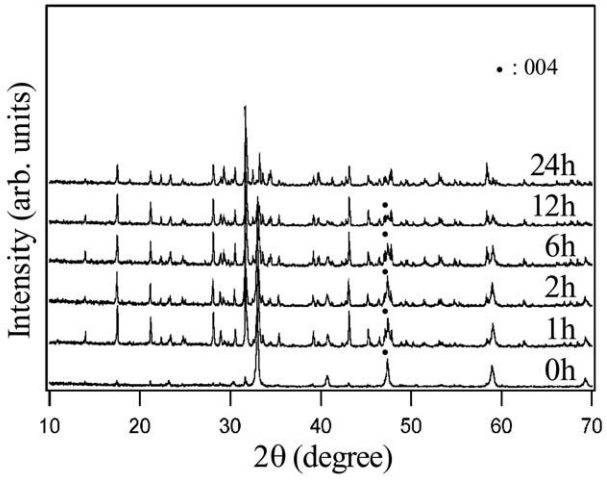

Fig. 3. XRD patterns of powders heat treated at 1100 °C for various times.

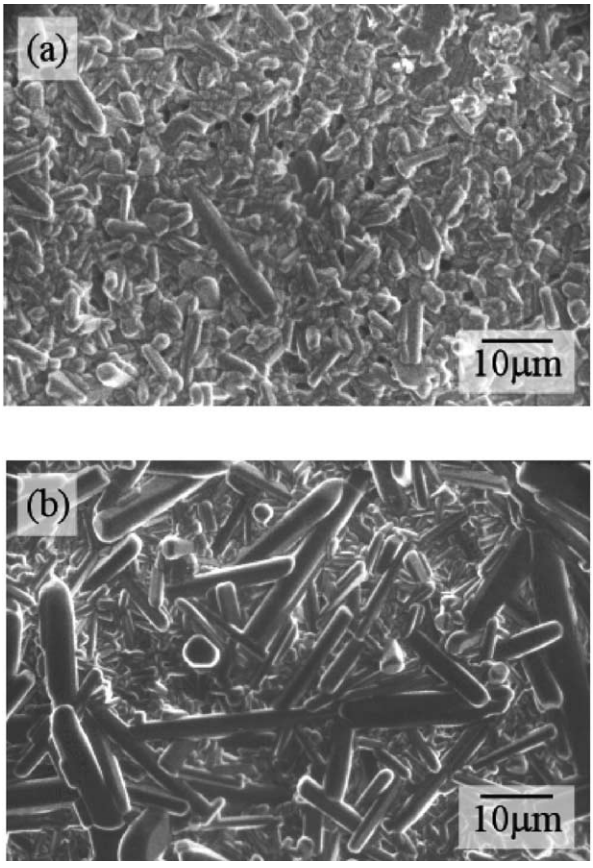

Fig. 4. SEM micrographs of the surface of (a) BST and (b) prepared with 10 wt.% columnar crystal sintered at 1460 °C for 2 h.

during the sintering process. While the degree of shrinkage perpendicular to the pressing direction decreases with the content of columnar crystals, that of shrinkage parallel to the pressing direction increases. For the specimens prepared with 15 wt.% columnar crystals, the shrinkage perpendicular to the pressing direction was approximately 3/4 times as small as that parallel to pressing direction. This is evidence of anisotropic grain growth within the microstructure. In other words, the growth rate of BST is faster for the *c*-axis direction than that for both the *a*- and *b*-axes. According to the experimental observation, columnar crystals tend to be dispersed perpendicular to the pressing direction in the green compact. The crystals act as seeds and promote anisotropic grain growth during the sintering process. Hence, shrinkage parallel to the pressing direction appeared large, compared with that perpendicular to the direction of pressing. Since the difference in the shrinkage between two directions was significant, anisotropic grain growth occurred at not only the surface region, but also the inside the specimen (as seen in Fig. 5). The relative density of BST ceramics, including these prepared with columnar crystals, sintered at 1460 °C was >94%.

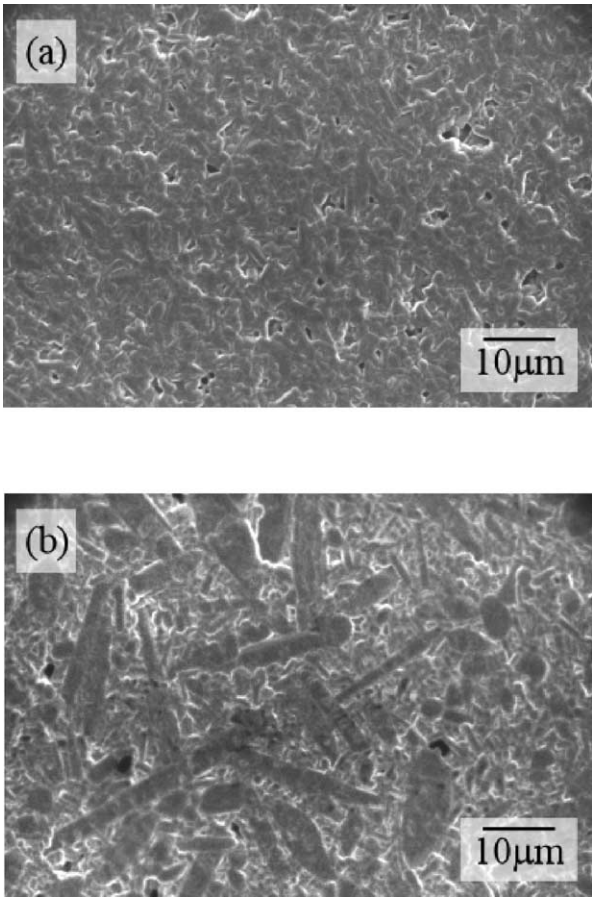

Fig. 5. SEM micrographs of the polished surface of (a) BST and (b) prepared with 10 wt.% columnar crystal sintered at 1460 °C for 2 h.

3.3. Microwave dielectric properties

Microwave dielectric properties of the sample as a function of the content of the columnar crystals are shown in Fig. 8. The most noteworthy point is that the τ_f value changed dramatically from negative to positive with the increasing content of columnar crystals. When the content of columnar crystal was 5 wt.%, 0 ppm/°C of τ_f was achieved successfully. On the other hand, $Q{\cdot}f$ value remained with a high value to near 10,000 GHz for sample containing up to 10 wt.% columnar crystals. The dielectric constant was also maintained ε_r 80. The reason why τ_f changed by addition of columnar crystal is not yet clear, but it is possible that the change in τ_f resulted from the anisotropy of the sample. It is known that τ_f is given by $\tau_f = (\alpha_l + \tau_\varepsilon /2)$, where α_l is a thermal expansion coefficient, and τ_ε is a temperature coefficient of dielectric constant. The thermal expansion coefficient for ceramics is generally about 10 ppm/°C. Therefore, if

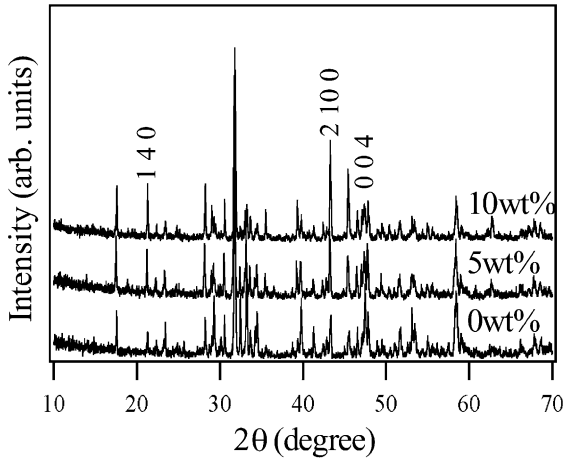

Fig. 6. XRD patterns of the surface of BST prepared with columnar crystal sintered at 1460 °C for 2 h.

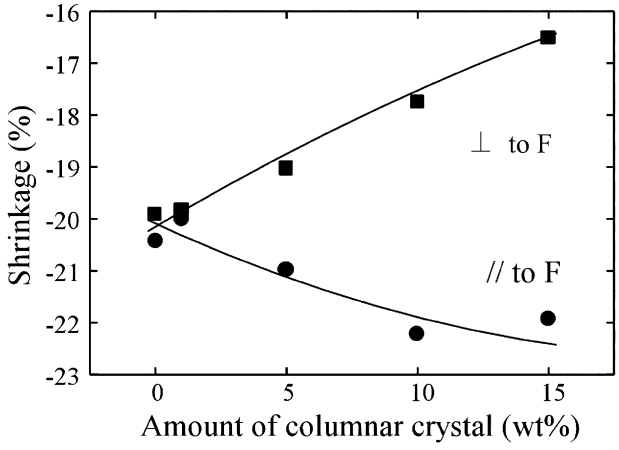

Fig. 7. Shrinkage of samples perpendicular and parallel to the pressing direction (F) as a function of columnar crystal content.

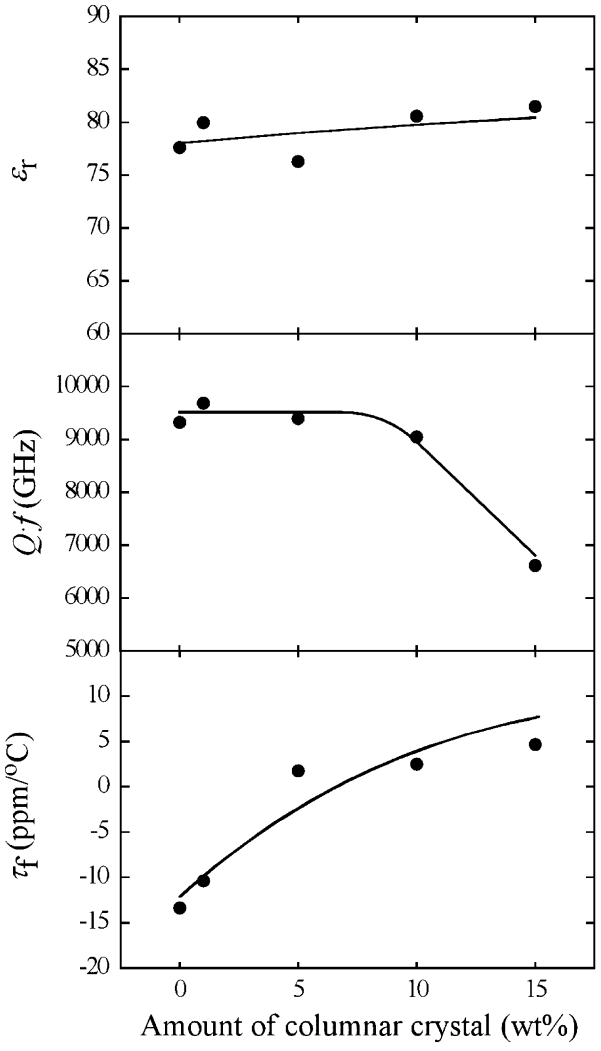

Fig. 8. Microwave dielectric properties of BST as a function of the amount of columnar crystals in the starting mixture.

it is assumed that BST crystal shows a large difference in the temperature coefficient of dielectric constant between the *c*-axis and the other axes, the sintered sample with elongated grains may show a difference in τ_f between perpendicular and parallel to the pressing direction.

4. Conclusions

Anisotropic samples were prepared using the NaCl–KCl molten salt method. BST single crystals with columnar shape have been successfully synthesized by heat treatments at temperature as low as 1100 °C. Soaking time for 24 h led to the formation of single-phase columnar BST crystals elongated along the crystallographic *c*-axis, with a length of 5–15 μm and width of 1–3 μm. The sintered ceramics samples including those prepared with the columnar crystals showed anisotropic grain growth. A difference in linear shrinkage during sintering, in directions perpendicular and parallel to the pressing direction occurred due to anisotropic grain growth within the sample. The temperature coefficient of resonant frequency τ_f was controlled by preferred orientation due to the templated growth of BST crystals. The best dielectric properties obtained in this study were as follows: $\varepsilon_r = 76.3$, $Q{\cdot}f = 9395.8$ GHz and $\tau_f = 1.76$ ppm/°C for samples prepared with 5 wt.% columnar crystals.

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