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Texture development and dielectric properties of $SrBi_2Ta_2O_9$ ceramics processed by templated grain growth

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Abstract

$SrBi_2Ta_2O_9$ (SBT) textured ceramics were produced by templated grain growth (TGG) using anisometric templates grown by self-flux solution method. SBT templates (5 wt.%) with the dimensions ∼40 μm × 40 μm × 8 μm were embedded in a fine-grained matrix of SBT powder containing a 3 wt.% of Bi_2O_3 excess and partially aligned by conventional uniaxial pressing. Textured SBT ceramics characterized by a Lotgering factor $f \approx 0.4$ could then be obtained after sintering at 1250 °C for 2 h. The influence of the pressing and sintering conditions on texture development was evaluated using scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). Significant improvement of the dielectric and ferroelectric properties was observed when measurements are performed perpendicularly to the pressing direction. This improvement was attested to the apparent alignment of the templates, dielectric anisotropy of SBT and texturing effect due to TGG.

Keywords: Bi-layered ferroelectrics; Ferroelectric properties

1. Introduction

Following a general trend of developing lead-free piezoelectric components, bismuth layer structure ferroelectrics (BLSF), in particular $SrBi_2Ta_2O_9$ (SBT), are recently emerged as promising candidates for high-temperature piezoelectric applications.[1] However, it is difficult to achieve high piezoelectric response in randomly oriented BLSF polycrystalline materials because of the two-dimensional character of ferroelectric switching.[2,3] Thus, the study of textured BLSF ceramics is of fundamental importance for tailoring their piezoelectric and dielectric properties and improving sensing and actuating capabilities of various devices.

One of the promising routes for the controlled texture development is a templated grain growth (TGG).[4–8] This process consists of the ceramics sintering mediated by a small amount of well-oriented anisometric template particles distributed in a fine-grained matrix. The template particles grow at the expense of the fine randomly oriented powder ensuring the large fraction of highly oriented grains.[9] Being based on a standard powder processing and sintering, TGG achieves texture at significantly lower cost as compared to other techniques including hot forging or hot pressing.

TGG has been reported for a variety of materials,[4–8] including some BLSFs.[4–6] However, because of the complexity of SBT single crystal synthesis, to the best of our knowledge, this technique has not been used for SBT so far. In this work, textured SBT ceramics were produced by TGG using anisometric SBT platelets and the anisotropy of the dielectric and ferroelectric properties was studied.

2. Experimental procedure

Plate-like SBT crystals were grown by a high-temperature self-flux solution method described elsewhere.[10] SBT crystals of rectangular shape with the [0 0 1] direction (*c*-axis) perpendicular to the major face were milled and sieved to obtain anisometric templates with an average size of ∼40 μm × 40 μm × 8 μm. Polycrystalline SBT powder was synthesized via solid-state reaction. Subsequently, a 3 wt.% of Bi_2O_3 excess for promoting liquid phase during TGG was added to the SBT powder together with the 5 wt.% of

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templates. The SBT powder–template mixture was stirred for 2 h and subsequently dried. Pellets were uniaxially pressed at 150 and 300 MPa followed by isostatical pressing at 200 MPa for homogenous compaction. Two different uniaxial pressures were used to evaluate the pressure effects on the texture development. The samples were sintered in air at 1250 °C for various times up to 24 h. For comparison, SBT ceramics with 3 wt.% of Bi_2O_3 excess but without templates were also sintered in the same conditions.

The crystallographic texture of the sintered samples was examined by X-ray diffraction analysis (XRD) using a conventional Rikagu/New diffractometer. The samples were scanned relative to the plane perpendicular to the pressing direction (⊥P). The degree of (0 0 l) orientation was evaluated in terms of the Lotgering factor, $f = (p - p_o)/(1 - p_o)$, where $p = \sum I(0\,0\,l)/I(h\,k\,l)$ for maximum intensities of each peak between $2\theta = 4°$ and 80°, and $p_o = p$ for the randomly oriented SBT powder.[11] The microstructure of the sintered samples was revealed by scanning electron microscopy (SEM) (Hitachi S-4100) on the polished and chemically etched cross-sections parallel to the pressing direction (//P). A stereological analysis was performed using an image analysis software (analySIS 3.2).

Dielectric properties of the sintered samples were measured using an HP4284A precision LCR Meter and an Eurotherm 2404 controller in the temperature range 25–400 °C. The specimens were polished and gold electrodes were sputtered onto the //P and ⊥P faces for measuring electrical properties. Ferroelectric hysteresis was measured via a Sawyer–Tower circuit at room temperature.

3. Results and discussion

Fig. 1 presents SEM pictures taken on the //P surface of a seeded SBT specimen uniaxially pressed at 300 MPa and sintered at 1250 °C for 0, 2 and 24 h. A bimodal microstructure dominated by a large number of interconnected big anisometric grains is clearly observed. These grains have plate-like morphology, similar to original SBT templates, with a final average length of ∼90 μm and average thickness of ∼14 μm for the sample sintered at 1250 °C/24 h. This is about twice the dimensions of the initial seeds. For unseeded ceramics sintered under the same processing conditions, only small plate-like and well-faceted matrix grains were observed, with a maximum grain size below 15 μm.[12]

With increasing the sintering time, the template particles grow faster along the length direction until the template impingement occurs. After sintering at 1250 °C/0 h the microstructure shows a few large grains that correspond roughly to the initial concentration of seed crystals. However, their average size was significantly increased to ∼74 μm × 9 μm and was accompanied with the corresponding increase (about 60%) of the aspect ratio to ∼8. In bismuth titanate ceramics textured by TGG the driving force for the template growth was ascribed to the anisotropy of grain boundary energies.[4]

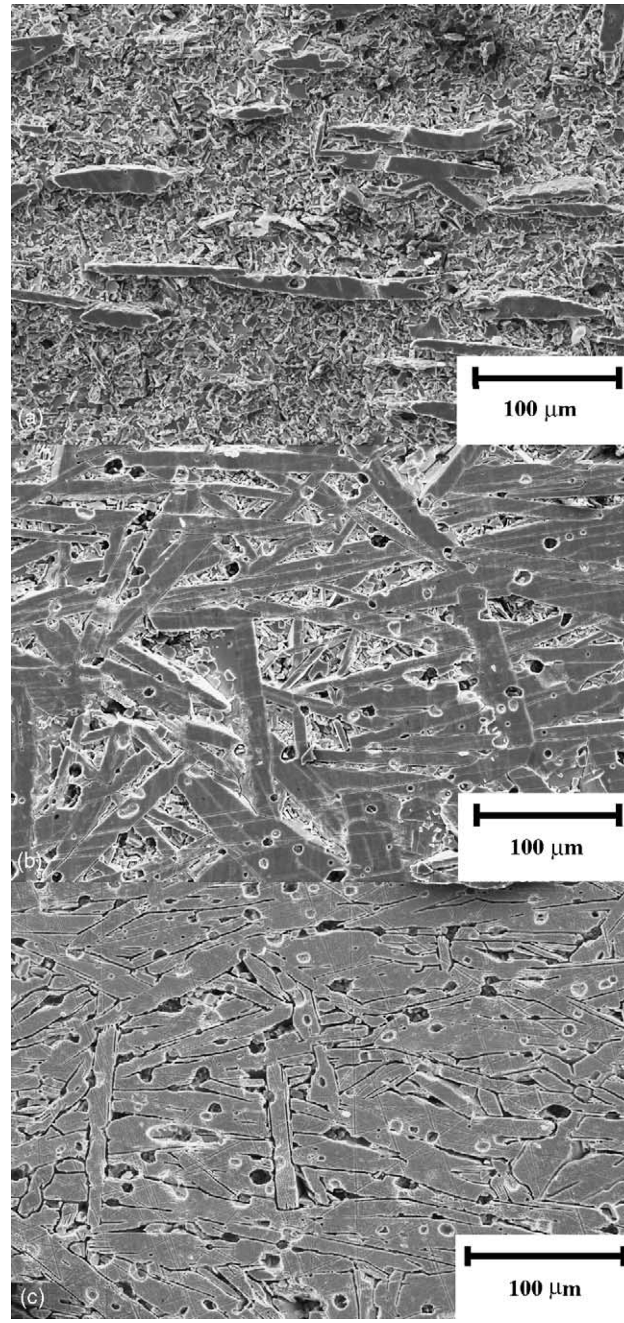

Fig. 1. SEM micrographs of the texture development as a function of the sintering time on the polished and etched cross-sections //P of seeded SBT specimens pressed at 300 MPa and sintered at 1250 °C: (a) 0 h; (b) 2 h and (c) 24 h.

Thus, the template lateral growth is preferred in order to maximize the area of low-energy faces perpendicular to the c-axis. Although slowed by matrix coarsening, the template lateral growth continues until templates impinge each other after 2 h. For longer sintering times, the aspect ratio decreases due to the thickening of the templates.

The densification results of unseeded and seeded SBT samples processed under different conditions are reported in Table 1. The presence of templates in seeded ceramics does

Table 1
Relative density (ρ_r) and degree of texture (Lotgering factor) of seeded and unseeded SBT ceramics under different pressing and sintering conditions

Sintering temperature (°C)	Sintering time (h)	Unseeded SBT 150 MPa		Seeded SBT 150 MPa		Seeded SBT 300 MPa	
		ρ_r (%)	Lotgering factor (%)	ρ_r (%)	Lotgering factor (%)	ρ_r (%)	Lotgering factor (%)
1250	0	94	8.4	94	11	93	13
1250	0.25	94	8.4	95	13	94	19
1250	1	96	8.5	97	15	94	27
1250	2	97	8.6	97	17	93	36
1250	24	96	8.9	95	25	91	46

not significantly affect the final density of the samples under the selected sintering conditions. However, the highest densities were obtained for the unseeded ceramics, while the lowest densities were observed for seeded samples that had been pressed at the highest uniaxial pressure (300 MPa). The maximum density is observed after a sintering time of 2 h in all cases, but decreases for longer sintering time. This behavior is tentatively attributed to the presence of liquid phase that increases the boundary mobility of templates throughout the matrix during sintering, promoting matrix grain rearrangement and mass transfer processes for short sintering times. However, after the template impingement, the trapped porosity between platelets becomes thermodynamically stable and difficult to be removed afterwards.

The texture degree of the ceramics was evaluated by XRD analysis performed on the ⊥P facets. With increasing sintering time, diffraction peaks from {0 0 1} planes progressively dominate the pattern, accounting for the most intensive peak of the spectrum as shown in Fig. 2 for seeded sample pressed at 300 MPa and sintered at 1250 °C/24 h. This result confirms a crystallographic texture in the seeded SBT ceramics by the preferential orientation of the elongated large grains with *c*-axis oriented parallel to the pressing direction and perpendicular to the major face of the templates.

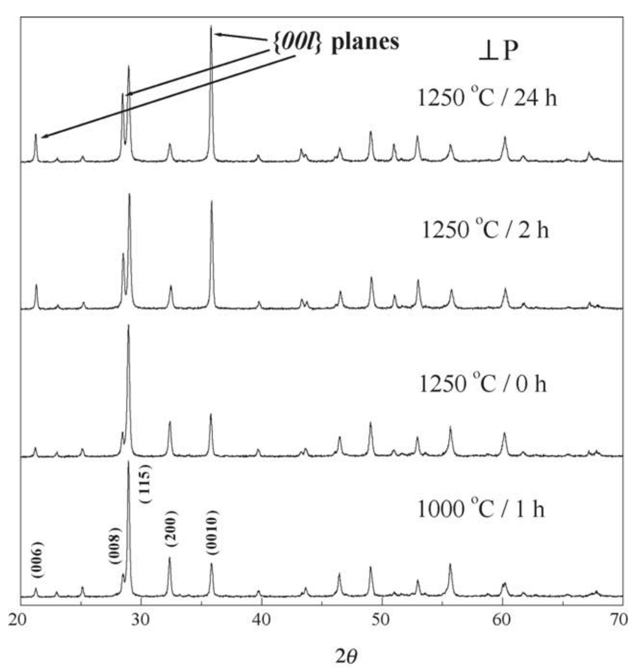

Fig. 2. XRD patterns on the cross sections ⊥P of seeded SBT ceramics with uniaxial pressure of 300 MPa and different sintering conditions.

The degree of orientation of the ceramics sintered under different conditions is included in Table 1. Whereas unseeded ceramics show a degree of orientation less than 0.1 even for 24 h of sintering time, seeded ceramics reach a maximum $f \approx 0.25$ for samples uniaxially pressed at 150 MPa and $f \approx 0.46$ for samples pressed at 300 MPa. For short sintering time (0 h) a similar degree of orientation was obtained in seeded samples corresponding to both pressure conditions, very close to that observed in the early state of the TGG process (seeded SBT sample sintered at 1000 °C/1 h, $f \sim 0.1$). When the sintering time increases, the seeded ceramics exhibit an initial fast texturing rate which tends to saturate after 2 h. The higher the uniaxial pressure in the green samples, the higher the initial orientation of the templates. Thus, it is the TGG of the oriented templates that results in texturing effect. Nevertheless, the *f*-values in our case are still lower than those typically reported for oriented ceramics produced by other texturing techniques like tape casting or hot forging.[4–8] Therefore, by using these techniques, higher degrees of texture are expected.

The ferroelectric characterization was done on samples with uniaxial pressure of 300 MPa, since they demonstrate the highest texture. Fig. 3 shows the temperature dependence

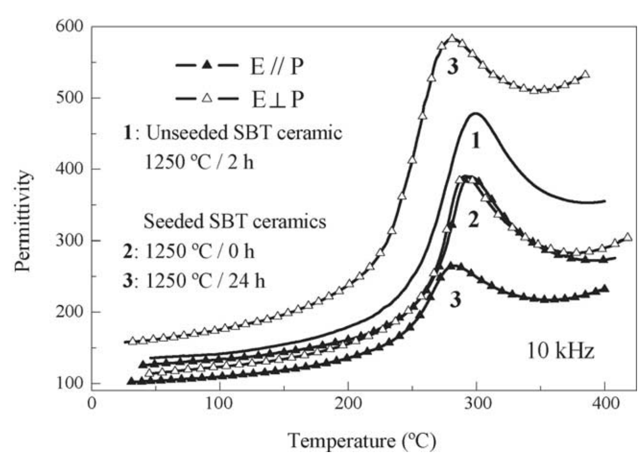

Fig. 3. Anisotropy in the temperature dependence of the permittivity measured with E//P and E⊥P for seeded SBT ceramics sintered at 1250 °C for 0 and 24 h. For comparison, the unseeded randomly oriented SBT ceramic sintered at 1250 °C/2 h is included.

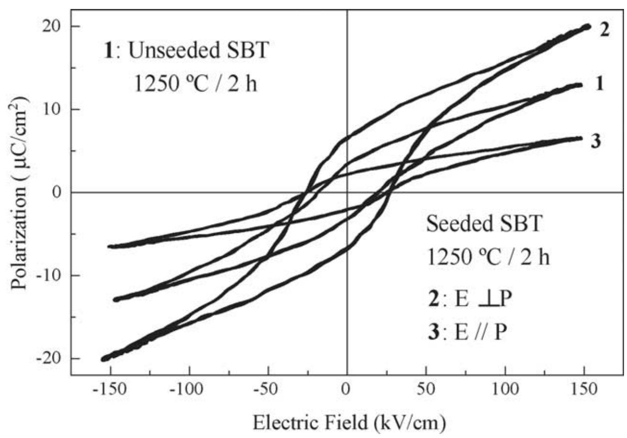

Fig. 4. Room temperature P–E hysteresis loops measured with E//P and E⊥P on textured SBT ceramics sintered at 1250 °C/2 h. The loop obtained for the unseeded SBT sintered at 1250 °C/2 h is also included for comparison.

of the permittivity at 10 kHz observed in seeded samples sintered at 1250 °C for 0 and 24 h, when the electric field is applied parallel (E//P) and perpendicular (E⊥P) to the pressing direction. For comparative purposes, the curve obtained for the unseeded SBT ceramic is also included. Anisotropy in the dielectric properties at room temperature as well as at the transition temperature can be observed in the seeded samples. The values obtained for seeded SBT ceramics sintered at 1250 °C/24 h [measured along the texture direction (E⊥P)] exceed those of unseeded SBT ceramics that are roughly isotropic and do not depend on the direction of applied electric field.

Fig. 4 shows the room temperature P–E hysteresis loops of seeded SBT ceramics sintered at 1250 °C/2 h, and measured with E//P and E⊥P. For comparative purpose, the loop obtained for the unseeded SBT ceramic is also included. In this case, the anisotropy of the remanent (P_r) polarization can be also observed between E//P and E⊥P directions. The polarization vector in the SBT orthorhombic structure lies entirely along *a*-axis.[13] Accordingly, the observed increase of permittivity and P_r values for the textured ceramics, when E⊥P is used, may be explained as an increased contribution from the highly polarizable *ab*-plane allowed by the favorable alignment of grains in the direction of the electric field. This contribution is expected to further increase with the ceramic texture degree. For the sample where E//P, the above mentioned contribution is partly lost and the permittivity and polarization values decrease.

4. Conclusions

Textured $SrBi_2Ta_2O_9$ ceramics were produced by TGG using anisometric SBT platelets. Bimodal microstructure with a high concentration of large anisometric grains was obtained after sintering at 1250 °C/2 h. Large grains are similar in shape to the SBT templates, but their dimensions are twice of the original seeds. A distinct preferential orientation of the elongated large grains, with the *c*-axis oriented perpendicular to the major face, was observed. Enhanced ferroelectric properties were measured perpendicularly to the uniaxial pressing direction with polarization values exceeding those of unseeded SBT ceramic, due to the increased contribution from the highly polarizable *ab*-plane allowed by the favorable alignment of grains in the direction of the applied electric field.

Acknowledgments

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