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# The orientation mechanism of (Ca,Sr)$Bi_4Ti_4O_{15}$ ceramics prepared by slip casting in high magnetic field and subsequent sintering

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**Abstract**

A high magnetic field of 10 T was introduced into a processing of slip casting for fabricating (Ca,Sr)$Bi_4Ti_4O_{15}$ (abbreviated as CSBT) ceramics. Feeble magnetic CSBT particles in green compacts were partially aligned through rotating a gypsum mold containing the CSBT slurry in the magnetic field. The green compacts were sintered at 1200 °C for different time without magnetic field. With increasing of the sintering time, the preferable orientation degree of CSBT ceramics rapidly went up at the initial stage, and then slowly increased at the medium and final stages. The mechanism of the orientation degree increasing during the sintering can be attributed to a processing in which large oriented particles coarsen small randomly oriented particle.


*Keywords:* Grain growth; Sintering; Slip casting; X-ray methods; Piezoelectric properties; (Ca,Sr)$Bi_4Ti_4O_{15}$

## 1. Introduction

Fabricating grain-oriented or textured microstructure is one of the most effective methods to enhance physical, mechanical and bioactive properties of some ceramics. Two techniques, templated grain growth[1–3] and high temperature deformation,[4–6] have been widely developed to prepare oriented ceramics. The former, which was realized in the processing of tape casting or layer manufacturing, is based on the morphological anisotropy of precursor powder, and the latter such as hot forging and hot pressing is based on the high temperature sliding of grain boundaries. Recently, with the advance of superconducting technologies, a high magnetic field has become a new tool for preparing oriented microstructure of feeble magnetic materials, which is based on anisotropic magnetic susceptibility ($\Delta\chi$) of crystals. When a paramagnetic or diamagnetic particle is placed in a magnetic field, it trends to rotate a certain angle to minimize the magnetization energy, which is expressed as the following formula:

$$\Delta E = \frac{\Delta\chi V B^2}{2\mu_0}, \qquad (1)$$

where $V$ is the volume of the particle, $B$ the applied magnetic field, and $\mu_0$ the permeability in vacuum. If a high magnetic field is introduced into the molding processing of feeble magnetic ceramics, green samples with oriented microstructure can be fabricated. Up to now, some highly oriented ceramics such as $Sr_{0.5}Ba_{0.5}Nb_2O_6$, AlN, ZnO, $Al_2O_3$, $Si_3N_4$ and hydroxyapatite[7–11] have been prepared through this novel technique.

The literature about oriented ceramics prepared by introducing a high magnetic field indicates that the sintering processing also has an important role on controlling the microstructure.[8,9,11] Generally, green compact prepared with the aid of a high magnetic field only exhibits partial orientation, but highly oriented ceramics can be obtained if it is sufficiently sintered. Although some efforts of optimizing the sintering parameters such as enhancing sintering temperature have been explored to increase the orientation degree of ceramics, the mechanism of the aforementioned phenomenon is seldom discussed and analyzed. Understanding and optimizing the material processing is vital to further improve physical properties. In this study, CSBT

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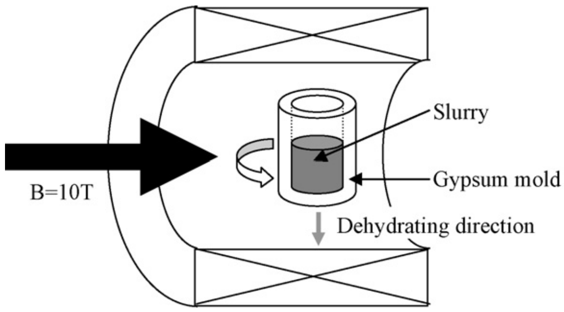


Fig. 1. Schematic view of experimental equipment.

ceramics, which recently has attracted great attention as one kind of high temperature piezoelectric material,[12–14] was prepared by slip casting in a high magnetic field of 10 T. The attained samples were sintered for different time to investigate the mechanism of the orientation degree increasing in the processing of sintering.

## 2. Experimental procedure

CSBT powder was synthesized via a conventional solid phase reaction. Reagent-grade powders of $Bi(OH)_3$, $Ti(OH)_4$, $SrCO_3$ and $CaCO_3$ were weighed according to the stoichiometric composition of $(Ca_{0.6}Sr_{0.4})Bi_4Ti_4O_{15}$, and then mixed by ball milling in deionized water for 48 h. After drying, the mixed powder was calcined at 850 °C for 2 h. The CSBT slurry with 25% solid loading was prepared by adding polyacrylic acid dispersant and milling again the synthesized powder in deionized water for 48 h. The slurry was poured into a gypsum mold for dehydrating along the direction parallel to the gravity. A horizontal magnetic field of 10 T was applied on the slurry during the slip casting. In order to realize a rotation magnetic field, according to the relative motion, the mold was rotated in the magnetic field at a ratio of 3 rpm along the axis parallel to the gravity. Fig. 1 shows the schematic view of experimental equipment. After consolidating and drying for 48 h in the mold, green compacts were taken out and densified with cold isostatic pressing, which could not disturb the particle orientation. Then the green compacts were calcined at 1200 °C for 0.5, 1, 2 and 4 h, respectively.

The crystal phase and grain orientation were investigated by X-ray diffraction (XRD) analysis (Rigaku, RINT2000) using CuKα radiation with a scan speed of 2°/min and a step width of 0.02°. Lotgering factor (*f*) is used to evaluate the degree of grain orientation, which is defined as:

$$f = \frac{p - p_0}{1 - p_0} \qquad (2)$$

where $p = \sum I(0\,0\,l)/\sum I(h\,k\,l)$, $p_0 = p$ for randomly oriented samples, and $\sum I(h\,k\,l)$ the sum of peak intensity in a XRD pattern. The particle size distribution of CSBT powder was measured by a laser particle analyzer (Horiba, LA-920). The microstructural morphologies of green compacts and sintered ceramics were observed by scanning electron microscopy (SEM) analysis (Keyence, VE7800). The sintered samples were cut and polished into slices with the top and bottom surfaces perpendicular or parallel to the rotating axis of the magnetic field. The CSBT slices were coated by sliver electrode on both top and bottom surfaces, and poled in silicon oil at 190 °C for 10–20 min with an electric field of 80–100 kV/cm. The dielectric and piezoelectric properties were investigated by an impedance analyser (HP 4294A). The piezoelectric coefficient was measured with a Berlincourt $d_{33}$ meter.

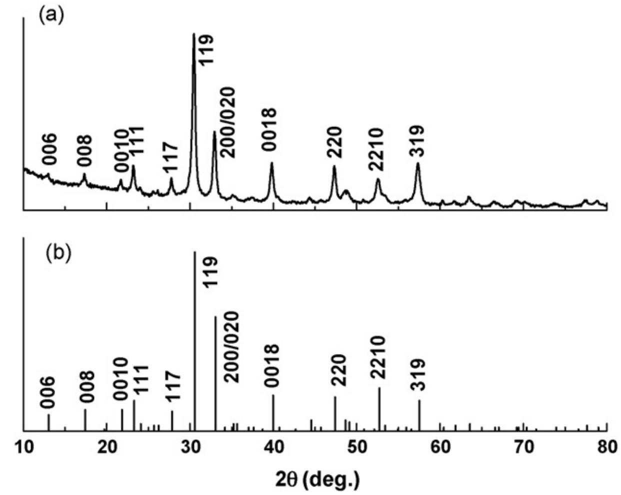


Fig. 2. XRD diffraction patterns of (a) CSBT powder synthesized at 850 °C for 2 h and (b) JSPDS card (no. 43-0973).

## 3. Experimental results and discussion

Fig. 2(a) shows the XRD pattern of CSBT powder synthesized at 850 °C for 2 h and Fig. 2(b) is that given by the data of JSPDS card (no. 43-0973). All the XRD peaks of synthesized CSBT powder can be correspondingly found in the JSPDS card. This fact implies only a layer-structured perovskite phase of CSBT was synthesized.

Fig. 3 shows the integral size distribution curve of CSBT powder synthesized at 850 °C for 2 h. It can be seen that the particle size is distributed in a wide range and a mass of powder is in a sub-micrometer scale. The median particle size $D_{50}$ is 163 nm, which means that the volume proportion of particles

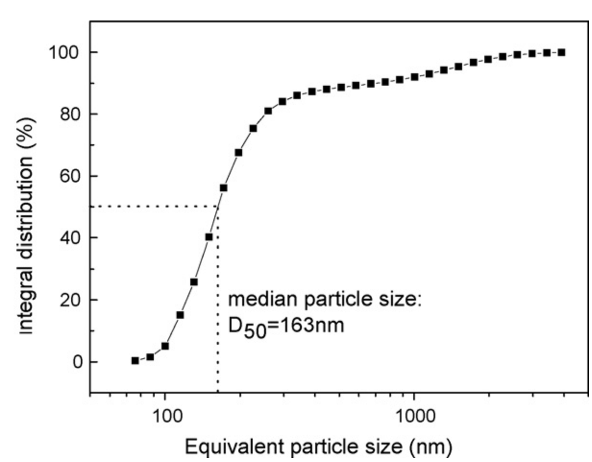


Fig. 3. Integral size distribution curve of synthesized CSBT powder.

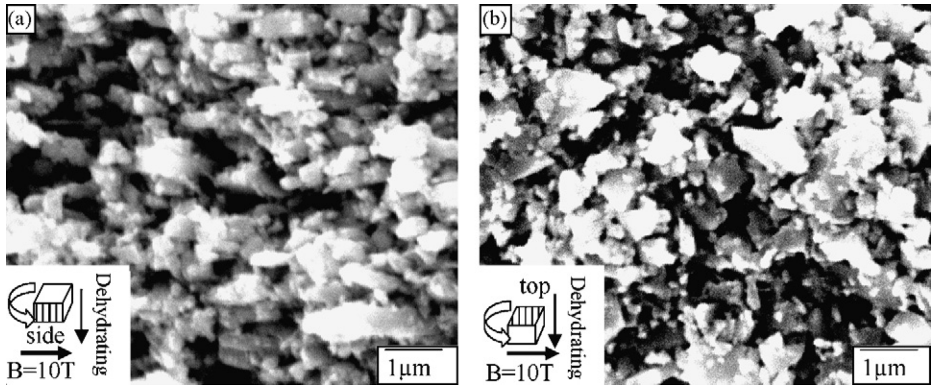


Fig. 4. SEM images of the side (a) and top (b) fracture surface of CSBT green compact prepared by slip casting in a magnetic field of 10T.

with size less than 163 nm is 50%. It should be noticed that the laser diffraction method is based on the presupposition that particles are sphere-like, so it only gives an equivalent value not the real size of the CSBT particles. In fact, the SEM image shown in Fig. 4 demonstrates that CSBT particles are plate-like and its width is far larger than its thickness.

Fig. 4(a and b) are the SEM images of the side and top fracture surfaces of CSBT green compact prepared by slip casting in the high magnetic field. It can be seen that most large plate-like CSBT particles are well aligned with its *c*-axis parallel to the rotating axis of the gypsum mold containing the CSBT slurry. A large number of small particles are partially agglomerated and distributed in the interspace of large particles, and its orientation cannot be clearly observed due to the resolution limit of the SEM equipment.

Fig. 5 shows the XRD patterns of the fracture surfaces of CSBT green compact prepared by slip casting in a magnetic field of 10 T. The relative intensity of $(0\,0\,l)$ peaks in the top fracture surface shown in Fig. 5(a) is evidently higher than that of the

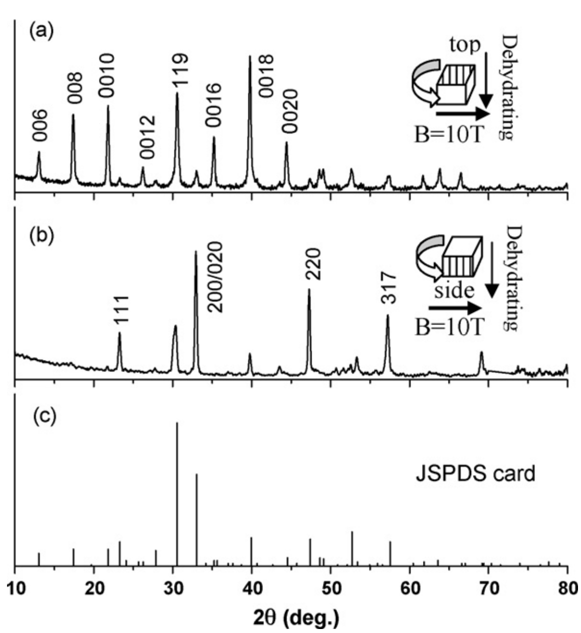


Fig. 5. XRD patterns of the top (a) and side (b) fracture surfaces of CSBT green compact prepared by slip casting in a magnetic field of 10 T.

JSPDS card. This indicates that some particles in green compact have been aligned with the $(0\,0\,l)$ crystallographic direction parallel to the rotating axis of the gypsum mold. On the other hand, the $(h\,k\,0)$ peaks in the side fracture surface shown in Fig. 5(b) are stronger, which coheres with the XRD pattern of the top fracture surface given in Fig. 5(a). The Lotgering factors of $(0\,0\,l)$ and $(h\,k\,0)$ in the top and side fracture surface are 0.56 and 0.49, respectively. The mechanism that CSBT particles in green compact are magnetically aligned can be ascribed to the relationship of $\chi_c < \chi_{a,b}$ (i.e. $U_c > U_{a,b}$ in a magnetic field), which had been analyzed in our other research.[15] The fact that the Lotgering factor in CSBT green compact was not so high further confirms that a lot of particles were not yet well aligned by the high magnetic field in the processing of slip casting. By taking into account of the SEM image shown in Fig. 4, which demonstrated that most large particles were highly oriented, it can be considered that most small particles are not well aligned.

Early research literatures reported that the motion of particles suspended in liquid is affected by not only magnetization force but also Brownian motion.[16,17] The smaller a particle is, the more active Brownian motion is. The effect of Brownian motion[17] can be neglected only when the particle radius is larger than the critical size given by $3\sqrt{3kT\mu_0/2\pi\Delta x B^2}$. In a magnetic field of 10 T, the critical size of a particle with different anisotropic magnetic susceptibility was calculated and given in Table 1. It can be seen that a feeble magnetic particle with nano-scale size is prone to be disturbed by Brownian motion, since the range of its anisotropic magnetic susceptibility is from $10^{-5}$ to $10^{-8}$ H/m. It is understood that a lot of nano-scale CSBT particles in the slurry could not be aligned well by the high magnetic field due to the disturbance caused by Brownian motion. Although the Lotgering factor of *c*-axis orientation in CSBT green compact

Table 1
Relation between anisotropic magnetic susceptibility and critical size (magnetic field: 10 T)

| Anisotropic magnetic susceptibility of $\Delta\chi$ (H/m) | Critical size (nm) |
|---|---|
| $1 \times 10^{-5}$ | 27.00 |
| $1 \times 10^{-6}$ | 58.20 |
| $1 \times 10^{-7}$ | 125.13 |
| $1 \times 10^{-8}$ | 270.00 |

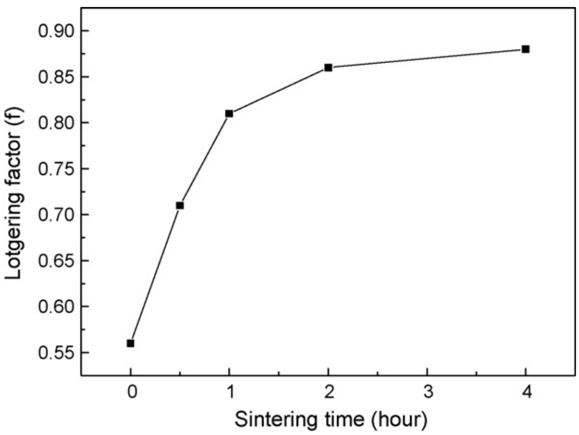


Fig. 6. Effect of sintering time on (0 0 1) orientation degree of CSBT ceramics prepared by slip casting in a magnetic field of 10 T.

reached 0.56, a large number of small CSBT particles probably kept random or partially random orientation.

Fig. 6 shows the effect of different sintering time on the (0 0 1) orientation degree of CSBT ceramics prepared by slip casting in the high magnetic field and then sintering at 1200 °C. The Lotgering factors of (0 0 *l*) peaks are 0.56, 0.71, 0.81, 0.86 and 0.88 for the samples sintered at 1200 °C for 0, 0.5, 1, 2 and 4 h, respectively. It can be seen that at the early stage of sintering, the orientation degree rapidly increases. However, longer the sintering time is, smaller the increasing ratio of the orientation degree. Fig. 7 shows the SEM images of the polished and thermally etched surfaces of CSBT ceramics prepared by slip casting in the magnetic field and then sintering at 1200 °C for 4 h. It can be seen that plate-like grains are well oriented and stacked with their *c* axis parallel to the rotating axis of the gypsum mold containing the CSBT slurry.

The effect of the sintering on the orientation degree of ceramics prepared in a high magnetic field were also found by Suzuki[8,9] and Akiyama,[11] respectively. Only Akiyama[11] gave a simple explanation to this phenomenon. He found that completely (0 0 1) oriented hydroxyapatite ceramics could be prepared by sintering partially (0 0 1) oriented green compact. He attributed his experimental result to the preferential grain growth of oriented crystals due to their lower angle grain boundary energy. Actually, this explanation is inconsistent with the thermodynamics laws. Generally, the lower the grain boundary energy is, the more stable the grain boundary is and the more difficultly it grows. Moreover, he could not explain how a large number of random crystals disappear in the sintering. Here, authors propose a new explanation from the view of the Ostwald ripening. Fig. 8 schematically shows the mechanism of the orientation degree increasing in the sintering of CSBT ceramics. The green compact prepared by slip casting in the high magnetic field consists of large highly oriented particles and small randomly oriented particles. During the sintering, for minimizing the total energy of system, small grains tend to be dissolved into large grains through an Ostwald ripening processing. The *a*–*b* plane of CSBT crystals possess low surface energy, and thus, trends to develop more fully during the sintering. So most of small randomly oriented grains were coarsened into the large (0 0 *l*)-oriented grains along their *a*–*b* plane. As a result, the volume fraction of the randomly oriented grains reduces, and concurrently the (0 0 *l*) orientation degree increases.

Table 2
Dielectric and piezoelectric properties of CSBT specimens prepared by slip casting in a rotating magnetic field

| Specimen | $\varepsilon/\varepsilon_0$ | Tan $\delta$ (%) | $T_c$ (°C) | $d_{33}$ ($\times 10^{-12}$ C/N) | $K_t$ (%) | $K_p$ (%) |
|---|---|---|---|---|---|---|
| Perpendicular | 133 | 0.10 | 672 | 5 | 6 | 2 |
| Parallel | 157 | 0.19 | 672 | 34 | 41 | 6 |
| Random[18] | 151 | 0.18 | 678 | 14.9 | | |

At the initial stage of the sintering, the relatively large size distribution among CSBT grains, which has been shown in Fig. 3, led to a high driving force for large grains coarsening small grains, and thus, the (0 0 *l*) orientation degree of CSBT ceramics rapidly reached 0.71 and 0.81 when the samples were sintered at 1200 °C for 0.5 and 1 h, respectively. At the medium and final stages of the sintering, because a lot of small grains had already been consumed, the size difference among CSBT grains became small and the driving force for large particles coarsening small grains fell off. As a result, the orientation degree slowly ascended to 0.86 and 0.88 when the sintering was further carried out 2 and 4 h, respectively.

Table 2 summarized the dielectric and piezoelectric properties of CSBT ceramic slices prepared by slip casting in the rotating magnetic field. The piezoelectric constant $d_{33}$ and elec-

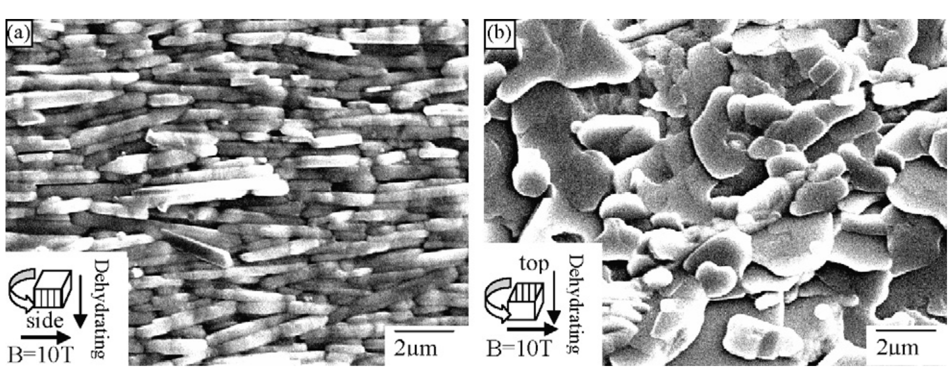


Fig. 7. SEM images of the side (a) and top (b) surfaces of CSBT ceramics prepared by slip casting in the magnetic field and then sintering at 1200 °C for 4 h.

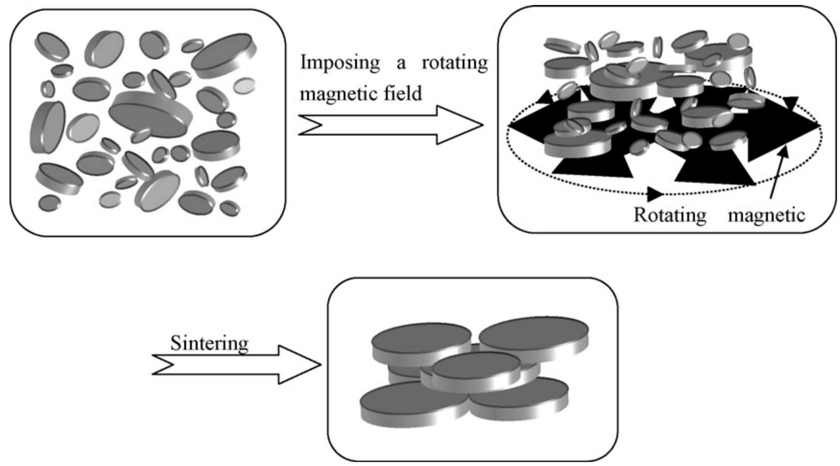


Fig. 8. Schematic view of the orientation degree augment in the sintering of CSBT ceramics.

tromechanical coefficient $k_t$ in the slices with both top and bottom surfaces parallel to the rotating axis of the magnetic field are evidently higher than those in the randomly oriented samples reported in the literature.[18] This confirms that introducing a high magnetic field into the preparation processing of piezoelectric ceramics is an effective method to increase the piezoelectric properties of materials.

## 4. Conclusion

CSBT ceramics were prepared by a processing of slip casting in a high magnetic field and then sintering at 1200 °C for different time. The following results have been obtained:

(1) Most of large CSBT particles were magnetically aligned in their slurry, which resulted from the requirement of minimizing the magnetization energy, but a large number of small particles still kept random or partially random orientation.
(2) The subsequently sintering procedure further enhanced the orientation degree of CSBT ceramics. The *c*-axis orientation degree reached 0.88 for the sample sintered at 1200 °C for 4 h.
(3) The mechanism of orientation degree augment in the sintering is attributed to the Ostwald ripening processing among CSBT grains.
(4) The CSBT ceramic slices with both top and bottom surfaces parallel to the rotating axis of the magnetic field demonstrated higher piezoelectric properties, which confirms that introducing a high magnetic field into the preparation processing is a useful approach to enhance piezoelectric properties of materials.

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