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Fabrication of textured ferroelectric ceramics by magnetic alignment via gelcasting

Weiwu Chen [a], Yoshiaki Kinemuchi [a], Takuya Tamura [b], Kenji Miwa [b], Koji Watari [a,*]

[a] *Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan*
[b] *Materials Research Institute for Sustainable Development, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, Japan*

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Abstract

Grain-oriented ferroelectric ceramics have attracted more interest recently because they may provide near single crystal properties. In the present study, a novel process combining magnetic alignment and gelcasting was explored to prepare grain-oriented ferroelectric ceramics with different crystal structures. In a strong magnetic field, ceramic particles in slurry were aligned by the magnetic force and then locked in situ by polymerization via a gelcasting technique. This process was found effective for ferroelectric ceramics with a bismuth layer structure ($Bi_4Ti_3O_{12}$) and tungsten bronze structure ($Sr_{0.5}Ba_{0.5}Nb_2O_6$). The sintered samples show highly anisotropic structure and enhanced physical properties. However for perovskite structured ferroelectric ceramics ($BaTiO_3$), the green compact shows grain orientation, while after sintering the sample become random again.

Thus for certain materials using the conventional ceramic processes, i.e., using conventional starting powders, gelcasting under strong magnetic fields (10 T) and pressure-less sintering, the preparation of dense grain-oriented ceramic materials is possible.

Keywords: Ferroelectrics; Shaping; Magnetic properties; Dielectric properties

1. Introduction

Grain-oriented polycrystalline ferroelectric ceramics have attracted a good deal of interest because they provide single crystal-like properties.[1] So far such kind ceramics were mainly achieved by mechanical force, namely: (1) at high temperature using high uniaxial pressure to rearrange grains and force grain oriented growth perpendicular to the pressure,[2–4] and (2) during green body forming using shear force to align large anisotropically shaped particles.[5–9] However a high uniaxial pressure at high temperature is required in the approach (1) and large anisotropically shaped templates are necessary in approach (2). Here we report a novel method to prepare grain-oriented ferroelectric ceramics by magnetic alignment without the requirement for large template and high uniaxial pressure. This method is based on the magnetic alignment and gelcasting techniques.

Generally, materials with non-cubic structure should have more or less anisotropic magnetic properties. In a magnetic field, a crystalline particle with an anisotropic magnetic susceptibility trends to rotate an angle to minimize the system energy, $\Delta E = \Delta XVB^2/2\mu_0$, where ΔX is the anisotropic magnetic susceptibility, V the particle volume, B the applied magnetic field, and μ_0 is the permeability in vacuum.[10] This is the driving force for magnetic alignment. For ferroelectric ceramic materials with weak anisotropic magnetic properties, due to low driving force the particle rotation is greatly inhibited by gravity, by steric hindrance, by thermal motion, etc., even in a strong magnetic field.

After dispersion in low viscosity slurry, the particle is relatively free and can rotate under the influence of the magnetic force. Gelcasting is a technique to prepare large and complex-shaped ceramic components.[11] The typical process consists of dispersing a ceramic powder in a solution containing organic monomers, casting the slurry in a mold, and initiating a polymerization reaction to form a gelled body. Temperature and catalysts are used to adjust the polymerization rate. In the present work, gelcasting provides an approach to lock in situ the particles after magnetic alignment in the slurry.[12]

Ferroelectric ceramics with perovskite structure, bismuth layer structure and tungsten bronze structure are the main classes, and grain-oriented microstructures have been sought

* Corresponding author.
E-mail address: koji-watari@aist.go.jp (K. Watari).

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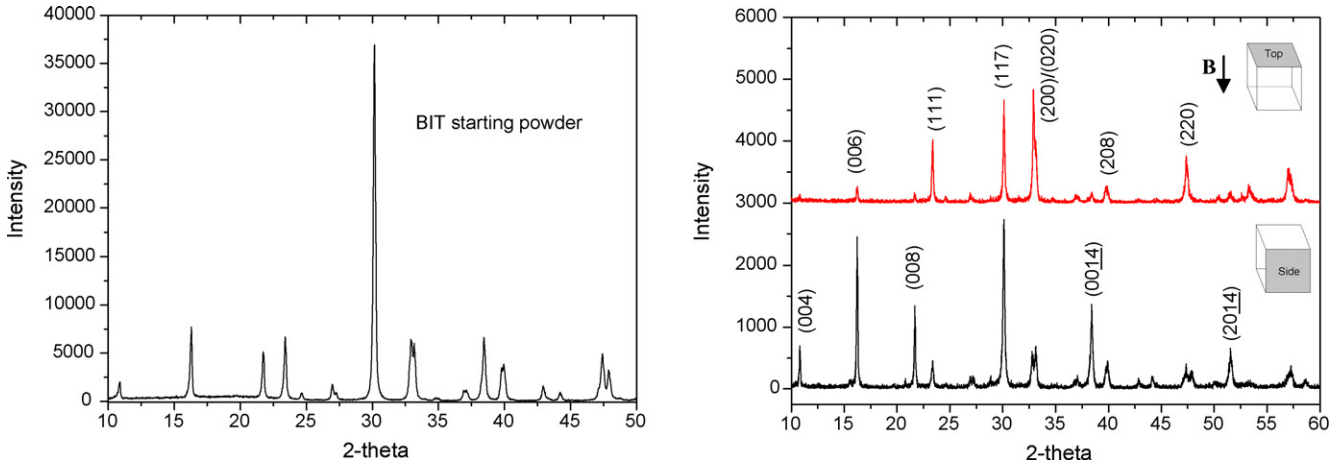

Fig. 1. XRD patterns of BIT starting powder and green compact with magnetic alignment.

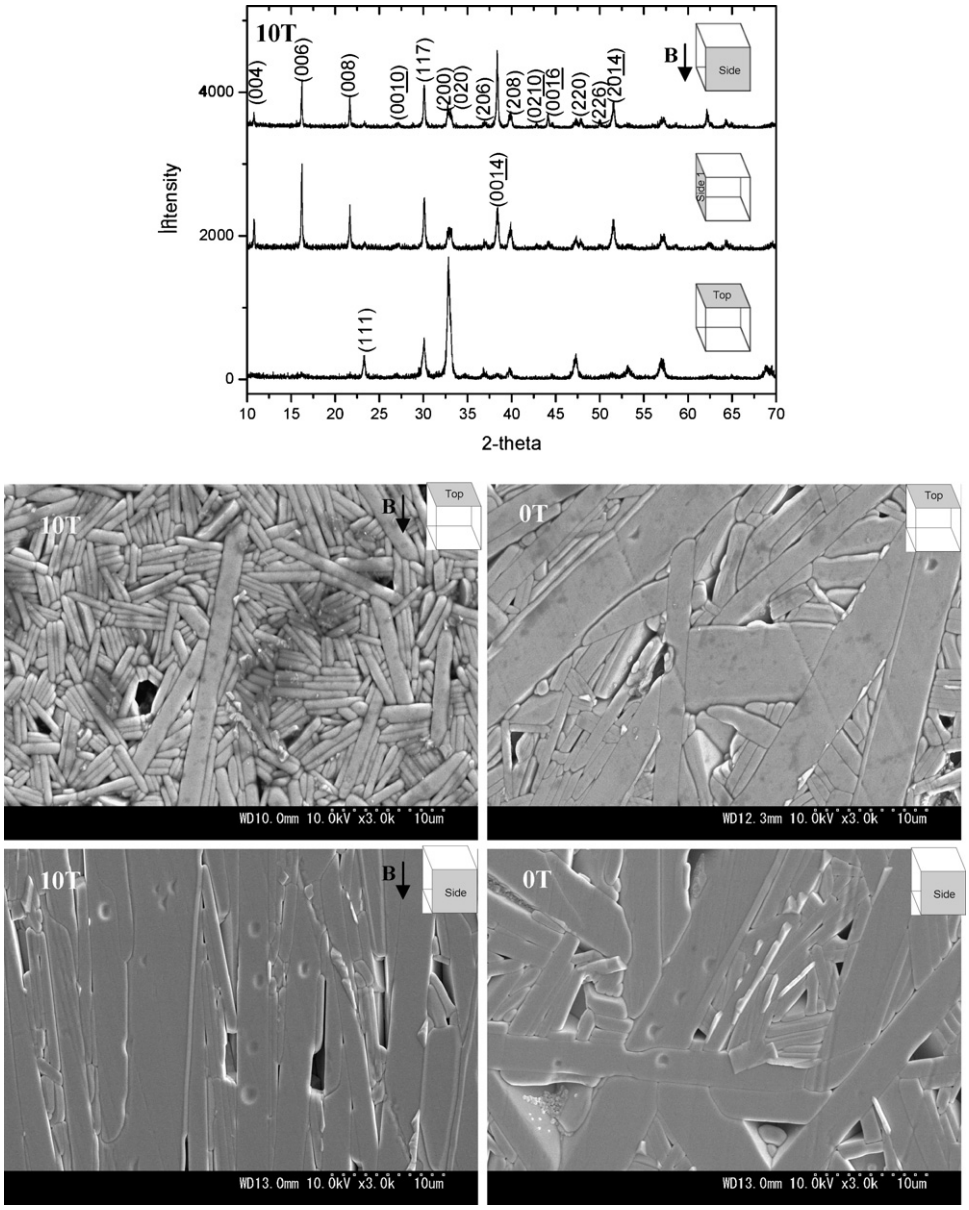

Fig. 2. XRD patterns of sintered BIT sample with magnetic alignment and SEM images of sintered BIT sample with (10 T) and without magnetic alignment (0 T).

using TGG, RTGG and hot forging.[2–9] In the present study, three typical ceramics, $Bi_4Ti_3O_{12}$ (BIT) with bismuth layer structure, $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN) with tungsten bronze structure and $BaTiO_3$ (BT) with perovskite structure were selected as model materials. The grain-orientation of green compacts and sintered samples were examined by XRD. The microstructure and dielectric properties were also characterized.

2. Experimental

2.1. Starting powders

BIT powder was solid-state synthesized from chemically pure Bi_2O_3 (Kojundo Co., Japan), TiO_2 (Wako Ltd., Japan) and Nb_2O_5 (Kojundo Co., Japan) by heating a powder mixture at 950 °C for 2 h and then ball-milled for 1 h.

SBN powder was solid-state synthesized by chemically pure $BaCO_3$ (Wako Ltd., Japan), $SrCO_3$ (Wako Ltd., Japan) and Nb_2O_5 (Wako Ltd., Japan) at 1250 °C for 4 h. The obtained SBN50 powder was ball-milled for 1 h. $BaTO_3$ starting powder was chemically pure from Sakai-Chem, Japan (BT05).

2.2. Processing

A typical gelcasting process was adopted in the current study. Acrylamide (AM) as monomer and methylenebisacrylamide (MBAM) as cross-linker were dissolved in distilled water to form a premix. 40 vol.% starting powder (BIT, SBN and BT respectively) and 1 wt.% dispersant was added into the premix and mixed. Before casting into a rubber mold at room temperature in a vertical 10 T magnetic field (JMTD-10T150, JASTEC, Japan), initiator (5 wt.% ammonium persulfate solution) and catalyst (tetramethylethylenediamine) were added. The magnetic alignment and casting time was made within 30 min by adjusting the amount of catalyst. After mold removal, the sample was dried 1 day in air at 28 °C. The green compact was then heated to 600 °C for burnout of the gel binder. After isotactically pressed at 300 MPa without disturbing the particle orientations,[13] samples were sintered at 1050 °C for BIT, 1400 °C for SBN and 1400 °C for BT. The soaking time was 2 h. For comparison, conventional gel cast samples were prepared in the same conditions without the magnetic alignment.

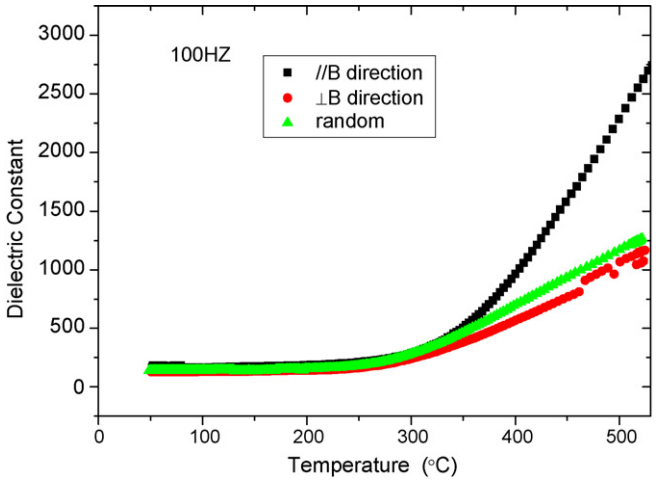

Fig. 3. Temperature dependence of dielectric constant at 100 kHz for random and magnetically aligned BIT samples.

2.3. Characterization

Grain orientation was examined using X-ray diffraction (XRD) (Rigaku, RINT2550). The apparent density was measured by the Archimedes method. The microstructure of sintered samples was observed by FE-SEM (HITICHI S-4300). The dielectric constants of Ag-electroded samples were measured between room temperature to 500 °C at 1–100 kHz (HP 4192A).

3. Results and discussion

3.1. Bismuth layer structure $Bi_4Ti_3O_{12}$

Fig. 1 shows the XRD patterns of BIT starting powder and magnetically aligned green compact. As shown the pattern of

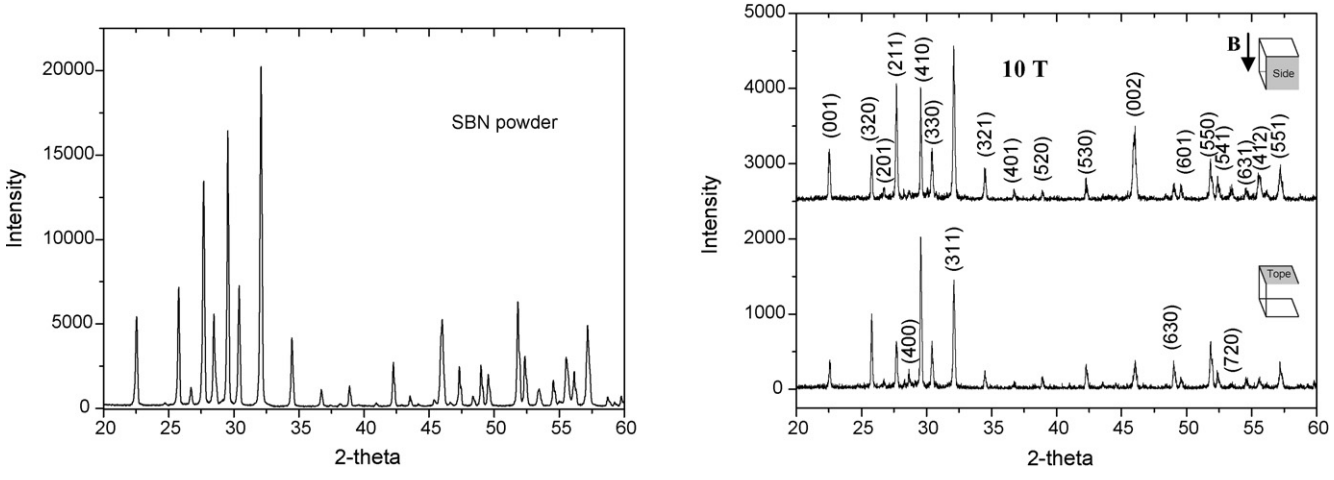

Fig. 4. XRD patterns of SBN starting powder and green compact with magnetic alignment.

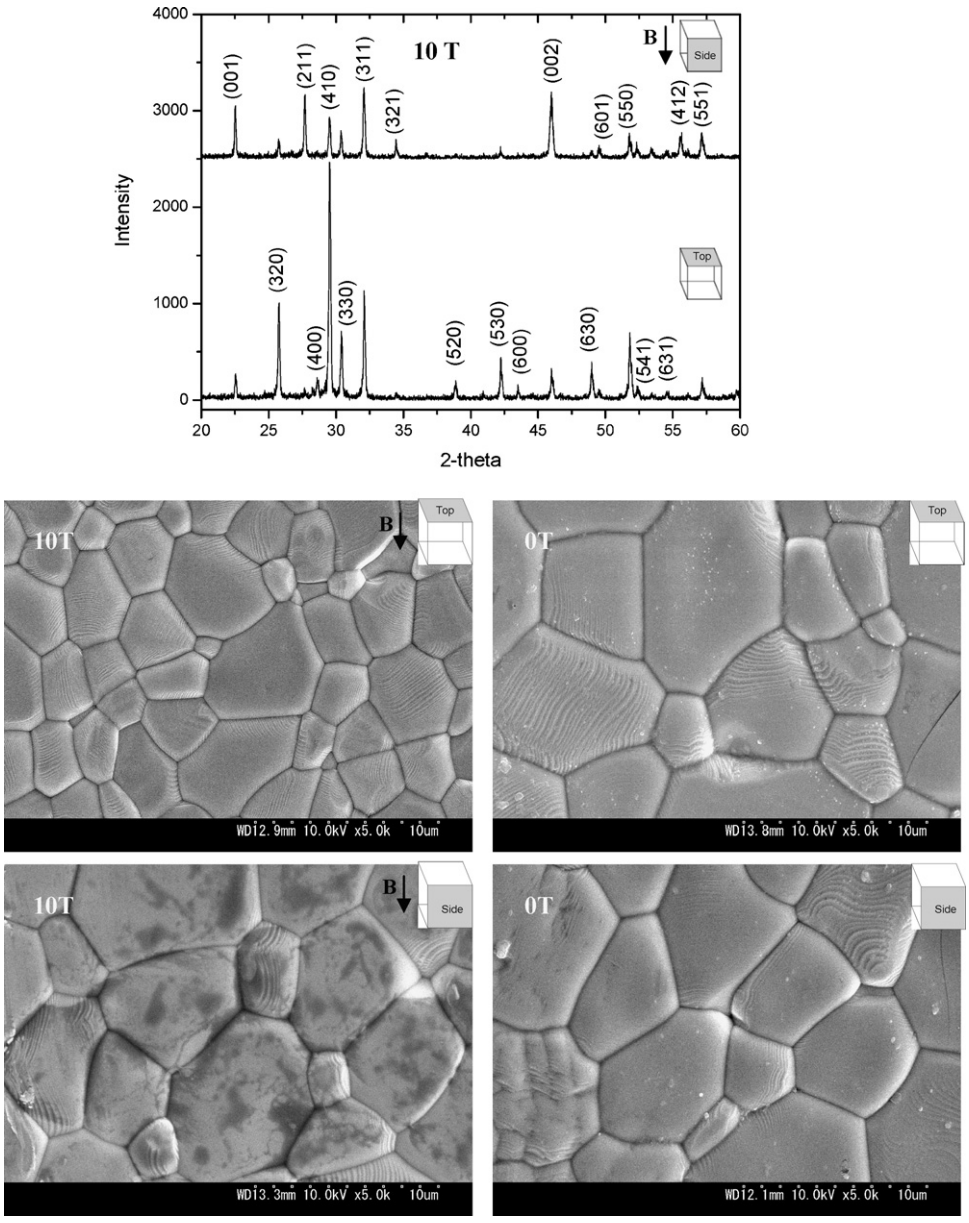

Fig. 5. XRD patterns of sintered SBN sample with magnetic alignment and SEM images of sintered SBN sample with (10 T) and without magnetic alignment (0 T).

the top surface ($\perp B$) is very different to that of the side surface ($\| B$). A BIT *a*–*b* plane orientation, i.e., stronger (2 0 0)/(0 2 0) peaks, are observed at the top surface while the *c*-plane orientation, i.e., stronger (0 0 *l*) peaks, is observed at the side surface. It indicates the magnetic alignment is effective for these BIT particles.

After sintering, the further grain growth promotes grain orientation, as shown by the XRD patterns in Fig. 2. Within the top surface BIT grains exhibit strong *a*–*b* plane orientation, while the (0 0 *l*) peaks, from the *c*-plane orientation, disappear. The similar XRD patterns with stronger (0 0 *l*) peaks were observed on the two perpendicular side surfaces that are parallel to the magnetic field direction. If observed by SEM from the top view, only grains with below 2 μm in width are observed in the magnetically aligned sample (10 T), while in the control sample (0 T) some grains reveal 5–6 μm in width. When observed from the side view, most grains are found parallel to the magnetic field direction in the magnetically aligned sample; while in the control sample grains are typically random. As we know, the BIT grains develop to plate-like shape with the largest surface being *c*-plane after sintering.[3,4] When combining the XRD and SEM results, the microstructure of the magnetically aligned samples show the *a*–*b* planes of BIT particle are aligned to parallel to the magnetic field direction. From the top view, only the *a*–*b* planes are observed, and from the side view, both *c*-plane and *a*–*b* plane can be observed. The temperature dependence of the dielectric constant and dielectric loss of magnetically aligned and random BIT samples measured at

100 kHz as shown in Fig. 3. The dielectric constant is improved obviously, i.e., 2500 in the plan parallel to the applied magnetic field compared to 1000 of the randomly oriented sample at 500 °C.

3.2. Tungsten bronze structure $Sr_{0.5}Ba_{0.5}Nb_2O_6$

Fig. 4 shows the XRD patterns of the SBN starting powder and the magnetically aligned green compact. In comparison with the pattern of randomly oriented powder, the relative intensity of (0 0 1), (0 0 2) and (2 1 1) peaks decreases, while that of (4 1 0) peak increases when observed at the top surface. Correspondingly, the side surface shows the relative intensity of the (0 0 1), (0 0 2) and (2 1 1) peaks increases, while that of the (4 1 0) peak decreases. It indicates that magnetic force is also effective in aligning SBN particles.

After sintering at 1400 °C for 2 h, the relative densities of samples reached 98% and the grain orientation in the magnetically aligned sample was enhanced, as shown in the XRD patterns in Fig. 5. From the side surface, the relative intensity of (0 0 1) and (0 0 2) peaks reach similar values to those for the (2 1 1) and (3 1 1) peaks; while the (4 0 0) peak disappears totally. The intensity of (4 1 0) and other $\{h\,k\,0\}$ peaks increases significantly in the top surface analysis. It also should be noted from the SEM images that in the magnetically aligned sample, the average grain size (3 μm) at the top surface is much smaller than the side surface (6 μm) and the randomly oriented sample (6 μm). It may be attributed to the different grain growth in the oriented SBN sample.

It is reported that the $\langle 0\,0\,l\rangle$-axis of SBN single crystal and $\langle 0\,0\,l\rangle$-axis textured SBN ceramics possess high dielectric and piezoelectric properties.[8,14] The magnetically aligned sample in the current study shows the orientation of $\langle 0\,0\,l\rangle$-axis being perpendicular to B direction. Fig. 6 shows the orientation and temperature dependence of the dielectric constant at 10 kHz, which indicates a very marked anisotropy in the magnetically aligned SBN sample.

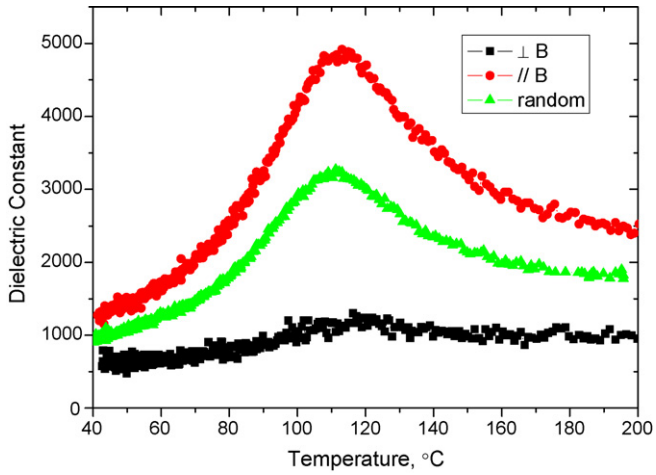

Fig. 6. Temperature dependence of dielectric constant at 10 kHz for random and magnetically aligned SBN samples.

3.3. Perovskite structure $BaTiO_3$

Fig. 7 shows the XRD patterns of BT starting powder and magnetically aligned green compact. In comparison with the pattern of randomly oriented powder, the relative intensity of (1 0 0) and (2 0 0) peaks increase to some extent at the top surface in the green compact. This indicates that some BT particles are aligned by the magnetic force in spite of their weak anisotropic structure.

However after sintering at 1400 °C for 2 h, the grain orientation can no longer be observed. As shown in Fig. 8, XRD patterns and microstructures at both top and side surfaces are similar. In addition, the dielectric constants in the two directions are very similar, as shown in Fig. 9. These results indicate that although some BT particles are aligned by magnetic force in the slurry and green compact, they are difficult to maintain after sintering. It may be attributed to the tetragonal–cubic–tetragonal phase transition during sintering process or the weak anisotropy of the properties and initial particle shapes.

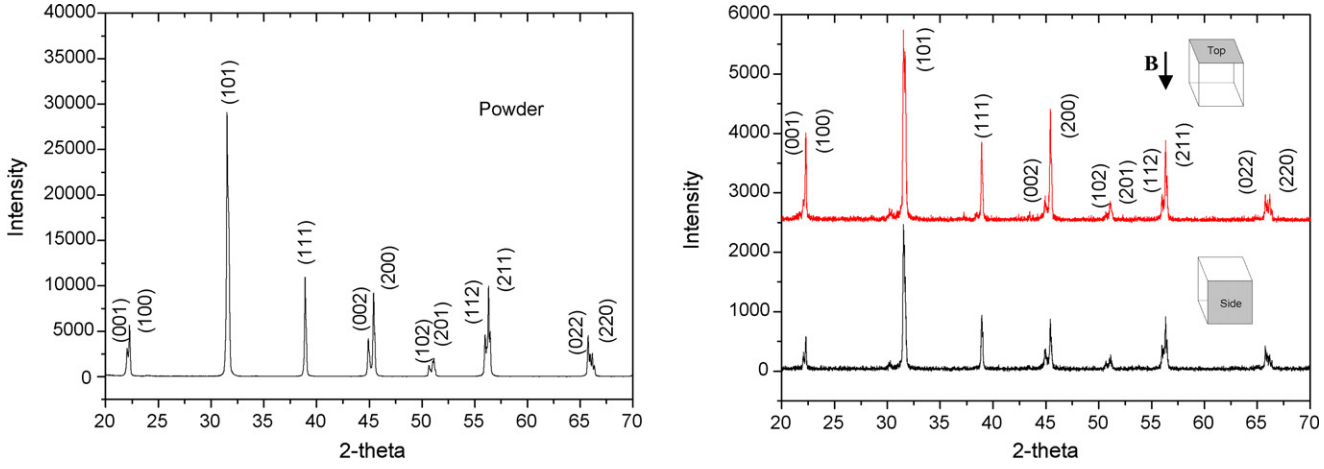

Fig. 7. XRD patterns of BT starting powder and the green compact with magnetic alignment.

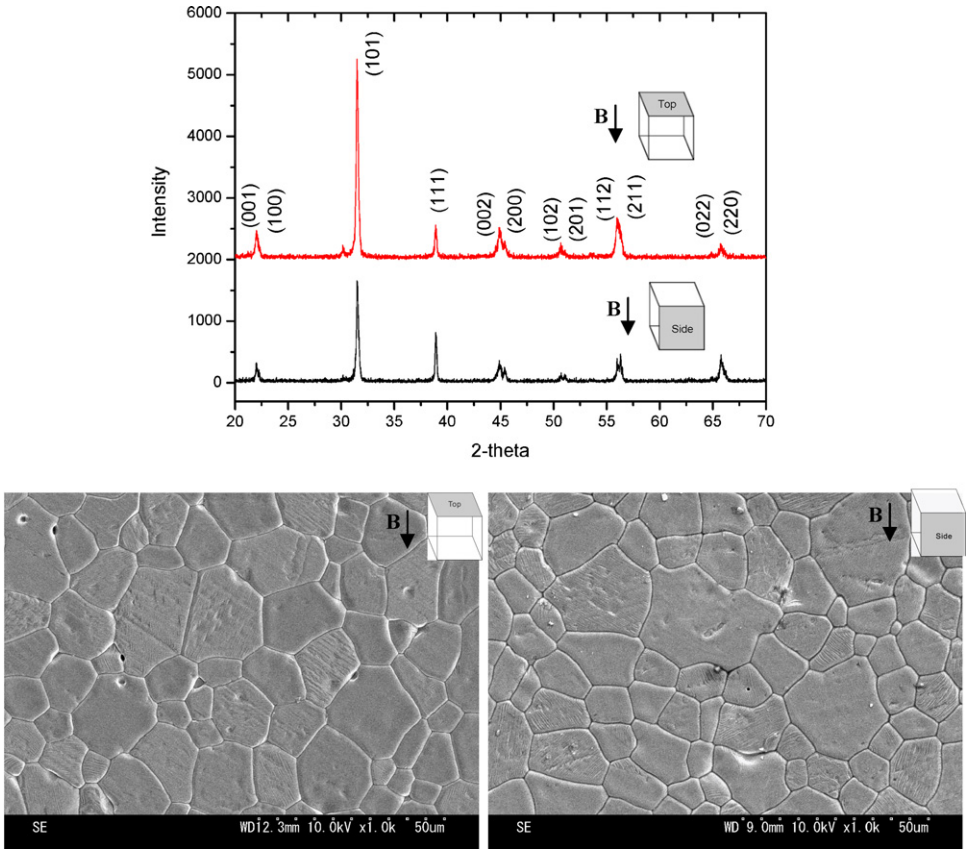

Fig. 8. XRD patterns and SEM images of sintered BT sample with magnetic alignment.

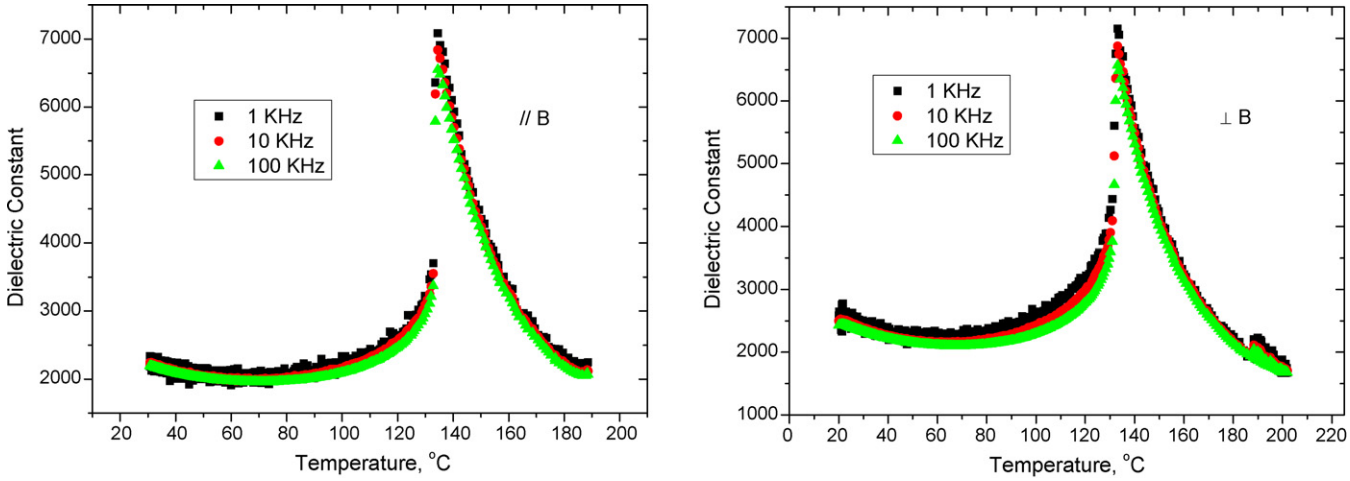

Fig. 9. Temperature dependence of dielectric constant for magnetically aligned BT sample in $\|B$ and $\perp B$ direction.

4. Conclusions

Magnetic alignment is a novel technique for preparing grain-oriented ceramics without the requirement for the templates or applied pressure. This method, using only the conventional ceramic processing, i.e., conventional starting powder, gelcasting forming technique and pressure-less sintering, should facilitate the preparation of large mass and dense grain-oriented ceramic materials. In ferroelectric material families, magnetic alignment is effective to prepare highly grain-oriented ceramics with bismuth layer structure and tungsten bronze structure, but for perovskite structure ceramics, the particle alignment is less significant and difficult to maintain after sintering.

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