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Fabrication and electrical properties of textured $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics by reactive-templated grain growth

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Abstract

Textured $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ (NKBT) ceramics with a relative density of >94% were fabricated by reactive-templated grain growth. Plated-like $Bi_4Ti_3O_{12}$ template particles synthesized by the NaCl–KCl molten salt process were aligned by tape casting in a mixture of original oxide powders. The effect of sintering temperature on the grain orientation and electrical properties of textured NKBT ceramics were investigated. The results show that the textured ceramics have a microstructure with plated-like grains aligning in the direction parallel to the casting plane. The degree of grain orientation increased at increasing sintering temperature. The textured ceramics show anisotropic electrical properties in the directions parallel and perpendicular to the casting plane. The dielectric constant parallel to $\{h\,0\,0\}$ plane is three times higher than that of the perpendicular direction in textured NKBT ceramics. The optimized sintering temperature is 1150 °C where the maximum dielectric constant is 2041, the remnant polarization is 68.7 $\mu C/cm^2$, the electromechanical coupling factor (k_{31}) and the piezoelectric constant (d_{33}) amount to 0.31 and 134 pC/N, respectively.

Keywords: A. Tape casting; A. Grain growth; C. Electrical properties; Lead-free ceramics; Texture

1. Introduction

Most widely used piezoelectric materials are lead-based ceramics including $Pb(Ti,Zr)O_3$ (PZT). However, it is very important to use lead-free piezoelectric materials for environmental protections [1]. Some of the lead-free materials, such as ferroelectric ceramics with perovskite structure, tungsten bronze-type oxides, and Bi-layer structure oxides, have been reported [2–4]. Among these materials, $(Na, K)_{0.5}Bi_{0.5}TiO_3$ solid solution is considered to be an excellent candidate for lead-free piezoelectric ceramics to replace lead-based piezoelectric materials [5,6]. But comparing with the conventional PZT piezoelectric ceramics, $(Na, K)_{0.5}Bi_{0.5}TiO_3$ ceramics still showed poor piezoelectric properties, which has restricted the applications of material.

Because the electrical properties of polycrystalline ceramics are determined not only by the composition but also by the microstructure, the control of microstructure with grain orientation is very important to obtain ceramics with better performances [7]. As an alternative to techniques such as hot pressing and hot forging, reactive-templated grain growth (RTGG) offers the possibility of fabricating grain-oriented polycrystalline ceramics. In this method, the textured microstructure is obtained by grain growth of anisometric template particles aligning in a fine-grained matrix. Template particles must be large and anisometric in shape, so that they can be oriented during tape casting and grown preferentially during sintering stage. It has been reported that anisometric template particles can develop textured microstructures using RTGG in bismuth layer-structured ferroelectrics [8,9].

In this study, plated-like $Bi_4Ti_3O_{12}$ template particles were prepared by NaCl–KCl molten salt synthesis (MSS) [10]. The fabrication and electrical properties of highly grain-oriented $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics by RTGG are described. Texture development, as well as the dielectric and piezoelectric

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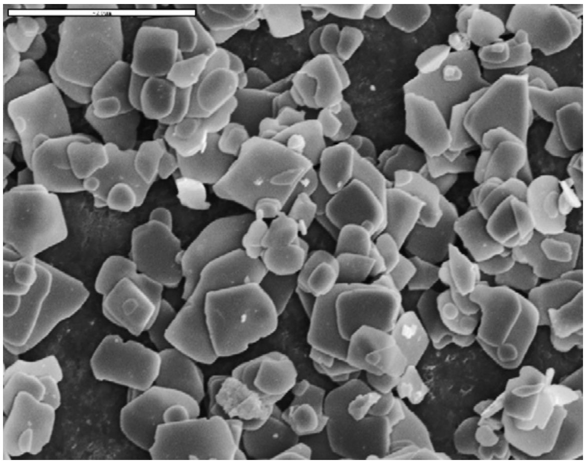


Fig. 1. SEM photograph of $Bi_4Ti_3O_{12}$ template particles.

properties, was investigated as a function of sintering temperature and the degree of orientation.

2. Experimental procedure

The general formula of the material studied was $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ (abbreviated as NKBT). Firstly, plated-like $Bi_4Ti_3O_{12}$ template particles were prepared by reacting Bi_2O_3 with TiO_2 in NaCl–KCl molten salt. An equal weight of NaCl–KCl mixture and reagent-grade oxides were ball milled in ethanol for 12 h and calcined at 1000 °C for 2 h. After cooling to the room temperature, the reaction product was washed with hot deionized water for 20 times until no free Cl^- ions were detected. The $Bi_4Ti_3O_{12}$ templates were obtained by drying at 80 °C for 10 h. Scanning electron microscopy (SEM) analysis (see Fig. 1) shows that $Bi_4Ti_3O_{12}$ powder is formed by plated-like particles with average diameter of 10 μm and a thickness of 1 μm. Secondly, reagent-grade Bi_2O_3, TiO_2, Na_2CO_3, K_2CO_3 powders and solvent, binder, plasticizer were mixed and ball milled for 48 h. After completion of the ball milling process for the slurry, 30 wt% plated-like $Bi_4Ti_3O_{12}$ template particles were added and mixed with the slurry for 4 h. Tape casting was performed on a plated steel surface with a blade gap of 150 μm. After 24 h of drying at room temperature, the green tapes were cut and laminated at a pressure of 100 MPa and then burned out at 500 °C for 2 h. Samples were sintered at 1100–1200 °C for 2 h. Sections, as shown in Fig. 2, were cut parallel (*a–b* plane) and perpendicular (*a–c* plane) to the tape-casting direction, to discuss the microstructure and the electrical properties. The sintered ceramics were polished and pasted with silver on both surface. Poling was performed by applying an electric field of 4 kV/mm at 130 °C for 20 min in silicone oil. The piezoelectric properties were measured after 24 h of aging at room temperature.

The texture was characterized using XRD (model DMX-IIC, Japan) and Lotgering factor was calculated by intensities of X-ray diffraction peaks. Microstructures of perpendicular-cut samples were observed using a scanning electron microscopy (SEM; Model Hitachi S-570, Japan). The dielectric constant (ε) and dielectric loss (tan δ) were measured by LCR precision electric bridge (Model HP4284, Hewlett-Packard). The piezoelectric constant (d_{33}) of the poled samples was measured with a quasistatic piezoelectric d_{33}-meter (ZJ-3D, Institute of Acoustics Academic Sinica, China). The electromechanical coupling factor (k_{31}) and the electromechanical quality factor (Q_m) were calculated from the resonance and anti-resonance frequencies using precise impedance analyzer (Model HP4294A, Hewlett-Packard, CA). The ferroelectric hysteresis loops were observed at room temperature by ferroelectric testing system. The samples were submerged in silicone oil to prevent arcing during testing.

3. Results and discussions

The relative densities and shrinkage of NKBT ceramics sintered at different temperature are shown in Fig. 3. It is found that the relative density and shrinkage increases quickly at temperature range from 1100 to 1130 °C. The maximum relative density, 94.5%, is achieved at 1150 °C. When the sintering temperature is higher than 1150 °C, the relative density decreases with increasing sintering temperature. Corresponding to the change of density, the shrinkage increases with increasing sintering temperature, but the increase rate of shrinkage at temperature higher than 1160 °C becomes much more quickly, which resulted from the evaporation of Bi, Na, and K at high temperature. The results indicate the narrow temperature range of well sintered NKBT ceramics (1130–1160 °C).

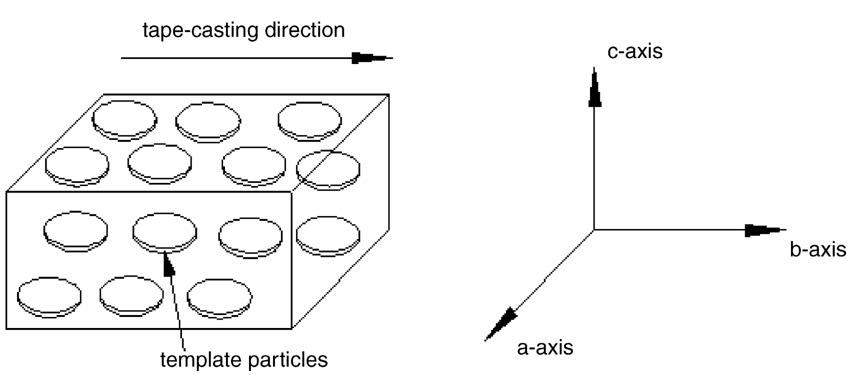


Fig. 2. Schematic depiction of the section in textured NKBT ceramics by RTGG method.

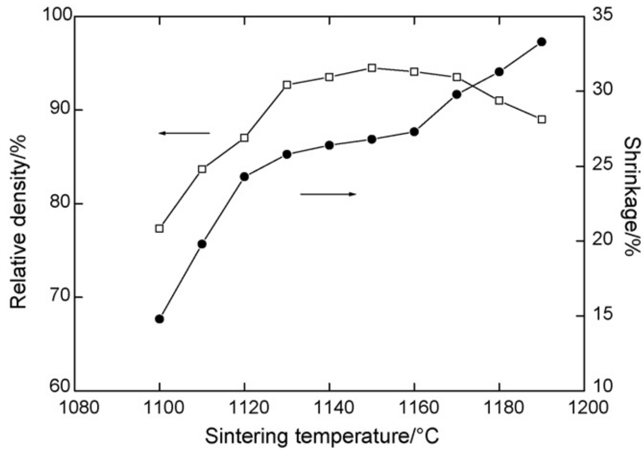


Fig. 3. Relative density and shrinkage of NKBT ceramics sintered at different temperature.

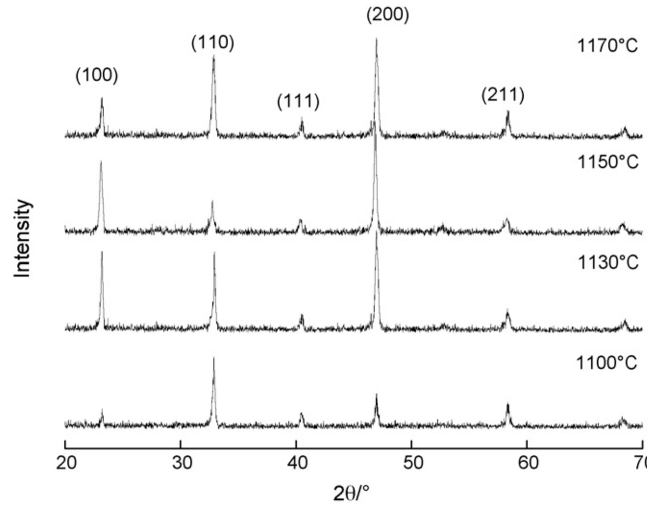


Fig. 5. XRD patterns of textured NKBT ceramics sintered at different temperature.

The microstructure of textured ceramics are shown in Fig. 4. All specimens are composed of two types of NKBT grains. One type is plated-like grains, which originated from plated-like $Bi_4Ti_3O_{12}$ particles. It can be seen that the plate face is parallel to the casting plane, and the thickness is larger than that of the original $Bi_4Ti_3O_{12}$ particles. The other type is equiaxed shaped grains. These two types of grains are called oriented and matrix grains, respectively. It is obviously that NKBT ceramics are not well sintered at temperature 1100 °C, a lot of pores appear in the microstructure, as shown in Fig. 4(a). The thickness of oriented grains increased as the sintering temperature increased. The matrix grains also grow and their shapes change to cubic above 1130 °C. It is difficult to distinguish them from oriented grains in the specimen sintered at 1170 °C.

Fig. 5 shows XRD patterns of textured NKBT ceramics. All samples consist of a single-phase, perovskite structure. The

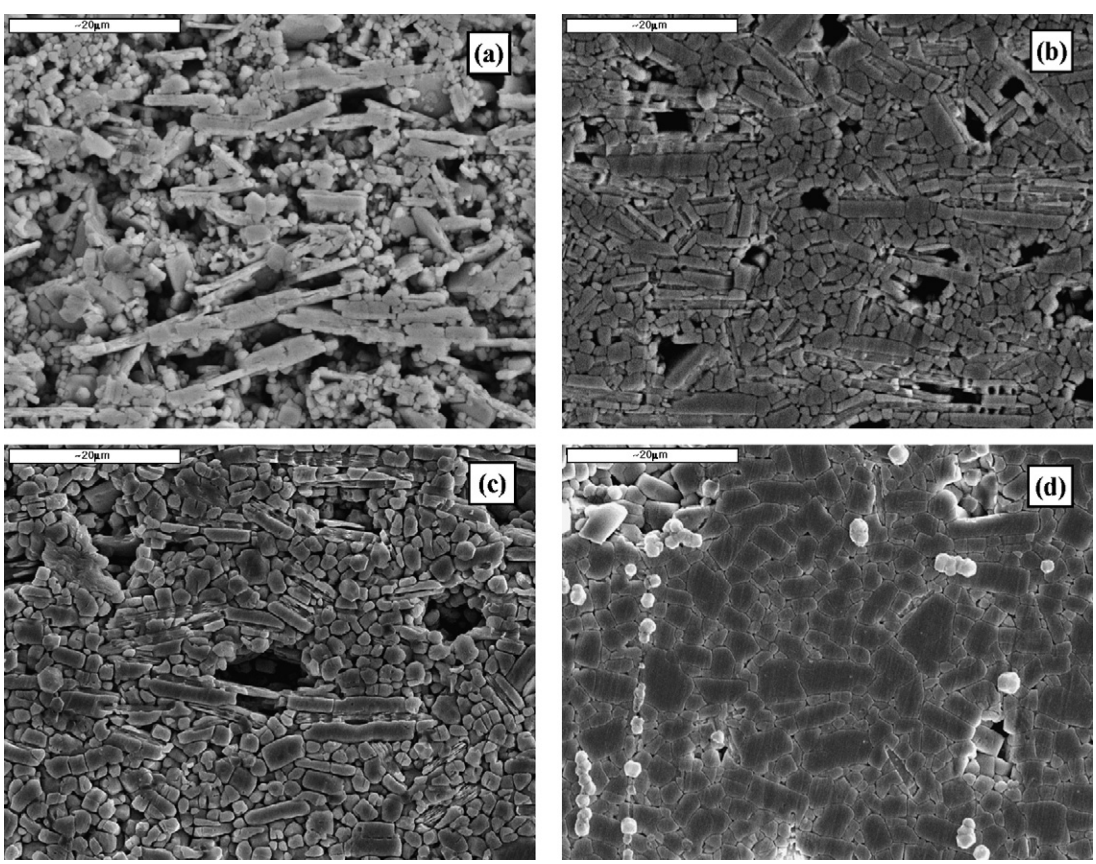


Fig. 4. SEM micrographs of textured NKBT ceramics sintered at (a) 1100 °C; (b) 1130 °C; (c) 1150 °C; (d) 1170 °C.

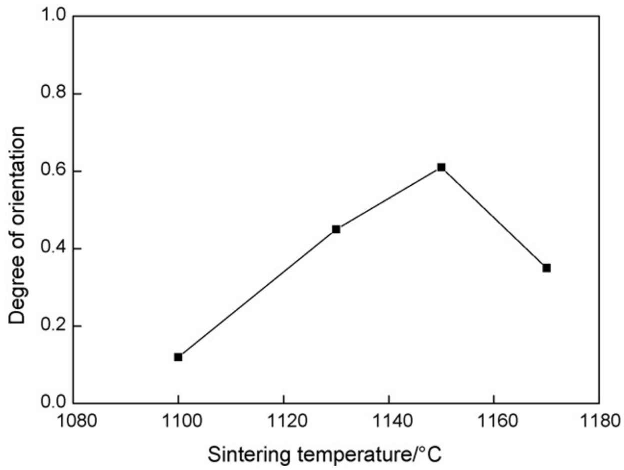


Fig. 6. Degree of orientation as a function of sintering temperature for NKBT ceramics.

(1 1 0) peak, which is the most intense peak for a specimen with randomly oriented grains, is the most intense peak in the samples sintered at 1100 °C, as shown in Fig. 5(a). But the (2 0 0) peak becomes the most intense peak as the sintering temperature is higher than 1100 °C. The intensities of the (1 0 0) and (2 0 0) peaks increase, while the intensities of (1 1 0), (2 1 1) peaks decrease as the sintering temperature increases from 1100 to 1150 °C. The results indicate that (*h* 0 0) texture is formed in the NKBT ceramics prepared by RTGG. When sintering temperature is 1170 °C, the relative intensity of (1 1 0) peak is higher than that of the same peaks in NKBT ceramics sintered at 1150 °C, as shown in Fig. 5(c) and (d).

The most convenient method to determine the degree of orientation is the Lotgering method [11]. The degree of orientation, *f*, is calculated using the following equations:

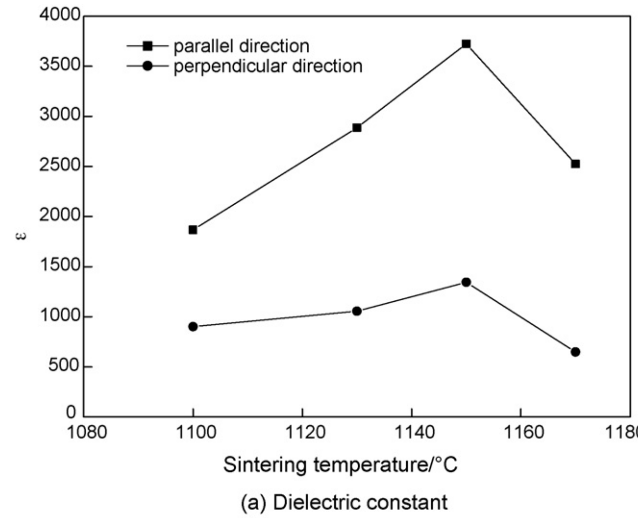
$$f = \frac{P - P_0}{1 - P_0} \tag{1}$$

$$P = \frac{\sum I_{\{h00\}}}{\sum I_{\{hkl\}}} \tag{2}$$

$$P_0 = \frac{\sum I_{0\{h00\}}}{\sum I_{0\{hkl\}}} \tag{3}$$

where I and I_0 are the peak intensities of the sintered compacts and randomly oriented NKBT, respectively. $\{h\,0\,0\}$ and $\{h\,k\,l\}$ are Miller indexes. The diffraction lines between $2\theta = 20°$ and $2\theta = 70°$ were used to calculate P and P_0. Fig. 6 shows the effect of sintering temperature on the degree of orientation for NKBT ceramics. The degree of orientation was small (0.12) in the samples sintered at 1100 °C. But *f* increases as the sintering temperature increases and the largest volume (0.61) appears at 1150 °C. It is indicated a more textured material with increasing sintering temperature from 1100 to 1150 °C. And NKBT ceramics sintered at 1150 °C has significant grain orientation.

It is revealed that the increase in the degree of orientation is caused by the growth of oriented grains at the expense of matrix grains, the growth rate of the oriented grains must be larger than that of the matrix grains at the initial stage of sintering. When the slurry passes blade gap, the templates tend to align under the shearing force from the blade and plated steel surface. Then the interaction between the templates and the fine particles makes the plated-like $Bi_4Ti_3O_{12}$ templates align in the same orientation in the casting process. As a result, the NKBT grains will tend to develop into a plate-like morphology during sintering, with their main surface planes parallel to the (*h* 0 0) crystal planes.



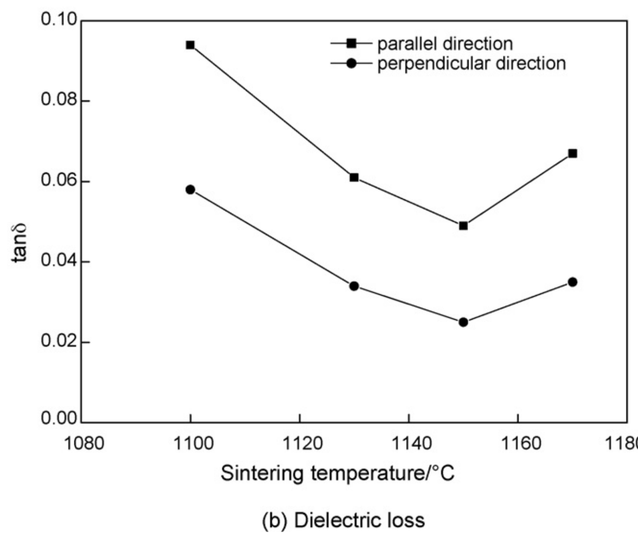


Fig. 7. Dielectric properties as a function of sintering temperature for NKBT ceramics.

Fig. 7 shows dielectric constant and dielectric loss of NKBT ceramics at room temperature in two different directions. It is obviously that NKBT ceramics show anisotropy dielectric properties and the more the degree of orientation is, the larger the dielectric constant is. The dielectric constant parallel to *a*–*b* plane is two times higher than that of perpendicular direction. Fig. 8 shows piezoelectric constant (d_{33}) and electromechanical coupling factor (k_{31}) of NKBT ceramics at different sintering temperature. It is revealed that NKBT ceramics have anisotropy piezoelectric properties. The piezoelectric constant d_{33} parallel

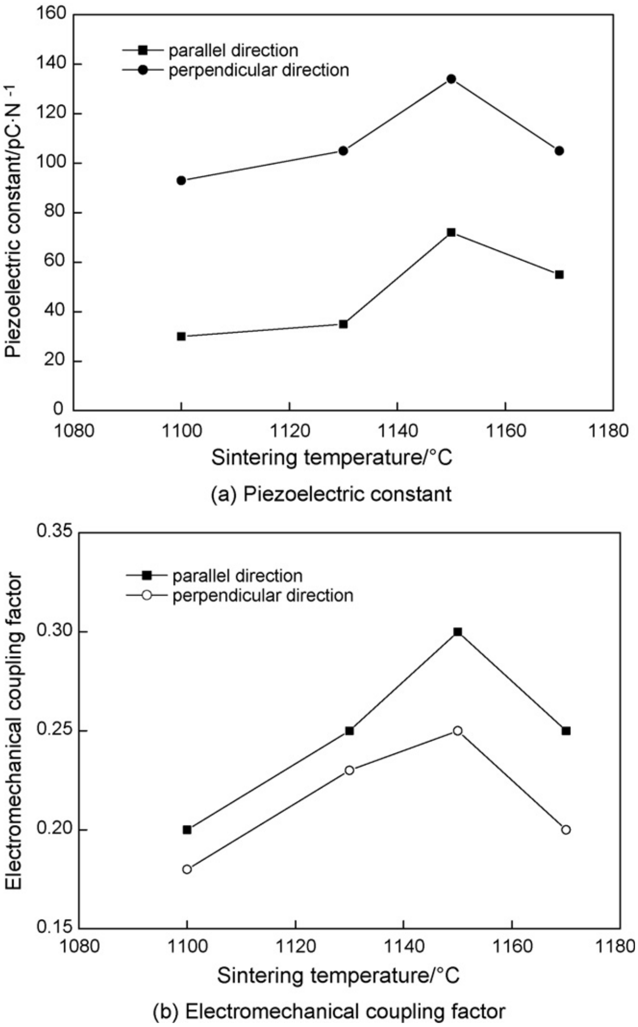


Fig. 8. Piezoelectric properties as a function of sintering temperature for NKBT ceramics.

to a–b plane is smaller than that of perpendicular direction, but k_{31} parallel to a–b plane is higher than that of perpendicular direction. Either parallel direction or perpendicular direction of textured ceramics shows the largest d_{33} and k_{31} as sintering

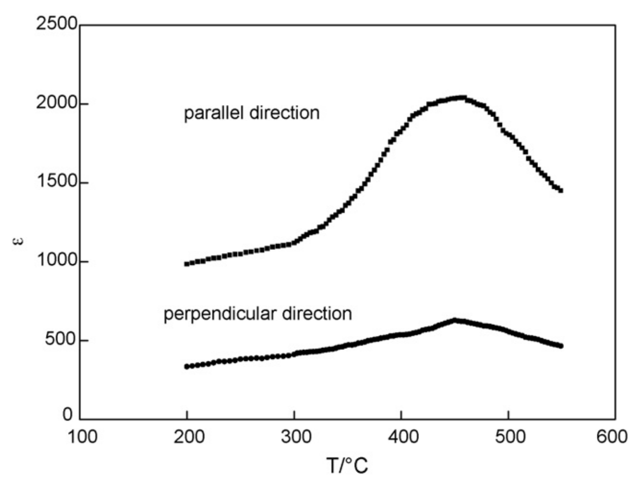


Fig. 9. The dielectric constant as a function of temperature for textured NKBT ceramics sintered at 1150 °C (1 kHz).

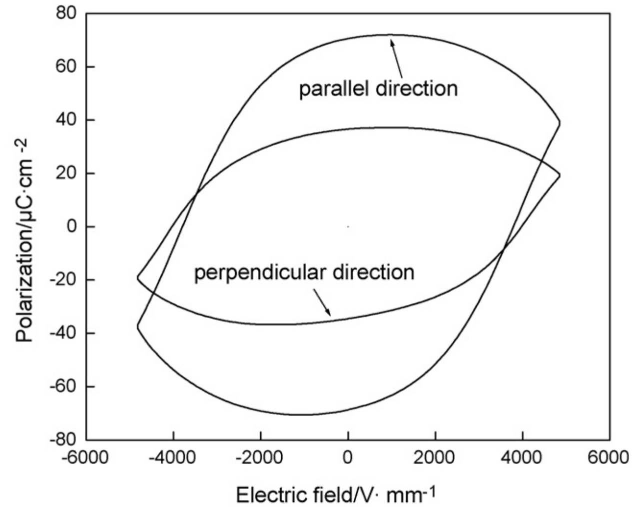


Fig. 10. Hysteresis loops of textured NKBT ceramics sintered at 1150 °C.

temperature is 1150 °C. It is concluded that the optimized sintering temperature for textured NKBT ceramics is 1150 °C.

Fig. 9 shows the orientation and temperature dependence of the dielectric constant for textured NKBT ceramics sintered at 1150 °C. It shows very high anisotropy in the dielectric constant between the perpendicular-cuts and parallel-cuts samples. The textured NKBT ceramics parallel to a–b plane exhibits dielectric constant three times higher than the value for the perpendicular-cuts ceramics. And the Curie temperature is 458 °C where the maximum dielectric constant amounts to 2041 in parallel direction.

P–E hysteresis loops of ceramics were recorded at room temperature and were shown in Fig. 10. It also shows very high anisotropy in P–E hysteresis loops between the perpendicular-cuts and parallel-cuts samples. The remnant polarization of $P_r = 68.7\ \mu C/cm^2$ is obtained in the parallel-cuts, which is much higher than the P_r value ($34.5\ \mu C/cm^2$) in the perpendicular-cuts. In contrast, the coercive field E_c (3771 V/mm) of the parallel-cuts is lower than that of perpendicular-cuts (3967 V/mm).

4. Conclusions

Textured $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ ceramics were fabricated by RTGG and tape-casting technique. The textured ceramics have a microstructure with developed plated-like grains aligned in the direction parallel to the casting plane. The ceramics exhibited $\{h\,0\,0\}$ preferred orientation with the degree of orientation larger than 0.6. The degree of grain orientation increases at increasing sintering temperature. The ceramics show anisotropic dielectric and piezoelectric properties in the directions parallel and perpendicular to the casting plane. The optimized sintering temperature is 1150 °C where the maximum dielectric constant is 2041, the remnant polarization is $68.7\ \mu C/cm^2$, the electromechanical coupling factor (k_{31}) and the piezoelectric constant (d_{33}) amount to 0.31 and 134pC/N, respectively.

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