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Microstructure and piezoelectric properties of textured $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ lead-free ceramics

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Abstract

Textured $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics were fabricated by reactive-templated grain growth in combination with tape casting. The effects of sintering conditions on the grain orientation and the piezoelectric properties of the textured $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics were investigated. The results show that the textured ceramics have microstructure with plated-like grains aligning in the direction parallel to the casting plane. The ceramics exhibit $\{h00\}$ preferred orientation and the degree of orientation is larger than 0.7. The degree of grain orientation increases with the increasing sintering temperature. The textured ceramics show anisotropy dielectric and piezoelectric properties in the directions of parallel and perpendicular to the casting plane. The ceramics in the perpendicular direction exhibit better dielectric and piezoelectric properties than those of the nontextured ceramics with the same composition. The optimized sintering temperature is 1150 °C where the maximum d_{33} of 134 pC/N parallel to casting plane, the maximum k_{31} of 0.31, and the maximum Q_m of 154 in perpendicular direction were obtained.

Keywords: Lead-free ceramics; Tape casting; Grain growth; Piezoelectric properties

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. Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), which considered to be an excellent candidate of lead-free piezoelectric ceramics to replace the lead-based piezoelectric materials, is a kind of perovskite ABO_3-type ferroelectrics discovered by Smolenskii.[1] But NBT has a drawback of high coercive field E_c which cause problems in the poling process.[2] To improve its properties, some modifications on NBT composition have been performed.[3–5] It has been reported that NBT-based compositions modified with $K_{0.5}Bi_{0.5}TiO_3$ (KBT) show improved piezoelectric properties and pole easily compared with pure NBT ceramics.[6,7] So $(Na,K)_{0.5}Bi_{0.5}TiO_3$ solid solution is an attractive ceramic as lead-free piezoelectric material.

But compared with the conventional PZT piezoelectric ceramics, $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics still show poor piezoelectric properties, which has restricted the applications of material. One of the approaches to enhance the piezoelectric properties of lead-free ceramics is to control the microstructure of ceramics by grain orientation.[8,9] Reactive-templated grain growth (RTGG) method has been used successfully to form crystallographically textured ceramic such as bismuth layer-structured ferroelectrics.[10,11] In RTGG method, the first step is to prepare particles with shape anisotropy, such as plated-like particles, needle-like particles. The second is to align particles with shape anisotropy in green compacts by tape casting. Then textured ceramics is formed after sintering with specific crystal axis of grains aligned in one direction, and high electrical properties are expected.

Our previous research showed that the ceramics with composition $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ lied near to the morphology phase boundary and had better piezoelectric properties. In the present study, plated-like $Bi_4Ti_3O_{12}$ template particles were prepared, and textured $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ ceramics were fabricated by RTGG in combination with tape casting. The effects of sintering conditions on the grain orientation and the piezoelectric properties of the textured $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ ceramics were investigated.

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2. Experimental procedure

2.1. Preparation of plated-like $Bi_4Ti_3O_{12}$ templates

Plated-like $Bi_4Ti_3O_{12}$ template particles were prepared by NaCl–KCl molten salt synthesis (MSS).[12] Reagent-grade Bi_2O_3, TiO_2, NaCl, and KCl were used as starting materials. An equal weight of NaCl–KCl mixture and reagent-grade oxides were ball milled in ethanol for 12 h and calcined in a sealed alumina crucible at 1000 °C for 2 h. After slowly cooling to the room temperature, the reaction product was washed with hot deionized water for twenty times until no free Cl^- ions were detected in the use of $AgNO_3$ solution. The $Bi_4Ti_3O_{12}$ templates were obtained by drying at 80 °C for 10 h. As shown in Fig. 1, the $Bi_4Ti_3O_{12}$ powder is formed by plated-like particles with average diameter of 10 μm and a thickness of 1 μm, which can meet the needs of RTGG method.

2.2. Fabrication of textured $(Na,K)_{0.5}Bi_{0.5}TiO_3$ ceramics by RTGG

The general formula of the material studied was $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ (NKBT). The samples were prepared by reactive-templated grain growth (RTGG) in combination with tape casting. 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. The solvents were ethanol and xylene. The binder and plasticizer were polyvinyl alcohol (PVA) and glycerin, respectively. 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. Then the slurry was degassed under vacuum and tape cast on a plated steel surface with a blade gap of 200 μm. The green tapes were cut into pieces of 100 mm × 100 mm and laminated at a pressure of 100 MPa for 15 min. After the laminated samples were cut into 10 mm × 10 mm square, the binder and plasticizer were burned out at 500 °C for 2 h with a heating rate of 1 °C/min. Then the samples were sintered at 1100–1200 °C for 2 h. The sintered ceramics were polished and pasted with silver on both surface. The samples were poled at 130 °C for 20 min under an electric field of 4 kV/mm in silicone oil. The piezoelectric properties were measured after 24 h of aging at room temperature.

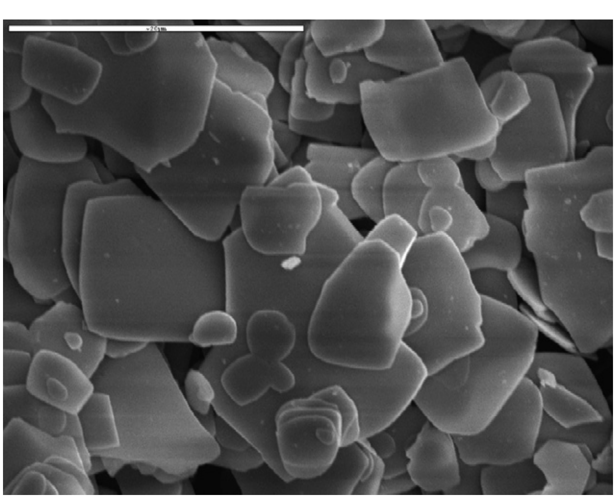


Fig. 1. SEM photograph of $Bi_4Ti_3O_{12}$ template particles.

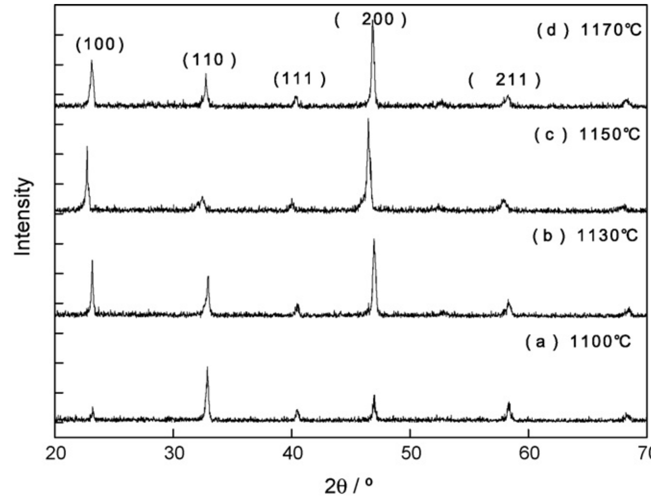


Fig. 2. XRD patterns of textured NKBT ceramics sintered at different temperature.

2.3. Characterization

The degree of grain orientation was examined by intensities of X-ray diffraction (XRD; model DMX-IIC, Japan) peaks. Microstructure was observed by a scanning electron microscopy (SEM; Model Hitachi S-570, Japan). The dielectric constant (ε) and dielectric loss ($\tan\delta$) in directions parallel and perpendicular to the casting plane were measured by LCR precision electric bridge (Model HP4284, Hewlett-Packard). The piezoelectric constant (d_{33}) 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 pre-

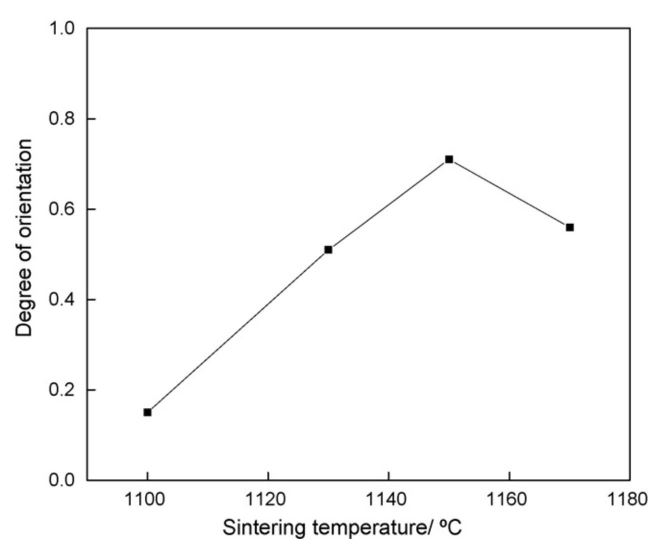


Fig. 3. Degree of orientation as a function of sintering temperature for NKBT ceramics.

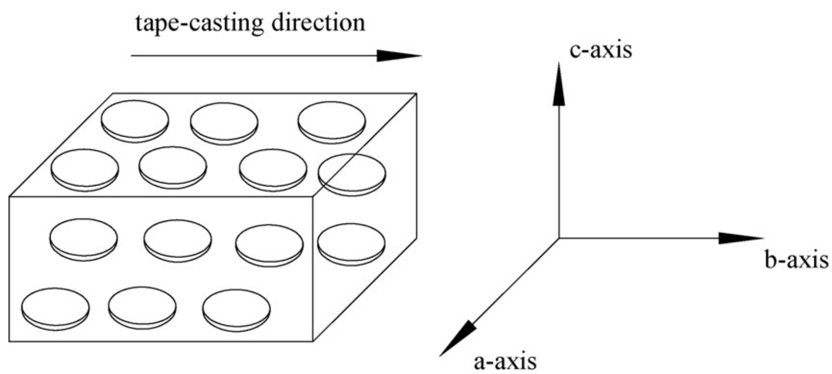


Fig. 4. The sketch map of textured NKBT ceramics by RTGG method.

cise impedance analyzer (Model HP4294A, Hewlett-Packard, California). The ferroelectric hysteresis loops were observed at room temperature by Radiant's RT6000 precision workstation ferroelectric testing system. The samples were submerged in silicone oil to prevent arcing during testing.

3. Results and discussion

Fig. 2 shows XRD patterns of sintered NKBT ceramics at temperature range from 1100 °C to 1170 °C. It is revealed that all samples consist of a single-phase, perovskite structure. The (1 1 0) peak is the most intense peak in the samples sintered at 1100 °C, just like that of the specimen with randomly oriented grains, as shown in Fig. 2(a). While the intensities of the (1 0 0) and (2 0 0) peaks increase, the intensities of others decrease as the sintering temperature increased from 1100 °C to 1150 °C. And the (2 0 0) peak becomes the most intense one in the textured NKBT ceramics as the sintering temperature is higher than 1100 °C. The results indicate that (*h* 0 0) texture is formed in the NKBT ceramics prepared by RTGG method. When sintering temperature is higher than 1150 °C, the relative intensity of (1 1 0) peak at 1170 °C is higher than that of NKBT ceramics sintered at 1150 °C, as shown in Fig. 2(c) and (d). The degree of orientation (*f*) is calculated by Lotgering method, as

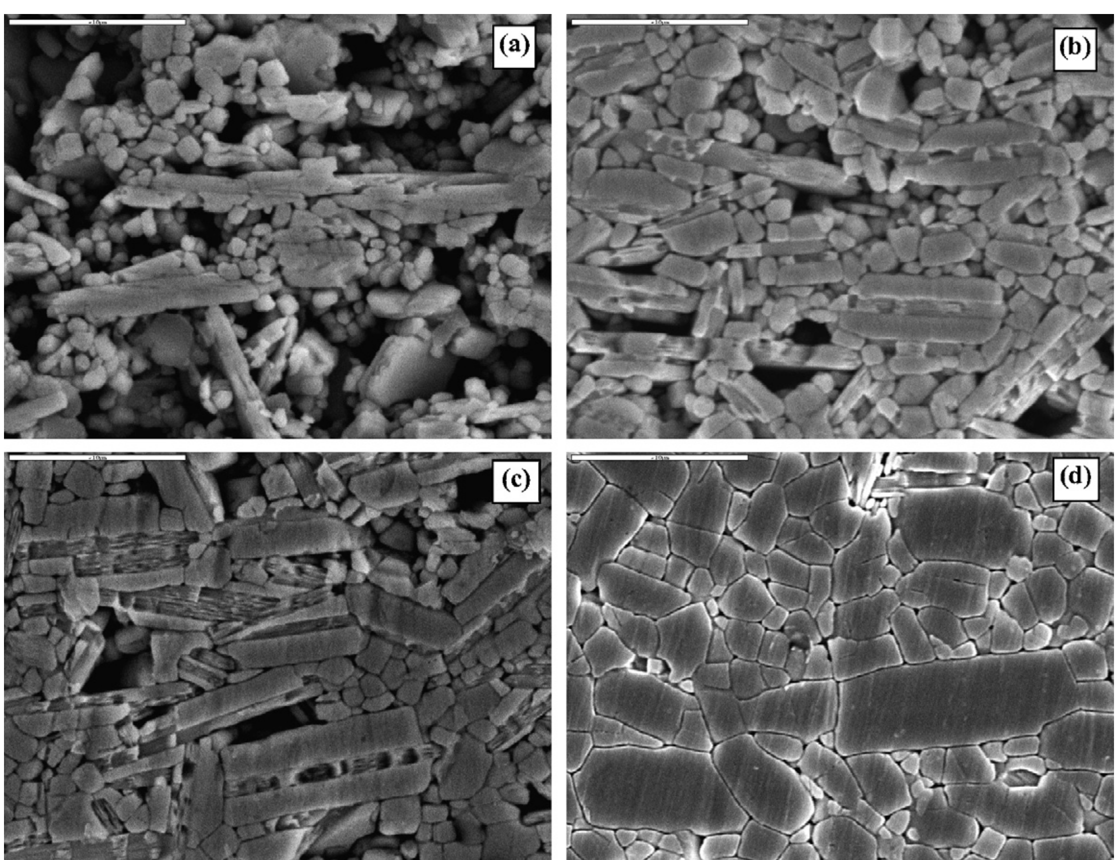


Fig. 5. SEM micrographs of textured NKBT ceramics sintered at (a) 1100 °C, (b) 1130 °C, (c) 1150 °C, and (d) 1170 °C.

the following equations shown[13]:

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

$$P = \frac{\sum I_{\{h\,0\,0\}}}{\sum I_{\{h\,k\,l\}}} \tag{2}$$

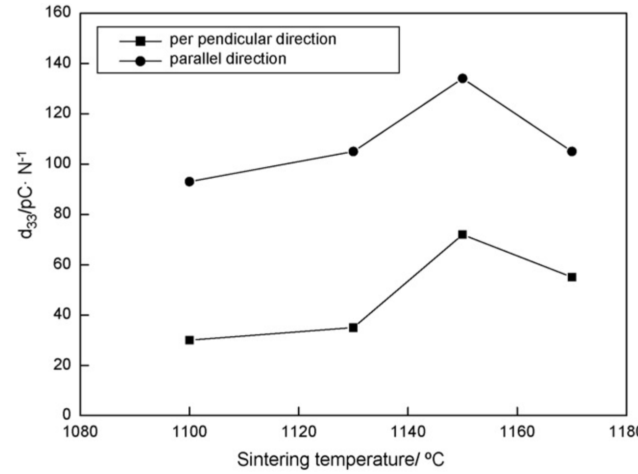
$$P_0 = \frac{\sum I_{0\{h\,0\,0\}}}{\sum I_{0\{h\,k\,l\}}} \tag{3}$$

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 $2\theta = 20^\circ$ and 70° were used to calculate P and P_0.

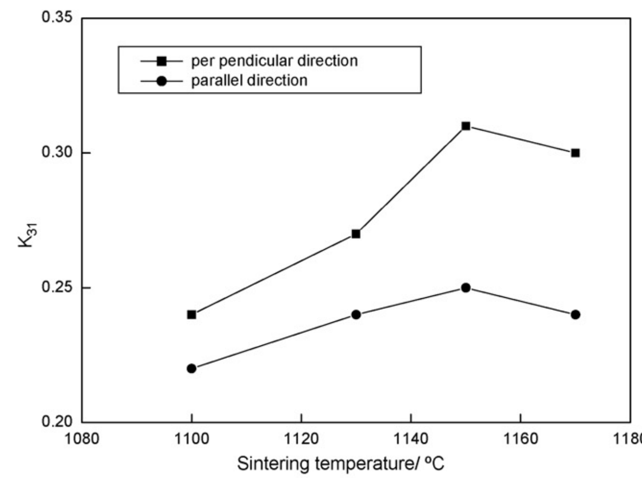
Fig. 3 shows the effect of sintering temperature on the degree of orientation for NKBT ceramics. The degree of orientation is small (0.15) in the samples sintered at 1100 °C. But the degree of orientation increases as the sintering temperature increases and the largest volume appears at 1150 °C where f amounts to 0.71. It is indicated a more textured material, which has significant grain orientation.

Samples were cut parallel (*a–b* plane) and perpendicular (*a–c* plane) to the tape-casting direction, as shown in Fig. 4, to discuss microstructure and electrical properties in two different directions. Fig. 5 shows the effect of sintering temperature on the microstructure of polished *a–c* plane in NKBT ceramics. It is obvious that NKBT ceramics is not well sintered at temperature lower than 1130 °C, and a lot of pores appear, as shown in Fig. 5(a) and (b). All specimens are composed of two types of NKBT grains. One is plated-like grains, which originated from plated-like $Bi_4Ti_3O_{12}$ particles. The other is fine, equiaxed shaped grains. Thy are called oriented and matrix grains, respectively, and the thickness of two types of grains' sizes increase when the sintering temperature increases. It is difficult to distinguish them from oriented grains at sintering temperature higher than 1170 °C.

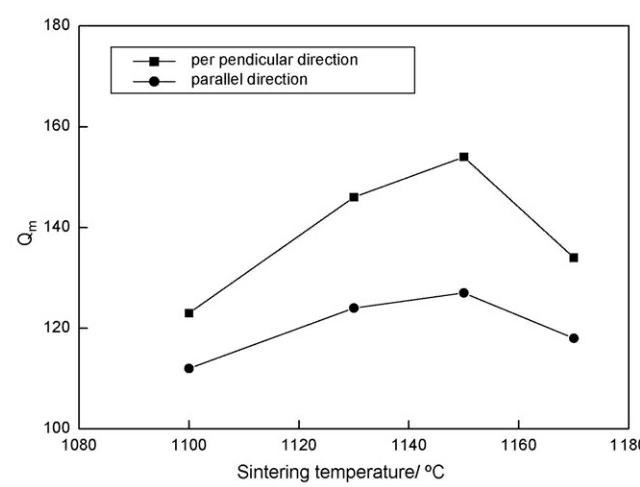
Because the grain size and the specific grain boundary area differ from the equiaxed grains and the plated-like grains, the small matrix grains tend to be consumed by the large oriented grains during sintering in order to reduce the grain boundary area and the internal energy of the system.[14] The plated-like grains oriented parallel to the $(h\,0\,0)$ planes form low-energy grain boundaries, and are difficult to be consumed. Some of them can grow large and eventually remain in the final product. In contrast, the fine matrix grains misaligned form high-energy grain boundaries and are easily consumed not only by the oriented grains but also by the more larger matrix grains. As a result, the volume fraction of the randomly oriented grains in the sample is reduced, and the degree of grain orientation increases with sintering temperature increased from 1100 °C to 1150 °C. When sintering temperature is higher than 1150 °C, matrix grains grow to a size comparable to that of oriented grains at the initial stage of sintering, and the growth rates of oriented and matrix grains become comparable. Some oriented grains may disappear during the grain growth of matrix grains because of the large growth rate of the matrix grains, which results in decreasing of the degree of orientation.



(a) Piezoelectric constant d_{33}



(b) Electromechanical coupling factor k_{31}



(c) Electromechanical quality factor Q_m

Fig. 6. Piezoelectric properties as a function of sintering temperature for NKBT ceramics.

Fig. 6 shows piezoelectric constant (d_{33}), electromechanical coupling factor (k_{31}), and electromechanical quality factor (Q_m) of NKBT ceramics at different sintering temperature. It is revealed that NKBT ceramics have anisotropy piezoelectric

Table 1
Piezoelectric properties of textured (RTGG) and nontextured (conventional) NKBT ceramics

Piezoelectric properties	k_{31}	Q_m	d_{33} (pC/N)	P_r (μC/cm^2)	E_c (V/mm)
RTGG					
Perpendicular direction	0.31	154	72	27.9	4378
Parallel direction	0.25	127	134	43.5	3643
Conventional Process	0.27	132	113	37.3	3988

properties and the more degree of orientation is, the larger values of d_{33}, k_{31} and Q_m are. The piezoelectric constant d_{33} parallel to *a*–*b* plane is higher than that of perpendicular direction, but k_{31} and Q_m parallel to *a*–*b* plane are smaller than those of perpendicular direction. Either parallel direction or perpendicular direction of textured ceramics shows the largest d_{33}, k_{31} and Q_m when sintering temperature is 1150 °C. It is concluded that the optimized sintering temperature for textured NKBT ceramics is 1150 °C.

Fig. 7 shows the orientation and temperature dependence of the dielectric constant for textured NKBT ceramics sintered at 1150 °C. It is observed that very high anisotropy in the dielectric constant between the perpendicular-cuts and parallel-cuts samples. The textured NKBT ceramics parallel to *a*–*b* plane exhibit dielectric constant two times higher than the values for the perpendicular-cuts ceramics. And the Curie temperature is 460 °C where the maximum dielectric constant amounts to 4661 in parallel direction and 2512 in perpendicular direction.

Fig. 8 shows the hysteresis loops of ceramics in parallel-cuts direction and perpendicular-cuts direction. It is also shown that very high anisotropy in *P*–*E* hysteresis loops. The remnant polarization of $P_r = 43.5$ μC/cm^2 were obtained in the parallel-cuts, which is much higher than the P_r values (27.9 μC/cm^2) in the perpendicular-cuts. In contrast, the coercive field E_c (3643 V/mm) in the parallel-cuts is lower than that of perpendicular-cuts (4378 V/mm) and the conventionally processed specimens (3988 V/mm), as shown in Table 1. The lower coercive field indicates that the textured NKBT ceramics can be more easily poled than the ceramics with grains unoriented.

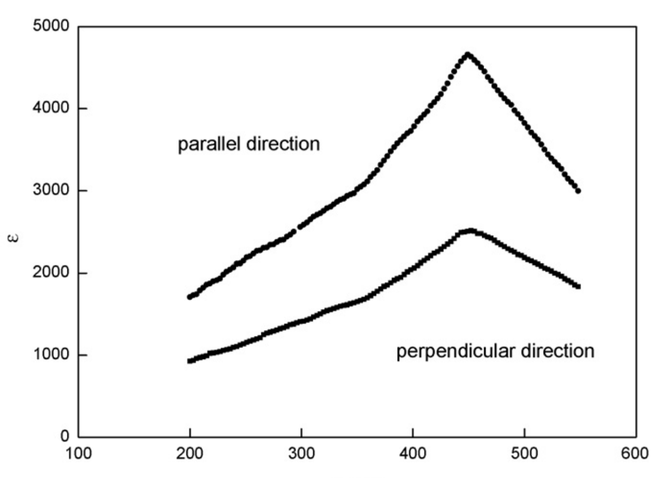


Fig. 7. The dielectric constant as a function of temperature for textured NKBT ceramics sintered at 1150 °C (1 KHz).

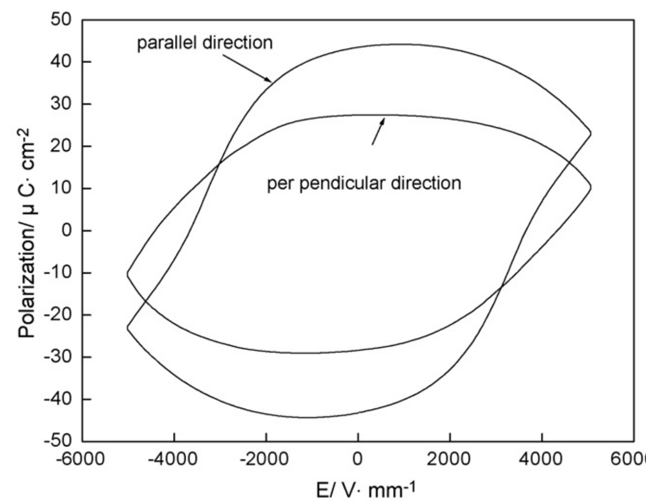


Fig. 8. Hysteresis loops of textured NKBT ceramics sintered at 1150 °C.

Table 1 lists piezoelectric properties of the textured NKBT ceramics and nontextured NKBT ceramics sintered at 1150 °C. The piezoelectric properties of the RTGG-processed NKBT were superior to those of the conventional process because of high grain orientation. The electromechanical coupling factor (k_{31}) and the electromechanical quality factor (Q_m) for the textured NKBT ceramics in perpendicular direction attained values of 0.31 and 154, respectively. The piezoelectric constant d_{33} parallel to casting plane amounts to 134 pC/N. Generally to say, the textured NKBT ceramics exhibited better piezoelectric properties than that of the nontextured ceramics with the same composition.

4. Conclusions

Highly textured $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ ceramics with enhanced piezoelectric properties were fabricated by RTGG method 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 NKBT ceramics exhibit $\{h00\}$ preferred orientation with the degree of orientation larger than 0.7. The degree of grain orientation increase with the increasing sintering temperature. The ceramics show anisotropy piezoelectric properties in the directions parallel and perpendicular to the casting plane. RTGG-processed NKBT ceramics in the parallel direction exhibited higher dielectric and piezoelectric properties than the values of the nontextured ceramics with the same composition. The optimized sintering temperature is 1150 °C which the electromechanical coupling factor (k_{31}) and the electromechanical quality factor (Q_m) in perpendicular direction attain values of 0.31 and 154, respectively, and the piezoelectric constant (d_{33}) parallel to casting plane amounts to 134 pC/N. What is more, the coercive field E_c in the parallel direction is lower than that of the conventionally processed specimens, which indicate that the textured NKBT ceramics can be more easily poled than the ceramics with grains unoriented.

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