Evolution of crystallographic grain orientation and anisotropic properties of $(K_{0.5}Na_{0.5})NbO_3$ ceramics using $BaTiO_3$ templates by reactive templated grain growth

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ABSTRACT

Platelike $BaTiO_3$ (BT) templates were used for the first time to fabricate $(0\,0\,1)$ textured $K_{0.5}Na_{0.5}NbO_3$ (KNN) piezoelectric ceramics. Plakelike BT templates with a thickness of 1–1.5 μm and a mean diameter of 10–15 μm were synthesized by the topochemical microcrystal conversion method using $Bi_4Ti_3O_{12}$ as precursor particles. A systematic investigation was conducted on illustrating the texture development and microstructure evolution as a function of heat-treatment conditions. It was found that the KNN–BT solid solution was formed between BT templates and matrix materials. The increase of sintering temperature and time induced an orthorhombic–tetragonal phase transition. And it was indicated that the dominant mechanism of texture development could be the abnormal grain growth in the textured KNN ceramics. A $(0\,0\,1)$ orientation degree of 80% was achieved at 1130 °C for 24 h. The textured ceramics showed anisotropic electrical properties in the direction of parallel and perpendicular to the casting plane. The orthorhombic–tetragonal polymorphic phase transition T_{o-t}, the tetragonal–cubic ferroelectric phase transition T_C, the dielectric constant ε_r and the remnant polarization P_r values for the perpendicular cut specimens were lower than the parallel cuts. The excellent electric properties at the parallel cuts were found to be the dielectric constant $\varepsilon_r = 810$, the piezoelectric charge constant $d_{33} = 163$ pC/N, and the electromechanical coupling factor $k_p = 0.37$.

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1. Introduction

The properties of ceramics are controlled not only by the composition designing or doping but by grain orientation methods. (reactive) templated grain growth ((R)TGG) method mainly relies on the preferentially oriented growth of large, anisotropic template grains through consuming the matrix grains during densification which has been generally used in textured $K_{0.5}Na_{0.5}NbO_3$ (KNN) based ceramics. In those textured ceramics, platelike $NaNbO_3$ grains were usually used as templates. On the one hand, (Li, Ta, Sb)-modified textured KNN ceramics exhibited an excellent piezoelectric properties [1–3]. On the other hand, CuO-doped KNN was demonstrated to improve the density and maximize the texture quality in textured KNN ceramics [4,5]. Moreover, Saito et al. synthesized polycrystalline platelike $KNbO_3$ [6] particles from $K_4Nb_6O_{17}$ precursor and fabricated textured KNN with a $(1\,0\,0)$ orientation degree and a piezoelectric constant d_{33} value of 39.7% and 68 pC/N, respectively.

$BaTiO_3$ (BT) crystal ($a_o = 3.992$ Å, $c_o = 4.036$ Å at room temperature) [7] was often chosen as templates for some perovskite sys-

tems such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ textured ceramics [8] owing to both similar structures, and chemical stability at high temperature. Remeika fabricated $(0\,0\,1)$ oriented tabular BT particles with a high chemical stability in KF solution [9]. However, large Remeika BT templates (average diameters >75 μm) resulted in extremely coarse microstructure and thus too low mechanical strength for most applications [8]. With regard to the synthesis of finer platelike BT particles (5–10 μm in diameter and 0.5 μm in thickness), Liu et al. synthesized BT platelets from $BaBi_4Ti_4O_{15}$ precursor by TMC method [10] and Su et al. also reported tabular BT prepared from $Bi_4Ti_3O_{12}$ (BIT) precursor by the same method [11]. Furthermore, Su et al. successfully enhanced performances of $0.94Na_{0.5}Bi_{0.5}TiO_3$–$0.06BaTiO_3$ textured ceramics using the BT templates [12]. Unfortunately, it was never successfully applied in textured KNN based ceramics although it seems to be an ideal candidate template as far as its composition and structure are concerned. In the previous reports, the KNN–BT ceramics, whose composition was located at the boundary of orthorhombic and tetragonal phases, were found to exhibit excellent piezoelectric properties [13].

In this study, the tabular BT templates were synthesized from BIT precursors, and then used to make textured KNN ceramics by RTGG method. First, we circumstantiate the change of phase

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structure and microstructure in the development of KNN ceramics during sintering. Then, we contrasted the electric properties of textured KNN ceramics samples in the direction parallel (//) and perpendicular (⊥) to the tape casting plane.

2. Experimental procedures

Platelike BT particles were prepared by a topochemical microcrystal conversion (TMC) method. First, Bi_2O_3 (⩾99.0%) and TiO_2 (⩾99.0%) as raw materials were mixed with the equal qualities of mixed molten salt (NaCl (⩾99.5%) and KCl (⩾99.5%) in a molar ratio of 1:1) and heated at 1100 °C for 6 h to synthesize plate-like BIT particles. The product was washed with distilled water many times. Secondly, platelike BT particles were prepared from obtained BIT and excessive $BaCO_3$ (⩾99.0%) (in a molar ratio of 1:10) at 1020 °C for 3 h in the mixed molten salt.

The equiaxed $NaNbO_3$ and $KNbO_3$ particles as matrix materials were prepared from Na_2CO_3 and Nb_2O_5 or K_2CO_3 and Nb_2O_5 via a calcination process twice at 750 °C for 3 h, respectively. The matrix materials, 6 mol% platelike $BaTiO_3$ particles and 2 mol% CuO as a sintering aid were mixed with a solvent (mixed solvent of ethanol and toluene (1/2 by molar ratio)), dispersant (triethyl phosphate, Sinopharm Chemical Reagent), plasticizers (dibutyl phthalate, Sinopharm Chemical Reagent) and binder (poly(vinyl butyral), Sinopharm Chemical Reagent) in turn to form a slurry. The slurry was degassed under vacuum and tape cast at 6.25 cm/s with a blade opening of 250 μm. After 24 h of drying at room temperature, the green tapes were cut, laminated into a multilayer sheet approximately 1.5 mm thick under a pressure of 60 MPa at 80 °C for 20 min. After removing organic substances from the green compacts by heating at 600 °C for 10 h in air, the textured KNN ceramics were prepared by sintering at 1110–1150 °C for 15–30 h in air. Random matrix KNN ceramics without CuO as a sintering aid were prepared through a conventional solid-state method.

The density of sintered samples was measured by using the Archimedes method. The phase structure and the Lotgering factor $F_{(00l)}$ were detected at room temperature by an X-ray diffractometer (XRD, D/Max-RB, Rigaku, Tokyo, Japan) using a Cu Kα1 radiation on polished sample surfaces (//). The microstructure of the samples (⊥) (shown in Fig. 1) was observed using a scanning electron microscope (SEM, SSX-550, Shimadzu, Kyoto, Japan). Before the SEM observation, the fractured surface was polished and etched by heating at 1030 °C for 30 min. Dielectric properties were measured as a function of temperature by an LCR meter (HP 4980A, Agilent, USA). Polarization versus electric field hysteresis (P–E) curves were measured by a ferroelectric measuring system (Precision LC, Radiant Technologies Inc., Albuquerque, NM). For measuring piezoelectric and electromechanical properties, samples were poled in stirring silicone oil at 110 °C under a dc field of 3.5 kV/mm for 30 min, and then cooled in the electric field. The piezoelectric constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinoceram, Yangzhou, China). The planar electromechanical coupling factor k_p was determined by a resonance–antiresonance method with an impedance analyzer (HP4192A, Hewlett–Packard, USA).

3. Results and discussion

Fig. 2 shows the morphology and XRD pattern of BT template particles synthesized by TMC method. All the diffraction peaks can be readily indexed to a perovskite-structured BT phase (JCPDS 05-0626), indicating that the obtained product is highly crystallized phase of pure BT. Moreover, it can be found that the (100) and (002) diffraction peaks were enhanced to some extent, indicating that the BT templates should be (100) faceted. The SEM image of BT particles (see the inset in Fig. 2) indicates a platelike particle morphology with a thickness of 1–1.5 μm and a mean diameter of 10–15 μm (the aspect ratio was approximately
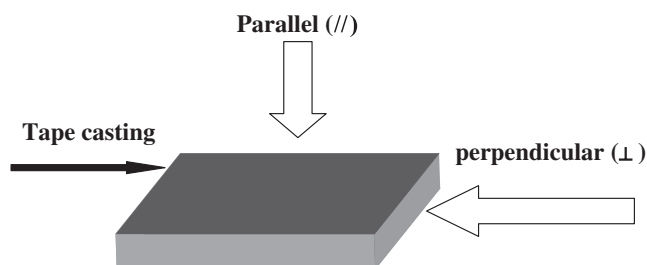

Fig. 1. A schematic view of parallel and perpendicular directions to the tape casting.
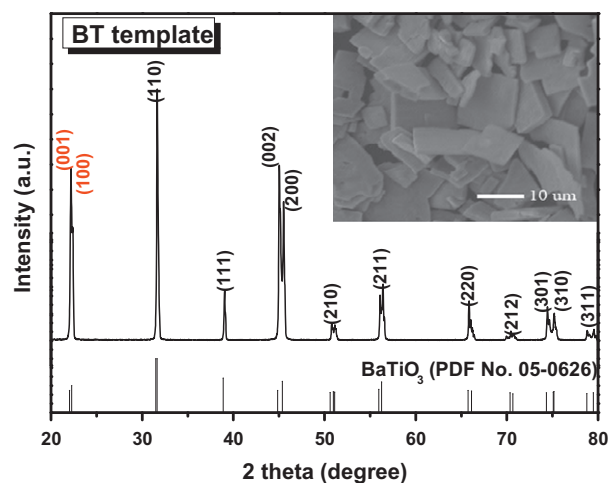

Fig. 2. XRD pattern of the BT template particles synthesized by DMSS (inset is the corresponding SEM image).

7–15). Thus, these seeds can be easily aligned or oriented under the applied shear force during tape-casting.

Fig. 3a shows the XRD patterns of KNN samples (//) using BT templates sintered at various temperatures for 15 or 24 h. All patterns show characteristic diffraction peaks of perovskite structures. Moreover, the coexistence of the orthorhombic and tetragonal phases can be clearly seen from the split (200) peaks, indicating the formation of KNN–BT solid solutions. It can be seen that the increase of sintering temperature has induced an orthorhombic–tetragonal phase transition. The impurity phases of $Ba_6Ti_2Nb_8O_{30}$ and $KTiNbO_5$ can be found in the textured ceramics, which also existed in the random KNN–BT solid solutions [14]. These phases can be related to the volatilization of Na_2O at higher sintering temperatures. The (110) diffraction lines are the strongest in the specimen heated at 1110 °C. The relative intensity of (100) and (200) peaks increases as the heating temperature is increased, reflects the texture degree in the (100) direction. The calculated Lotgering factor f of the (100) orientation was shown in Table 1.

The main difference in the phase structure of different samples can be easily detected in {200} reflection lines near 45°. To obtain a precise phase analysis, the {200} reflection lines (solid lines) were fitted using Pearson-VII function as shown in Fig. 3b. Because of the complexity between orthorhombic and tetragonal phase (totally four peaks for (200) diffraction lines and a certain degree overlap of the (200) peaks), the distinct phase boundary is difficult to distinguish. But, according to the real intensity values (Fig. 3a), the ideal orthorhombic and tetragonal symmetry and multiplicity factor for compositions with coexistence of orthorhombic and tetragonal phases, the content of tetragonal phases (F_T) can be calculated by the following equations: $I_{Small-Brag} = 1/3SI_T + 2/3SI_O$, $I_{Large-Brag} = 2/3SI_T + 1/3SI_O$, and $F_T = SI_T/(SI_T + SI_O)$ [15], where $I_{Small-Brag}$ and $I_{Large-Brag}$ are the intensities of (200) peaks with small Brag angles and large Brag angles, respectively, and SI_T and SI_O are the sums of peak intensities for tetragonal and orthorhombic phases, respectively. The F_T values for textured ceramics sintered under different conditions are listed in Table 1.

At 1110 °C for 15 h, KNN–BT solid solution ceramics were formed through the reaction between the matrix materials and BT templates (F_T = 44.37%), but the oriented grain growth did not occur (f = 0). It is thought that, in this stage, the contact area between the BT template and the matrix materials is not sufficiently large to allow for the oriented grain growth. Considering that the relative density is too low (<90%). As sintering at 1130 °C for 15 h, the f value of the as-prepared ceramics increases abruptly
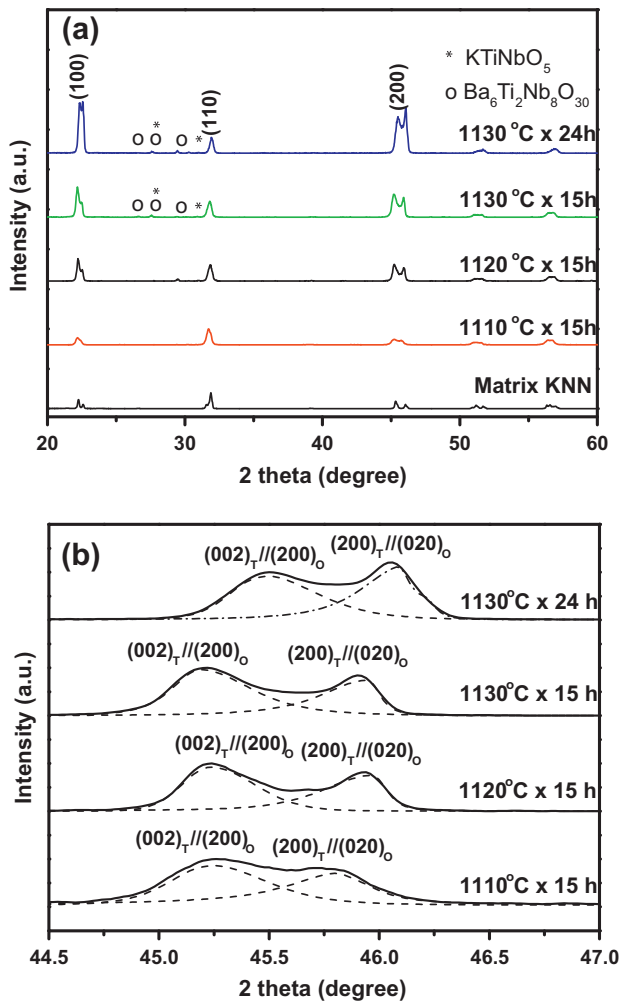
Fig. 3. (a) XRD patterns of random and textured KNN ceramics using BT templates (//) at different sintering conditions and (b) fitted (2 0 0) lines near $2\theta = 46°$ (solid lines denote original experimental results and dash lines fitted lines).

to 64% and the sample density reaches above 90%. At this stage, the oriented grain growth was still accompanied by the reaction of the BT templates with the matrix materials. Further elongating the sintering time to 24 h at 1130 °C would increase the f value and relative density up to 80% and 94%, respectively. But the F_T value of 52.49% is found to be lower than the F_T value of 0.94KNN–0.06BT (76.20%) [13], which indicates that the oriented grain growth occurs on the surface of the BT template before completion of the formation of KNN–BT solid solutions. The F_T value of 52.49% also indicates that the composition of the as-prepared textured ceramics would be between 0.97KNN–0.03BT ($F_T = 41.8\%$) and 0.96KNN–0.04BT ($F_T = 67.4\%$) [13]. The relationship between the oriented grain growth and the formation of KNN–BT solid solution is quite

Table 1
Relative densities, Lotgering factors and contents of tetragonal phases at different sintering conditions.

Sintering condition		Relative density (%)	Degree of orientation f (%)	F_T (%)
Temperature (°C)	Time (h)			
1110	15	83	0	43.37
1120	15	88	23	44.02
1130	15	92	64	44.69
1130	24	94	80	52.49

similar to that in KNN textured ceramics by platelike $NaNbO_3$ templates [4].

The microstructure on the surface (⊥) shown in Fig. 4 reveals that the KNN grains were textured by the growth of BT template grains at the expense of the matrix compositions. Fig. 4a shows the microstructure of the specimen heated at 1110 °C for 15 h. It can be seen that the matrix was only partially densified without visible templated grain growth. With increasing the sintering temperature and time the growth of template grains continues, whereas the volume of matrix grains decreases (Fig. 4b), and the specimen is finally composed of large brick-like grains and a little amount of small matrix grains (Fig. 4c). These characteristics, such as an abrupt increase in the degree of orientation, the formation of large brick-like grain in the matrix of small grains and the presence of pores, are quite similar to those observed in (K, Na, Li)(Nb, Ta)O_3 ceramics textured by platelike $NaNbO_3$ template grains [16] and in BT ceramics textured by platelike $Ba_6Ti_{17}O_{40}$ hetero-template grains [17], in which the abnormal grain growth acts as a dominant mechanism for the texture evolution.

Fig. 5 shows the temperature dependence of dielectric constant (ε_r) at 10 kHz for textured KNN ceramic cuts (// and ⊥) using BT templates sintered at 1130 °C for 24 h. It is obvious that the textured KNN ceramic cuts all exhibit two phase transition temperatures: the orthorhombic–tetragonal polymorphic phase transition (T_{o-t}) and the tetragonal–cubic ferroelectric phase transition (T_C). But, there is an obvious anisotropy in the two cuts. The perpendicular cuts show lower T_{o-t}, T_c and ε_r values than the parallel cuts. In particular, the T_{o-t} value of the perpendicular cuts moves below room temperature and at the same time the phase transition at T_C becomes more broadening. Furthermore, it is to be noted that there is an obvious dielectric anomaly near 400 °C in the perpendicular cuts, which illustrated that the composition fluctuation and the structure fluctuation become more obvious in the perpendicular ones. This abnormal dielectric peak can originate from the some matrix grains which keep the compositions of the stoichiometric KNN, because these KNN grains do not react with BT templates. Moreover, because of larger particle size and larger ion sizes of the BT templates, Ba^{2+} and Ti^{2-} ions are difficult to diffuse into the matrix grains, which results in the low BT content and low F_T value in the place far away from the templates regions.

As well known, a perovskite ceramic spontaneous polarization is along the [0 0 1] and [1 1 0] directions for the tetragonal symmetry and orthorhombic symmetry phases respectively [7]. According to the SEM and XRD results, an anisotropic response of the polarization can be expected between the (//) and (⊥) cuts of the textured KNN ceramics. Moreover, the highest polarization values should be found in the (//) cuts, for compositions with coexistence of tetragonal and orthorhombic phases, and, in the (⊥) cuts, for some matrix grains which keep the compositions of the stoichiometric KNN without reacting with BT templates. The P–E hysteresis loops at room temperature for textured KNN ceramic cuts (// and ⊥) sintered at 1130 °C for 24 h are shown in Fig. 6. The remnant polarization $P_r = 29.5\ \mu C/cm^2$ was obtained in the (//) cuts, which was much higher than the P_r value (14.4 $\mu C/cm^2$) in the (⊥) cuts. It is an expected result that shows a very high anisotropy in the ferroelectric properties between the (//) and (⊥) cuts. And the anisotropy is higher than that observed for the textured KNN ceramics using $NaNbO_3$ templates [18], for compositions with orthorhombic phases. This strong anisotropy in the hysteresis loops was already observed in the other textured ceramics [19–21].

The effect of the change in the crystal structure of textured ceramics will be obvious in electrical properties. Table 2 summarizes the dielectric and piezoelectric properties of random and textured KNN ceramics. Textured KNN ceramics using BT templates sintered at 1130 °C for 24 h have a lower T_c of 320 °C than random matrix KNN ceramics. This is mainly because both the
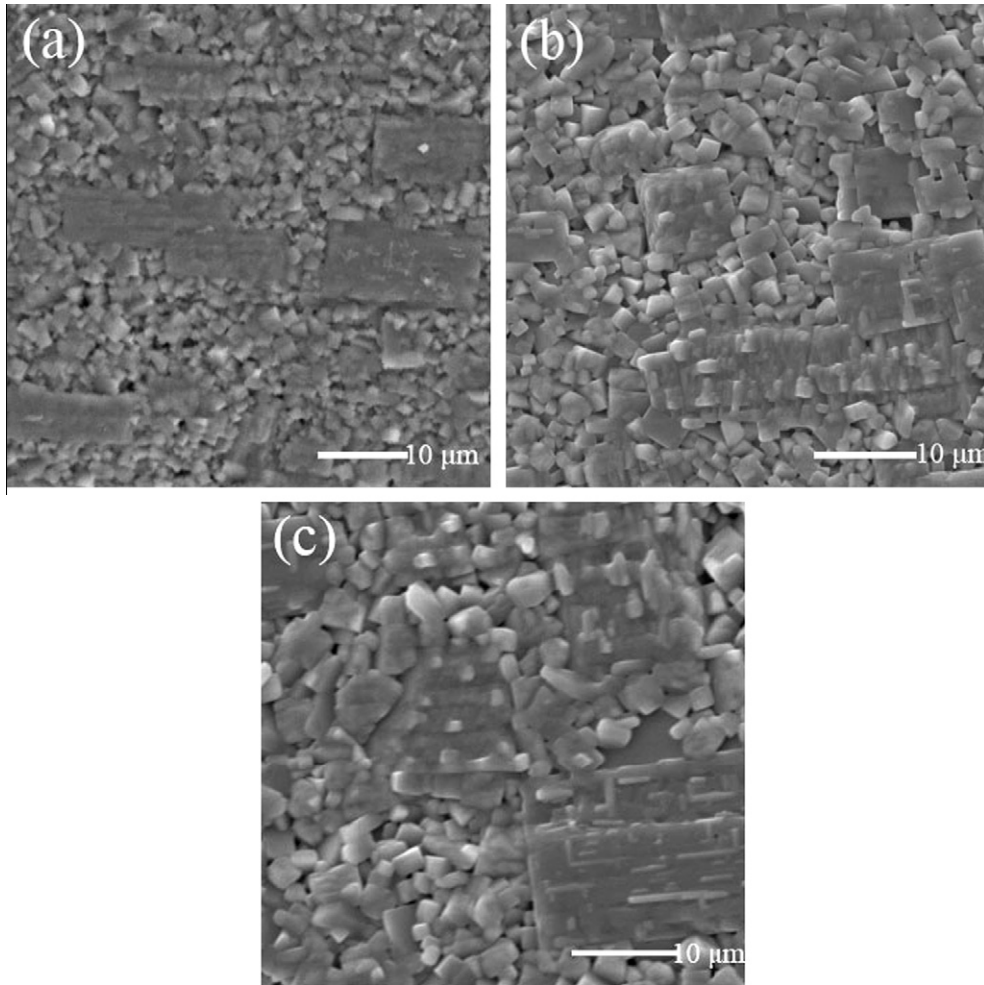
Fig. 4. SEM images of textured ceramics (⊥) heated at different conditions: (a) 1110 °C for 15 h; (b) 1130 °C for 15 h and (c) 1130 °C for 24 h.
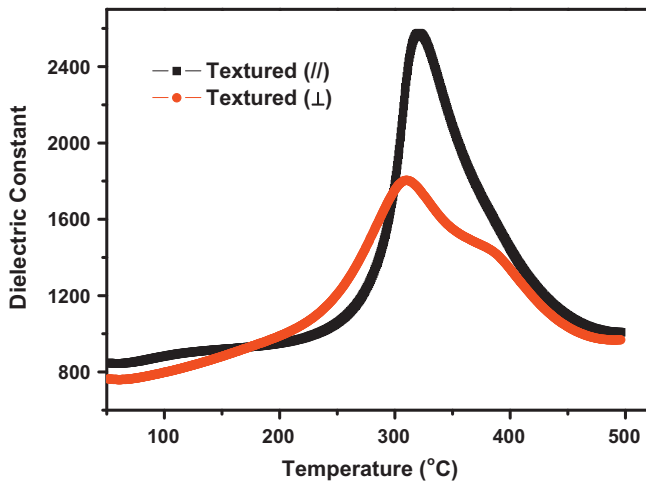

Fig. 5. Temperature dependence of dielectric constant at 10 kHz for textured ceramics sintering at 1130 °C for 24 h (// and ⊥).

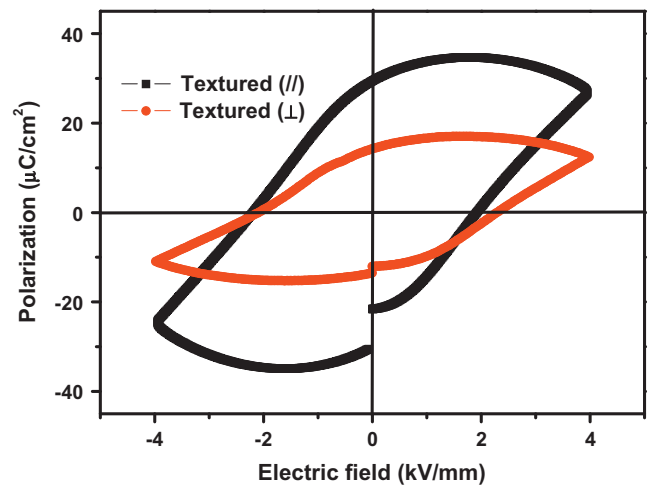**Fig. 6.** P–E hysteresis loops of textured ceramics sintering at 1130 °C for 24 h (// and ⊥).

formation of KNN–BT solid solutions and usage of CuO a sintering aid [22] would lead to the reduction of the T_c value. Textured KNN ceramics using BT templates exhibit substantially twice higher dielectric constant ε_r (810), 40% higher piezoelectric constant d_{33} (163 pC/N) and 20% higher electromechanical coupling factor k_p (0.37) than random KNN ceramics. However, because of the lower

content of BT in the final textured ceramics and the deviation away from the orthorhombic and tetragonal phase coexistence zone, their d_{33} value was lower than that of the 0.95KNN–0.05BT ceramics. Moreover, the lower densification ability for the textured ceramics would be another reason. The piezoelectric properties

Table 2
Electrical properties of random and textured ceramics.

	T_c (°C)	ε_r (10 kHz)	d_{33} (pC/N)	k_p
0.95KNN–0.05BT [13]	320	–	225	0.36
Matrix KNN	420	362	115	0.30
Textured (//)	320	810	163	0.37
Textured (⊥)	310	732	89	0.14

between the perpendicular-cuts and parallel-cuts samples show very high anisotropy. The piezoelectric properties of the perpendicular-cuts are considerable low.

4. Conclusions

The platelike BT templates were applied for the first time to make (0 0 1)-textured KNN ceramics by RTGG method. It is found that the formation of KNN–BT solid solutions between BT templates and matrix materials was accompanied by the templated grain growth during sintering. The increase of sintering temperature and time tend to induce an orthorhombic–tetragonal phase transition near room temperature. It is indicated that the dominant mechanism of the texture development can be the abnormal grain growth in the textured KNN ceramics. A high (0 0 1) orientation degree of 80% is achieved as the sample was sintered at 1130 °C for 24 h and the excellent electrical properties of ε_r = 810, d_{33} = 163 pC/N, and k_p = 0.37 are reached. Moreover, the textured ceramics show anisotropic electrical properties in the (// and ⊥) cuts. The (⊥) cuts have lower T_{o-t}, T_c, ε_r and P_r values than the (//) cuts.

Acknowledgements

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