



(Reactive) Templated Grain Growth of Textured Sodium Bismuth Titanate ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$) Ceramics—II Dielectric and Piezoelectric Properties

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Abstract. ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-BaTiO}_3$ (<6.5% BaTiO_3) ceramics with $\langle 001 \rangle_{\text{pc}}$ orientation were fabricated by Templated Grain Growth (TGG) or Reactive Templated Grain Growth (RTGG) using tabular SrTiO_3 template particles. The maximum electrically-induced strain was 0.26% at 70 kV/cm. d_{33} coefficients over 500 pC/N were obtained for highly textured samples ($f \sim 90\%$) when driven at high electric fields. Under these conditions, the materials show considerable hysteresis in the strain—field response, even after poling. Berlincourt piezoelectric coefficients for the same samples gave d_{33} of 200 pC/N.

Keywords: texture, sodium bismuth titanate, piezoelectric, dielectric, template grain growth

Introduction

Sodium bismuth titanate-barium titanate, ($\text{Na}_{1/2}\text{Bi}_{1/2}$)- $\text{TiO}_3\text{-BaTiO}_3$ (NBT-BT), is a potentially important lead-free piezoelectric material because single crystals at the morphotropic phase boundary (i.e., ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$) have been shown to have comparatively high piezoelectric response [1]. ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-BaTiO}_3$ ceramics have a lower density than lead zirconate titanate (PZT) and solid solutions of lead magnesium niobate and lead titanate (6 g/cm³ vs. 7.5–8.5 g/cm³) and higher elastic moduli (100–110 GPa vs. 60–80 GPa in PZT) [1]. Consequently, rhombohedrally distorted ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-BaTiO}_3$ single crystals have been reported to have an actuation energy density 1.4 times greater than polycrystalline $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) [2].

($\text{Na}_{1/2}\text{Bi}_{1/2}$) TiO_3 has a relatively high Curie temperature ($T_c \sim 230^\circ\text{C}$) and a large remanent polarization (38 $\mu\text{C}/\text{cm}^2$) [3]. In the $\langle 001 \rangle_{\text{pc}}$ direction, a d_{33} coefficient as high as 450 pC/N [1] has been reported

for flux grown single crystals at the morphotropic phase boundary with BaTiO_3 [4]. Undoped, polycrystalline ($\text{Na}_{1/2}\text{Bi}_{1/2}$) TiO_3 ceramics on the other hand, have been reported to have d_{33} values of 125 pC/N [3]. If the reported single crystal properties can be achieved in a ceramic, while simultaneously reducing the level of hysteresis [1], the resulting material would be an attractive alternative for lead-based piezoelectrics. One approach to achieving this economically is to texture a polycrystalline sample. The generation of macroanisotropy in ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$ ceramics by TGG was the focus of part I.

The electromechanical properties of single crystal ($\text{Na}_{1/2}\text{Bi}_{1/2}$) $\text{TiO}_3\text{-5.5 mol\% BaTiO}_3$ are anisotropic and the electromechanical properties are largest along $\langle 001 \rangle_{\text{pc}}$, as is the case for many rhombohedrally-distorted perovskites [2]. Therefore, ceramics with grains oriented along $\langle 001 \rangle_{\text{pc}}$ should display higher electromechanical properties than randomly oriented ceramics. This paper reports the electrical and piezoelectric properties of $\langle 001 \rangle$ textured NBT-BT ceramics with compositions near the morphotropic phase boundary as a function of composition and the degree of texture.

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Experimental Procedure

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics were textured using either SrTiO_3 platelets (TGG approach) or $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT) platelets (RTGG approach). Both TGG and RTGG approaches resulted in $\langle 001 \rangle_{\text{pc}}$ textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics. Details of sample preparation procedures were described in [5]. As a reference, randomly-oriented ceramics were made by sintering matrix powder at 1200°C for 12 h without any template addition. It was found that the weight loss from the sample at 1200°C was 0.6% after a 1 min hold and 1% after a 12 h hold. To minimize the impact of this nonstoichiometry on the properties, at least $250\ \mu\text{m}$ of material was removed from the top and bottom surfaces before measurements. Thus, $\langle 001 \rangle_{\text{pc}}$ oriented surfaces were first fine polished using 5000 grit paper and then sputtered with Pt for electrical property measurements. As a result, no compositional gradient was detected by microprobe analysis across the sample thickness. A multi-frequency meter (HP 4284A LCR meter) was used in conjunction with a computer-controlled temperature chamber (Delta Design Inc., Model MK 9023) to measure the dielectric constant as a function of temperature on heating and cooling (0 to 475°C) at frequencies between 1 and 100 kHz. Samples were heated and cooled at $2^\circ\text{C}/\text{min}$. The samples were poled by applying 60 kV/cm at 100°C for 15 min and then cooling to room temperature while maintaining the field. Berlincourt d_{33} measurements were made on poled samples.

Simultaneous polarization (P) and strain (S) hysteresis curves were measured up to 80 kV/cm on $\langle 001 \rangle_{\text{pc}}$ textured ceramics using a computer-controlled modified Sawyer Tower system and a linear variable displacement transducer (LVDT) sensor driven by a lock in amplifier (Stanford Research Systems, Model SR830). Electric fields as high as 80 kV/cm were applied using an amplified triangular wave form at 0.2 Hz, using a Trek 609C-6 high voltage DC amplifier. During testing, the samples were submerged in Flourinert (FC-40, 3M, St. Paul, MN), an insulating liquid, to prevent arcing. The same system was used to measure unipolar strain of poled $\langle 001 \rangle_{\text{pc}}$ textured ceramics, with a unipolar wave form. The value of d_{33} was determined from the decreasing slope of the unipolar strain vs. electric field curve from 0 to 10 kV/cm.

Results and Discussion

X-Ray Diffraction Analysis

Ferroelectric $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ with low BaTiO_3 concentrations has rhombohedral symmetry ($R3c$) with a small rhombohedral distortion ($90^\circ - \alpha < 0.05^\circ$) at room temperature [6]. The structure of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ solid solution becomes tetragonal with increasing BaTiO_3 concentration. The MPB (morphotropic phase boundary) is located at $\sim 5.5\ \text{mol}\%$ BaTiO_3 [3].

The rhombohedral distortion close to the MPB was checked with textured samples in order to determine if the presence of SrTiO_3 affected the position of the MPB. Figure 1 shows the variation of the (200) peaks with BaTiO_3 doping and SrTiO_3 . Diffraction data were collected at 0.01° steps with a hold of 13 seconds at each step. The $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ samples are predominantly rhombohedral in the composition range

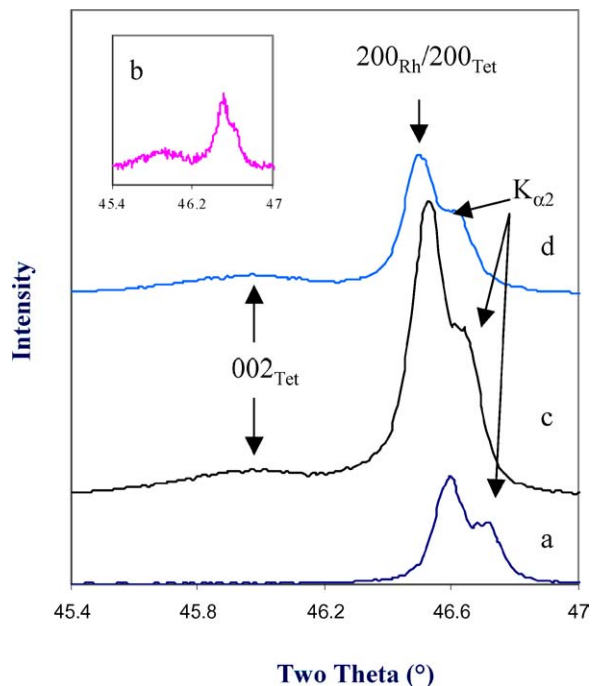


Fig. 1. (a) (200) X-ray pattern of SrTiO_3 templates, (b) randomly oriented $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol}\%$ BaTiO_3 , (c) textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-5.5 mol}\%$ BaTiO_3 , and (d) textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-6.5 mol}\%$ BT ceramics (textured ceramics contain 5 vol% SrTiO_3 templates), sintered at 1200°C for 12 h.

studied, although the weak broad peaks at lower 2θ angles might indicate a small amount of tetragonal phase.

High Field Electrical Properties of Textured ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ Ceramics-Polarization

The polarization vs. electric field curves for undoped and 5.5 mol% BaTiO_3 doped samples were reasonably square and saturated, as seen in Fig. 2. A small leakage contribution is evident from the rounding of the tops of the loops, especially in the random samples. As expected, textured ceramics have lower remanent polarizations than randomly oriented ceramics.

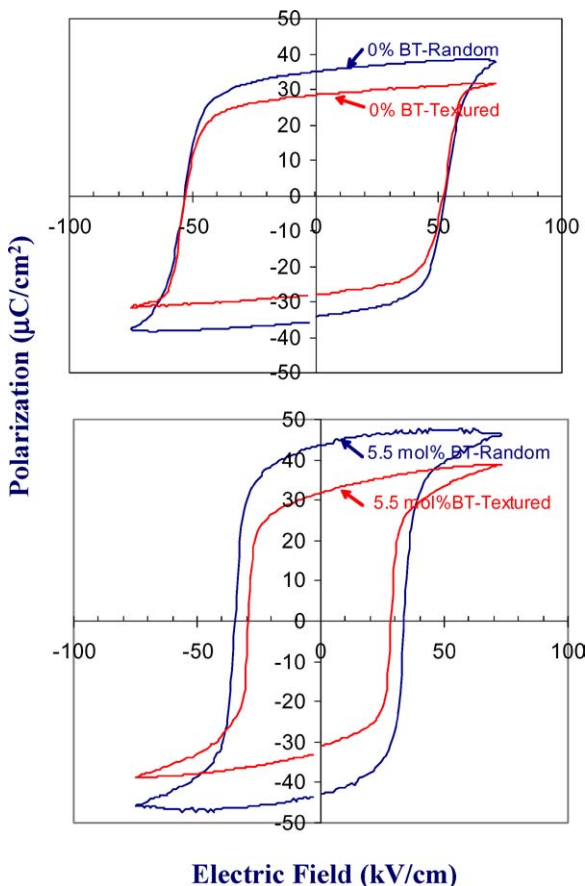


Fig. 2. Polarization vs. electric field for randomly oriented and textured (5 vol% SrTiO_3) ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-5.5 mol% BaTiO}_3$ ceramics. All samples were sintered at 1200°C for 12 h.

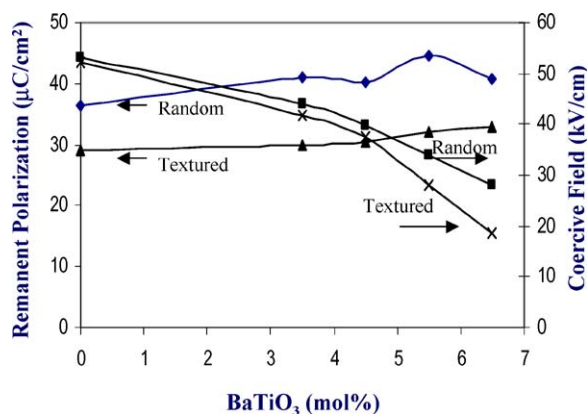


Fig. 3. Polarization and coercive field of randomly oriented and textured (5 vol% SrTiO_3) ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ ceramics as function of BaTiO_3 content (sintered at 1200°C for 12 h).

The variation of the polarization and the coercive field as a function of BaTiO_3 content for randomly oriented ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ ceramics is shown in Fig. 3. Undoped ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$) has a remanent polarization of $36 \mu\text{C}/\text{cm}^2$ and a coercive field of $53 \text{ kV}/\text{cm}$. The coercive field of undoped ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$) is large compared to lead-based ferroelectrics like PZT and PMN-PT ceramics. Coercive fields up to $73 \text{ kV}/\text{cm}$ have been reported in the literature for NBT-BT ceramics [3, 4]. It is therefore difficult to pole samples. For compositions close to the MPB (5.5 mol% BaTiO_3), the remanent polarization increases to $45 \mu\text{C}/\text{cm}^2$ and the coercive field decreases to $34 \text{ kV}/\text{cm}$. The remanent polarization and coercive field values for NBT-BT ceramics containing 6.5 mol% BaTiO_3 were $41 \mu\text{C}/\text{cm}^2$ and $28 \text{ kV}/\text{cm}$, respectively. The maximum remanent polarization of $45 \mu\text{C}/\text{cm}^2$ was achieved for ceramics at the MPB of 5.5 mol% BaTiO_3 NBT-BT.

The remanent polarization and coercive field for ($\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-BaTiO}_3$ ceramics textured with 5 vol% SrTiO_3 template particles are plotted as a function of BaTiO_3 content in Fig. 3. The remanent polarization of a $(001)_{\text{pc}}$ oriented rhombohedral single crystal must be $1/\sqrt{3} P_{\text{S}}$. In randomly oriented ceramics, $(001)_{\text{pc}}$ is randomly distributed in 3-D space. The angle between the measurement direction and the polarization direction ($(111)_{\text{pc}}$) varies from 0 to 54.7° , with equal pole density in between. For textured ceramics, the angle between the measurement direction (texture direction) and polarization direction ($(111)_{\text{pc}}$) is about 54.7° [5], similar to the $(001)_{\text{pc}}$ oriented rhombohedral

single crystal case. Therefore, due to the averaging of polarization of each domain in 3-D space, randomly oriented ceramics have a higher P_r than $\langle 001 \rangle_{pc}$ textured materials.

In textured ceramics, ~ 5 vol% SrTiO_3 templates persist due to the limited interdiffusion at the sintering temperature. Since SrTiO_3 is a non-ferroelectric phase, its contribution to the switchable polarization is negligible. Thus, the remanent polarizations of the textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics were decreased by the smaller polarizable volume of the templates. It is also possible that the dielectric and elastic mismatch between the template and the matrix reduce the efficiency of polarization reversal.

The coercive fields of randomly oriented and textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics using 5 vol% SrTiO_3 template particles are shown in Fig. 3. Undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics (random or textured) have similar coercive fields (~ 52 kV/cm), whereas at compositions close to the MPB, textured ceramics have appreciably lower coercive fields than randomly oriented ceramics. The coercive field of randomly oriented $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics was 34 kV/cm, whereas it was 28 kV/cm for textured ceramics with the same amount of BaTiO_3 doping. The difference between the coercive fields of randomly oriented and textured ceramics with 6.5 mol% BaTiO_3 doping level was ~ 10 kV/cm.

Different levels of texture in $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics were obtained by keeping the sintering temperature fixed at 1200°C and varying the sintering time from 1 min to 12 h. Densities were greater than 90% (up to 98%) for all samples sintered longer than 1 h. Since those samples have comparable densities, the polarization was more or less determined by texture fraction alone. It was observed that sintering for 1 h resulted in a polarization of $33 \mu\text{C}/\text{cm}^2$ for NBT-BT with a Lotgering factor of 69%. This polarization is lower than that of the randomly oriented ceramic ($45 \mu\text{C}/\text{cm}^2$), as explained above. Further increases in sintering time resulted in a higher texture fraction and therefore slightly lower polarization values. Sintering for 12 h resulted in a remanent polarization of $32 \mu\text{C}/\text{cm}^2$ with a Lotgering factor of 94%. It is important to note that the decreasing polarization is opposite to that the expected based on increased sample density. From microprobe analysis only 0.7 mol% SrTiO_3 diffused into the NBT-BT matrix. Thus, the decrease in remanent polarization with increasing texture fraction cannot be related to Sr diffusion alone.

Electromechanical Properties

The piezoelectric coefficients of randomly oriented and textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics from Berlincourt measurements are given in Table 1. In all cases, the textured samples show superior properties. As expected, the properties peak near the MPB. At that composition, the low field piezoelectric coefficient was $d_{33} \sim 200$ pC/N, appreciably higher than the data for the random sample at the MPB (110 pC/N). It is not clear why the d_{33} values for the random NBT ceramics are lower than literature reports of 125 pC/N [3].

In order to assess how useful these materials would be in actuator applications, measurements were also made of the strain response under high electric field excitation. Figure 4 shows the variation of the maximum electrically-induced strain of randomly oriented ceramics as a function of BaTiO_3 content. Samples were sintered at 1200°C for 12 h. Undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ reached 0.06% strain at 50 kV/cm and 0.09% strain at 70 kV/cm. For $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 , maximum strains of 0.12% at 50 kV/cm and 0.17% at 70 kV/cm were obtained in random ceramics.

In Fig. 5, unipolar strain measurements are shown for textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics. Figure 6 shows the variation of maximum strain of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics as a function of BaTiO_3 content. In all cases, 5 vol% SrTiO_3 templates were added, and samples were sintered at 1200°C for 12 h. The highest strains obtained for textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 were 0.16% strain at 50 kV/cm and 0.26% strain at 70 kV/cm. The

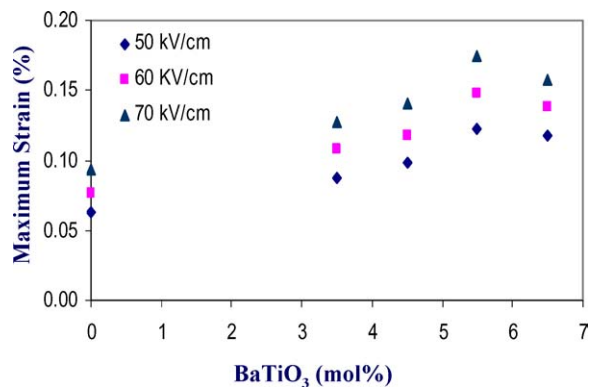


Fig. 4. Unipolar maximum strain of randomly oriented ceramics plotted as a function of BaTiO_3 content (sintered at 1200°C for 12 h).

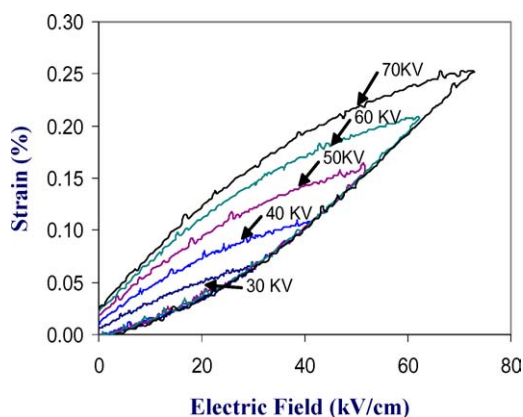


Fig. 5. Unipolar maximum strain of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5% BaTiO_3 ceramics textured with 5 vol% SrTiO_3 .

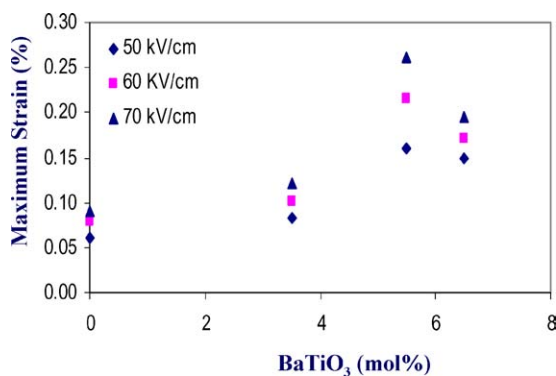


Fig. 6. Unipolar maximum strain of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics textured with 5 vol% SrTiO_3 plotted as function of BaTiO_3 content.

0.26% strain is 62% higher than for random ceramics and close to the maximum strain of 0.3% of single crystals of similar composition [1].

Figure 7 shows the piezoelectric coefficient of randomly oriented ceramics as a function of BaTiO_3 content. d_{33} was estimated from the slope of the unipolar strain vs. electric field E curve. First, a unipolar electric field was applied, and then, a linear fit was made to the 0 to 10 kV/cm segment of the decreasing electric field curve. The d_{33} coefficients of undoped random $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics ranged between 120 pC/N at 30 kV/cm and 170 pC/N at 70 kV/cm. The highest d_{33} was obtained for random $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics, which showed d_{33} coefficients between 230 pC/N at 30 kV/cm and 360 pC/N at 70 kV/cm. In all cases, these values are substantially higher than the low field numbers shown in Table 1.

Table 1. Piezoelectric coefficients of randomly oriented and SrTiO_3 templated $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics from Berlincourt measurements.

mol% BaTiO_3	d_{33} random (pC/N)	d_{33} textured (pC/N)	% Increase
0	65	95	46
3.5	90	110	22
4.5	95	110	16
5.5	110	200	82
6.5	105	170	62

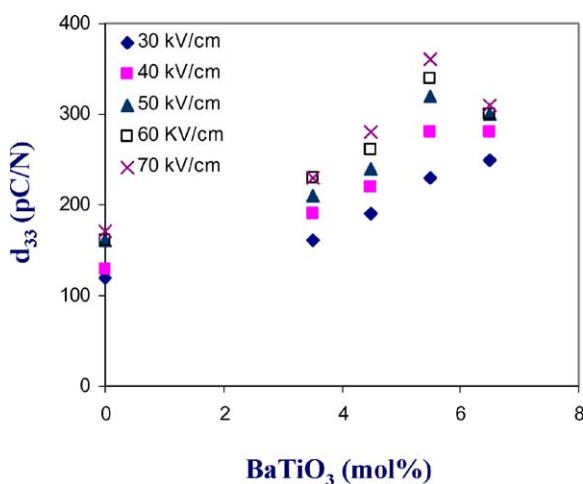


Fig. 7. d_{33} coefficients of random ceramics plotted as a function of BaTiO_3 content.

Figure 8 shows the variation of the piezoelectric coefficient of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics (5 vol% SrTiO_3) as a function of BaTiO_3 content. Textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics showed d_{33} coefficients from 120 pC/N at 30 kV/cm to 150 pC/N at 70 kV/cm. Again, the highest d_{33} values were obtained for $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 textured ceramics, which showed large signal d_{33} coefficients between 270 pC/N at 30 kV/cm and 520 pC/N at 70 kV/cm (Berlincourt value ~ 200 pC/N). A d_{33} of 520 pC/N is 44% higher than random ceramics and close to the 450 pC/N reported for single crystals of similar composition [1]. Since the d_{33} coefficients for ceramics are unlikely to be larger than single crystal values with similar domain status, it is likely that the higher value is due to the higher hysteresis in the textured ceramics. This would be consistent with the substantial field dependence of the piezoelectric coefficient. It does, however, draw into question whether the high field

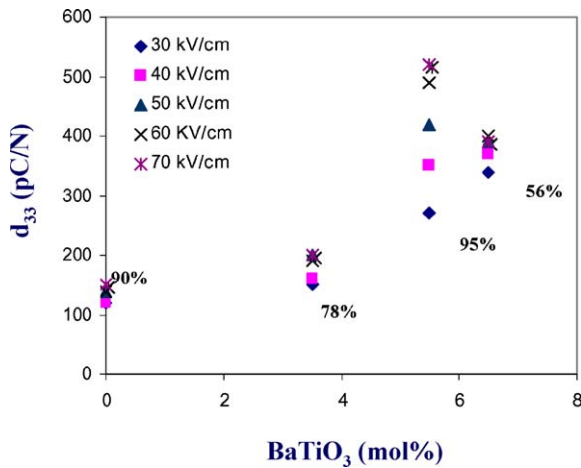


Fig. 8. d_{33} coefficients of textured ceramics plotted as function of BaTiO_3 content (sintered at 1200°C for 12 h with 5 vol% SrTiO_3 templates). Numbers specify amount of texture (Lotgering factor).

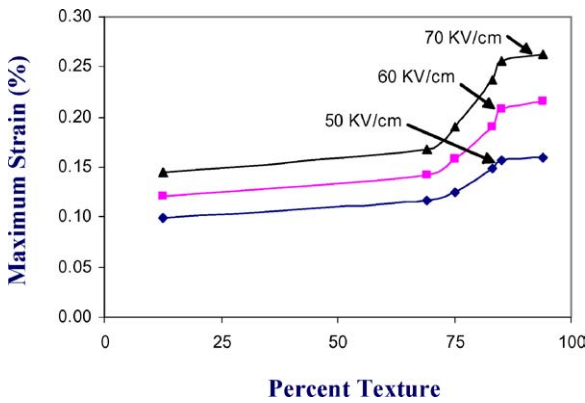


Fig. 9. Unipolar maximum strain of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics textured with 5 vol% SrTiO_3 plotted as function of Lotgering factor.

numbers reported for flux grown crystals are similarly inflated [1].

Figure 9 shows the maximum unipolar strain of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics textured with 5.5 vol% SrTiO_3 template particles plotted as function of Lotgering factor. It seems that for texture fractions lower than 70%, the maximum strain shown is a weak function of texture. For texture fractions greater than 70% the maximum strain shown by the sample starts to increase when measured for the same driving field. The sample with 94% texture shows 0.26% strain when measured at 70 kV/cm.

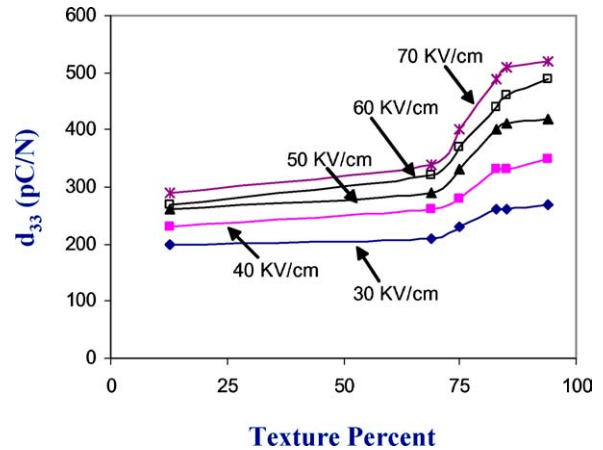


Fig. 10. d_{33} coefficient of textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics textured with 5 vol% SrTiO_3 plotted as function of Lotgering factor, sintered at 1200°C for 12 h.

Figure 10 shows the variation of the d_{33} coefficient of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics sintered at 1200°C for 12 h with 5 vol% SrTiO_3 template particles. d_{33} coefficients were measured from the slope of unipolar strain-electric field curve as explained above. Measurements were performed at electric fields between 30 and 70 kV/cm. Piezoelectric coefficients for 70% textured ceramics were similar to coefficients of random ceramic (i.e., $\sim 360 \text{ pC/N}$ @ 70 kV/cm). Ceramics with high texture ($f > 70\%$) showed enhanced actuation (d_{33}). The highest d_{33} coefficient (520 pC/N) was obtained for the ceramic with 94% texture.

Hysteresis in $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 Ceramics

In all cases, the unipolar strain curves were accompanied by substantial hysteresis. Two approaches were taken to quantify the hysteresis. First, the hysteresis in the strain response was normalized, that is the maximum opening in the increasing and decreasing electric field curves was divided by the maximum strain in the sample. Secondly, the large signal $\tan \delta$ was calculated as in [7]. The results as a function of composition are given in Fig. 11 for a driving electric field of 70 kV/cm. The first point to notice is that textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics were less hysteretic than the randomly oriented ceramics. The normalized hysteresis and large signal $\tan \delta$ for textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics were 15 and

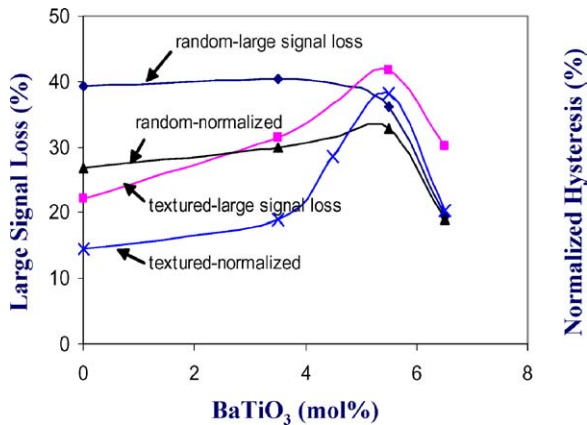


Fig. 11. Comparison of large signal dielectric loss factor and normalized hysteresis at 70 kV/cm for random and textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics with different BaTiO_3 contents.

22%, respectively. In contrast, the normalized hysteresis and large signal $\tan \delta$ for randomly oriented $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics were 27 and 39%, respectively. For undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics the coercive field is high (~ 52 kV/cm) and almost the same for random and textured ceramics (Fig. 3).

The amount of hysteresis was also tracked as a function of the amplitude of the driving field. For undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$, textured samples were less hysteretic than randomly oriented samples for all field levels investigated (30 to 70 kV/cm). Thus, at 70 kV/cm, the large signal $\tan \delta$ was 22 and 39% for textured and randomly oriented ceramics, respectively. Textured samples with MPB compositions were less hysteretic than the randomly oriented samples only if the driving fields were below the coercive field (< 40 kV/cm). When the driving fields exceeded the coercive field (> 50 kV/cm), the hysteresis for the textured MPB composition was large compared to the random sample. Thus, at 30 kV/cm, the large signal $\tan \delta$ was 20 and 32% for textured and randomly oriented ceramics, respectively. At 70 kV/cm, the large signal $\tan \delta$ was 42 and 36% for textured and randomly oriented ceramics, respectively. It is believed that there are two competing mechanisms at work. Orientation control favors low hysteresis, whereas ease of domain movement, due to the low coercive field of textured ceramics, increases the hysteresis.

Chiang et al. [1] reported that 5.5 mol% BaTiO_3 doped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ single crystals showed 0.24% free strain at 60 kV/cm. A normalized hysteresis of about 20% was reported for the same sample.

In the $\langle 001 \rangle_{\text{pc}}$ direction, a d_{33} coefficient as high as 450 pC/N [1] was reported. In contrast, textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics reached 0.26% strain at 70 kV/cm, which is 62% higher than random ceramics. A d_{33} coefficient of 520 pC/N, accompanied by high hysteresis, was measured.

It is clear from the review of the literature that the largest piezoelectric coefficients observed to date in $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -based single crystals are coupled with substantial hysteresis [1]. One possible cause for high hysteresis in the unipolar strain curve is related to the high temperature ferroelastic phase transition. The ferroelastic domain structure is set at high temperature, and does not move with electric field. It is possible that the presence of this domain structure imposes some type of restoring force on the ferroelectric domain walls, so that an electric field applied to the rhombohedral phase only temporarily moves the domain boundary. If the field is removed, the original domain configuration may be recovered, yielding appreciable hysteresis. An alternative explanation is that the electric field required to induce a phase transition is low in the $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ - BaTiO_3 system. This would be consistent with the substantial poling strain observed in the work of Chiang and co-workers [1]. If so, then the extent of hysteresis should depend on the proximity of the sample composition to the MPB.

A third possibility is that some of the hysteresis is associated with either microheterogeneity or large concentrations of point defects. This is reasonable in $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ due to the volatility of Na, Bi, and O. In NBT ceramics, A site vacancies can be formed due to vaporization of Na and/or Bi from the perovskite lattice and lead to V'_{Na} or $V'''_{\text{Bi}}-(V_{\text{O}}^{\bullet\bullet})$ defect dipole formation. One of the consequences of defect dipole formation is that domain boundary motion might be partially pinned, becoming mobile only when substantial electric fields are applied, and thus, contribute to the high levels of hysteresis.

Dielectric Properties

In this section, all dielectric properties are reported at 1 kHz unless otherwise noted. Ceramics were poled before measurement and the loss $\tan \delta$ was about 1% for all samples. Sample densities were $> 96\%$ of theoretical. Undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ has a room temperature dielectric constant of ~ 350 . For compositions close to the morphotropic phase boundary, the

dielectric constant increases and the highest dielectric constants were measured for $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -6.5 mol% BaTiO_3 ceramics. The room temperature dielectric constant for randomly oriented ceramics was ~ 750 whereas the dielectric constant for a textured ceramic with the same composition was ~ 950 . The maximum dielectric constant, measured for 5.5 mol% BaTiO_3 doped ceramics, was $\varepsilon_{\text{max}} \approx 6600$ for randomly oriented ceramics and $\varepsilon_{\text{max}} \approx 5800$ for textured ceramics.

The transition temperatures (T_{tr}) were obtained based on dielectric property measurements. The transition from rhombohedral to tetragonal for undoped $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ starts at $\sim 230^\circ\text{C}$ [3]. In our measurements, this transition temperature was lower than reported in the literature because of the presence of Mn (0.3 wt% MnCO_3) doping to increase the resistivity and enhance grain growth. A T_{tr} of $\sim 184^\circ\text{C}$ was measured for randomly oriented ceramics, whereas a T_{tr} of $\sim 146^\circ\text{C}$ was measured for textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ ceramics with 5 vol% SrTiO_3 templates. The further lowering of the transition temperature with texturing may be attributed to dissolution of the small SrTiO_3 template particles (0.7 mol% SrTiO_3 was detected in the matrix). In all of the compositions studied, T_{tr} was lower for textured ceramics than randomly oriented ceramics. All the measurements were done on heating of poled ceramics.

Figure 12 shows the dielectric constant vs. temperature behavior of randomly oriented and textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 (5 vol% SrTiO_3 template particles) ceramics sintered at 1200°C for 12 h. The rhombohedral-tetragonal transition temperature for randomly oriented and textured ceramics were 125 and 105°C , respectively. The rhombohedral-tetragonal transition temperature of textured samples did not change with sintering time. The maximum dielectric constant was also suppressed for the textured ceramic relative to the random materials, probably due to the presence of a low dielectric constant phase, i.e., SrTiO_3 template particles.

It was found that the room temperature dielectric constant of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics textured using 5 vol% SrTiO_3 template was a relatively weak function of texture fraction. The dielectric constant increases with increasing texture fraction from ~ 510 for randomly oriented ceramic to ~ 650 for 94% textured ceramics, with the majority of the rise occurring for $f > 75\%$. The maximum dielectric constant of many rhombohedral ferroelectric perovskites

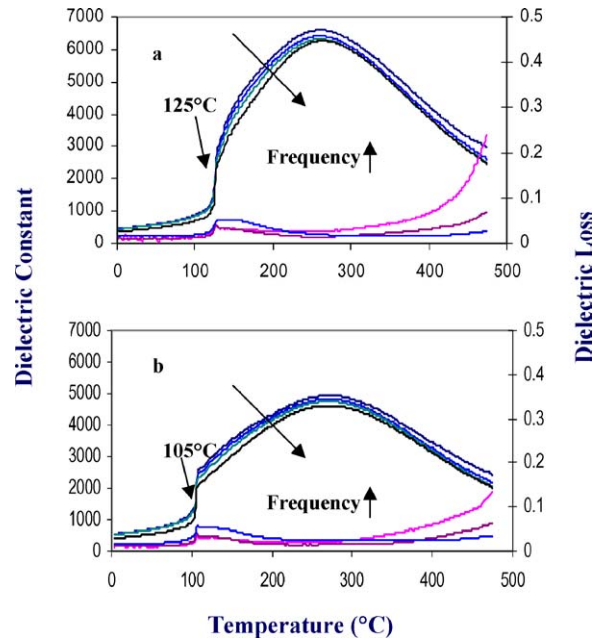


Fig. 12. Dielectric constant at 1, 10, 100, and 1000 kHz vs. temperature for (a) randomly oriented and (b) textured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics, sintered at 1200°C for 12 h and measured on heating. Dielectric loss is reported at 1, 10 and 100 kHz.

is observed in the direction perpendicular to the polarization direction [9]. So, for the textured ceramic, the maximum dielectric constant is located 35.3° away from the measurement direction. However, for the randomly oriented ceramic, in which the pole density of maximum dielectric constant is equal in all directions, the averaging of the dielectric constant in all possible directions resulted in a lower dielectric constant than textured ceramics.

Electrical Properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Templated $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 Ceramics

The objective in studying the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ templated ceramic was to compare the electrical properties to the ceramic textured using SrTiO_3 templates. The $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 composition was textured using 6 vol% $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ template particles. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ templated systems were very sensitive to the pre-reaction condition.

In Fig. 13 the dielectric constant measured as a function of temperature for textured and untextured $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics is given.

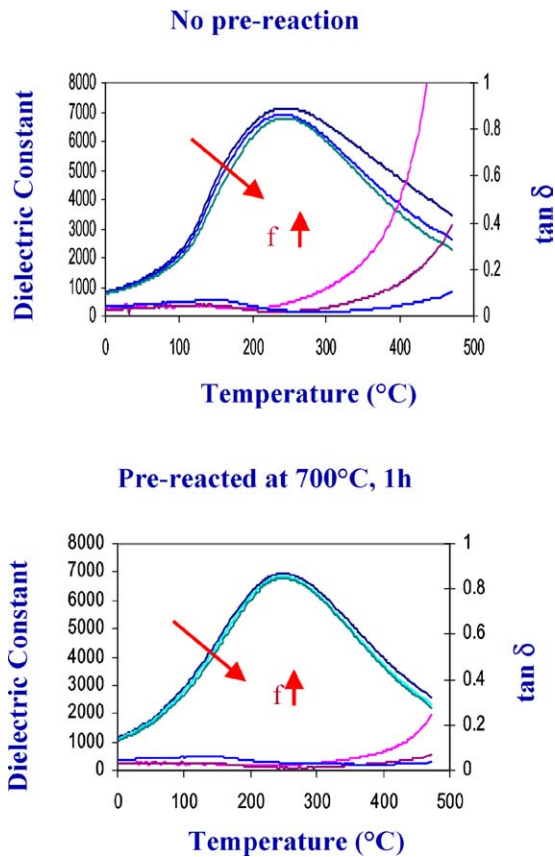


Fig. 13. Dielectric constant of $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics: (a) randomly oriented ceramics and (b) textured using 6 vol% $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ template particles. Data reported for 1, 10, and 100 kHz.

These measurements were performed for unpoled ceramics. The room temperature dielectric constant for the textured ceramic (~ 1400) was higher than the randomly oriented ceramics (~ 1000), as is expected. The maximum dielectric constants and the corresponding T_{max} for textured and untextured ceramics were 7000–250°C and 7100–245°C, respectively.

The amount of texture in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ templated systems is dependent on the pre-reaction temperature and time. The unipolar strain curves for ceramics prepared using different pre-reaction conditions are given in Fig. 14. Those ceramics were all sintered at 1200°C for 12 h. However, two of them were pre-reacted at either 700 or 800°C for 1 h before they were heated to the sintering temperature. Ceramics that were directly heated to the sintering temperature did not develop any texture. The maximum unipolar strain in this random sample was $\sim 0.15\%$ with a d_{33} of ~ 260 pC/N

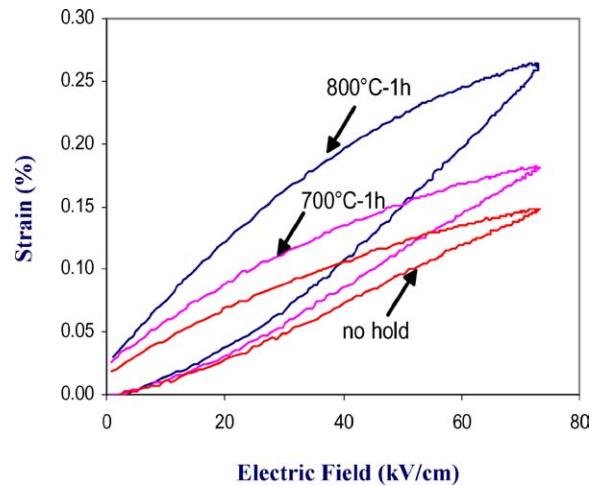


Fig. 14. Unipolar strain curves of three $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ -5.5 mol% BaTiO_3 ceramics at different pre-reaction conditions.

at 70 kV/cm. However, pre-reacted ceramics were 80% textured. The ceramic that was pre-reacted at 800°C for 1 h had a maximum unipolar strain of $\sim 0.26\%$ with a d_{33} of ~ 490 pC/N at 70 kV/cm.

It should be noted that for the textured ceramics, the unipolar strain curve is more hysteretic. This result is consistent with the hysteresis behavior of SrTiO_3 templated MPB composition ceramics, where textured ceramics were more hysteretic than randomly oriented ceramics. The normalized hysteresis for the $\sim 80\%$ textured ceramic was $\sim 34\%$, whereas it was $\sim 28\%$ for untextured ceramics. Untextured ceramics obtained either by sintering the matrix powder without any template particles or by sintering $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ templated ceramics without any pre-reaction yield similar unipolar maximum strain ($\sim 0.15\%$) and normalized hysteresis ($\sim 30\%$). At 70 kV/cm, the large signal $\tan \delta$ was 20% for an untextured (no hold) ceramic, and 25 and 34% for textured ceramics pre-reacted at either 700 or 800°C for 1 h, respectively.

Conclusions

$(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics with 0 to 6.5 mol% BaTiO_3 were textured using 5 vol% SrTiO_3 template particles. Texture fractions up to 94% were obtained. There is a good correlation between texture fraction and the electrical and electromechanical properties but significant enhancements in the properties were not observed until the texture fraction exceeded 70%.

$\langle 001 \rangle_{pc}$ oriented rhombohedral single crystals show high strain and piezoelectric coefficients. The same is also valid for $\langle 001 \rangle_{pc}$ oriented rhombohedral $(\text{Na}_{1/2}\text{Bi}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics. Piezoelectric coefficients higher than randomly oriented ceramics, but close to the single crystal values, were obtained. The highest piezoelectric coefficient of 520 pC/N was measured for a textured sample with 5.5 mol% BaTiO_3 doping, on the rhombohedral side of the MPB. Considerable hysteresis in the strain response was observed. Possible reasons for the hysteresis include partial pinning of the domain structure by ferroelastic walls, point defects, and the possibility of a field-forced phase transition. The Berlincourt piezoelectric coefficient for the same sample was $d_{33} \sim 200$ pC/N, confirming that a substantial fraction of the piezoelectric response measured in unipolar strain curves was associated with domain wall motion.

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