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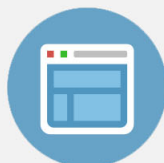
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Complete set of material constants of $0.95(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - 0.05BaTiO_3 lead-free piezoelectric single crystal and the delineation of extrinsic contributions

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Lead-free piezoelectric single crystal $0.95(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ (NBT)- 0.05BaTiO_3 was grown by top-seeded solution growth method, which has rhombohedral symmetry with composition near morphotropic phase boundary. Full set of dielectric, piezoelectric, and elastic constants for $[001]_c$ poled domain-engineered single crystal was determined. Excellent electromechanical properties and low dielectric loss ($d_{33} = 360 \text{ pC/N}$, $d_{31} = -113 \text{ pC/N}$, $d_{15} = 162 \text{ pC/N}$, $k_{33} = 0.720$, $k_t = 0.540$, and $\tan \delta = 1.1\%$) make it a good candidate to replace lead-based piezoelectric materials. The depolarization temperature ($T_d = 135^\circ\text{C}$) is the highest among all NBT-based materials and its electromechanical coupling properties are very stable below T_d . Extrinsic contributions to piezoelectric properties were investigated by Rayleigh analysis. © 2013 AIP Publishing LLC.

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Research on lead-free piezoelectric materials has gained momentum over the last decade because almost all piezoelectric materials in use today are lead based, while both Pb and PbO produced during the fabrication process are toxic. Among all lead-free piezoelectric materials up to date, the sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ (NBT) based material is one of the most promising candidates due to its large remnant polarization, high Curie temperature, and relatively good piezoelectric properties.^{1,2}

Among these NBT-based solid solutions, BaTiO_3 (BT) modified NBT system, $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - $x\text{BaTiO}_3$ (NBBT) is the most attractive, showing excellent piezoelectric properties when the composition is near the rhombohedral-tetragonal morphotropic phase boundary (MPB) with $x = 0.06 - 0.07$.³⁻⁵ Although the exact composition of the MPB is still under debate, the best piezoelectric and dielectric properties are always obtained near the composition of $x = 0.06 - 0.07$.⁶⁻⁸ It has been reported that the piezoelectric constant d_{33} of In_2O_3 doped 0.93NBT - 0.07BT ceramic is as high as 205 pC/N .² In order to obtain higher piezoelectricity through domain engineering strategy, growth of larger size NBBT single crystals are extensively studied in recent years. Relatively high longitudinal piezoelectric coefficient, dielectric constant, and thickness electromechanical coupling factor were reported for NBBT single crystals.^{1,9-12} For device design and theoretical analysis on domain engineering, it is necessary to know the complete set of dielectric, piezoelectric, and elastic properties of NBBT single crystals. However, in the literature, only longitudinal dielectric constant ϵ_{33}^T , piezoelectric coefficient d_{33} and d_{31} , and the thickness electromechanical coupling factor k_t have

been reported, other components of dielectric, piezoelectric, and elastic tensors properties have not been measured up to date. In fact, there is not even one complete set of dielectric, piezoelectric, and elastic constants for NBT materials in the literature. It is well known that piezoelectric properties can be divided into intrinsic and extrinsic contributions.^{13,14} In order to gain further insight into the nature of high piezoelectric activities in domain engineered single crystal, it is necessary to delineate the level extrinsic contributions.

In this letter, we report the growth of high quality NBBT single crystal with the size of 35 mm in diameter and 12 mm in height from which a complete set of materials coefficients were measured. We have also delineated the extrinsic contributions to the enhanced piezoelectric effect in domain engineered multidomain NBBT single crystal.

Although the NBBT system with the composition of $x = 0.06 \sim 0.07$ exhibits the best piezoelectric and dielectric properties, the structure of the MPB composition is complicated due to the coexistence of two phases, so that the properties are difficult to control.^{4,15} For this reason, we chose to grow NBBT single crystal with the composition of $0.95(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - 0.05BaTiO_3 (NBBT95/5), which has pure rhombohedral structure but close to the MPB, therefore, high piezoelectric performance can be expected.

The NBBT95/5 single crystal was grown by the top-seeded solution growth method. Powders of Na_2CO_3 , Bi_2O_3 , TiO_2 , and BaCO_3 with purity of 99.99% were used as raw materials. They were mixed in proper proportions and calcined at 1000°C for 10 h in air. The obtained polycrystalline powders were mixed with excess 30 mol. % Bi_2O_3 and Na_2CO_3 as self-fluxes and put into a Pt crucible, which was heated in a resistance furnace up to melt ($\sim 1400^\circ\text{C}$), then kept for 2 h to ensure that the melt became stable. A $[001]_c$ oriented NBT seed was used to pull the crystal out of the

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TABLE I. Measured and derived constants of NBBT95/5 single crystal poled along $[001]_c$ (Density: $\rho = 5777 \text{ kg/m}^3$).

Elastic stiffness constants: c_{ij}^E and c_{ij}^D (10^{10} N/m^2)											
c_{11}^E *	c_{12}^E	c_{13}^E	c_{33}^E *	c_{44}^E *	c_{66}^E *	c_{11}^D	c_{12}^D	c_{13}^D	c_{33}^D *	c_{44}^D *	c_{66}^D
15.9	9.5	7.5	8.1	7.5	7.8	16.0	9.6	7.1	11.4	9.4	7.8
Elastic compliance constants: s_{ij}^E and s_{ij}^D ($10^{-12} \text{ m}^2/\text{N}$)											
s_{11}^E *	s_{12}^E	s_{13}^E	s_{33}^E *	s_{44}^E	s_{66}^E	s_{11}^D	s_{12}^D	s_{13}^D	s_{33}^D *	s_{44}^D	s_{66}^D
12.2	-3.4	-8.2	27.7	13.4	12.9	10.8	-4.8	-3.7	13.3	10.7	12.9
Piezoelectric coefficients: $e_{i\lambda}$ (C/m^2), $d_{i\lambda}$ (10^{-12} C/N), $g_{i\lambda}$ (10^{-3} Vm/N), and $h_{i\lambda}$ (10^8 V/m)											
e_{15}	e_{31}	e_{33}	d_{15} *	d_{31} *	d_{33} *	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
12.1	-1.7	12.0	162	-113	360	16.7	-12.5	39.8	15.6	-3.9	27.7
Dielectric constants: ε_{ij} (ε_0) and β_{ij} ($10^{-4}/\varepsilon_0$)						Electromechanical coupling factors					
ε_{11}^T *	ε_{33}^T *	ε_{11}^S *	ε_{33}^S *	β_{11}^T	β_{33}^T	β_{11}^S	β_{33}^S	k_{15} *	k_{31} *	k_{33} *	k_t *
1099	1021	877	489	9.1	9.8	11.4	20.4	0.449	0.341	0.720	0.540

*Directly measured properties.

melt at the rate of $0.1 \sim 0.15 \text{ mm/h}$, and the pulling rod was rotated with an angular velocity of $10\text{--}20 \text{ rpm}$. After the growth was completed in $2\text{--}3$ days, the crystal was cooled down to room temperature at the rate of 40°C/h .

The density of the crystal determined by the Archimedes' method is 5777 kg/m^3 . Based on the measurement using inductively coupled plasma mass spectrometer (ICP-MAS), the BaTiO_3 content is around 0.05 . All samples were cut from the same single crystal and poled at room temperature along $[001]_c$ pseudo-cubic direction under a field of 30 kV/cm for 10 min . The dielectric constant was determined using an HP 4284A multi-frequency LCR meter, and the resonance and antiresonance frequencies were measured using an Agilent 4294A impedance-phase analyzer. Piezoelectric coefficients and electromechanical coupling factors were determined based on the IEEE piezoelectric standard. A piezo- d_{33} meter (ZJ-2) was also used to estimate the d_{33} value, which is often larger than the value measured by the resonance method. The electric-field-induced strain was measured at 1 Hz frequency, using a linear variable differential transducer driven by a lock-in amplifier (Stanford Research system, Model SR830).

The spontaneous polarization of the NBBT single crystal in the rhombohedral phase is along the eight $\langle 111 \rangle_c$ pseudo-cubic directions. After poling along $[001]_c$, only four of the eight spontaneous polarizations ($[111]_c$, $[\bar{1}\bar{1}1]_c$, $[\bar{1}1\bar{1}]_c$, and $[1\bar{1}\bar{1}]_c$) are left. The effective macroscopic symmetry of the multidomain NBBT95/5 sample becomes tetragonal 4mm , which has a total of 11 independent material constants, i.e., 6 elastic, 3 piezoelectric, and 2 dielectric constants. The combined resonance and ultrasonic methods were used to determine the complete sets of the elastic, dielectric, and piezoelectric constants.^{16–18}

The complete set of elastic, piezoelectric, and dielectric constants of the NBBT95/5 single crystal poled along $[001]_c$ are listed in Table I. Material constants marked with star (*) were determined directly by the resonance or ultrasonic measurements, others were derived constants. Of particular interest is the high piezoelectric coefficients of this crystal: $d_{33} = 360 \text{ pC/N}$, $d_{31} = -113 \text{ pC/N}$, $d_{15} = 162 \text{ pC/N}$, and the

high electromechanical coupling factors: $k_{33} = 0.720$ and $k_t = 0.540$. The longitudinal piezoelectric coefficient d_{33} measured by the piezo- d_{33} meter at 60 Hz is 420 pC/N , which is much higher than that obtained by the resonance method. Based on our experience, the directly measured value using the piezo- d_{33} meter is usually higher than that determined by the resonance method because the sample geometry does not meet the requirement of the standard test sample. These piezoelectric properties are comparable to the popular $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT) piezoelectric ceramics, hence, the NBBT95/5 single crystal can be used to replace lead based piezoelectric materials in many practical applications.

Figure 1 shows the dielectric constant and dielectric loss as a function of temperature for unpoled and poled $[001]_c$ oriented NBBT95/5 single crystal. At room temperature, both dielectric constant and dielectric loss for the unpoled sample are higher than those of the poled sample. There are two dielectric abnormalities in the measured temperature

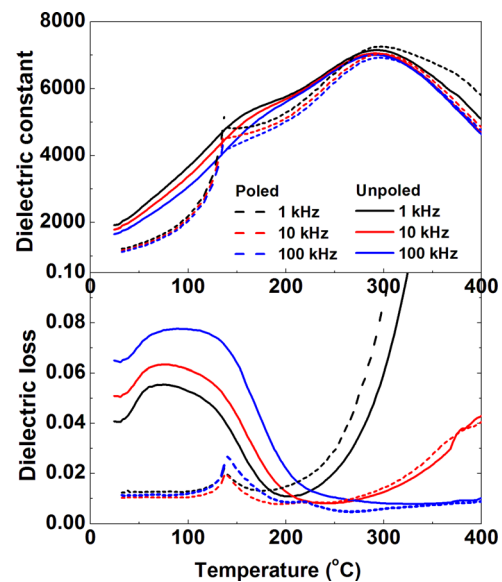


FIG. 1. Temperature dependence of dielectric constant and dielectric loss for unpoled sample and (b) poled sample of NBBT95/5 single crystal.

range for both unpoled and poled samples. For the unpoled sample, the dielectric abnormality at around 160 °C is generally regarded as the ferroelectric to anti-ferroelectric phase transition, called T_{F-A} .^{5,19} The dielectric peak at 295 °C (called T_m) corresponds to the anti-ferroelectric to paraelectric phase transition. For the poled sample, the sharp increase of the dielectric constant at around 135 °C (called T_d) corresponds to the randomization of domain structures, leading the disappearance of the piezoelectric properties, while T_m is the same as that of the unpoled sample.

The temperature dependence of lateral electromechanical coupling factor k_{31} was measured by the resonance method in the temperature range of 0 °C–140 °C and the piezoelectric coefficient d_{31} is calculated according to the formula: $d_{31} = k_{31} \sqrt{s_{11}^E \epsilon_{33}^T}$. As shown in Fig. 2, k_{31} increases slightly from 0.331 to 0.453 as the temperature increases from 0 °C to 130 °C, showing good temperature stability. On the other hand, the increase of d_{31} with temperature is much more intense compared with k_{31} , from 105 pC/N at 0 °C to 303 pC/N at 130 °C, due to the rapid increase of dielectric constant ϵ_{33}^T . The increase of piezoelectric properties should be ascribed to the combined effect of easier domain wall motion and the softening of lattice structures at higher temperatures. Both k_{31} and d_{31} reach their maximum values at 130 °C, and then drastically decrease to zero at 135 °C, indicating the disappearance of piezoelectricity at T_d , at which the aligned domain structure with 4 mm symmetry becomes randomized due to the back switching of domains caused by poling generated strain.

We found that the depolarization temperature T_d (135 °C) of the NBBT95/5 single crystal is about 20–30 °C lower than that of T_{F-A} . This phenomenon was also found in other NBT-based materials.^{20,21} This may be understood as follows: Internal stresses were formed during poling induced domain switching, so that the poled state is in a metastable state with increased elastic energy. As temperature increases, polar vector rotation and domain wall motions become easier, the system will try to minimize the elastic energy by back switching to the random state. This can explain the fact that the depolarization temperature T_d is always lower than the ferroelectric-antiferroelectric phase transition temperature T_{F-A} .

Table II lists some important parameters of our NBBT95/5 single crystal. Corresponding parameters of some reported NBT-based materials with similar composition and PZT ceramics are also listed in the table for comparison. It

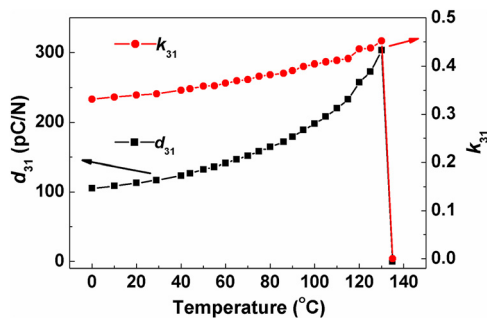


FIG. 2. Temperature dependence of lateral piezoelectric coefficient d_{31} and electromechanical coupling factor k_{31} of NBBT95/5 single crystal.

TABLE II. Comparison of some important coefficients for several NBT-based ceramics and single crystals poled along $[001]_c$.

Materials	d_{33} (pC/N)	d_{33}^* (pC/N)	k_t	ϵ_{33}^T	$\text{tg}\delta$	T_d (°C)
NBBT95/5 crystal ^a	420	360	0.54	1021	0.011	135
NBBT94/6 crystal (Ref. 9)	360	...	0.62	1710	0.021	120
NBBT95/5 crystal (Ref. 10)	280	...	0.50	1050	0.023	130
NBBT96/4 crystal (Ref. 12)	283	...	0.50	1230	0.018	131
NBBT94/6 ceramics (Ref. 3)	122	...	0.40	601	0.018	100
PZT (Ref. 22)	223	...	0.51	730	0.004	386

* d_{33} determined by the resonance method.

^aThis work.

should be pointed out that the d_{33} values reported by others are all measured by the piezo- d_{33} -meter, which often over estimates the piezoelectric d_{33} coefficient. It can be seen from Table II that our NBBT95/5 single crystal possesses significantly higher piezoelectric property, lower dielectric loss, higher electromechanical coupling factors, and higher depolarization temperature. Considering such excellent piezoelectric and electromechanical coupling properties, low dielectric loss, and relatively high depolarization temperature, our NBBT95/5 lead-free single crystal is a very attractive candidate to replace lead-based materials in many practical applications.

In order to understand domain wall contributions to the piezoelectric response in the $[001]_c$ poled NBBT95/5 domain engineered single crystal, we have performed Rayleigh analysis. The Rayleigh law can be expressed as follows:²³

$$s(E) = (d_{\text{init}} + \alpha E_0)E \pm \alpha(E_0^2 - E^2)/2, \quad (1)$$

$$d(E_0) = (d_{\text{init}} + \alpha E_0), \quad (2)$$

where $S(E)$ is the electric-field-induced strain, E_0 is the amplitude of the electric field, and $d(E_0)$ is the piezoelectric coefficient under E_0 , d_{init} is the intrinsic portion of the piezoelectric coefficient, and the coefficient “ α ” is the irreversible Rayleigh parameter, resulting from the irreversible motion of internal interfaces (e.g., domain walls and phase boundaries). The term αE_0 represents the extrinsic contribution to the total piezoelectric response.²⁴ The piezoelectric coefficient d_{33} can be calculated from the slope of the unipolar strain measured at small amplitudes as shown in Fig. 3. The

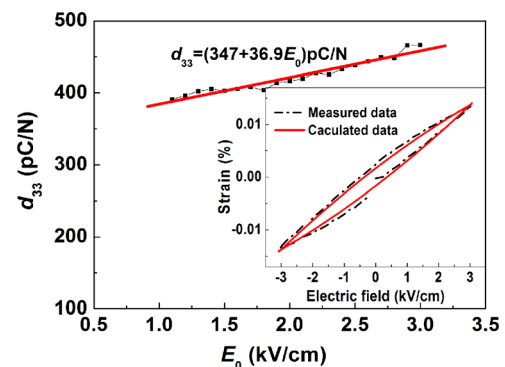


FIG. 3. Electric field dependence of piezoelectric coefficient d_{33} of NBBT95/5 crystal at 1 Hz. The inset shows the comparison between the measured and calculated strain vs. electric field hysteresis loop.

parameter d_{init} and α can be obtained by fitting the d_{33} curve using Eq. (2), which were found to be 347 pm/V and 36.9 cm/kV, respectively. One may conclude from this result that the extrinsic contribution to the piezoelectric response is on the order of 10% under the applied field of 1 kV/cm and 24% under the field level of 3 kV/cm. In comparison, the extrinsic contributions for the NBBT95/5 single crystals is much higher than that in PbTiO₃-based relaxor single crystals,^{24–26} indicating the easy motion of domain walls in NBBT95/5 under external electric field. The composition of the crystal in this study is near the MPB composition, which is partly responsible for the high extrinsic contribution in this system.^{24,27} From the obtained d_{init} and α , the strain-electric field loop was calculated according to Eq. (1) and is given in the inset of Fig. 3, showing excellent agreement with the actual measured data.

In summary, we have grown a large size high quality lead-free piezoelectric NBBT95/5 single crystal by the top seeded solution growth method, which is in the rhombohedra phase. Using samples cut from this compositionally uniform single crystal, the full set of dielectric, piezoelectric, and elastic constants for [001]_c poled multidomain NBBT95/5 single crystal have been determined by combined resonance and ultrasonic method. This complete set of material coefficients will be of great help for theoretical analysis on this lead-free system and can facilitate simulation design of electromechanical devices using this lead-free piezoelectric material. The [001]_c poled NBBT95/5 multidomain single crystal show large piezoelectric effect ($d_{33} = 360$ pC/N, $d_{15} = 162$ pC/N, and $d_{31} = -113$ pC/N), high electromechanical coupling factors ($k_{33} = 0.720$ and $k_t = 0.540$), low dielectric loss ($\tan \delta = 1.1\%$), and relatively high depolarization temperature ($T_d = 135^\circ\text{C}$). Hence, the crystal is a very promising lead-free material to replace PZT piezoelectric ceramic for many electromechanical device applications. By using the Rayleigh analysis, we have extracted the extrinsic contribution from experimental data, which shows that the extrinsic contributions in the lead-free domain engineered single crystal are much higher than that in relaxor-PbTiO₃ based domain engineered crystals. In general, the extrinsic contribution is a function of applied field, which accounts for 10% and 24% of the total piezoelectric effect under the electric field level of 1 kV/cm and 3 kV/cm, respectively.

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