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Large piezoelectric coefficient and ferroelectric nanodomain switching in $\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_{3-0.5}(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ nanofibers and thin films

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Abstract

Currently available low-dimensional piezoelectric materials show a low piezoelectric coefficient d_{33} of merely 100 pm V⁻¹ with $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ -based materials at the high end. Here, we report very large piezoelectricity in $\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_{3-0.5}(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ (BTZ-0.5BCT) lead-free nanostructures sintered as thin films ($d_{33} = 140$ pm V⁻¹) and nanofibers ($d_{33} = 180$ pm V⁻¹). The influences of lateral size, geometry, and the clamping effect on the piezoelectric performance were investigated for both thin films and nanofibers. Combining a high piezoelectric coefficient with environmental benefits, the BTZ-0.5BCT nanostructures provide the superior functions sought for highly efficient piezoelectric devices and electromechanical systems. 2014 AIP Publishing LLC.

Keywords

nanofibers, TiO_3 , thin, films, 70ca, ba0, 5, o3, 20, 30, 80zr0, large, TiO_3 , ba, switching, nanodomain, ferroelectric, coefficient, piezoelectric

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Currently available low-dimensional piezoelectric materials show a low piezoelectric coefficient d_{33} of merely 100 pm V^{-1} with $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ -based materials at the high end. Here, we report very large piezoelectricity in $\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_3\text{-}0.5(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ (BTZ-0.5BCT) lead-free nanostructures sintered as thin films ($d_{33} = 140 \text{ pm V}^{-1}$) and nanofibers ($d_{33} = 180 \text{ pm V}^{-1}$). The influences of lateral size, geometry, and the clamping effect on the piezoelectric performance were investigated for both thin films and nanofibers. Combining a high piezoelectric coefficient with environmental benefits, the BTZ-0.5BCT nanostructures provide the superior functions sought for highly efficient piezoelectric devices and electromechanical systems. © 2014 AIP Publishing LLC.

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Integration of high performance piezoelectrics in piezoelectric devices and micro-/nano-electromechanical systems (MEMS, NEMS) is a viable approach to enhance their efficiency. Low-dimensional piezoelectric and ferroelectric materials have been exploited widely in nanogenerators, sensors, transducers, MEMS devices, and other applications such as microwave varactors and ferroelectric field effect transistors.^{1–6} For instance, high performance piezoelectric nanostructures can enhance the output power of piezoelectric generators that convert the kinetic energy of vibrations, displacements, or applied force to electricity.^{7–11}

There are three challenging issues that need to be addressed, however, for low-dimensional piezoelectric materials and their devices: (1) Although scaling down the devices to the nanoscale provides significant benefits such as suppressing the energy consumption, the ferroelectric and piezoelectric properties are often suppressed in small dimensions due to intrinsic or extrinsic effects depending on factors such as lateral size, geometry, particle size, in-plane stress, and domain wall mobility. (2) Confinement of the nanosized piezoelectric components by the substrate causes them to develop internal stress in their interface with the substrate (clamping effect), which leads to a direct suppression of their piezoelectric performance. (3) Although piezoelectric single crystals possess remarkably high piezoelectric coefficients, growing single crystals on the nanoscale, such as in nanowires, nanorods, or nanoribbons, while retaining their superior performance, is very difficult in practice, due to the complex phase formation dynamics, in particular, for ternary piezoelectric systems.

Enormous efforts have been undertaken to innovate with new piezoelectric materials and improve their piezoelectric response by varying their composition and shape in the form of thin films, nanowires, and nanofibers. However, the best piezoelectric response reported for polycrystalline thin films and nanofibers so far has been less than 160 pm V^{-1} .^{12–26} Grain boundaries create pinning sites for ferroelectric

domain wall motion. A high density of grain boundaries restricts domain walls' mobility in nanostructured materials. As a consequence, the electromechanical response becomes smaller compared to bulk ceramics containing single crystals and coarse grains with a lower density of grain boundaries.²⁷

Recently, a lead-free $\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_3\text{-}x(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ (BTZ- x BCT) piezoelectric system with optimal composition of $x = 0.5$ was reported to show superior room temperature piezoelectricity, with the piezoelectric coefficient $d_{33} = 620 \text{ pC N}^{-1}$, the piezoelectric voltage constant $g_{33} = 15.38 \times 10^{-3} \text{ V m N}^{-1}$, and the electromechanical (inverse piezoelectric) response as high as 1140 pm V^{-1} . These superior piezoelectric properties are comparable to or higher than those of state-of-the-art $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) or other lead-free piezoelectric compounds, due to the low polarization anisotropy and low energy barrier for lattice distortions in the morphotropic phase boundary (MPB) region.²⁸ The large d_{33} obtained in bulk BTZ-0.5BCT ceramics makes this compound a promising candidate as a component for low-dimensional piezoelectric devices. However, its low Curie temperature ($T_c = 93^\circ\text{C}$)²⁸ limits its applications around room temperature²⁹ due to domain instability at elevated temperatures. It is expected that nanowires, nanofibers, or thin films of this compound would have piezoelectric properties comparable to those of PZT and other piezoelectric materials.

In the study of piezoelectricity, conventional piezoresponse force microscopy (PFM) has been widely used to measure the piezoelectric response and the domain and domain wall dynamics. It is difficult, however, to achieve high spatial resolution for ferroelectric domains in nanowires or nanofibers with curving surfaces.

In this study, we report our observations on the high piezoelectric response achieved in BTZ-0.5BCT nanofibers and thin films and our visualization of ferroelectric nanodomains with high spatial resolution using PFM. The influences of lateral size, geometry, and the clamping effect on the piezoelectric performance were also investigated for both thin films and nanofibers.

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The BTZ-0.5BCT nanofibers and thin films were fabricated according to Ref. 30. Field-emission scanning electron microscopy (FE-SEM, JEOL JSM 7500FA) was used to examine the surface morphology and microstructure of the cross-section of the thin film with a 3.8 mm working distance under 1 kV acceleration voltage. A Raman spectrometer (HORIBA JobinYvon, HR800 spectrometer) was employed to study the state of crystallization and lattice vibration modes. Un-polarized spectra were collected at room temperature using 632.8 nm light pumping from a He-Ne laser and a charge coupled device (CCD) detector in this experiment.

PFM (Asylum Research, MFP-3D) was used for our experiments. The PFM measurements were performed at a low frequency 25 Hz and in electric field, ranging from -300 kV/cm to $+300$ kV/cm. Bottom electrode is Ir layer on Si wafer and the top electrode is PtIr-coated Si tip with deflection sensitivity: 73.6 nm V^{-1} for our experiments, respectively.

A typical three-dimensional (3D) atomic force microscope (AFM) image of a 400×400 nm² surface area of a BTZ-0.5BCT thin film spin-coated on Si/SiO₂/Ti/Ir substrate³⁰ and heat-treated at 700°C for 1 h is shown in Fig. 1(a). The films have a smooth surface with a surface root mean square (rms) roughness equal to 2.1 nm, with an average particle size of 33 nm. The FE-SEM cross-sectional image of the 200 nm thick BTZ-0.5BCT film in Fig. 1(b) reveals randomly oriented particles. The image was collected at 3.8 mm working distance under 1 kV acceleration voltage. Fig. 1(c) depicts an individual nanofiber annealed at 700°C for 1 h.³⁰ The average particle size is 46 nm. Since its diameter of 200 nm is close to the BTZ-0.5BCT film thickness, the image was collected to study how the geometry, lateral size, and clamping effect influence the piezoelectric properties on the nanoscale.

Local atomic environments in BTZ-0.5BCT nanofibers and films were examined by Raman spectroscopy at room temperature.³⁰ These spectra are displayed in Fig. 2. Spectra of bulk BTZ-0.5BCT ceramics prepared by conventional solid state reaction at 1450°C were used as Ref. 30. All features characteristics of the perovskite structure of bulk BaTiO₃ were verified in the Raman spectra of bulk BTZ-0.5BCT ceramics in different forms.^{31,32} Two A_1 transverse optical modes [$A_1(\text{TO})$] and a longitudinal optical mode [$A_1(\text{LO})$], together with a combined mode [$B_1, E(\text{TO} + \text{LO})$], are located in the range of 100 – 300 cm⁻¹. Raman shifts at around 260 and 300 cm⁻¹ are attributed to the T-O bond vibrations. Ba-O bonds produce two mixed modes, [$A_1, E(\text{TO})$] and [$A_1, E(\text{LO})$], at the high frequencies of about 520 and 725 cm⁻¹.^{31,33} The A_1 and E modes are present in both Raman and infrared spectra, however, the B_1 mode is only Raman active.³¹ The low intensity peak at 164 cm⁻¹, assigned to the transverse optical mode [$A_1(\text{TO})$], has been observed only in the rhombohedral phase of nanocrystalline barium titanate,³⁴ while the other vibration modes exist in both tetragonal and rhombohedral phases. The coexistence of these two ferroelectric phases in the Raman spectra confirms the crystallization of the BTZ-0.5BCT nanofibers and thin films in the MPB region.

Strain developed at the BTZ-0.5BCT nanostructure-substrate interface together with the substitution of Ca^{2+} and Zr^{4+} , with ionic radii of 114 and 86 pm, respectively, for Ba^{2+} and Ti^{4+} (with ionic radii of 146 pm and 74.5 pm, respectively) could be responsible for the shift in the Raman

FIG. 1. (a) 3D image of topography of BTZ-0.5BCT thin film annealed at 700°C for 1 h, showing 2 nm rms roughness of the surface. (b) FE-SEM image of cross-section of BTZ-0.5BCT thin film about 200 nm in thickness with an average particle size of 33 nm. (c) 3D topographical image of a single BTZ-0.5BCT nanofiber prepared from the same precursor solution as the thin film and annealed under the same conditions. Its diameter of about 200 nm is the same as the BTZ-0.5BCT film thickness. (d) FE-SEM image of BTZ-0.5BCT nanofibers annealed at 700°C for 1 h, showing an average particle size of 46 nm and average diameter of 200 nm.

spectra of bulk BTZ-0.5BCT thin films and nanofibers compared to the polycrystalline BaTiO₃.³²

PFM was employed to quantify the piezoelectric coefficient in the BTZ-0.5BCT films and fibers. The deflection signal was calibrated by using the force-distance curve for the cantilever used for PFM measurements.³⁰ Hysteretic electric field dependencies of the phase of the piezo-signal, the displacement, and the piezoelectric coefficient in Figs. 3(a)–3(c) manifest the switching of local ferroelectric domains in the BTZ-0.5BCT thin film and nanofiber. These measurements were performed at a low frequency 25 Hz to eliminate the mechanical amplification induced by the tip-sample system. An electric field, ranging from -300 kV/cm to $+300$ kV/cm, was employed. The PFM phase hysteresis loops in Fig. 3(a)

FIG. 2. Raman spectra of BTZ-0.5BCT nanofibers and 200 nm thick BTZ-0.5BCT film spin-coated on Si/SiO₂/Ti/Ir substrate annealed at 700°C for 1 h in air. All features are characteristic of the polar structure of BaTiO₃ and indicate successful evolution of perovskite structure in all samples. The existence of a peak at 164 cm⁻¹ [$A_1(\text{TO})$] is only observed in the rhombohedral symmetry, while the other peaks, which appear in both tetragonal and rhombohedral symmetries, indicate the crystallization in MPB region.

FIG. 3. (a) Local PFM phase hysteresis loops and (b) piezoelectric butterfly loops of the BTZ-0.5BCT thin film and nanofiber obtained by switching the voltage from -5 to $+5$ V (± 300 kV cm $^{-1}$ electric field) at 25 Hz. 180° domain switching in the phase hysteresis loop shows the switching phenomenon of spontaneous electrical dipoles built up in the BTZ-0.5BCT thin film. (c) d_{33} hysteresis loop calculated by using the converse piezoelectric equation, $\Delta z = d_{33}$ (V), which indicates a significant enhancement compared to the bulk of $d_{33} = 141$ pm V $^{-1}$ in the thin film and $d_{33} = 180$ pm V $^{-1}$ in the BTZ-0.5BCT nanofiber. (d) Schematic illustration of lateral size and contact area in the nanofiber and thin film with different geometries.

show the 180° rotation of the electrical polarization of domains in the BTZ-0.5BCT film and nanofiber. Switching of polarization occurs as an inhomogeneous nucleation and anisotropic growth of domains³⁵ in external electric field applied between the bottom electrode (Ir layer on Si wafer) and the top electrode (PtIr-coated Si tip). The asymmetric shape of the hysteresis loops and their shift toward the positive field (PtIr tip as anode) is due to the difference in work functions, respectively, in the bottom and top electrodes: 4.23 eV for Ir and 5.6 eV for PtIr.^{36,37}

Fig. 3(b) shows the displacement Δz of the tip caused by the deformation of ferroelectric samples under applied electric field E . Hysteretic curves exhibit an irreversible converse piezoelectric effect in BTZ-0.5BCT nanofiber and thin film. According to the definition of the converse piezoelectric effect, the piezoelectric coefficient d_{33} can be calculated from the equation³⁸

$$d_{33} = \frac{\Delta z}{V}, \quad (1)$$

d_{33} values as high as 141 pm V $^{-1}$ in film and 180 pm V $^{-1}$ in fiber were obtained from the slope of the linear part of the Δz vs. E curve at very low electrical field. The observed piezoelectric coefficients in our nanofiber and thin film are comparable to or higher than those of PZT. Table I compares the piezoelectric coefficient d_{33} of lead-containing and lead-free ferroelectric nanostructures fabricated in the form of nanofibers and thin films. The d_{33} obtained in our nanostructured BTZ-0.5BCT fibers and films appeared to be significantly higher than in the known Pb-free and Pb-containing piezoelectric structures. Compared to PZT nanofibers, BaTiO $_3$ thin films, ZnO nanorods/pillars, and NaNbO $_3$ nanowires exploited recently in high-power piezoelectric generators^{7-9,39,40} (see Fig. 4), our fibers and films seem to be capable of significantly increased efficiency and output power in self-powered nanodevices and energy harvesting systems. For example, according

FIG. 4. Comparison of piezoelectric coefficient d_{33} in nanostructured components used to build piezoelectric generators with d_{33} in our BTZ-0.5BCT films and fibers.

to Fig. 4, d_{33} in BTZ-0.5BCT nanostructures exhibits more than 100% enhancement compare to the PZT nanofibers.²¹

The reason for the high d_{33} values in our nanofibers and thin films is because the BTZ-0.5BCT bulk ceramics exhibit a very large piezoelectric effect compared to other piezoelectric bulks. The large value ($d_{33} = 1146$ pm/V) in the BTZ-0.5BCT bulk ceramics is caused by crystallization in the vicinity of the rhombohedral-cubic-tetragonal critical point (critical triple point) which approaches the MPB region in the BTZ-BCT phase diagram.²⁸ For this composition, the polarization anisotropy vanishes, leading to a strong dependence of the electrical polarization on elastic deformations, thus significantly increasing the piezoelectricity. It is important to note that even a very low change in stoichiometry of the BTZ-0.5BCT, as low as 5%, can result in drastic suppression of d_{33} in the final system of up to 40%.²⁸

Equation (2) relates T (stress), E (electric field), s_{13}^E (elastic compliance), and d_{33} (inverse piezoelectric coefficient) to S (strain) in an unclamped piezoelectric crystal⁴¹

$$S_3 = s_{13}^E(T_1 + T_2) + s_{33}^E T_3 + d_{33} E_3. \quad (2)$$

It is well known that clamping to the substrate suppresses the strain and consequently the measured converse piezoelectric coefficient in thin films and nanofibers. The normal component of the electric field induces in-plane elastic stress, $\sigma_{\text{effective}}$. This affects normal deformations of the sample if a ferroelectric material is tightly bonded with a rigid substrate. We assume the clamped nanofibers and the thin films as the one-dimensional and the two-dimensional objects, respectively. Without applying stress on their free surfaces, $T_2 = T_3 = 0$ and $T_3 = 0$ for the nanofibers and the thin films, respectively. The rigid substrate can be considered as an isotropic object, therefore, $T_1 = T_2 = T$ in the thin films and $T_1 = T$ in the nanofibers. The T represents the effective stress.

Re-arranging Eq. (2) with respect to the stress distributions in the nanofibers and the thin films gives the effective piezoelectric coefficient d_{33f} for the one-dimensional (Eq. (3)) and the two-dimensional (Eq. (4)) objects

$$\frac{S_3}{E_3} = d_{33f} = d_{33} + \frac{s_{13}^E \sigma_{\text{effective}}}{E_3}, \quad (3)$$

$$\frac{S_3}{E_3} = d_{33f} = d_{33} + \frac{2s_{13}^E \sigma_{\text{effective}}}{E_3}. \quad (4)$$

TABLE I. Piezoelectric coefficient d_{33} of nanofibers and thin films.

Materials	Geometry	Orientation	d_{33} (pm V ⁻¹)	Ref.
(Ba _{0.85} Ca _{0.15})(Ti _{0.90} Zr _{0.10})O ₃	NF ^a	Random	180	Current study
Pb(Zr _{0.3} Ti _{0.7})O ₃	NF	Random	83	21
0.65Pb(Mg _{1/3} Nb _{2/3})O ₃ -0.35PbTiO ₃	NF	Random	50	43
CoFe ₂ O ₄ -Pb(Zr _{0.52} Ti _{0.48})O ₃	NF	Random	157	24
Bi _{3.4} Ce _{0.6} Ti ₃ O ₁₂	NF	Random	158	23
(Na _{0.82} K _{0.18})0.5Bi _{0.5} TiO ₃	NF	Random	96	44
Bi _{3.15} Nd _{0.85} Ti ₃ O ₁₂	NF	Random	89	45
ZnO-V	NF	Random	121	46
(Na _{0.5} Bi _{0.5}) _{0.94} TiO ₃ -Ba _{0.06} TiO ₃	NF	Random	102	44
(Ba _{0.85} Ca _{0.15})(Ti _{0.90} Zr _{0.10})O ₃	TF ^b	Random	141	Current study
BaTiO ₃	TF	(100)	30	18
BaTiO ₃	TF	Single crystal	80–100	47
0.5(Ba _{0.7} Ca _{0.3} TiO ₃)-0.5[Ba(Zr _{0.2} Ti _{0.8})O ₃]	TF	(111)	80	48
Pb _{0.76} Ca _{0.24} TiO ₃	TF	Random	70	19
Bi _{0.83} Sm _{0.17} FeO ₃	TF	(002)	110	20
BiFeO ₃	TF	(001)	70	12
0.34BiScO ₃ -0.66PbTiO ₃	TF	(001)	130	49
0.948(K _{0.5} Na _{0.5})NbO ₃ -0.052LiSbO ₃	TF	Random	50	50
(K _{0.44} Na _{0.52} Li _{0.04})(Nb _{0.84} Ta _{0.1} Sb _{0.06})O ₃	TF	(001)	53	51
Pb(Zr _{0.6} Ti _{0.4})O ₃	TF	(100)	100	52
		(111)	63	
		Random	77	
0.7 Pb(Mg _{1/3} Nb _{2/3})O ₃ -0.3PbTiO ₃			79	
0.9 Pb(Mg _{1/3} Nb _{2/3})O ₃ -0.1PbTiO ₃			64	
Pb(Zr _{0.6} Ti _{0.4})O ₃	TF	(111)	85	53
(K _{0.5} Na _{0.5})NbO ₃ with 20 mol. % extra K and Na.	TF	Random	40	54

^aNF: Nanofiber.^bTF: Thin film.

Using $d_{33} = 1140$ pm/V (Ref. 28) and $s_{13}^E = -7.4 \times 10^{-12}$ m²/N,⁴² experimentally obtained in bulk BTZ-0.5BCT ceramics, we present the effective piezoelectric coefficient d_{33f} and the effective stress $\sigma_{\text{effective}}$ calculated from Eqs. (3) and (4) in Table II.

Since the elastic compliance s_{13}^E has a negative value, therefore, an additional term proportional to the elastic compliance in the effective piezoelectric coefficient is subtracted from the bulk coefficient d_{33} .

Figs. 3(a) and 3(c) demonstrate that the nanofibers have half the coercive field and higher d_{33f} compared to the film. We explain this by the much smaller lateral size of the fiber-substrate interface and the fiber-to-substrate contact area, as shown in Fig. 3(d). Reduction of the residual ferroelectric-substrate interface strain increases the piezoelectric response in the nanofibers.

Figs. 5(a) and 5(b) present 3D PFM patterns of the surface of a 200 nm thick BTZ-0.5BCT film. Simultaneous recording of 3D profiles of the PFM phase and amplitude

signals enables a visualization of ferroelectric domains. These 3D images were acquired using a lock-in amplification technique with a PtIr-coated silicon cantilever in contact mode, which was ac-biased with a voltage of 1.0 V. Ferroelectric domains have a lateral size of 20 to 40 nm. 180°

FIG. 5. 3D PFM phase (a) and amplitude (b) images of the surface of 200 nm thick BTZ-0.5BCT film. Ferroelectric domain patterns in the phase image (a) display the opposite polarity of ferroelectric domains 20 to 40 nm in size. These domains are revealed by 180° phase difference contrast. The amplitude image (b) reproduces the domain shape. Sharp contrast around domains visualizes domain boundaries. In (c), phase and amplitude profiles recorded along the marked lines in (a) and (b) are overlaid on an AFM topographical image. All three images were collected simultaneously under 1.0 V ac modulation voltage.

TABLE II. Calculated effective stress induced by electric field in the nanofiber/thin film-substrate interface.

Geometry	Maximum d_{33f} (pm V ⁻¹)	E_c^A (kV cm ⁻¹)	d_{33f} (pm V ⁻¹) ^a	$\sigma_{\text{effective}}$ (MPa)
Thin film	141	45	122	302.7
Nanofiber	180	20	151	284

^a d_{33} measured in coercive field.

PFM phase contrast in Fig. 5(a) distinctly shows that ferroelectric domains have antiparallel out-of-plane polarization. The PFM amplitude pattern in Fig. 5(b) reproduces the shape of the domains. In Fig. 5(c), phase and amplitude cross-sectional profiles recorded along the marked line are overlaid on the topographical image taken from Fig. 1(a). Sharp 180° PFM phase contrast occurs when the conducting cantilever crosses narrow domain boundaries.

In conclusion, we report very large piezoelectricity in $\text{Ba}(\text{Ti}_{0.80}\text{Zr}_{0.20})\text{O}_{3-0.5}(\text{Ba}_{0.70}\text{Ca}_{0.30})\text{TiO}_3$ (BTZ-0.5BCT) lead-free nanostructured thin films ($d_{33} = 141 \text{ pm V}^{-1}$) and nanofibers ($d_{33} = 180 \text{ pm V}^{-1}$). These values are comparable to or higher than those for PZT films and nanofibers, respectively. Strong reduction of the coercive field induced by interface stress and improved piezoelectric response makes BTZ-0.5BCT nanofibers a promising candidate for integration in piezoelectric nanodevices and power generator systems.

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