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Electrical poling below coercive field for large piezoelectricity

Abstract

Isotropic polycrystalline ferroelectric ceramics have to be electrically poled to develop a net macroscopic polarization and hence piezoelectricity. It is well accepted that a sufficient poling can only be realized under an electric field that is much higher than the coercive field. In this study, we observed in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics that large piezoelectricity can develop at poling fields far below the measured coercive field. Using *in situ* transmission electron microscopy, such an unusual behavior, is interpreted with the polarization alignment of polar nanodomains in the non-ergodic relaxor phase.

Keywords

Piezoelectric fields, Relaxor ferroelectrics, Polarization, Ceramics, Sodium, Transmission electron microscopy, Coercive force, Ferroelectric phase transitions, Piezoelectricity, Phase transitions

Disciplines

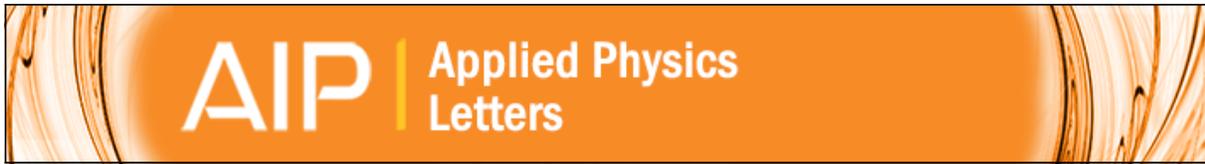
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Comments

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Electrical poling below coercive field for large piezoelectricity

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Isotropic polycrystalline ferroelectric ceramics have to be electrically poled to develop a net macroscopic polarization and hence piezoelectricity. It is well accepted that a sufficient poling can only be realized under an electric field that is much higher than the coercive field. In this study, we observed in $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ ceramics that large piezoelectricity can develop at poling fields far below the measured coercive field. Using *in situ* transmission electron microscopy, such an unusual behavior, is interpreted with the polarization alignment of polar nanodomains in the non-ergodic relaxor phase. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794866>]

Piezoelectric materials are key to numerous important technologies, including energy harvesting,¹ noise cancellation,² and minimally invasive surgery.³ The defining property is a third rank tensor, which requires a macroscopically broken spatial-inversion symmetry in order to exhibit non-zero values.⁴ For an originally isotropic polycrystalline ferroelectric ceramic, a polar symmetry (∞m) needed for the existence of piezoelectricity can be brought by a poling process, where a strong direct current electric field is applied to switch ferroelectric domains and align spontaneous polarizations.^{5,6} Therefore, it is commonly believed that poling fields have to be much greater than the coercive field E_C , which characterizes the difficulty of polarization reversal in ferroelectrics.⁶ Such an empirical rule is based on and supported by numerous experimental observations on all of the widely studied piezoelectrics so far, including $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ -based,⁷ BaTiO_3 -based,⁸ $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based,⁹ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based¹⁰ compositions; optimal piezoelectricity of these systems (represented by the d_{33} coefficient) can only be achieved when poled at or above $2E_C$. Poling fields below or around E_C only yield very small d_{33} values that are close to zero.^{8,10} In this study, we report the observation of large piezoelectricity realized at poling fields significantly below experimentally measured E_C . This peculiar behavior occurs in a limited composition range of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$, the most extensively studied lead-free piezoelectric system.^{11–15} The observed phenomenon is rationalized using the electric-field *in situ* transmission electron microscopy (TEM) technique.

The preparation of polycrystalline ceramic samples of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$ ($x=6\%$, 7% , 8% , 9%) was described previously.¹⁶ Hot-pressed $\text{Pb}_{0.92}\text{La}_{0.08}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT8/65/35) ceramic was acquired from a commercial source (Boston Applied Technologies, MA, USA). The electric field-induced volume strain was calculated from the strains measured parallel and perpendicular to the field direction simultaneously at 0.62 Hz. The details about this technique can be found in the previous reports.^{17,18} The polarization versus electric field hysteresis loops were measured with the standardized ferroelectric test system (RT-66A, Radiant Technologies, Albuquerque, NM, USA) at room temperature at 4 Hz. For piezoelectric characterization, the ceramic specimens were poled

at various electric fields at room temperature (25°C) for 20 min. The piezoelectric coefficient d_{33} was measured with a piezo- d_{33} meter (ZJ-4B, Institute of Acoustics, Chinese Academy of Sciences) 24 h after poling. Electric-field *in situ* TEM experiments were carried out on a Phillips CM30 microscope operated at 300 kV. Experimental details were described in previous articles.^{19–22}

The abnormal poling behavior is illustrated in Fig. 1, using the $93\%(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}7\%\text{BaTiO}_3$ ceramic as an example. This composition was observed to experience a transition from the $P4bm$ phase to long-range-ordered ferroelectric phases at a critical field (referred to as E_F in the present work) during poling, and the induced ferroelectric phases persist after removal of fields.^{15,17,23,24} Figure 1(a) shows the evolution of volume strain and the simultaneously measured polarization during the very first cycle of electric field. The anomaly on the volume strain curve, resulted from the unit cell volume change, marks the critical phase transition field E_F .¹⁷ Accompanied with this volume strain anomaly is a slope change in the polarization curve, from which E_F is determined as 2.5 kV/mm for $x=7\%$. The comparison between the volume strain and polarization curves in Fig. 1(a) clearly suggests a significant amount of macroscopic polarization is developed in the $P4bm$ phase. Figure 1(b) presents the $E > 0$ portion of the polarization P vs. electric field E hysteresis loop measured in the second electric field cycle. A coercive field E_C of 2.4 kV/mm is recorded. Figure 1(c) shows the piezoelectric coefficient d_{33} as a function of poling field. An abrupt increase in d_{33} is observed at 1.5 kV/mm . This critical poling field is denoted as E_P . It is noted that d_{33} only slightly increases and quickly saturates beyond E_P . Figure 1 unambiguously indicates that E_P is significantly lower than both E_F and E_C in the $93\%(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}7\%\text{BaTiO}_3$ ceramic.

The highly unusual phenomenon is also observed in other compositions with the $P4bm$ phase in the virgin state ($x=6\%$, 8% , and 9%). For all of these compositions, a remarkable jump of piezoelectric coefficient d_{33} is also clearly observed in the poling field dependence of the d_{33} curves shown in Fig. 2(a). Again, the d_{33} value of all these compositions barely increases when the poling field beyond E_P is applied. Figure 2(b) displays the values of E_F , E_C , and E_P of these compositions, which are determined in the same way

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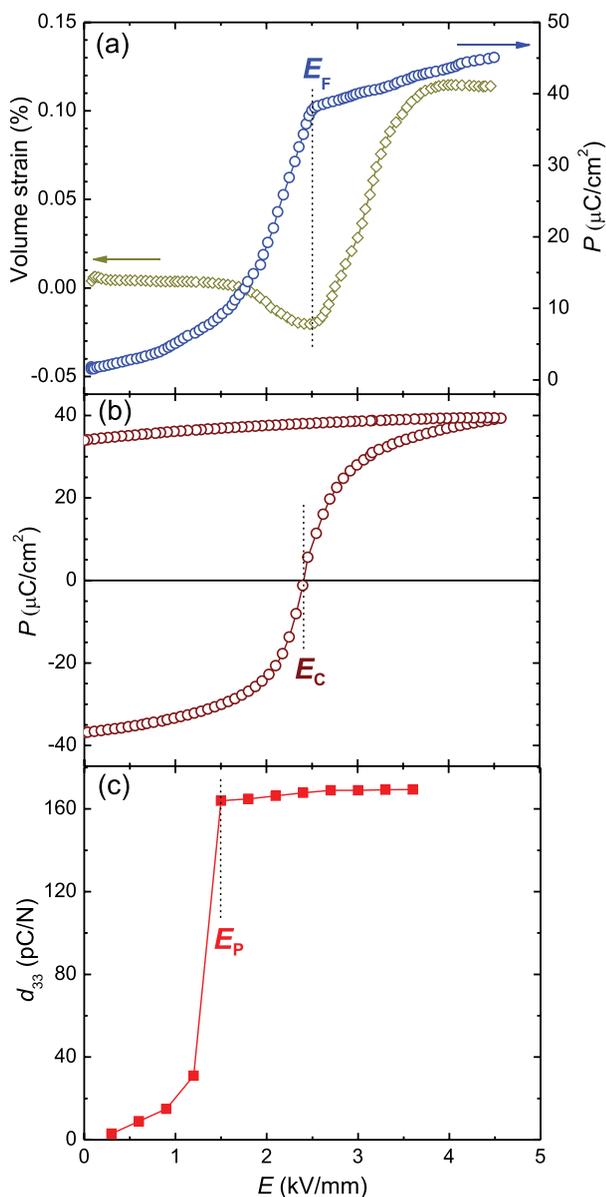


FIG. 1. The three critical fields defined from data of the 93%(Bi_{1/2}Na_{1/2})TiO₃-7%BaTiO₃ ceramic. (a) E_F , the critical field for the electric field-induced $P4bm$ -to- $P4mm$ phase transition; (b) E_C , the coercive field; (c) E_P , the critical poling field where d_{33} abruptly increases.

as in Fig. 1. Similar to $x = 7\%$, the critical poling field E_P is much lower than the coercive field E_C in all of them. For $x = 9\%$, E_P is even smaller than one third of its E_C .

One possible explanation for the results shown in Figs. 1 and 2 is that E_P is determined under DC field while E_C is under AC field and is known to be strongly frequency dependent.²⁵⁻²⁷ However, it should be pointed out that such an unusual poling behavior is not observed in compositions in the $R3c$ and $P4mm$ ferroelectric phase regions in $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3$, but only in those with the $P4bm$ phase. The frequency effect is hence not the primary factor here.

Furthermore, the fact that E_P , where the d_{33} coefficient suddenly increases and then saturates, is significantly lower than E_F , where phases with long-range ferroelectric order emerge, also rules out any possible contributions from phase transition to d_{33} at E_P . As a result, the observed phenomenon

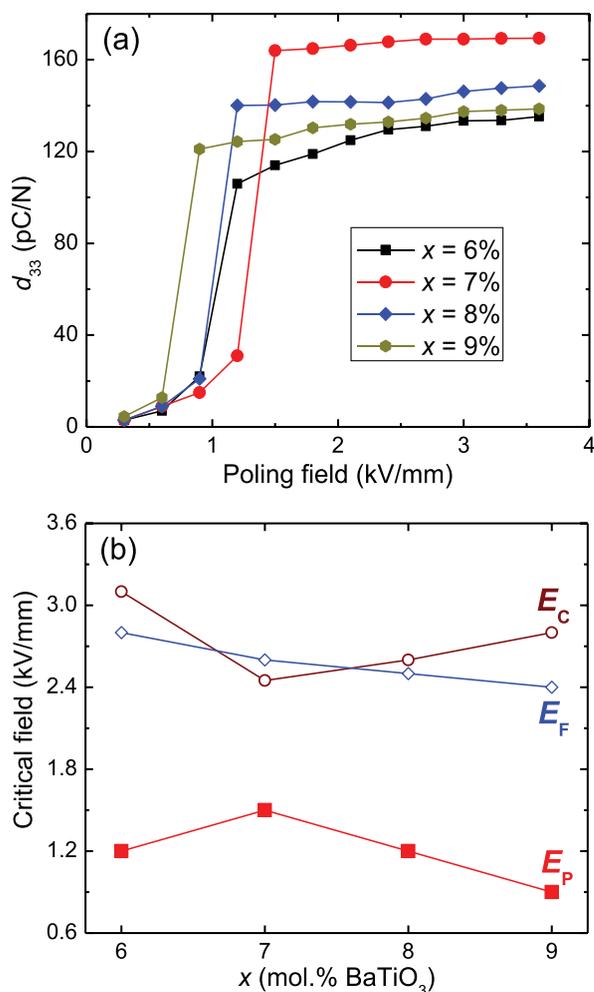


FIG. 2. Electrical properties of $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-x\text{BaTiO}_3$ ($x = 6\%$, 7% , 8% , 9%) polycrystalline ceramics. (a) Poling field dependence of the piezoelectric coefficient d_{33} ; (b) critical fields E_F , E_C , and E_P .

must be rooted in the $P4bm$ phase: The high d_{33} developed below E_C is a result of the poling of the $P4bm$ phase.

In the virgin state prior to poling, ceramics with these compositions crystallize in the $P4bm$ space group, with polar nanodomains in microstructure and strong frequency dispersion in their dielectric permittivity.^{13,14,16} The polar $P4bm$ space group allows for the presence of dipole moment within the tetragonal unit cell,²⁸ and hence these compositions are referred to as relaxor ferroelectric with a spontaneous polarization.^{23,24} The $P4bm$ phase undergoes an irreversible electric-field-induced phase transition to ferroelectric phases with large domains during poling.²⁴ The large domains in the ferroelectric $R3c$ and $P4mm$ phases are disrupted into $P4bm$ nanodomains when heated to the thermal depolarization temperature T_d ,¹⁴ which is equivalent to the freezing temperature in Pb-containing relaxor ferroelectrics.^{18,29} It was reported that the T_d for the compositions concerned here ($6\% \leq x \leq 9\%$) is above 100°C .³⁰

Therefore, these compositions should be characterized as non-ergodic relaxor ferroelectric at room temperature with static polar nanodomains. These nanodomains, unlike the dynamically fluctuating polar nanoregions in ergodic relaxors, can be poled and aligned under applied field to develop piezoelectricity.

Using the electric-field *in situ* TEM technique,^{19–22} the domain switching process during the poling of the $P4bm$ non-ergodic relaxor ferroelectric phase in composition $x = 7\%$ is directly imaged and displayed in Fig. 3. A representative grain along its $[112]$ zone axis is selected for study. As shown in Fig. 3(a), at zero field it consists of polar nanodomains, which shows the $P4bm$ symmetry as indicated by the presence of $1/2\{ooe\}$ and absence of $1/2\{ooo\}$ spots (o and e stand for odd and even Miller indices, respectively).^{13,14} When a nominal field of 1.4 kV/mm is applied (Fig. 3(b)), the nanodomains coalesce into a tweed structure, and some regions near the grain boundary transform to thin lamellar domains. However, the diffraction pattern still

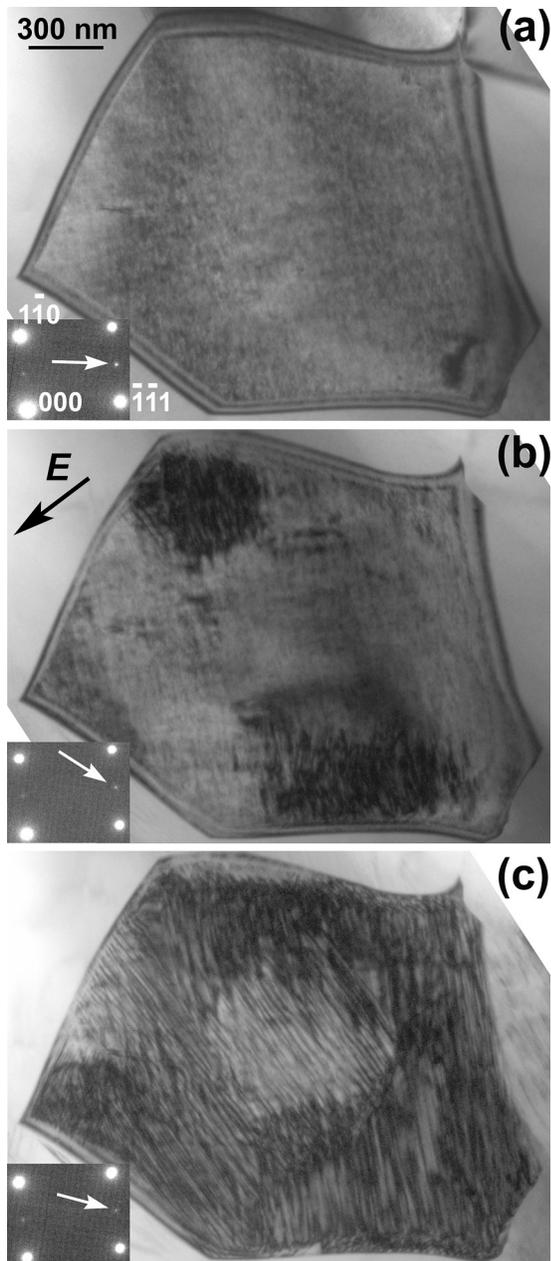


FIG. 3. Electric field *in situ* TEM results of a representative grain in the $93\%(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}7\%\text{BaTiO}_3$ ceramic studied along the $[112]$ zone-axis. Bright-field micrographs at (a) 0 kV/mm, (b) 1.4 kV/mm, and (c) 2.8 kV/mm are displayed. The *in situ* electric field direction is indicated by the dark arrow. The selected area diffraction pattern at each field is shown in the insets, with $1/2\{ooe\}$ spots highlighted by the bright arrow.

suggests the $P4bm$ symmetry across the entire grain, indicating no phase transition has occurred. At 2.8 kV/mm, the volume with nanodomains is completely consumed by that with thin lamellar domains (Fig. 3(c)). Again, electron diffraction indicates that the symmetry is still $P4bm$. These $P4bm$ lamellar domains persist at least two hours after removal of fields in TEM.

It should be noted that the microstructural response to poling field in composition $x = 7\%$ displayed in Fig. 3 appears to be inconsistent with our previous observations where $P4bm$ nanodomains directly transform to thick lamellar $P4mm$ domains.²³ The discrepancy is reconciled with the fact that the electric field in the TEM specimen is not uniform due to the presence of a central perforation and randomly oriented grains. Since the actual field value is not known, we report the nominal values (the applied voltage divided by the electrode spacing). As explained previously,²¹ there are areas along the rim of the central perforation with intensified as well as diluted electric fields. All our previous *in situ* TEM experiments were focused on the field intensified area, but the present one examined a grain out of this area in order to focus on the responses at low poling fields. The results in Fig. 3 reveal the changes in the $P4bm$ phase prior to the transition to the $P4mm$ phase and directly support the poling field E_{pol} vs. composition x phase diagram,²⁴ which indicates that the $P4bm$ phase is stable against poling field up to ~ 3.0 kV/mm.

The *in situ* TEM observations (Fig. 3) reveal that the poling of the $P4bm$ non-ergodic relaxor ferroelectric phase takes place through the irreversible coalescence of individual nanodomains into thin lamellar domains. The electric field required for such a coalescence to occur is lower than the field triggering the high-field ferroelectric phases (E_F) in the first quarter cycle. The measurement of the coercive field E_C takes place after the high-field ferroelectric phases are formed, and hence E_C in these compositions represents the resistance for switching the induced large ferroelectric domains, not the $P4bm$ nanodomains. Apparently, the critical field E_P is the onset field for the alignment of the polarizations associated with $P4bm$ nanodomains. This provides the microstructural origin for the observed strong piezoelectricity below E_F and E_C .

This unusual poling behavior is also observed in lead-containing relaxor ferroelectric ceramics such as $(\text{Pb}_{0.92}\text{La}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ (PLZT8/65/35). This composition is a non-ergodic relaxor at room temperature with a freezing temperature of $(36 \pm 2)^\circ\text{C}$.^{31,32} An exceptionally low E_P value of 0.25 kV/mm is found for this composition, which is lower than both E_C (0.3 kV/mm) and E_F (0.5 kV/mm). The result suggests the high d_{33} coefficient in this composition^{28,29} is also originated from the coalescence of the polar nanodomains during poling.³³

In summary, well-developed piezoelectric properties are observed in polycrystalline $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}x\text{BaTiO}_3$ ceramics with the $P4bm$ relaxor ferroelectric phase even when they are poled at fields significantly lower than both the phase transition field and the coercive field. The microstructural origin for this behavior is attributed to the electric field-induced irreversible nanodomains coalescence into thin lamellar domains prior to the phase transition. The discovery suggests

that non-ergodic relaxors should be included in the search of lead-free piezoelectrics for replacing the industrial standard, but environmentally hazardous, lead-containing ones.

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