

## Nonlinear Piezoelectricity in Epitaxial Ferroelectrics at High Electric Fields

Alexei Grigoriev,<sup>1</sup> Rebecca Sichel,<sup>1</sup> Ho Nyung Lee,<sup>2</sup> Eric C. Landahl,<sup>3</sup> Bernhard Adams,<sup>3</sup>  
Eric M. Dufresne,<sup>3</sup> and Paul G. Evans<sup>1</sup>

<sup>1</sup>*Department of Materials Science and Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA*

<sup>2</sup>*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

<sup>3</sup>*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*

(Received 28 July 2007; published 18 January 2008)

Nonlinear effects in the coupling of polarization with elastic strain have been predicted to occur in ferroelectric materials subjected to high electric fields. Such predictions are tested here for a  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  ferroelectric thin film at electric fields in the range of several hundred MV/m and strains reaching up to 2.7%. The piezoelectric strain exceeds predictions based on constant piezoelectric coefficients at electric fields from approximately 200 to 400 MV/m, which is consistent with a nonlinear effect predicted to occur at corresponding piezoelectric distortions.

DOI: [10.1103/PhysRevLett.100.027604](https://doi.org/10.1103/PhysRevLett.100.027604)

PACS numbers: 77.65.-j, 68.37.Yz, 77.84.Dy, 78.47.-p

Ferroelectric materials are sensitive to applied electric fields, temperature, and pressure due to a strong coupling between electrical polarization and elastic distortion [1–3]. This sensitivity to external parameters leads to large piezoelectric strains, high dielectric susceptibility, and can allow structural phase transitions to be driven by applied stresses or electric fields [4,5]. Changes in the structure of perovskite oxide ferroelectrics have been predicted to occur at high electric fields, but these predictions have yet to be tested experimentally. In this Letter, we describe the piezoelectricity of epitaxial ferroelectrics at electric fields up to  $\sim 500$  MV/m and show that very high piezoelectric strains of 2.7% can be reached in perovskite thin films. The changes in piezoelectric response at high field are indicative of interatomic interactions predicted in computational studies to be common to all perovskite ferroelectrics [6,7]. Low-frequency dielectric breakdown in these materials has previously limited studies of high-field properties of ferroelectrics to a narrow range of low electric fields. This problem can be overcome by applying electric fields for short periods of time.

Calculations of the structure and properties of ferroelectrics at high electric fields have recently become possible by adapting density functional theory to problems in which periodic boundary conditions do not apply [8]. The increase in electrical polarization at high external fields results in stronger short-range repulsive forces acting on cations and anions of a  $\text{PbTiO}_3$  ferroelectric lattice to compensate for further compression of Ti-O and Pb-O bonds. In this new regime, the displacement of cations and anions in response to an applied field occurs as a motion of rigid Ti-O and O-Pb-O groups of atoms with effective net charges of about +2 and -2, respectively [6]. These calculations predict that it will be harder to introduce elastic displacements at high electric fields. The linear piezoelectric coefficient  $d_{33}$  of a  $\text{PbTiO}_3$  ferroelectric is predicted to monotonically decrease as the field

increases [6,9]. The  $d_{33}$  component of the piezoelectric tensor describes the coupling of the piezoelectric strain  $\epsilon_3$  to the electric field  $E_3$  applied along the direction of measured strain as  $\epsilon_3 = d_{33} E_3$ . It has been predicted that  $d_{33}$  for a  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  (PZT) thin film decreases from 45 pm/V at zero electric field to 34 pm/V at 100 MV/m [9,10]. Measuring piezoelectric coefficients at high electric fields thus tests the present understanding of electromechanical response and provides an important input for the practical application of ferroelectrics in extreme electric fields.

Predictions of the structure of a  $\text{PbTiO}_3$  ferroelectric at high negative pressure forecast a sudden increase of the tetragonality ratio  $c/a$  [Fig. 1(a)] from  $\sim 1.1$  to  $\sim 1.21$  with increasingly negative pressure [7]. This effect has been attributed to an elongation of one of the Ti-O bonds, similar to large structural effects observed in other non-ferroelectric systems [11,12]. In a material undergoing such a change, the electrical polarization is predicted to increase significantly. We may thus expect an increase of the piezoelectric coefficient  $d_{33}$  at large fields, in contrast to the predicted decrease of  $d_{33}$  [9]. If the piezoelectric coefficient  $d_{33} = 45$  pm/V were constant at all fields, an electric field of 250 MV/m would be needed to reach a tetragonality of 1.1 in a PZT thin film epitaxially grown on a  $\text{SrTiO}_3$  substrate [9,13]. This corresponds to the distortion at which one of the Ti-O bonds is predicted to elongate [7].

Electric fields in the range of several hundred MV/m can be reached in thin ferroelectric films. We have probed the structure of a 35-nm-thick tetragonal  $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$  film epitaxially grown by pulsed laser deposition on an epitaxial 4-nm-thick  $\text{SrRuO}_3$  conducting oxide film on a  $\text{SrTiO}_3$  single-crystal substrate. The surface normal was along the [00L] crystallographic direction. The 50- $\mu\text{m}$ -diameter top electrodes of the ferroelectric capacitors were made of polycrystalline Pt. The remnant electri-

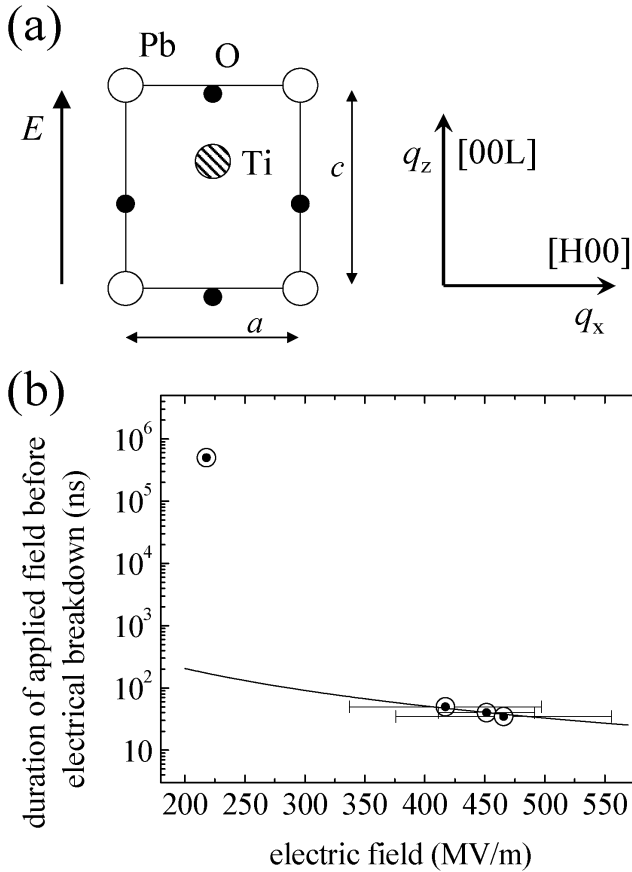


FIG. 1. (a) Orientations of the crystallographic axes and electric field in the experiment. (b) Elapsed time before dielectric breakdown as a function of the amplitude of the electric field. The low-field data point near 200 MV/m was measured using quasistatic triangular electric-field pulses and the high-field points were measured using a series of square-wave pulses of fixed durations. The points at high electric fields are fit with  $t \propto (E_{\text{bd}})^{-2}$ .

cal polarization of the ferroelectric capacitors was  $P_r \approx 0.8 \text{ C/m}^2$  [13]. Both the  $\text{SrRuO}_3$  bottom electrode and the PZT film are coherently strained on the  $\text{SrTiO}_3$  substrate with in-plane lattice constant  $a = 3.905 \text{ \AA}$ . The epitaxial coherence increases the tetragonality  $c/a$  from  $4.148 \text{ \AA}/3.95 \text{ \AA} = 1.05$  in bulk PZT to  $4.25 \text{ \AA}/3.905 \text{ \AA} = 1.088$  in the film [13,14]. The chemical composition of the film favors a tetragonal crystal structure for any feasible induced strain and guarantees that the film always consists of a single crystalline phase [15].

Even in thin films, it is a challenge to reach high electric fields because the low-frequency breakdown field for perovskite ferroelectrics is typically in the range of 100 to 200 MV/m [16]. The dominant mechanism for breakdown in ferroelectric thin films is thermal runaway initiated by field emission from electrodes. The characteristic time  $t$  for which the field can be applied without breakdown at electric field  $E_{\text{bd}}$  is  $t \propto (E_{\text{bd}})^{-2}$  [16]. There is thus a practically useful opportunity to avoid breakdown by using short

electric-field pulses. The duration of applied electric-field pulses that lead to breakdown is shown as a function of the magnitude of the applied electric field in Fig. 1(b). The magnitude of the electric field was taken to be the quotient of the voltage and the thickness. The low-frequency breakdown field of 215 MV/m was measured using triangular voltage pulses for which the duration was 50 ms. The time required for the low-frequency breakdown,  $\sim 0.5 \text{ ms}$ , was estimated by monitoring the current supplied to the capacitor. The threshold for breakdown at high fields and short times was measured using square voltage pulses of fixed duration. The breakdown fields are shown at the midpoint between the maximum field that does not lead to the breakdown and the field at which the ferroelectric was electrically destroyed. The high-frequency data are fit with  $t \propto (E_{\text{bd}})^2$  shown in Fig. 1(b) [16]. Electric fields of 400–500 MV/m can be applied to the PZT capacitors using electrical pulses for which the duration is 50 ns or shorter. Even higher fields may be possible with shorter electrical pulses unless a new breakdown mechanism intervenes.

We used time-resolved x-ray microdiffraction at sector 7 of the Advanced Photon Source of the Argonne National Laboratory to probe the structural changes that occur during short electric-field pulses [17]. The 10 keV photon beam was focused to a 400-nm spot on a ferroelectric capacitor using Fresnel zone plate optics. The diffraction experiments measured the intensity of the diffracted radiation as a function of wave vectors  $q_x$  and  $q_z$  along the  $H$  and  $L$  directions in reciprocal space [Fig. 1(a)]. The x-ray pulses were synchronized to electrical pulses applied to the ferroelectric capacitor and the data were accumulated over several thousand pulses [18].

The (103) PZT Bragg peak has components along both  $H$  and  $L$  crystallographic directions and can thus be used to simultaneously measure lattice constants  $a$  and  $c$ . At an electric field of 354 MV/m applied along the [00L] direction, the (103) peak is shifted along the [00L] direction and its projection on the [H00] axis remained unchanged (Fig. 2). The  $a$  lattice constant was clamped by the substrate and the  $c$  lattice constant reached  $\sim 1.8\%$  piezoelectric strain. The structural changes induced by the electric field are therefore restricted to the lattice parameter  $c$ , which can be measured using, for instance, the (002) PZT Bragg peak.

The piezoelectric strains resulting from the expansion of the  $c$  lattice parameter during 35 to 50 ns electric-field pulses are shown in Fig. 3 for applied fields from 0 to 491 MV/m. Different symbols correspond to four different ferroelectric capacitors. The line is drawn for  $\epsilon_3 = d_{33} E_3$  with  $d_{33} = 45 \text{ pm/V}$ , the low-field piezoelectric coefficient of the PZT film. A linear fit of the data in Fig. 3 with  $\epsilon_3 = d_{33} E_3$  for electric fields up to 160 MV/m gives  $d_{33}$  from 44 to 46 pm/V, a surprisingly good match to the low-field coefficient. Calculations predicting the decrease of

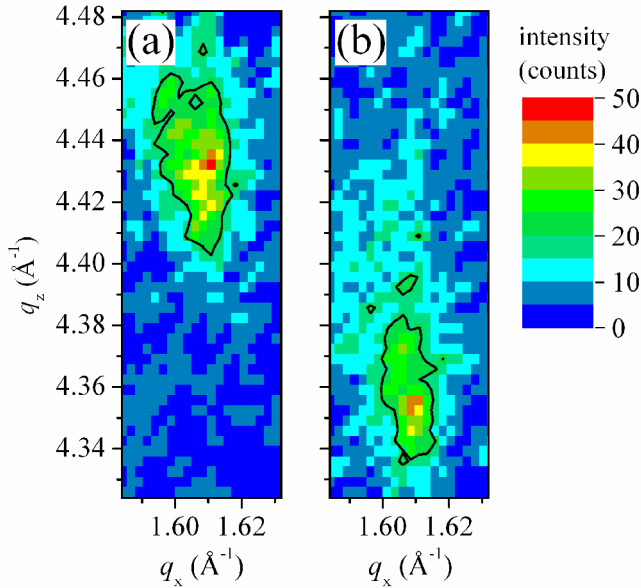


FIG. 2 (color online). The (103) PZT Bragg peak (a) before (at zero field) and (b) during 65-ns electric-field pulses of magnitude  $E = 354$  MV/m.

$d_{33}$  at high electric fields thus significantly overestimate the changes of the piezoelectric coefficient at intermediate electric fields. This discrepancy is potentially due to employing field-independent parameters to parametrize the free energy that is used in calculations of the piezoelectric constants [6,9].

The piezoelectric response becomes stronger at  $\sim 200$  MV/m, which results in a strain that exceeds the  $\epsilon_3 = d_{33} E_3$  line by 10% at 218 MV/m. The standard deviation of this measurement was 2.9% of the strain based

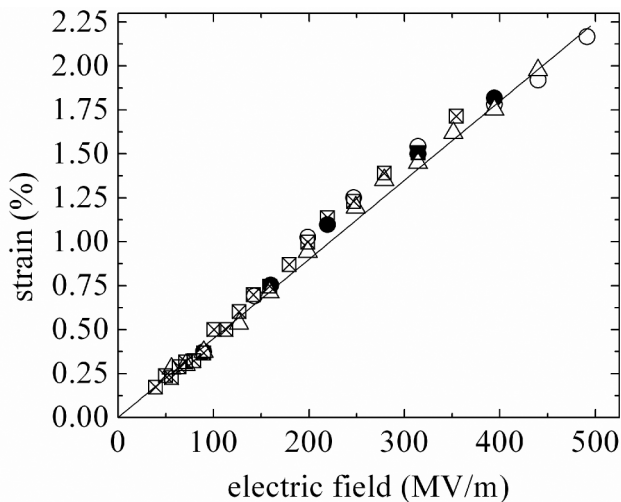


FIG. 3. Piezoelectric strain measured at applied electric fields from 0 to 491 MV/m for four ferroelectric capacitors (shown with different symbols). The solid line is  $\epsilon_3 = d_{33} E_3$ , with  $d_{33} = 45$  pm/V.

on repeated measurements on four capacitors. At this electric field, the tetragonality ratio reaches  $c/a = 1.1$ , which is the point at which the Ti-O bond elongation effect is predicted to occur in the  $\text{PbTiO}_3$  lattice under negative pressure [7]. The strengthened piezoelectric response in a window of electric fields from 180 to 220 MV/m is consistent with predictions for the ferroelectric undergoing the Ti-O bond elongation transition. The tetragonality enhancement predicted in [7] involves considerable in-plane compression not observed here due to epitaxial clamping of the ferroelectric thin film. The comparison of the strengthened piezoelectric response with the tetragonality enhancement is possible, however, because the tetragonality enhancement predicted in Ref. [7] depends strongly on the  $c$ -axis elongation, and much less on the in-plane compression.

As the electric field continues to increase, the piezoelectric response decreases and at 395 MV/m the strain again crosses the  $\epsilon_3 = d_{33} E_3$  line. The decrease of the response for electric fields higher than 220 MV/m can be understood using the predictions that interatomic repulsion plays an increasingly important role at high electric fields [6]. Nonlinear effects in the piezoelectric response at high electric fields are in agreement with the predicted changes of interatomic interactions. The linear response at fields up to  $\sim 200$  MV/m, however, apparently indicates the quantitative disagreement with the piezoelectric coefficients that are predicted to monotonically decrease with field.

Higher fields than those shown in Fig. 3 can be applied by further reducing the duration of the electric-field pulses. With 24.4 V 8-ns electrical pulses, the strain reaches 2.7% (Fig. 4), the highest piezoelectric strain yet reported in a ferroelectric oxide thin film [19]. Pulses of this duration are comparable to the capacitive rise time of the ferroelectric capacitors and the electric field is thus difficult to estimate

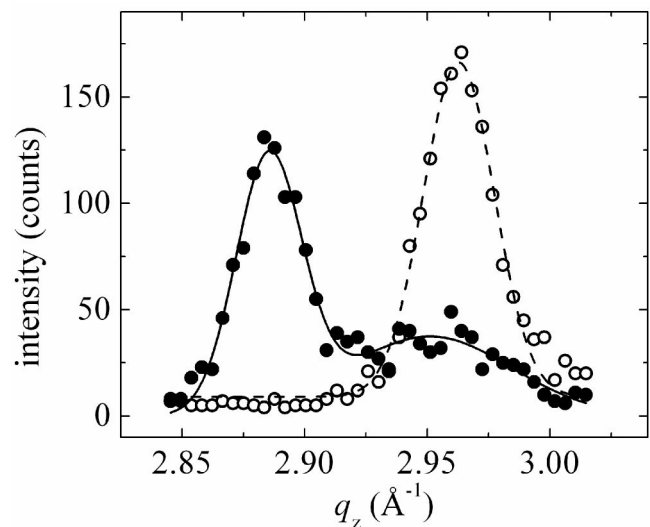


FIG. 4. The PZT (002) Bragg peak before (open symbols) and during (solid symbols) 8-ns electrical pulses of 24.4 V.

accurately. The diffraction scan shown in Fig. 4 for the highest electric field reveals a small additional Bragg peak, which is presumably due to a fraction of the PZT film that is not responding to the applied field. The additional peak could be explained by an interfacial layer of  $\sim 10$  nm for which the piezoelectric properties are remarkably different from the rest of the film. If such a layer were conductive, it would increase the effective electric field applied to the remainder of the PZT layer by up to 40%, and the piezoelectric coefficient would decrease even more dramatically at high electric fields. Since the existence of an interfacial layer has been proposed on multiple occasions as an explanation for the electrical properties of dielectric capacitors [20,21], it will be interesting in the future to address the effects that are responsible for the additional x-ray reflection observed at the high electric fields.

Using the broad range of available piezoelectric strains from 0% to 2.7%, it becomes feasible to extend the search for electric-field induced phase transitions to a number of important ferroelectric and multiferroic thin films [5,15,22]. In  $\text{BiFeO}_3$ , a multiferroic material, the electrical polarization vector can rotate from the [111] direction towards the [001] direction that is predicted to change significantly the remnant polarization, while the magnetic structure remains essentially unchanged [22]. It is now possible to experimentally test these predictions at high piezoelectric strains using short electric-field pulses.

The piezoelectric response is qualitatively well explained at high fields by the predictions of recent structural calculations. The surprisingly linear response at fields up to  $\sim 200$  MV/m disagrees with the present theoretical descriptions, which predict a significantly weaker piezoelectric response already at 100 MV/m. The strengthening of the piezoelectric response that starts at 180 MV/m is consistent with the nonlinear bond elongation effect that is predicted to be a fundamental property of perovskite ferroelectrics.

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences. One of

the authors (H.N.L.) was sponsored by the LDRD Program of ORNL, managed by UT-Battelle, LLC for the U.S. Department of Energy. Use of the Advanced Photon Source was supported by the DOE, BES, under Contract No. DE-AC02-06CH11357.

- 
- [1] K. M. Rabe and U. V. Waghmare, *Phil. Trans. R. Soc. A* **354**, 2897 (1996).
  - [2] M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
  - [3] R. E. Cohen, *Nature (London)* **358**, 136 (1992).
  - [4] X. Ren, *Nat. Mater.* **3**, 91 (2004).
  - [5] B. Noheda *et al.*, *Phys. Rev. B* **65**, 224101 (2002).
  - [6] N. Sai, K. M. Rabe, and D. Vanderbilt, *Phys. Rev. B* **66**, 104108 (2002).
  - [7] S. Tinte, K. M. Rabe, and D. Vanderbilt, *Phys. Rev. B* **68**, 144105 (2003).
  - [8] I. Souza, J. Iniguez, and D. Vanderbilt, *Phys. Rev. Lett.* **89**, 117602 (2002).
  - [9] L. Chen *et al.*, *J. Appl. Phys.* **94**, 5147 (2003).
  - [10] V. Nagarajan *et al.*, *Appl. Phys. Lett.* **81**, 4215 (2002).
  - [11] M. Ueno *et al.*, *Phys. Rev. B* **49**, 14 (1994).
  - [12] L. Bellaïche, K. Kunc, and J. M. Besson, *Phys. Rev. B* **54**, 8945 (1996).
  - [13] H. N. Lee *et al.*, *Phys. Rev. Lett.* **98**, 217602 (2007).
  - [14] J. Frantti *et al.*, *Jpn. J. Appl. Phys.* **39**, 5697 (2000).
  - [15] N. A. Pertsev *et al.*, *Phys. Rev. B* **67**, 054107 (2003).
  - [16] J. F. Scott, *Ferroelectric Memories* (Springer-Verlag, New York, 2000).
  - [17] A. Grigoriev *et al.*, *Phys. Rev. Lett.* **96**, 187601 (2006).
  - [18] A. Grigoriev *et al.*, *Rev. Sci. Instrum.* **78**, 023105 (2007).
  - [19] S.-E. Park and T. R. ShROUT, *J. Appl. Phys.* **82**, 1804 (1997).
  - [20] A. Jiang *et al.*, *Jpn. J. Appl. Phys.* **42**, 6973 (2003).
  - [21] M. Stengel and N. A. Spaldin, *Nature (London)* **443**, 679 (2006).
  - [22] C. Ederer and N. A. Spaldin, *Phys. Rev. B* **71**, 224103 (2005).