

Very large spontaneous electric polarization in Bi Fe O 3 single crystals at room temperature and its evolution under cycling fields

D. Lebeugle, D. Colson, A. Forget, and M. Viret

Citation: [Applied Physics Letters](#) **91**, 022907 (2007); doi: 10.1063/1.2753390

View online: <http://dx.doi.org/10.1063/1.2753390>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/91/2?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Effects of SrRuO 3 buffer layer thickness on multiferroic \(Bi 0.90 La 0.10 \) \(Fe 0.95 Mn 0.05 \) O 3 thin films](#)
J. Appl. Phys. **106**, 054115 (2009); 10.1063/1.3213335

[Microstructure and frequency dependent electrical properties of Mn-substituted Bi Fe O 3 thin films](#)
J. Appl. Phys. **102**, 094109 (2007); 10.1063/1.2812594

[Antiferroelectricity in multiferroic Bi Cr O 3 epitaxial films](#)
Appl. Phys. Lett. **89**, 162904 (2006); 10.1063/1.2362585

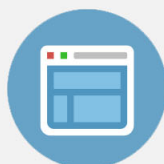
[Sol-gel derived multiferroic Bi Fe O 3 ceramics with large polarization and weak ferromagnetism](#)
Appl. Phys. Lett. **89**, 092910 (2006); 10.1063/1.2345603

[Enhanced ferroelectric properties of Cr-doped Bi Fe O 3 thin films grown by chemical solution deposition](#)
Appl. Phys. Lett. **88**, 132901 (2006); 10.1063/1.2189453



Re-register for Table of Content Alerts

Create a profile.



Sign up today!



Very large spontaneous electric polarization in BiFeO₃ single crystals at room temperature and its evolution under cycling fields

D. Lebeugle,^{a)} D. Colson, A. Forget, and M. Viret

Service de Physique de l'Etat Condensé, DSM/DRECAM, CEA Saclay, 91191 Gif-Sur-Yvette Cedex, France

(Received 19 April 2007; accepted 7 June 2007; published online 11 July 2007)

Electric polarization loops are measured at room temperature on highly pure BiFeO₃ single crystals synthesized by a flux growth method. Because the crystals have a high electrical resistivity, the resulting low leakage currents allow the authors to measure a large spontaneous polarization in excess of 100 $\mu\text{C cm}^{-2}$, a value never reported in the bulk. During electric cycling, the slow degradation of the material leads to an evolution of the hysteresis curves eventually preventing full saturation of the crystals. © 2007 American Institute of Physics. [DOI: 10.1063/1.2753390]

Recently, the perovskite-type oxides, which display electric and magnetic orders, have raised renewed interest since the two orders may interact as evidenced by magnetoelectric measurements. There is also a great interest in their potential application in spintronic devices where the magnetic state of some compounds could be affected by an electric field.¹ So far, the vast majority of compounds in which ferroelectricity and magnetism are coupled have low ordering temperatures, and room-temperature operation has not been demonstrated yet. BiFeO₃ is a good candidate as its space group *R3c* allows the existence of both antiferromagnetic and ferroelectric orders with very high transition temperatures.^{2,3} BiFeO₃ is antiferromagnetic below the Néel temperature $T_N=643$ K (neutron powder diffraction⁴) with a long range cycloidal spiral, incommensurate with the lattice;⁵ it is also ferroelectric below $T_C=1143$ K (dielectric measurements⁶ and x-ray single crystals diffraction⁴).

From an experimental point of view, revealing the ferroelectric behavior of the multiferroic BiFeO₃ at room temperature has proven to be a difficult task. Indeed, electrical measurements are very sensitive to the presence of grain boundaries in polycrystalline samples and impurities such as inclusions in single crystals. These defects, presumably more conducting than the pure BiFeO₃ crystal, induce high leakage currents which generally prevent the application of high electric fields on the sample and make the measurement of a hysteresis loop quite difficult. This remains a persistent problem in the electrical measurements of bulk samples and to date there has been no report of polarization versus electric field loops (*P-E* loops) at room temperature on single crystals of BiFeO₃.

Theoretical studies using density functional theory predict a large ferroelectric polarization of 90–100 $\mu\text{C cm}^{-2}$,⁷ consistent with the atomic displacements of the Bi³⁺ and Fe³⁺ ions. The effect is expected not to change significantly between 0 K and room temperature because of the high Curie temperature $T_C=1143$ K [extrapolated from electrical measurements made on solid solutions of BiFeO₃ with Pb(Ti,Zr)O₃ (Ref. 6)]. Recently, a ferroelectric polarization in the range of 50–90 $\mu\text{C cm}^{-2}$ has been observed in thin films at room temperature.⁸ In ceramic samples, much lower values of the polarization have been measured (8.9 $\mu\text{C cm}^{-2}$ at room temperature^{9,10}) as well as in single crystals

[6.1 $\mu\text{C cm}^{-2}$ at 77 K (Ref. 11)] revealing nonsaturated hysteretic loops. According to the authors, the difficulty in obtaining a well saturated *P-E* loop comes from the high conductivity of their samples for temperatures above 190 K probably due to the presence of impurities in the measured compounds. At the present time, the situation is still unclear concerning the real polarization of the pure compound. There is still a controversy concerning the origin of the large electric polarization found in thin films.^{8,12} Indeed, recent calculations show a value of 90–100 $\mu\text{C cm}^{-2}$ in unstrained BiFeO₃.⁷

In this letter, we present the polarization loops obtained at room temperature on highly pure single crystals and their evolution under cycling electric fields. The single crystals were grown by a spontaneous crystallization in air from a Bi₂O₃–Fe₂O₃ flux, as detailed in Ref. 13. With this procedure, we obtain millimeter sized platelets as required for electrical measurements. Electron microprobe analysis confirms the cationic stoichiometry of BiFeO₃. The possible oxygen nonstoichiometry was studied by thermogravimetry in controlled atmosphere between 25 and 800 °C. No compositional variation was detected in the studied temperature range, both under oxygen and argon, confirming a stoichiometric compound. The structural x-ray characterization has been performed on a 0.3 × 0.2 × 0.02 mm³ single crystal at 293 K with a four-circle Kappa X8 APPEX II Bruker diffractometer (Mo *Kα* radiation, $\lambda=0.71073$ Å). The data of the x-ray analysis revealed a rhomboedrally distorted perovskite-type cell with lattice constants $a_{\text{hex}}=5.571$ Å and $c_{\text{hex}}=13.868$ Å. The space group is determined to be *R3c* with six formula units per hexagonal unit cell. Three main distortions are responsible for the existence of the spontaneous polarization along the [001]_{hex} direction (i.e., [111]_{cub}): the oxygen octahedra are distorted with minimum and maximum O–O distances of 2.71 and 3.02 Å and rotated by about $\pm\alpha=13.8^\circ$ around the threefold axis, and bismuth and iron atoms are shifted by 0.54 and 0.13 Å, respectively, along the threefold axis.¹⁴ Considering these large atomic displacements, a large electric polarization is expected in the BiFeO₃ phase.

The millimeter sized single crystals of BiFeO₃ with a high resistivity [$\rho(300\text{ K}, 100\text{ V})\sim 6.10^{10}$ Ω cm] have been selected for electrical measurements. A standard *P(E)* loop method, as described in Ref. 13, has been used. It consists in measuring the current flowing in a simple resistive circuit as

^{a)}Electronic mail: dorothee.colson@cea.fr

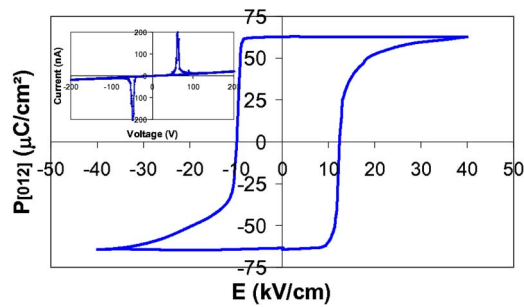


FIG. 1. (Color online) First full P - E hysteresis loop of the single crystal of BiFeO_3 at room temperature. The remnant polarization $P_{[012]}$ is $60 \mu\text{C cm}^{-2}$ and the coercive field is 12 kV/cm . The inferred full saturation polarization along the $[001]_{\text{hex}}$ direction is close to $100 \mu\text{C cm}^{-2}$. (Insert) Raw $I(V)$ data.

a function of the voltage applied to the sample [$I(V)$ characteristic] using a picoamperemeter and a voltage source. Silver electrodes are deposited on both sides of the major face of the crystal which corresponds to the $(012)_{\text{hex}}$ plane [i.e., $(010)_{\text{cub}}$]. Hence, the perpendicular plane makes an angle of $54^\circ 44'$ with the hexagonal c axis which contains the easy polarization axis. Measurement of the charge current versus applied electric field during the first electric loading reveals that most of the crystals are single (ferroelectric) domain. Indeed, if the electric field is applied in the same direction as the spontaneous polarization, no current flows in the circuit, and when the polarity is reversed, we observe an abrupt peak of the current due to the polarization switching of the only electrical domain. When integrating the charge current of two successive switching in the positive and negative voltages, a $P(E)$ cycle can be reconstructed, as shown in Fig. 1, where the first full hysteresis cycle is shown. From this, we extract the polarization and coercive field of our BiFeO_3 single crystal at room temperature and we find a remnant polarization $P_{[012]}$ of $60 \mu\text{C cm}^{-2}$ and a coercive field of 12 kV/cm . Considering that our measurement is not along the easy direction (but canted from it by $54^\circ 44'$), the inferred full saturation polarization along the $[001]_{\text{hex}}$ direction is close to $100 \mu\text{C cm}^{-2}$. Such a large value of polarization, so far only measured in thin films,⁸ has been attributed to a structural modification imposed by the substrate. Our measurements on single crystals demonstrate that this polarization is, in fact, an intrinsic property of the BiFeO_3 phase, as expected theoretically.⁷

We have measured several polarization loops in BiFeO_3 crystals in order to assess the reproducibility of the cycles

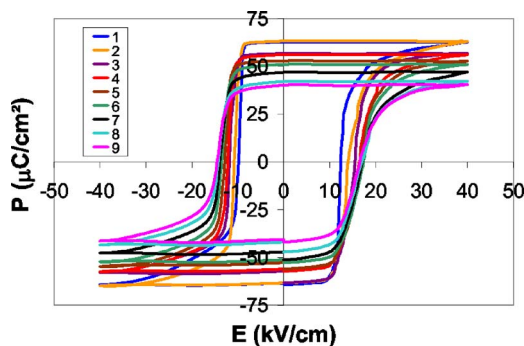


FIG. 2. (Color online) Gradual modification of the shape of the $P(E)$ loops during electric field cycling. The loops lose their squareness and the quantities most affected are the coercive and saturation fields as well as the remnant polarization.

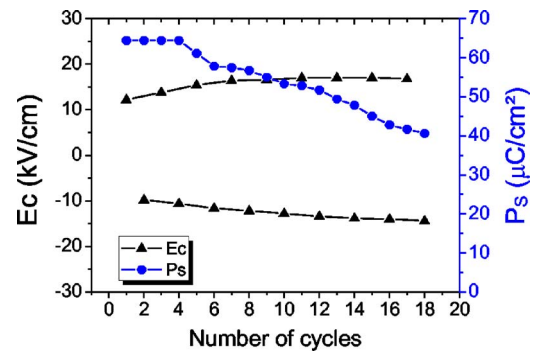


FIG. 3. (Color online) Decrease of the spontaneous polarization as well as the increase of the coercive field during electric field cycling as a consequence of a gradual increase of leakage current.

and check if any “fatigue” occurs. Because of their piezoelectric properties, it is well known that electric cycling of ferroelectric materials induces mechanical stresses which degrade the material. As a consequence, the reliability of their electric switching is reduced.^{15–17} This phenomenon is generally called the fatigue of the material and refers to the gradual electrical degradation of the compounds under cycling electric fields above the coercivity.

In the case of BiFeO_3 single crystals, we observe a gradual modification of the shape of the $P(E)$ loops during electric field cycling (Fig. 2). Visually, the loops lose their squareness and the quantities most affected are the coercive and saturation fields as well as the remnant polarization. Observations with an optical microscope confirm that microcracks appear during reversal, presumably preventing domain walls from moving easily through the sample. Hence, full saturation is obtained at progressively larger fields for which, eventually, the leakage current induces significant Joule heating. When these large leakage currents are reached, it becomes impossible to fully saturate the crystals and their polarization decreases, as can be seen in Fig. 3. Eventually, temperature effects further damage the samples and the coercive fields cannot be reached anymore. Hence, measurements performed after cycling become unrepresentative of the intrinsic properties of the material.

In summary, we showed here that highly pure single crystals of BiFeO_3 have a high enough resistivity to allow us to measure a clear polarization loop at room temperature. The as-synthesized crystals are also found to be ferroelectrically single domain. We infer from the first polarization loop a large intrinsic electric polarization of $100 \mu\text{C cm}^{-2}$ at room temperature, which is consistent with that predicted from the perfect BiFeO_3 unit cell. Hence, this large value of polarization previously thought to be a property of thin films is, in fact, intrinsic to the pure BiFeO_3 phase. Measurements of several successive polarization loops show that the samples become harder to polarize as coercivity and saturation fields increase with cycling, eventually reaching fields where leakage currents prevent the application of a large enough voltage.

The authors are grateful to S. Poissonnet for performing electron microprobe chemical analysis and also to R. Guillot for x-ray diffraction measurements on single crystals. One of the authors (D. C.) wants to acknowledge the Conseil Régional de l’Île de France (Sésame 2002-2006) and the MIAT project “Matériaux à Propriétés Remarquables” for

their financial supports. This research was supported by the Agence Nationale de la Recherche, Project “FEMMES” NT05-1_45147.

- ¹W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature (London)* **442**, 759 (2006).
- ²C. Tabares-Munoz, J.-P. Rivera, A. Bezings, A. Monnier, and H. Schmid, *Jpn. J. Appl. Phys., Suppl.* **24**, 1051 (1985).
- ³T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, *Nat. Mater.* **5**, 829 (2006).
- ⁴J. M. Moreau, C. Michel, R. Gerson, and W. J. James, *J. Phys. Chem. Solids* **32**, 1315 (1971).
- ⁵I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, *J. Phys. C* **15**, 4835 (1982).
- ⁶R. T. Smith, G. D. Achenbach, R. Gerson, and W. J. James, *J. Appl. Phys.* **39** 70 (1968).
- ⁷J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).
- ⁸J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ⁹Y. P. Wang, G. L. Yuan, X. Y. Chen, J.-M. Liu, and Z. G. Liu, *J. Phys. D* **39**, 2019 (2006).
- ¹⁰A. K. Pradhan, K. Zhang, D. Hunter, J. B. Dadson, G. B. Loutts, P. Bhattacharya, R. Katiyar, J. Zhang, D. J. Sellmer, U. N. Roy, Y. Cui, and A. Burger, *J. Appl. Phys.* **97**, 093903 (2005).
- ¹¹J. R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* **8**, 1073 (1970).
- ¹²W. Eerenstein, F. D. Morrison, J. Dho, M. G. Blamire, J. F. Scott, and N. D. Mathur, *Science* **307**, 1203 (2005).
- ¹³D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, *Phys. Rev. B*, in press.
- ¹⁴F. Kubel and H. Schmid, *Acta Crystallogr., Sect. B: Struct. Sci.* **46**, 698 (1990).
- ¹⁵J. Shieh, J. E. Huber, and N. A. Fleck, *J. Eur. Ceram. Soc.* **26**, 95 (2006).
- ¹⁶C. S. Lynch, L. Chen, W. Yang, Z. Suo, and R. M. McMeeking, *J. Intell. Mater. Syst. Struct.* **6** 191 (1995).
- ¹⁷H. Cao and A. G. Evans, *J. Am. Ceram. Soc.* **77** 1783 (1994).