Nonstoichiometric BiFe$_{0.9}$Ti$_{0.05}$O$_3$ multiferroic ceramics with ultrahigh electrical resistivity

Yan Hong Gu,[1] Yu Wang,[2] Feng Chen,[2] Helen Lai Wah Chan,[2] and Wan Ping Chen[1,a)]

[1]*Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education and School of Physics and Technology, Wuhan University, Wuhan 430072, China*
[2]*Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hong Kong, China*

BiFeO$_3$, BiFe$_{0.9}$Ti$_{0.1}$O$_3$, and BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics of relatively high perovskite phase content were prepared for a comparison study. While both BiFe$_{0.9}$Ti$_{0.1}$O$_3$ and BiFe$_{0.9}$Ti$_{0.05}$O$_3$ exhibit similarly improved weak ferromagnetism over BiFeO$_3$, there exists a major difference in the x-ray diffraction patterns of BiFe$_{0.9}$Ti$_{0.1}$O$_3$ and BiFe$_{0.9}$Ti$_{0.05}$O$_3$, and the leakage current of BiFe$_{0.9}$Ti$_{0.05}$O$_3$ is decreased by five orders of magnitude from that of BiFe$_{0.9}$Ti$_{0.1}$O$_3$. With an ultrahigh electrical resistivity, over 1×10^{14} Ω cm, BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramic displays an especially low dielectric loss, 0.015 at 100 Hz, a remanent polarization P_r of 0.23 μC/cm^2 and a remanent magnetization M_r of 0.13 emu/g at room temperature. It is proposed that the Fe-deficiency in BiFe$_{0.9}$Ti$_{0.05}$O$_3$ decreases the amount of Fe^{2+} and leads to the ultrahigh electrical resistivity. Nonstoichiometric compositions should receive more attention for developing high quality BiFeO$_3$ multiferroic materials. © *2010 American Institute of Physics*. [doi:10.1063/1.3506526]

I. INTRODUCTION

With a high Curie temperature (810–830 °C) and a high Neel temperature (370 °C), BiFeO$_3$ shows both ferroelectric and magnetic orderings above room temperature and is of great attraction for multiferroic exploring and applications.[1,2] However, BiFeO$_3$ usually exhibits a relatively high leakage current that is detrimental to ferroelectric performance and often makes BiFeO$_3$ practically unusable.[3,4] As a matter of fact, Fe^{3+} tends to be partially reduced to Fe^{2+} and electronic conduction occurs through electron hopping between Fe^{3+} and Fe^{2+} in most ferrites, including BiFeO$_3$, and it is difficult to obtain a really high electrical resistivity in them. The electrical resistivity of BiFeO$_3$ is usually much lower than that of perovskite type titanates, which are typical ferroelectric materials. It is also difficult to derive weak ferromagnetism in pure BiFeO$_3$,[5] whose space-modulated spin structure may lead to a cancellation of the possible nonzero remnant magnetization permitted by the canted G-type antiferromagnetic order.[6,7] These problems have to be satisfactorily overcome before BiFeO$_3$ can be regarded as an ideal multiferroic material. Upon extensive investigations in the past decade, it is quite encouraging to find that BiFeO$_3$ can be greatly tailored toward an ideal multiferroic material through doping[8–10] and/or forming solid-state-solution with other perovskite type oxides,[11] and through epitaxial strain and interfacial coupling for BiFeO$_3$ thin films in addition.[12]

Among various kinds of doping reported, Ti substitution for Fe, which can be expressed *as* BiFe$_{1-x}$Ti$_x$O$_3$, seems especially attractive. It could not only decrease the leakage current but also induce a remanent magnetization in BiFeO$_3$.[13,14] In other words, Ti substitution is promising for simultaneously solving two main problems of BiFeO$_3$ as a multiferroic material. However, the decrease in leakage current varies quite significantly among different reports, some of which are listed here: a decrease by three orders of magnitude upon 2% Ti substitution in thin films prepared through pulsed laser deposition,[8] a decrease by two orders of magnitude upon 5% Ti substitution in thin films prepared through sol-gel spin-coating technique,[15] a decrease by approximately six orders of magnitude upon 25% Ti substitution in bulk ceramics,[13] a decrease by only a factor of three upon 5% Ti substitution in thin films prepared through chemical solution deposition.[16] The leakage current was even increased upon Ti substitution in a couple of other cases.[16,17] Perhaps such a great variety suggests that the influence of Ti substitution is sensitive to some additional factors. Obviously, more studies are highly desirable to obtain a clear understanding and make the influence of Ti substitution more reliable or even further optimized. In all these previous investigations, a fraction of Fe was substituted by the same amount of Ti to maintain stoichiometry. Presently, we have extended the study on Ti substitution to some nonstoichiometric formulas and observed an ultrahigh electrical resistivity, over 1×10^{14} Ω cm at room temperature, in nonstoichiometric BiFe$_{0.9}$Ti$_{0.05}$O$_3$. As far as we know, this is by far the highest electrical resistivity obtained for BiFeO$_3$ ceramics and thin films. It demonstrates the great extent to which the properties of BiFeO$_3$ can be tailored and should highlight the importance of defect subsystem associated with nonstoichiometric compositions in developing high quality BiFeO$_3$ multiferroic materials.

II. EXPERIMENTAL

Analytical grade Bi$_2$O$_3$, Fe$_2$O$_3$, and TiO$_2$ powders were used as the starting precursors. The powders were carefully weighed and mixed to obtain compositions of BiFeO$_3$,
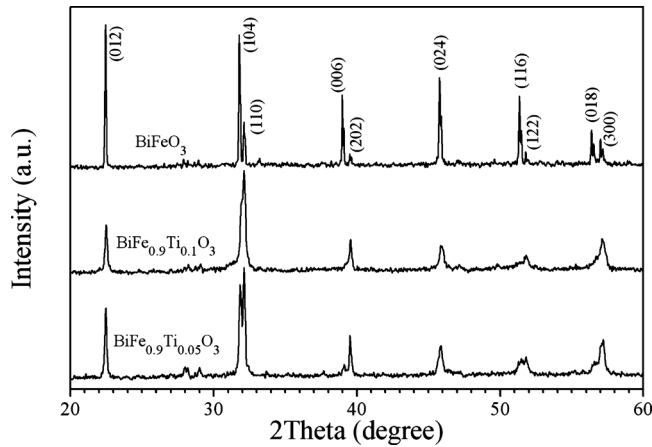
a)Electronic mail: wpchen@whu.edu.cn.

FIG. 1. XRD patterns taken on the surface of $BiFeO_3$, $BiFe_{0.9}Ti_{0.1}O_3$, and $BiFe_{0.9}Ti_{0.05}O_3$ ceramics.

$BiFe_{0.9}Ti_{0.1}O_3$, and $BiFe_{0.9}Ti_{0.05}O_3$, and ball-milled for 24 h using deionized water as medium and then dehydrated in an oven at 120 °C for 12 h. The powders were granulated and uniaxially pressed into pellets of 10 mm in diameter and 1 mm thick by applying a pressure of 7 MPa. In order to obtain samples with high perovskite phase content and possibly high electrical resistivity, for every composition, a series of sintering systems were tested and then an optimum sintering system was chosen. The optimum sintering system adopted for $BiFeO_3$ was heating at 850 °C for 30 min and then annealing in air to room temperature, for $BiFe_{0.9}Ti_{0.1}O_3$ it was heating at 900 °C for 30 min and annealing in air to room temperature, and for $BiFe_{0.9}Ti_{0.05}O_3$ it was heating at 810 °C for 120 min and furnace-cooling to room temperature.

The crystal structure and phase content of the sintered samples were examined by x-ray diffraction (XRD) on an x-ray diffractometer (Brucker D8 Discover) using Cu $K\alpha$ radiation. The microstructure of the samples was observed using scanning electron microscopy (SEM). *I-V* characteristics of the samples were recorded through a Keithley electrometer/high resistance meter (6517A). The dielectric constant and dielectric loss were measured using an impedance analyzer (Agilent 4294A). The ferroelectric hysteresis loop was characterized by a ferroelectric tester (Precision Premier Workstation Radiant Technology, USA). The magnetization hysteresis (*M-H*) loop was evaluated using a physical properties measurement system (Quantum Design PPMS-9).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns taken on the surfaces of three ceramic pellets we prepared according to nominal compositions of $BiFeO_3$, $BiFe_{0.9}Ti_{0.1}O_3$, and $BiFe_{0.9}Ti_{0.05}O_3$. It can be seen that they are all of relatively high perovskite phase content and the content of secondary phases in them is small. It is interesting to note that there are some noticeable differences among their perovskite phases. On one hand, some similar changes can be observed in the perovskite phases of $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$, e.g., their (006), (116), and (018) peaks are dramatically depressed upon Ti substitution. On the other hand, there is a major
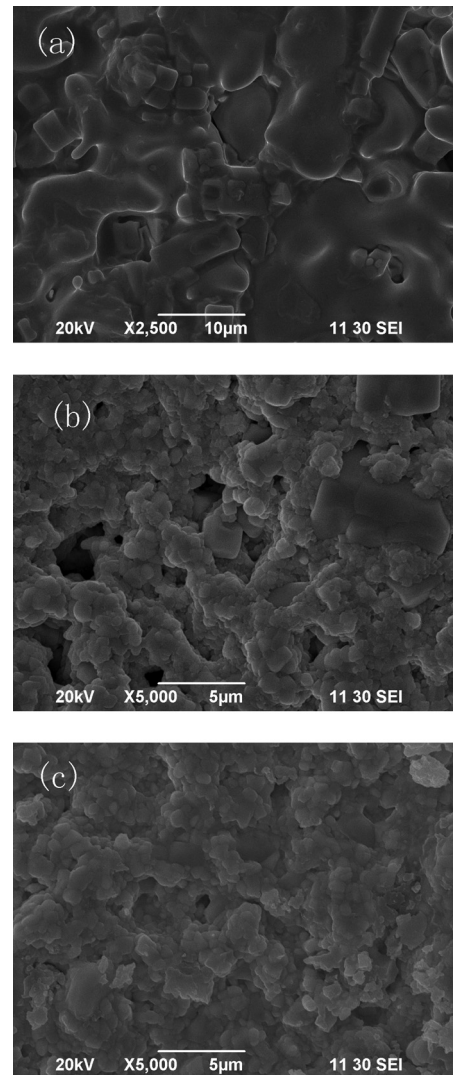

FIG. 2. SEM micrographs taken on the as-sintered ceramic surface of (a) $BiFeO_3$, (b) $BiFe_{0.9}Ti_{0.1}O_3$, and (c) $BiFe_{0.9}Ti_{0.05}O_3$.

difference between the perovskite phases of $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$. For $BiFeO_3$, the peaks of (104) and (110) are clearly split; while for $BiFe_{0.9}Ti_{0.1}O_3$, this peak splitting almost cannot be observed. This disappearance of peak splitting [(104)/(110)] in the XRD pattern has been commonly observed for Ti substitution.[13,14,16,17] While for $BiFe_{0.9}Ti_{0.05}O_3$, this peak splitting remains upon Ti substitution. It implies that Ti substitution leads to some changes in the crystal structure of $BiFeO_3$ and there exist some subtle differences in those of $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$, representative of stoichiometric and nonstoichiometric formulas with Ti substitution, respectively.

As shown in Fig. 2, these three kinds of ceramics exhibit quite different surface morphologies. A rapid liquid phase sintering has been proved effective for preparing undoped $BiFeO_3$ ceramics of high phase purity.[18] Liquid phase sintering should also have occurred in the $BiFeO_3$ ceramics here and some features of melt, including unclear grain boundaries, can be obviously observed in Fig. 2(a). On the other hand, for the other two ceramics with Ti substitution, their grain boundaries are relatively clear and very fine grains are
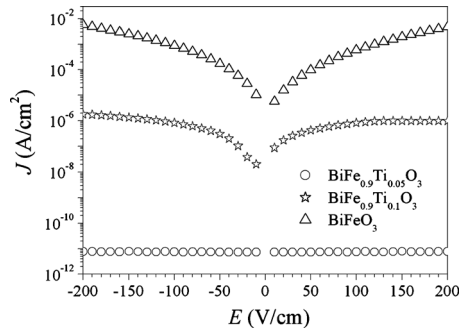
FIG. 3. *J-E* characteristics measured for $BiFeO_3$, $BiFe_{0.9}Ti_{0.1}O_3$, and $BiFe_{0.9}Ti_{0.05}O_3$ ceramics.

FIG. 4. Frequency spectra of dielectric properties measured for $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$ ceramics.

observed. Ti substitution should be very effective to suppress the appearance of liquid phases so the $BiFe_{0.9}Ti_{0.1}O_3$ ceramic has clearer grain boundaries than the $BiFeO_3$ ceramic even though it was sintered at a temperature 50 °C higher. Similar images have been observed by other researchers.[13,19] The sintering shrinkage of diameter is 7%, 8.4%, and 10% for the ceramics of $BiFeO_3$, $BiFe_{0.9}Ti_{0.1}O_3$, and $BiFe_{0.9}Ti_{0.05}O_3$, respectively. Less pores can be observed in the ceramic of $BiFe_{0.9}Ti_{0.05}O_3$ than $BiFe_{0.9}Ti_{0.1}O_3$ from the surface morphologies.

Figure 3 shows the current density versus electric field (*J-E*) characteristics of the ceramics measured at room temperature. As expected for Ti substitution, the leakage current density of $BiFe_{0.9}Ti_{0.1}O_3$ is decreased from that of $BiFeO_3$ by more than three orders of magnitude in our study. It is quite surprising that $BiFe_{0.9}Ti_{0.05}O_3$ exhibits an extremely small leakage current, which actually cannot be detected in our measurement. It is decreased from that of $BiFeO_3$ by about nine orders of magnitude, from that of $BiFe_{0.9}Ti_{0.1}O_3$ by more than five orders of magnitude. An ultrahigh electrical resistivity, over 1×10^{14} Ω cm at room temperature, was calculated out for $BiFe_{0.9}Ti_{0.05}O_3$ ceramic, using the data obtained at an electric field of 500 V/cm. Such a high electrical resistivity has been quite unexpected for $BiFeO_3$ as a ferrite. As pointed out by Qi *et al.*,[8] the charge compensation required by substitution of Ti^{4+} for Fe^{3+} can be achieved through three mechanisms: filling of oxygen vacancies, decrease in cation valence, and creation of cation vacancies. Decrease in cation valence, namely, Fe^{3+} is partially reduced to Fe^{2+}, will result in electronic conduction and should not be considered for the case of decreased leakage current. As for the other two mechanisms, each of them has been proposed to be the dominant charge compensation mechanism for Ti substitutions by some researchers.[8,14,15] Our results here clearly show that the leakage current can be further greatly deceased in nonstoichiometric $BiFe_{0.9}Ti_{0.05}O_3$ with some Fe-deficiency, or V'''_{Fe}. The difference in crystal structure between $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$ revealed through XRD analyses may be regarded as a sign for the difference in their defect subsystems. Supposed that 5% $Ti^{\bullet}_{Fe}$ and 5% V'''_{Fe} are formed in $BiFe_{0.9}Ti_{0.05}O_3$, the negative charge from V'''_{Fe} is more than the positive charge from $Ti^{\bullet}_{Fe}$, which will decrease other negative charge already present, including Fe'_{Fe}, to reach electric neutrality. In this way the amount of Fe^{2+} is decreased and electron hopping between Fe^{3+} and Fe^{2+} is
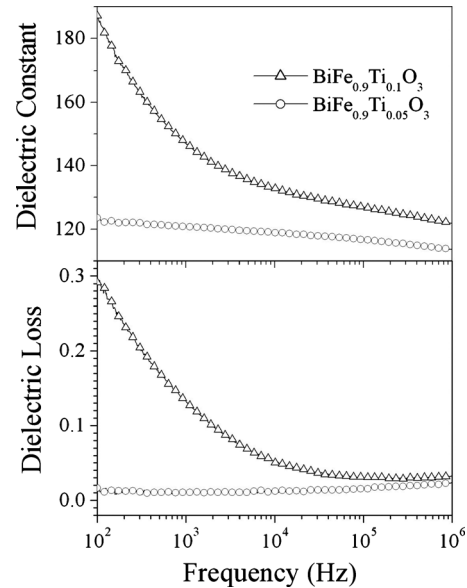
therefore suppressed and an ultrahigh electrical resistivity is observed. So the Fe-deficiency in $BiFe_{0.9}Ti_{0.05}O_3$ is the main reason responsible for the ultrahigh electrical resistivity. Further investigations on the defect subsystem in Ti-substituted nonstoichiometric formulas, especially the relationship between $Ti^{\bullet}_{Fe}$ and V'''_{Fe}, are being conducted.

The dielectric constant and dielectric loss as a function of frequency at room temperature for $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$ ceramics are shown in Fig. 4. The dielectric loss of $BiFeO_3$ ceramic is too high so the data for $BiFeO_3$ are not included. The dielectric loss of $BiFe_{0.9}Ti_{0.1}O_3$ ceramic is 0.30 at 100 Hz and decreases quickly with increasing frequency. Similar values of dielectric loss have been reported for Ti-substituted $BiFeO_3$ ceramics prepared by other researchers.[13] In contrast, the dielectric loss of $BiFe_{0.9}Ti_{0.05}O_3$ ceramic is only 0.015 at 100 Hz and almost remains unchanged with increasing frequency. Such a low dielectric loss is in agreement with the ultrahigh electrical resistivity observed and is attractive to most ferroelectric materials. Both the dielectric constant and dielectric loss of $BiFe_{0.9}Ti_{0.05}O_3$ show a much weaker dependence on frequency than those of $BiFe_{0.9}Ti_{0.1}O_3$, indicating that the leakage current has obviously influenced the dielectric properties of $BiFe_{0.9}Ti_{0.1}O_3$ at low frequencies. Figure 5 plots the polarization hysteresis (*P-E*) loops of $BiFe_{0.9}Ti_{0.1}O_3$ and $BiFe_{0.9}Ti_{0.05}O_3$ ceramics at room temperature. Due to the high leakage current, the ferroelectric hysteresis loop of $BiFeO_3$ ceramics has not been achieved. As shown in Fig. 5(a), the unsaturated loose *P-E* loop of $BiFe_{0.9}Ti_{0.1}O_3$ ceramic has rounded corners, which indicates a significant conductive loss and is consistent with the previous electric (*J-E*) properties. It is obvious that a much improved polarization hysteresis loop is observed for $BiFe_{0.9}Ti_{0.05}O_3$ ceramic, showing a saturation polarization P_S of 0.61 $\mu C/cm^2$ and a remanent polarization P_r of 0.23 $\mu C/cm^2$. Its P_r is almost equal to that of $BiFe_{0.8}Ti_{0.2}O_3$ ceramic prepared by Kumar *et al.*,[20] whereas is about one third of that of a
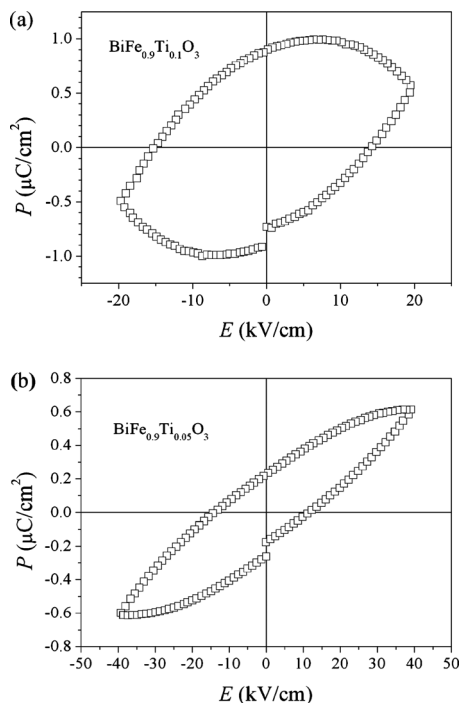
FIG. 5. Polarization hysteresis *P-E* loops of (a) BiFe$_{0.9}$Ti$_{0.1}$O$_3$ and (b) BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics.

(PLZT)$_{0.3}$(BiFeO$_3$)$_{0.7}$ solid solution,[11] whose ferroelectricity should have been enhanced through introducing PLZT.

The magnetization hysteresis (*M-H*) loops of the ceramics for the maximum magnetic field (H_m) of 60 kOe at room temperature are shown in Fig. 6. No hysteresis loop is observed for BiFeO$_3$ ceramic, which is common for undoped BiFeO$_3$ ceramics as we have mentioned before. It is evident that BiFe$_{0.9}$Ti$_{0.1}$O$_3$ and BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics both show improved weak ferromagnetism with remanent magnetization (M_r) of 0.11 emu/g and 0.13 emu/g, respectively. As a matter of fact, weak ferromagnetism has been observed in Ti-substituted BiFeO$_3$ ceramic samples prepared by different groups.[13,14] Some possible mechanisms, including destruction of the space-modulated antiferromagnetic state through structural distortion,[21,22] breakdown of the balance between the antiparallel sublattices due to substitutions with ions of different valences,[23] have been proposed. It should be pointed out that the *M-H* loops of BiFe$_{0.9}$Ti$_{0.1}$O$_3$ and BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics are actually very close to each

other, indicating that they should have a quite similar spin ordering despite of the great difference in electronic conduction. It is interesting to note that the magnetic behavior is not degraded when the electrical resistivity is so greatly increased through introduction of some Fe-deficiency. So for those BiFeO$_3$ materials whose weak ferromagnetism has been much enhanced,[9] their overall multiferroic behavior should be further improved when their electrical resistivity is greatly increased through similarly adopting some nonstoichiometric compositions.

IV. CONCLUSION

We have achieved an ultrahigh electrical resistivity, over 1×10^{14} Ω cm at room temperature, and an especially low dielectric loss, 0.015 at 100 Hz, in nonstoichiometric BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics, which also exhibit a polarization hysteresis *P-E* loop with a remanent polarization P_r of 0.23 μC/cm^2 and a magnetization hysteresis *M-H* loop with a remanent magnetization M_r of 0.13 emu/g at room temperature. With BiFeO$_3$ and BiFe$_{0.9}$Ti$_{0.1}$O$_3$ ceramics as references, Ti substitution is proved effective to induce weak ferromagnetism and Fe vacancies play a vital role in suppressing electronic conduction in BiFeO$_3$. The small amount of Ti-substitution and Fe-deficiency in BiFe$_{0.9}$Ti$_{0.05}$O$_3$ may reveal a great potential of tailoring the defect subsystem in BiFeO$_3$ for developing high-performance BiFeO$_3$ multiferroic materials.

FIG. 6. (Color online) Magnetization hysteresis *M-H* loops of BiFeO$_3$, BiFe$_{0.9}$Ti$_{0.1}$O$_3$, and BiFe$_{0.9}$Ti$_{0.05}$O$_3$ ceramics.

[1] J. 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).
[2] G. Catalan and J. F. Scott, Adv. Mater. **21**, 2463 (2009).
[3] W. Eerenstein, F. D. Morrison, J. Dho, M. G. Blamire, J. F. Scott, and N. D. Mathur, Science **307**, 1203a (2005).
[4] G. W. Pabst, L. W. Martin, Y. H. Chu, and R. Ramesh, Appl. Phys. Lett. **90**, 072902 (2007).
[5] J. Dho, X. D. Qi, H. Kim, J. L. MacManus-Driscoll, and M. G. Blamire, Adv. Mater. **18**, 1445 (2006).
[6] B. Ruette, S. Zvyagin, A. P. Pyatakov, A. Bush, J. F. Li, V. I. Belotelov, A. K. Zvezdin, and D. Vieland, Phys. Rev. B **69**, 064114 (2004).
[7] F. Bai, J. Wang, M. Wuttig, J. F. Li, N. Wang, A. P. Pyatakov, A. K. Zvezdin, L. E. Cross, and D. Vieland, Appl. Phys. Lett. **86**, 032511 (2005).
[8] X. D. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, Appl. Phys. Lett. **86**, 062903 (2005).
[9] G. L. Yuan, S. W. Or, J. M. Liu, and Z. G. Liu, Appl. Phys. Lett. **89**, 052905 (2006).
[10] C.-H. Yang, J. Seidel, S. Y. Kim, P. B. Rossen, P. Yu, M. Gajek, Y. H. Chu, L. W. Martin, M. B. Holcomb, Q. He, P. Maksymovych, N. Balke, S. V. Kalinin, A. P. Baddorf, S. R. Basu, M. L. Scullin, and R. Ramesh, Nature Mater. **8**, 485 (2009).
[11] T. Kanai, S. I. Ohkoshi, A. Nakajima, T. Watanabe, and K. Hashimoto, Adv. Mater. **13**, 487 (2001).
[12] R. Ramesh and N. A. Spaldin, Nature Mater. **6**, 21 (2007).
[13] M. Kumar and K. L. Yadav, J. Appl. Phys. **100**, 074111 (2006).
[14] I. O. Troyanchuk, N. V. Tereshko, A. N. Chobot, M. V. Bushinsky, and K. Barner, Physica B **404**, 4185 (2009).

[15]Y. Wang and C. W. Nan, Appl. Phys. Lett. **89**, 052903 (2006).

[16]N. M. Murari, R. Thomas, R. E. Melgarejo, S. P. Pavunny, and R. S. Katiyar, J. Appl. Phys. **106**, 014103 (2009).

[17]G. D. Hu, S. H. Fan, C. H. Yang, and W. B. Wu, Appl. Phys. Lett. **92**, 192905 (2008).

[18]Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu, and Z. G. Liu, Appl. Phys. Lett. **84**, 1731 (2004).

[19]M. Kumar and K. L. Yadav, Appl. Phys. Lett. **91**, 112911 (2007).

[20]M. Kumar and K. L. Yadav, J. Phys.: Condens. Matter **18**, L503 (2006).

[21]M. M. Kumar, S. Srinath, G. S. Kumar, and S. V. Suryanarayana, J. Magn. Magn. Mater. **188**, 203 (1998).

[22]J. Wang, A. Scholl, H. Zheng, S. B. Ogale, D. Viehland, D. G. Schlom, N. A. Spaldin, K. M. Rabe, M. Wuttig, L. Mohaddes, J. Neaton, U. Waghmare, T. Zhao, and R. Ramesh, Science **307**, 1203b (2005).

[23]K. Ueda, H. Tabata, and T. Kawai, Appl. Phys. Lett. **75**, 555 (1999).