

Electrical behavior of $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{FeO}_3$ thin films grown by the soft chemical method

F.B. Destro^a, F. Moura^b, C.R. Foschini^c, M.G. Ranieri^a, E. Longo^c, A.Z. Simões^{a,*}

^aUniversidade Estadual Paulista (UNESP), Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Pedregulho, CEP 12516-410 Guaratinguetá-SP, Brazil

^bUniversidade Federal de Itajubá (UNIFEI), Campus Itabira, Rua São Paulo, 377, Bairro: Amazonas, CEP 35900-37 Itabira, MG, Brazil

^cLaboratório Interdisciplinar em Cerâmica (LIEC), Departamento de Físico-Química, Instituto de Química, UNESP, CEP: 14800-900 Araraquara, SP, Brazil

Received 19 December 2013; accepted 15 January 2014

Available online 25 January 2014

Abstract

This paper focuses on the electrical properties of $\text{Bi}_{0.95}\text{Nd}_{0.05}\text{FeO}_3$ thin films (BNFO05) deposited on Pt/TiO₂/SiO₂/Si (100) substrates by the soft chemical method. A BNFO05 single phase was simultaneously grown at a temperature of 500 °C for 2 h. Room temperature magnetic coercive field indicates that the film is magnetically soft. The remanent polarization (P_r) and the coercive field (E_c) measured were 51 $\mu\text{C}/\text{cm}^2$ and 65.0 kV/cm, respectively, and were superior to the values found in the literature. XPS results show that the oxidation state of Fe is purely 3+, which is beneficial for producing a BNFO05 film with low leakage current. The polarization of the Au/BNFO05 on Pt/TiO₂/SiO₂/Si (100) capacitors with a thickness of 230 nm exhibited no degradation after 1×10^8 switching cycles at a frequency of 1 MHz. Experimental results demonstrated that the soft chemical method is a promising technique for growing films with excellent electrical properties, and can be used in various integrated device applications.

© 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Chemical synthesis; Electron diffraction; Ferroelectricity; Thin films

1. Introduction

Ferroelectromagnets are a class of materials exhibiting the coexistence of magnetic and ferroelectric orderings in a certain range of temperature [1]. Therefore, these materials not only can be used in magnetic and ferroelectric devices, but also have the potential ability to couple electric and magnetic polarizations which provide an additional degree of freedom in device design and applications. Consequently, ferroelectromagnetism is the subject of intensive investigation because this phenomenon potentially offers a whole range of applications, including the emerging fields of spintronics, data-storage media, and multiple-state memories [2–6]. Ferromagnetic and ferroelectric ordering parameters are widely used to store binary information in magnetoresistive random access memory (MRAM) devices [7] and ferroelectric random access memory

(FeRAM) devices [8]. Unfortunately, ferroelectric ferromagnets (or ferrimagnets) are very scarce and the search for a material with both large and finite polarization and magnetization at room temperature is still in progress. To reach this goal, the first step is to obtain materials with magnetoelectric coupling. Among all known multiferroics, the only compound that satisfies these criteria is bismuth ferrite (BFO). First synthesized in the late 1950s [9], BFO was shown to be a G-type antiferromagnet with a Néel temperature of 630 K by Kiselev et al. [10]. Later, Sosnowska et al. showed that the magnetic order of bulk BFO is not strictly collinear and that a cycloidal modulation with a period of 62 nm is present [11]. One property required for ferroelectric memories is long term stability. The application of ferroelectric thin films to the microelectronic industry is currently limited by the degradation of the polarization state. Device reliability (including factors such as fatigue, imprint and retention) constitutes the main obstacle to the commercialization of FeRAM devices [12]. FeRAMs have not been yet introduced beyond 130 nm

*Corresponding author. Tel./fax: +55 31 3834 6472/6136.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

complementary metal-oxide-semiconductor (CMOS) technology due to integration issues (etching, deposition techniques, and electrode developments) and not only due to polarization state degradation. Many attempts have been made to improve the ferroelectricity and magnetization of BiFeO₃. Cheng et al. [13] reported the fabrication of BiFeO₃ ceramics by the sol–gel method with large remanent polarizations: however, only negligible weak ferromagnetism was observed at room temperature. An effective way to improve the magnetic properties is ion substitution. Room temperature magnetic hysteresis loops have been observed in BiFeO₃ doped by Sr, Eu, Gd, Ba, La, Dy, etc. [14–19]. Recently, Li et al. reported the enhanced magnetic properties and large polarization in BiFeO₃ ceramics prepared by a high-pressure synthesis [20] which indicated the possible realization of ferromagnetism in non-doped BiFeO₃. A fast sintering process will maintain the high defect concentration induced at a high sintering temperature, which might induce more defects and lattice distortion to influence the spin arrangement of Fe³⁺ ions [21].

For large magnetoelectric coupling, ferroelectricity and spontaneous magnetization should coexist within the same structural phase. The coexistence of spontaneous magnetization and electric polarization has been reported in Bi_{1–x}Ln_xFeO₃ (Ln=lanthanides) systems in a relatively wide concentration range [22–29]. The crystal structure of Bi_{1–x}Nd_xFeO₃ system was studied and crystal symmetry lowering was observed from rhombohedral ($x < 0.14$) system down to the triclinic ($x > 0.14$) system. The unit cell of a $x=0.175$ composition was described with the non-central symmetric tetragonal space group P4mm whereas the central symmetric P4/mmm one was used to describe the $x=0.2$ composition [30–33]. Magnetic measurements show that the spontaneous magnetization starts to develop near the concentration of the structural transition (where R3c symmetry disappears) and increases almost linearly with increasing rare-earth ion content [34]. However, magnetic studies have been carried out in relatively small magnetic fields, and magnetization saturation was not observed.

To the knowledge of this group, no literature is currently available on the fatigue properties of neodymium modified bismuth ferrite thin film (BNFO05) grown onto Pt/TiO₂/SiO₂/Si (100) substrates by the soft chemical method. Thus, the goal of this study is to investigate the improved reliability when Nd is used as a dopant in BFO thin films. The structural and electrical properties of the films (mainly related to ferroelectric and magnetic behaviors) were investigated by using various techniques with a view to explore their technological applications.

2. Experimental procedure

BFO and BNFO05 thin films were prepared by using the soft chemical method as described elsewhere [35]. A phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) patterns recorded on a Rigaku-DMAX 2000PC model with Cu-K α radiation in the 2θ range from 20° to 60° at 0.3°/min. The annealed thin film thickness was determined by using scanning electron microscopy (SEM)

(Topcom SM-300) and by evaluating the transversal section where back-scattered electrons were utilized. Three measurements were performed to obtain an average thickness value. Raman measurements were performed using an ISAT 64000 triple monochromator. An optical microscope with 80 $\times$ objective was used to focus on the 514.5-nm radiation from a Coherent Innova 99 Ar⁺ laser on the sample. The same microscope was used to collect the back-scattered radiation. The scattering light dispersed was detected by a charge-coupled device (CCD) detection system. A PHI-5702 multi-function X-ray photoelectron spectrometer (XPS) was used, with an Al-K α X-ray source of 29.35 eV passing energy. The chamber pressure during the experiments was about 4.5×10^{-9} Torr. The calibration of the binding energy scale was controlled by using the C1s line which appears in photoelectron spectra of the as-grown samples. The surface morphology of BFO and BNFO05 thin films was measured by atomic force microscopy (AFM) using the tapping mode technique and scanning electron microscopy (SEM). Then, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition on the top electrode, the film was subjected to a post-annealing treatment in a tube furnace under an oxidant atmosphere flow of 50 mL/min at 300 °C for 1 h. Here, the desired effect was to eventually decrease present oxygen vacancies.

The hysteresis loop measurements were carried out on the films with a Radiant Technology RT6000HVS. These loops were traced using the Charge 5.0 program included in the software of the RT6000HVS in a virtual ground mode test device. For the fatigue measurements, internally generated 8.6 μ s wide square pulses or externally generated square pulses were used. The J – V measurements were recorded on the Radiant Technology tester in the current–voltage mode, with a voltage changing from 0 to +10 V, from +10 to –10 V and then back to 0 V. All measurements were performed at room temperature. Magnetization measurements were performed using a vibrating-sample magnetometer (VSM) from Quantum Design™.

3. Results and discussion

Fig. 1 shows the XRD pattern of BFO and BNFO05 thin films deposited on Pt/TiO₂/SiO₂/Si (100) substrates at 500 °C for 2 h. The polycrystalline film exhibits a pure perovskite phase. Furthermore, except for the Si (100) and Pt (111) peaks, no peaks of impurity phases such as Bi₂Fe₄O₉ and Bi₄₆Fe₂O₇₂ were observed, so pure phase BNFO05 films were obtained by using the soft chemical method. However, the presence of an impurity phase such as Bi₂Fe₄O₉ was detected in addition to the major BFO phase for the pure BFO thin film. The polycrystalline nature of the film can be attributed to the differences in nucleation energy between the ferroelectromagnetic material and the bottom electrode. According to the pattern, the film has a tetragonal perovskite structure.

The surface morphology of the BFO and BNFO05 thin films was evaluated by AFM measurements (Fig. 2). AFM studies

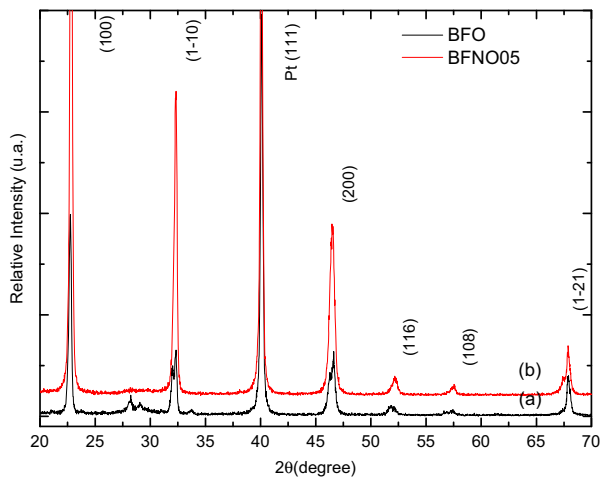


Fig. 1. X-ray diffraction of a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

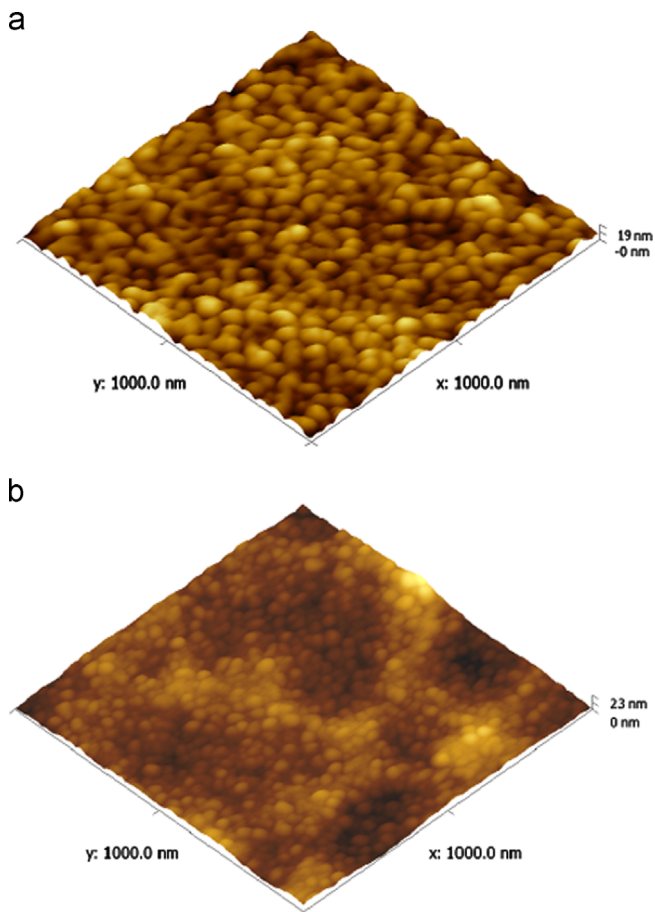


Fig. 2. AFM surface image of a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

demonstrated that Nd dopant reveals a homogeneous surface indicating that the soft chemical method allows the preparation of films with controlled morphology. The average surface roughness value is 6.2 nm for the BFO thin film with an average grain size of 85 nm. BNFO05 thin film consists of

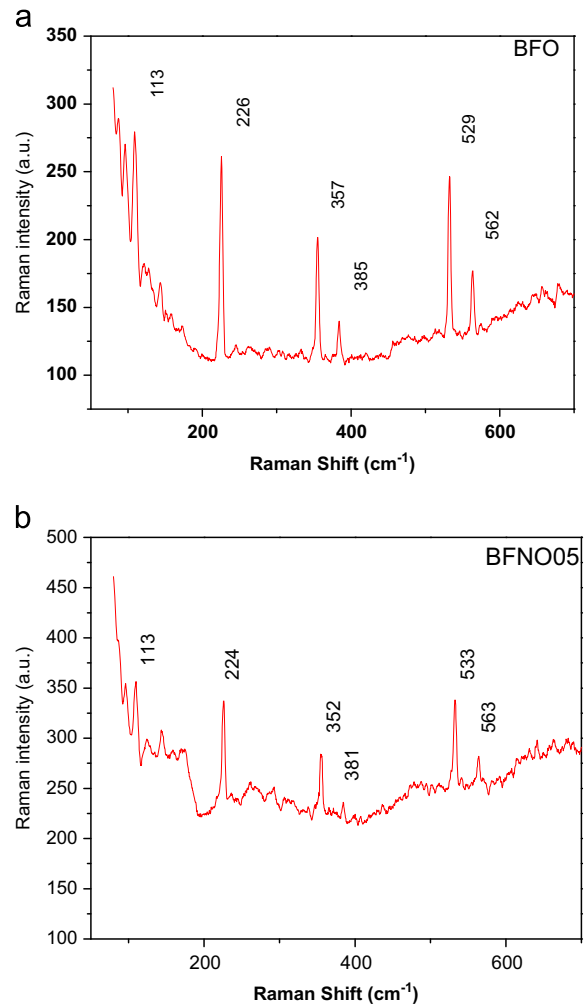


Fig. 3. Micro-Raman analysis of a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

small grains (58 nm) with a statistical roughness and a root mean square (RMS) of approximately 5.5 nm. Nd-substitution was found to be effective in improving the surface morphology of synthesized BFO-based films, because the precursor film underwent an optimized nucleation and growth process which produced films with a homogeneous and dense microstructure. In addition, the homogeneous microstructure of BNFO05 films may affect the ferroelectric properties, because the voltage can be applied uniformly onto it.

Raman analysis shows the order–disorder degree of the atomic structure at short range see Fig. 3(a) and (b). The modes further split into longitudinal and transverse components due to long electrostatic forces associated with lattice ionicity. The substitution of neodymium at the A-site lattice reduces the distortion of octahedral clusters having little influence in the relative intensity of the bands. The vibrational modes located at 226, 357, 385, 529, and 562 cm^{-1} result from the FeO_6 octahedron ($\text{Fe}=5$ or $\text{Fe}=6$). The band located below 200 cm^{-1} is due the site occupied by bismuth within the perovskite layer. Slight changes which occur above 200 cm^{-1} in BNFO05 can be associated with structural distortion and the

reduction of vibrations in the FeO_5 octahedra. Neodymium substitution has a marginal influence in the interactions between $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite structure. The vibrational modes of the BNFO05 thin film tend to disappear when compared to the BFO thin film. Structural rearrangements take place during the energy transfer process creating distortion across the octahedral (FeO_6) and dodecahedral (BiO_{12}) clusters. In this way, there is a symmetry breaking process along the network of both $[\text{FeO}_6]$ and $[\text{BiO}_{12}]$ clusters leading to lower symmetry. This can be related to structural disordering at short range, as well as a phase transition for an ordering crystal structure. The structural changes developed at the Pt interface create localized levels in the band gap and an inhomogeneous charge distribution between valence and conduction bands.

To identify the chemical bonding of BFO and BNFO05 thin films, XPS measurements were performed on the deposited surface. The wide-range spectrum of BNFO05 thin films deposited is shown in Fig. 4a. The spectrum expanded from 700 eV to 745 eV see Fig. 4(b). The 3/2 and 1/2 spin-orbit doublet components of the Fe 2p photoemission located at 711.1 and 724.6 eV, respectively, were identified as Fe^{3+} ; no

Fe^{2+} and Fe were found. XPS results show that BNFO05 thin films have a single phase with a Fe^{3+} valence state. The oxidation state of Fe was purely 3+, which was advantageous for producing thin films with low leakage current. BFO thin films reveal the same XPS spectra with the 3/2 and 1/2 spin-orbit doublet components of the Fe 2p photoemission located at 711.1 and 724.6 eV (not shown in the text).

A typical leakage current characteristic for the films is illustrated in Fig. 5(a) and (b). The curves were recorded with a voltage step width of 0.1 V and an elapsed time of 1.0 s for each voltage, and the results were plotted in measured logarithmic current density ($\log J$) versus the voltage (V), evidenced by two clearly different regions. The current density increases linearly with the external voltage in the region of low applied voltage magnitude which suggests an ohmic conduction. At higher field strengths, the current density increases exponentially which implies that at least one contribution for the conductivity results from the Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V for the BFO thin film is $2.2 \times 10^{-9} \text{ A/cm}^2$. The leakage current density decreased for the BNFO05 thin films being considered at 1.0 V is equal to $3.8 \times 10^{-11} \text{ A/cm}^2$. The main reason for such a small value can be attributed to changes in the surface roughness and the reduction of microcracks due to modification in the lattice volume after the addition of neodymium.

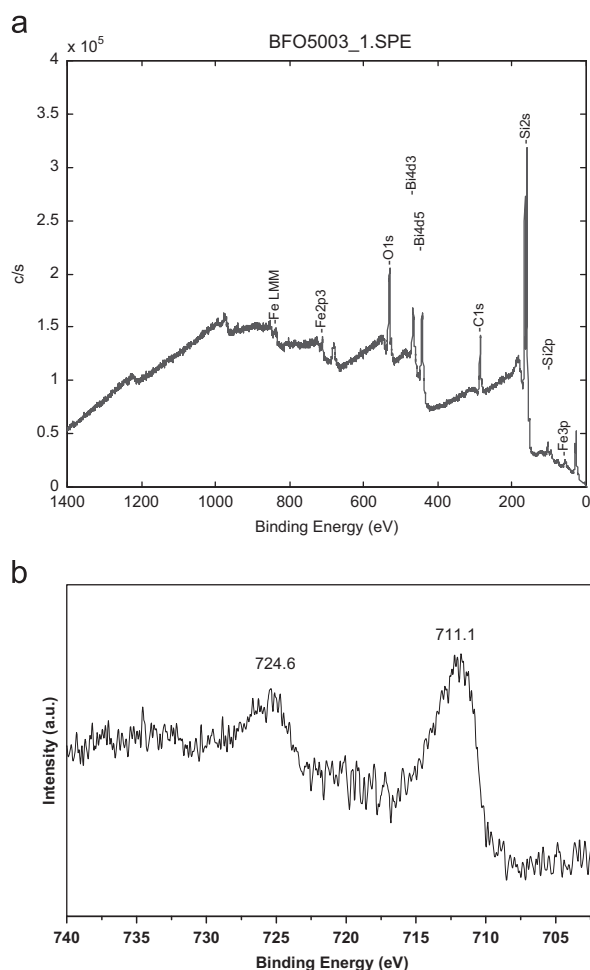


Fig. 4. XPS analysis of a multiferroic BNFO05 thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) wide-range spectrum and (b) Fe 2p peaks.

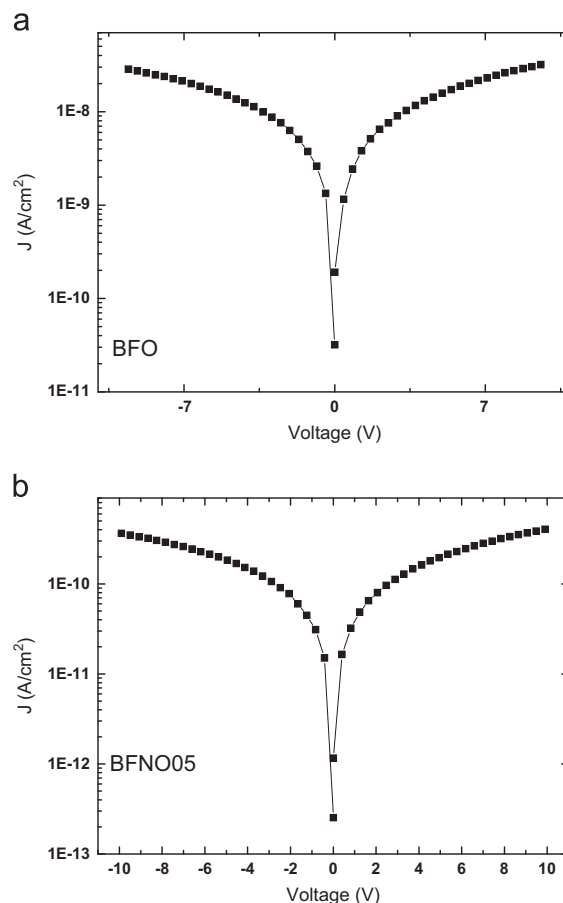


Fig. 5. Leakage current density versus applied voltage for a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

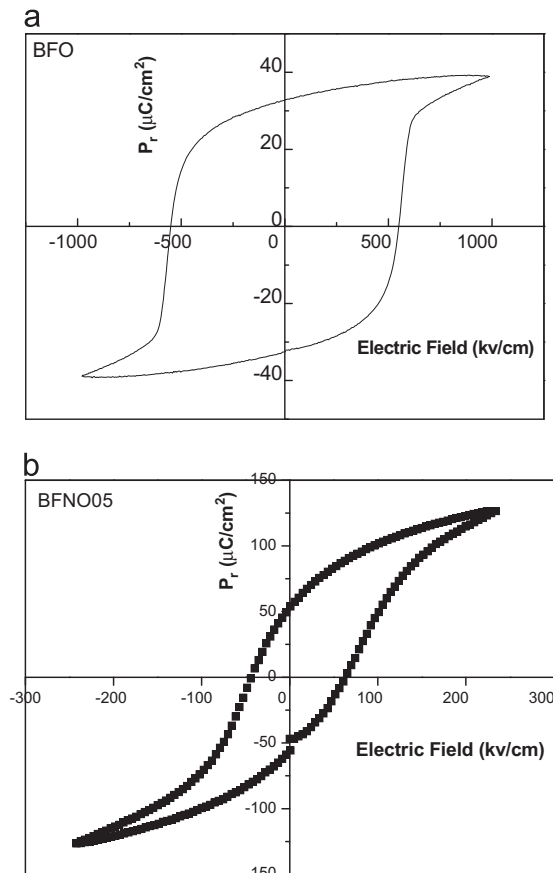


Fig. 6. Hysteresis loop of a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

Also, this might be attributed to that the Nd substitution can enhance distortion of FeO_6 octahedra and reduce the oxygen vacancy density. This may be responsible for the improved leakage behavior because oxygen vacancy plays a detrimental role in the conductivity of the film-electrode interface.

The room temperature P - E hysteresis loop of BFO and BNFO05 thin films is shown in Fig. 6(a) and (b). The BFO film presents well-saturated hysteresis characteristics with a remanent polarization (P_r) of $31 \mu\text{C}/\text{cm}^2$ and a coercive field (E_c) of 560 kV/cm at a maximum applied electric field of 1000 kV/cm. According to Wang et al. [5], the BFO ferroelectricity originates from the relative displacements of a Bi ion and a Fe-O octahedron along the (111) orientation in epitaxial BFO thin films, and the projection polarization along the (110) orientation is larger than the polarization of the (100) orientation. Since the films produced here were randomly oriented, a reasonably larger polarization was not expected. The loop for the BNFO05 thin film is well saturated with P_r of $51 \mu\text{C}/\text{cm}^2$ under an applied field of 65 kV/cm. Liu et al. [36] have reported substantially reduced leakage of BiFeO_3 films by introducing a LaNiO_3 intermediate layer. Although a saturated hysteresis loop was observed, they obtained only a remanent polarization of $26.9 \mu\text{C}/\text{cm}^2$ under 1.25 MV/cm. To the knowledge of this group, there have been very few reports on a large P_r of BNFO05 films obtained from chemical methods [37,38].

Meanwhile, the hysteresis loop in this study is more saturated than some of the BFO films on the Pt bottom electrode by the chemical solution deposition (CSD) method [39]. In fact, the pure BFO film loops on the Pt bottom electrode are unsaturated in some cases. Gonzalez et al. [40] observed saturated hysteresis loops at room temperature in pure BFO films on a Pt bottom electrode while they observed only a small remanent polarization of $36 \mu\text{C}/\text{cm}^2$ at 800 kV/cm. In other typical studies from Singh et al. [41], Hu et al. [42], and Uchida et al. [43], unsaturated loops were observed under 10 kHz at room temperature. The results in this study are comparable to the results observed in the epitaxial BFO films on a (100) SrTiO_3 substrate prepared by the PLD method [44]. The smaller coercive field of Nd-doped BFO films was consistent with the decrease of the concentration of oxygen vacancies according to defect chemistry. The increased P_r values should be attributed to the following factor: the oxygen vacancy, which mainly resides at a perovskite block and is closely followed by Bi vacancy because of its volatile property, which can induce domain pinning; therefore, the intrinsic ferroelectricity is difficult to be drawn out [45–48]. However, for BNFO05 thin film, the nonvolatile Nd substituted for volatile Bi in the perovskite block can stabilize the oxygen ions in Fe-O octahedra, thus decreasing oxygen vacancy density and minimizing the oxygen vacancy effects on ferroelectricity. Therefore, it is reasonable that BNFO05 thin films have greater P_r than BFO films at the same electrical field.

Fig. 7 plots the degradation of normalized switchable polarization $\Delta P = P^* - \hat{P}$ of the BFO and BNFO05-based films versus the number of switching cycles. P^* represents the switching polarization between two pulses with opposite polarity, and $\hat{P}$ represents the nonswitching polarization between two pulses with the same polarity. Fatigue resistance was observed up to 10^8 cycles for the BNFO05-based films suggesting a good potential for applications in ferroelectric memories. The value of nonvolatility of the BFO film decreased by 25.0%, while that of BNFO05 film decreased by 6.4%, suggesting that the Nd substitution could improve the fatigue resistance property of BFO. As described earlier, the oxygen vacancy density in BNFO05 films is less than that in BFO films. This should be responsible for the improved fatigue property of BNFO05 than BFO because oxygen vacancy plays a detrimental role in ferroelectric fatigue [49–50]. The substitution of Bi for Nd can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BFO thin films. Since a Nd^{3+} ion has no outer electron (in contrast to a Bi^{3+} ion which has a lone pair of 6s electrons) less hybridization with O 2p should lead to less structural distortion. As a consequence, the in-plane lattice constant, a , decreases while b increases as Nd is substituted, resulting in decrease in the crystal symmetry which suggests that the relaxation of the structural distortion arises from the substitution.

Measurements of magnetization (M) versus magnetic field (H) loops were recorded at room temperature (Fig. 8). The film magnetization was observed with a magnetic field of 1.3 emu/g. A weak ferromagnetic response was noticed, although enhanced magnetization was observed as compared to bulk specimens.

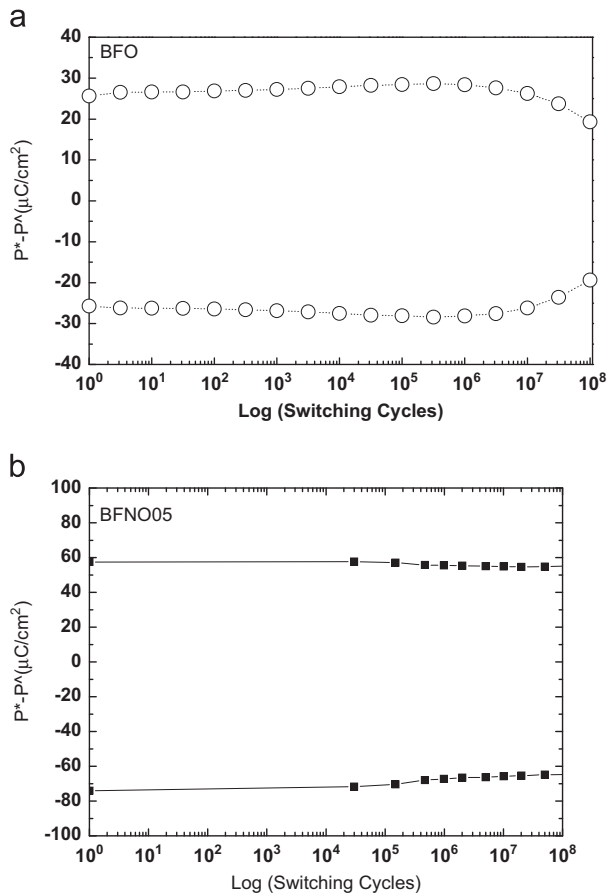


Fig. 7. Fatigue properties of a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

Gehring [51], and Goodenough and Lango [52] suggested that the statistical distribution of an Fe^{3+} ion in octahedra or the creation of lattice defects might lead to bulk magnetization and weak ferromagnetism. The appearance of weak ferromagnetism in this compound may be attributed to either the canting of the antiferromagnetically ordered spins by a structural distortion [53–55] or the breakdown of the balance between the antiparallel sublattice magnetization of Fe^{3+} due to metal ion substitution with a different valence [56]. The magnetization linearly increases with the applied magnetic field, which is a characteristic for antiferromagnets and can be changed by introducing a small fraction of rare-earth additives which will change the pure bismuth ferrite magnetic structure. A change in the magnetic properties in this case is explained not only by different magnetic moments and ion radii of neodymium (the Nd atom does not possess any intrinsic magnetic moment), but also by the anisotropy of the magnetic moments of Nd ions. The magnetization appears enhanced due to magnetic ordering on Nd substitution. This enhancement may be attributed to different factors such as (i) structural distortion due to Nd substitution, (ii) variation in the oxygen stoichiometry or Fe^{2+} ion, (iii) reduction in grain size and (iv) change in the magnetic anisotropy [57,58]. The low coercive magnetic fields of

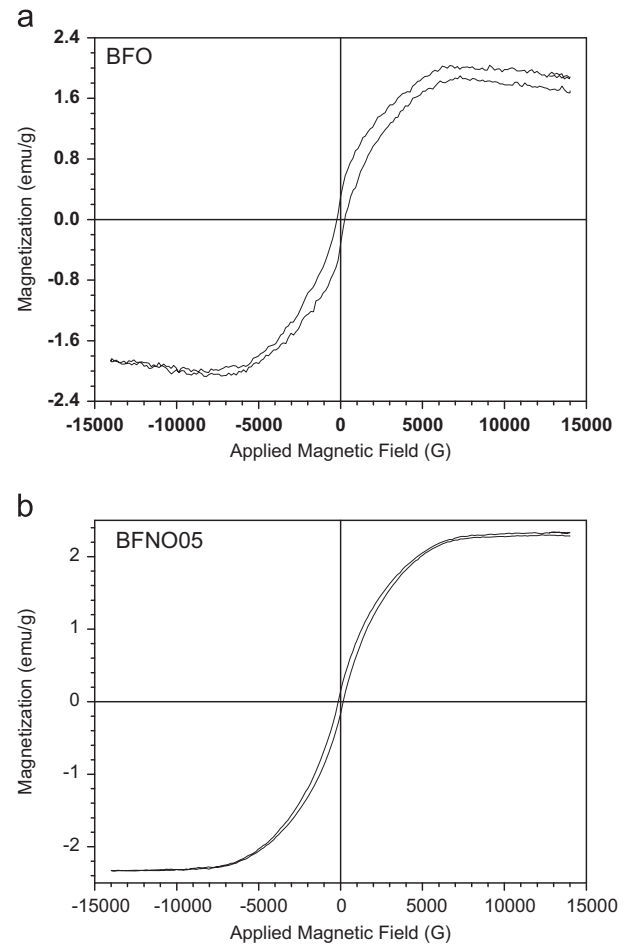


Fig. 8. Field dependency of the magnetization obtained for a multiferroic thin film deposited by the soft chemical method and annealed at 500 °C in static air for 2 h: (a) BFO and (b) BNFO05.

BNFO05 films are indicative of their magnetically soft nature and suitability for device applications.

4. Conclusions

In summary, we have demonstrated a viable chemical deposition process which enables the growth of good quality BFO and Nd-based BiFeO_3 multiferroic thin films. The leakage-current density of the BNFO05 film was around 10^{-11} A/cm^2 with a remanent polarization P_r of $51 \mu\text{C/cm}^2$ at room temperature. The low conductivity of the BNFO05 film is a consequence of oxygen vacancies ordering which prevents oxygen ions from migrating and lessens conditions for the trapping of electrons. In-plane magnetization-field curves revealed magnetization of the BFO and BNFO05 films. The neodymium substitution was found to effectively induce spontaneous magnetization in antiferromagnetic BiFeO_3 which exhibited good ferroelectric properties. The BNFO05 film exhibited no degradation after 1×10^8 switching cycles at a frequency of 1 MHz. For practical applications, a reduction in the coercive field is necessary. Thus, a careful study is required on the defect chemistry of the films as well as the growth of epitaxial film under an oxide electrode.

Acknowledgments

The financial support of this research project by the Brazilian Research Funding Agencies CNPq and FAPESP is gratefully acknowledged.

References

- [1] E.H. Salje, in: *Phase Transitions in Ferroelastic and Co-Elastic Crystals*, Cambridge University Press, Cambridge, 1990.
- [2] M. Fiebig, T. Lottermoser, D. Fröhlich, A.V. Golsev, R.V. Pisarev, Observation of coupled magnetic and electric domains, *Nature* 419 (2002) 818–820.
- [3] N.A. Hill, Why are there so few magnetic ferroelectrics?, *J. Phys. Chem. B* 104 (2000) 6694–6709.
- [4] G.A. Smolenskii, I.E. Chupis, *Ferroelectromagnets*, *Sov. Phys. Uspekhi* 25 (1982) 475–493.
- [5] 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, R. Ramesh, Epitaxial BiFeO₃ multiferroic thin film heterostructures, *Science* 299 (2003) 1719–1722.
- [6] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruetter, A.P. Pyatakov, A.K. Zvezdin, D. Viehland, Dramatically enhanced polarization in (001), (101) and (111) BiFeO₃ thin films due to epitaxial-induced transitions, *Appl. Phys. Lett.* 84 (2004) 5261–5263.
- [7] W.J. Gallagher, S.S.P. Parkin, Development of the magnetic tunnel junction MRAM at IBM: from first junctions to a 16-Mb MRAM demonstrator chip, *IBM J. Res. Dev.* 50 (2006) 5–23.
- [8] M. Dawber, K.M. Rabe, J.F. Scott, Physics of thin-film ferroelectric oxides, *Rev. Mod. Phys.* 77 (2005) 1083–1130.
- [9] P. Royen, K. Swars, Das system wismutoxyd-eisenoxyd im bereich von 0 bis 55 mol% eisenoxyd, *Angew. Chem.* 24 (1957) 779–781.
- [10] S.V. Kiselev, R.P. Ozerov, G.S. Zhdanov, Detection of magnetic order in ferroelectric BiFeO₃ by neutron diffraction, *Sov. Phys. Dokl.* 7 (1963) 742–744.
- [11] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, Spiral magnetic ordering in bismuth ferrite, *J. Phys. C* 15 (1982) 4835–4846.
- [12] Z.G. Zhang, Y.N. Wang, J.S. Zhu, F. Yan, X.M. Lu, H.M. Shen, J.S. Liu, Retention characteristics of SrBi₂Ta₂O₉ thin films prepared by metalorganic deposition, *Appl. Phys. Lett.* 73 (1998) 3674–3676.
- [13] Z.X. Cheng, A.H. Li, X.L. Wang, S.X. Dou, K. Ozawa, H. Kimura, S.J. Zhang, T.R. ShROUT, Structure, ferroelectric properties, and magnetic properties of the La-doped bismuth ferrite, *J. Appl. Phys.* 103 (2008) 07E507.
- [14] F. Chen, Q.F. Zhang, J.H. Li, Y.J. Qi, C.J. Lu, X.B. Chen, X.M. Ren, Y. Zhao, Sol–gel derived multiferroic BiFeO₃ ceramics with large polarization and weak ferromagnetism, *Appl. Phys. Lett.* 89 (2006) 092910–092912.
- [15] L.Y. Wang, D.H. Wang, H.B. Huang, Z.D. Han, Q.Q. Cao, B.X. Gu, Y.W. Du, The magnetic properties of polycrystalline Bi_{1-x}Sr_xFeO₃ ceramics, *J. Alloys Compd.* 469 (2009) 1–3.
- [16] V. Raghavendra Reddy, D. Kothari, A. Gupta, S.M. Gupta, Study of weak ferromagnetism in polycrystalline multiferroic Eu doped bismuth ferrite, *Appl. Phys. Lett.* 94 (2009) 082505–082507.
- [17] V.A. Khomchenko, D.A. Kiselev, I.K. Bdikin, V.V. Shvartsman, P. Borisov, W. Kleemann, J.M. Vieira, A.L. Kholkin, Crystal structure and multiferroic properties of Gd-substituted BiFeO₃, *Appl. Phys. Lett.* 93 (2008) 262905–262907.
- [18] M. Li, M. Ning, Y. Ma, Q. Wu, C.K. Ong, Room temperature ferroelectric, ferromagnetic and magnetoelectric properties of Ba-doped BiFeO₃ thin films, *J. Phys. D* 40 (2007) 1603–1607.
- [19] V.R. Palkar, K. Prashanthi, Observation of magnetoelectric coupling in multiferroic Bi_{0.7}Dy_{0.3}FeO₃ thin films at room temperature, *Appl. Phys. Lett.* 93 (2008) 132906–132908.
- [20] Y. Lin, Q. Jiang, Y. Wang, C. Nan, L. Chen, J. Yu, Enhancement of ferromagnetic properties in BiFeO₃ polycrystalline ceramic by La doping, *Appl. Phys. Lett.* 90 (2007) 172507–172509.
- [21] J. Osorio-Guillén, S. Lany, S.V. Barabash, A. Zunger, Nonstoichiometry as a source of magnetism in otherwise nonmagnetic oxides: magnetically interacting cation vacancies and their percolation, *Phys. Rev. B* 75 (2007) 184421.
- [22] Y.E. Roginskaya, Y.N. Venevtsev, S.A. Fedulov, G.S. Zhdanov, *Sov. Phys. Crystallogr.* 8 (1964) 490.
- [23] Y.E. Roginskaya, Y.N. Venevtsev, G.S. Zhdanov, *Sov. Phys. JETP* 44 (1963) 1418.
- [24] M. Polomska, W. Kaczmarek, Z. Pajak, Electric and magnetic properties of (Bi_{1-x}La_x)FeO₃ solid solutions, *Phys. Status Solidi A* 23 (1974) 567–574.
- [25] V.A. Murashov, D.N. Rakov, I.S. Dubenko, A.K. Zvezdin, V.M. Ionov, *Sov. Phys. Crystallogr.* 35 (1990) 538.
- [26] Z.V. Gabbasova, M.D. Kuz'min, A.K. Zvezdin, I.S. Dubenko, V.A. Murashov, D.N. Rakov, I.B. Krynetsky, Bi_{1-x}R_xFeO₃ (R=rare earth): a family of novel magnetoelectrics, *Phys. Lett. A* 158 (1991) 491–498.
- [27] S.T. Zhang, Y. Zhang, M.-H. Lu, et al., Substitution-induced phase transition and enhanced multiferroic properties of Bi_{1-x}La_xFeO₃ ceramics, *Appl. Phys. Lett.* 88 (2006) 162901–162903.
- [28] V.R. Palkar, D.C. Kundaliya, S.K. Malik, S. Bhattacharya, Magnetoelectricity at room temperature in the Bi_{0.9-x}Tb_xLa_{0.1}FeO₃ system, *Phys. Rev. B* 69 (2004) 212102.
- [29] Q.-H. Jiang, C.-W. Nan, Z.-J. Shen, Synthesis and properties of multiferroic La-modified BiFeO₃ ceramics, *J. Am. Ceram. Soc.* 89 (2006) 2123–2127.
- [30] G.L. Yuan, S.W. Or, Multiferroicity in polarized single-phase Bi_{0.875}Sm_{0.125}FeO₃ ceramics, *J. Appl. Phys.* 100 (2006) 024109.
- [31] G.L. Yuan, S.W. Or, Enhanced piezoelectric and pyroelectric effects in single-phase multiferroic Bi_{1-x}Nd_xFeO₃ (x=0–0.15) ceramics, *Appl. Phys. Lett.* 88 (2006) 062905–062907.
- [32] G.L. Yuan, S.W. Or, J.M. Liu, Z.G. Liu, Structural transformation and ferroelectromagnetic behavior in single-phase Bi_{1-x}Nd_xFeO₃ multiferroic ceramics, *Appl. Phys. Lett.* 89 (2006) 052905–052907.
- [33] G.L. Yuan, S.W. Or, H.L.W. Chan, Raman scattering spectra and ferroelectric properties of Bi_{1-x}Nd_xFeO₃ (x=0–0.2) multiferroic ceramics, *J. Appl. Phys.* 101 (2007) 064101.
- [34] J.R. Sahu, C.N.R. Rao, Beneficial modification of the properties of multiferroic BiFeO₃ by cation substitution, *Solid State Sci.* 9 (2007) 950–954.
- [35] A.Z. Simões, R.F.C. Pianno, E.C. Aguiar, J.A. Varela, E. Longo, Effect of niobium dopant on fatigue characteristics of BiFeO₃ thin films grown on Pt electrodes, *J. Alloys Compd.* 479 (2009) 274–279.
- [36] H. Liu, Z. Liu, K. Yao, Improved electric properties in BiFeO₃ films by the doping of Ti, *J. Sol-Gel Sci. Technol.* 41 (2007) 123–128.
- [37] X.J. Meng, J.G. Cheng, J.L. Sun, H.J. Ye, Growth of (100)-oriented LaNiO₃ thin films directly on Si substrates by a simple metalorganic decomposition technique for the highly oriented PZT thin films, *J. Cryst. Growth* 220 (2000) 100–104.
- [38] W. Zhu, M.S. Tse, W. Lu, Raman, X-ray and electrical properties of MOD PZT/PLZT thin films, *Integr. Ferroelectr.* 12 (1996) 167–175.
- [39] J.K. Kim, S.S. Kim, W. Kim, Enhanced ferroelectric properties of Cr-doped BiFeO₃ thin films grown by chemical solution deposition, *Appl. Phys. Lett.* 88 (2006) 132901–1–132901-3.
- [40] A.M. Gonzalez, A.Z. Simões, L.S. Cavalcante, Soft chemical deposition of BiFeO₃ thin films, *Appl. Phys. Lett.* 90 (2007) 052906.
- [41] S.K. Singh, H. Ishiwara, K. Maruyama, Room temperature ferroelectric properties of Mn-substituted BiFeO₃ thin films deposited on Pt electrodes using chemical solution deposition, *Appl. Phys. Lett.* 88 (2006) 262908–262910.
- [42] G.D. Hu, X. Cheng, W.B. Wu, C.H. Yang, Effects of Gd substitution on structure and ferroelectric properties of BiFeO₃ thin films prepared using metal organic decomposition, *Appl. Phys. Lett.* 91 (2007) 232909–232911.
- [43] H. Uchida, R. Ueno, H. Funakubo, S. Koda, Crystal structure and ferroelectric properties of rare-earth substituted BiFeO₃ thin films, *J. Appl. Phys.* 100 (2006) 014106–1–014106-9.

- [44] Y. Wang, C.W. Nan, Enhanced ferroelectricity in Ti-doped multiferroic BiFeO₃ thin films, *Appl. Phys. Lett.* 89 (2006) 052903–052905.
- [45] H. Uchida, H. Yoshikawa, I. Okada, H. Matsuda, T. Iijima, T. Watanabe, T. Kojima, H. Funakubo, Approach for enhanced polarization of polycrystalline bismuth titanate films by Nd³⁺/V⁵⁺ cosubstitution, *Appl. Phys. Lett.* 81 (2002) 2229–2231.
- [46] U. Chon, H.M. Jang, M.G. Kim, C.H. Chang, Layered perovskites with giant spontaneous polarization for nonvolatile memories, *Phys. Rev. Lett.* 89 (2002) 087601.
- [47] Y. Noguchi, M. Miyayama, Large remanent polarization of vanadium-doped Bi₄Ti₃O₁₂, *Appl. Phys. Lett.* 78 (2001) 1903–1905.
- [48] Y. Shimakawa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, F. Izumi, Z. Hiroi, Crystal and electronic structures of Bi_{4–x}La_xTi₃O₁₂ ferroelectric materials, *Appl. Phys. Lett.* 79 (2001) 2791–2793.
- [49] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, Fatigue-free ferroelectric capacitors with platinum electrodes, *Nature* 374 (1995) 627–629.
- [50] D. Dimos, H.N. Al-Shareef, W.L. Warren, B.A. Tuttle, Photoinduced changes in the fatigue behavior of SrBi₂Ta₂O₉ and Pb(Zr,Ti)O₃ thin films, *J. Appl. Phys.* 80 (1996) 1682–1687.
- [51] G.A. Gehring, On the microscopic theory of the magnetoelectric effect, *Ferroelectrics* 161 (1994) 275–285.
- [52] J.B. Goodenough, J.M. Lango, Landolt–Bornstein Numerical Data and Functional Relationships in Science and Technology, vol III/4a, Springer, New York, 1978.
- [53] M.M. Kumar, S. Srinath, G.S. Kumar, S.V. Suryanarayana, Spontaneous magnetic moment in BiFeO₃–BaTiO₃ solid solutions at low temperatures, *J. Magn. Magn. Mater.* 188 (1998) 203–212.
- [54] T. Kanai, S.I. Ohkoshi, A. Nakajima, T. Watanabe, K. Hashimoto, A ferroelectric-ferromagnet composed of (PLZT)_x(BiFeO₃)_{1–x} solid solution, *Adv. Mater.* 13 (2001) 487–490.
- [55] J. Wang, A. Scholl, H. Zheng, S.B. Ogale, L. Viehland, D.G. Schlom, N.A. Spaldin, K.M. Rabe, M. Wuttig, L. Mohaddes, J. Neaton, U. Waghmare, T. Zhao, R. Ramesh, Response to Comment on ‘Epitaxial BiFeO₃ multiferroic thin film heterostructures, *Science* 307 (2005) 1203–1204.
- [56] K. Ueda, H. Tabata, T. Kawai, Coexistence of ferroelectricity and ferromagnetism in BiFeO₃–BaTiO₃ thin films at room temperature, *Appl. Phys. Lett.* 75 (1999) 555–557.
- [57] G.L. Yuan, Siu Wing Or, J.M. Liu, Z.G. Liu, Structural transformation and ferroelectromagnetic behavior in single-phase Bi_{1–x}Nd_xFeO₃ multiferroic ceramics, *Appl. Phys. Lett.* 89 (2006) 052905–052907.
- [58] F. Huang, X. Lu, W. Lin, X. Wu, Y. Kan, J. Zhu, Effect of Nd dopant on magnetic and electric properties of BiFeO₃ thin films prepared by metal organic decomposition, *Appl. Phys. Lett.* 89 (2006) 242914–242916.