

Contents lists available at ScienceDirect

# **Physics Letters A**





# Possible misleading interpretations on magnetic and transport properties in BiFeO<sub>3</sub> nanoparticles caused by impurity phase



Fabian E.N. Ramirez, Gabriel A.C. Pasca, Jose A. Souza\*

Universidade Federal do ABC, CEP 09090-400, Santo André, SP, Brazil

#### ARTICLE INFO

Article history: Received 20 February 2015 Received in revised form 26 March 2015 Accepted 27 March 2015 Available online 2 April 2015 Communicated by L. Ghivelder

Keywords: Multiferroic nanoparticles Magnetic properties Electrical polarization Impurity phase

#### 1. Introduction

Multiferroic materials, which show coexistence of ferromagnetic (FM) and ferroelectric ordering, are of great interest because of many technological applications [1–5]. The possible coupling between magnetic and electric properties implies that the spontaneous magnetization can be reoriented by an applied electrical field and the spontaneous polarization can be reoriented by an applied magnetic field, opening exciting opportunities for designing microelectronic devices with multifunctional nature [6–11].

Perovskite BiFeO<sub>3</sub> is unique because it exhibits both ferroelectricity and antiferromagnetic (AFM) order simultaneously over a wide temperature range above room temperature [12,13]. This raises the possibility of developing potential devices based on magnetoelectric coupling operating at room temperature. The ferroelectric Curie temperature  $T_C$  and the Neel temperature  $(T_N)$ of bulk compound are  $T_C \sim 1100$  K [14,15] and  $T_N = 643$  K [16], respectively. Recently, it has been demonstrated that BiFeO<sub>3</sub> nanoparticles and nanostructured thin films possess functional properties that are distinct from the bulk [8,17].

The practical applications of this compound have been prevented by the leakage current problems, which lead to low electrical resistivity, due to nonstoichiometry region within the sample. This is mostly because of the difficulty in obtaining a stoichiometric single-phase materials. Indeed, it is well known that synthe-

# ABSTRACT

BiFeO<sub>3</sub> nanoparticles were synthesized by a wet chemical method. X-ray powder diffraction indicated single phase samples. The sample S1 shows a ferromagnetic-like behavior whereas S2 exhibits an antiferromagnetic-like character with lower magnetic moment and coercive field. Magnetic measurements at high temperature reveal two phase transitions, one related to BiFeO<sub>3</sub> and another from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> magnetic impurity in contrast to X-ray diffraction. We observed an increase of remanent polarization, coercive electrical field, and the appearance of interfacial polarization due to higher leakage current density. We discuss how an apparently single phase sample can lead to misleading interpretations in magnetic and dielectric properties.

© 2015 Elsevier B.V. All rights reserved.

sizing a pure phase of BiFeO<sub>3</sub> is difficult through the traditional solid-state method. Various processing techniques have been used to improve the synthesis of bismuth ferrite nanostructured samples [18–23]. The  $T_C$  and  $T_N$  of the magnetic nanoparticles obtained by these methods are strongly synthesis dependent [19,20]. Some works have shown that small amount of ferromagnetic impurity phase, such as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>, is present in the grain boundary of BiFeO<sub>3</sub> nanocrystals [24,25]. However, a comprehensive understanding on the influence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> impurity phase on the magnetic and electrical properties of BiFeO<sub>3</sub> is important for future works.

In the present work, we have performed a systematic study on the magnetic and electric properties of BiFeO<sub>3</sub> nanoparticles. We have employed a wet chemical method to obtain two sets of apparently single-phase BiFeO<sub>3</sub> nanoparticles with crystallite average size of  $\sim$  75–90 nm. Magnetic measurements obtained at low temperature lead to an interpretation that a set of samples shows a ferromagnetic-like behavior whereas the other one exhibits an antiferromagnetic-like character. These possible results reveal that the samples have different magnetic character. However, magnetic measurements at high temperature suggest two phase transitions with strong irreversibility indicating the presence of a second magnetic phase,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> impurity, which is in contrast to X-ray powder diffraction obtained at room temperature. On the other hand, in the electrical properties, we have observed an increase of the remanent polarization and coercive field which is also explained in terms of leakage current density due to presence of impurities. We discuss how an apparently single phase sample can lead to

<sup>\*</sup> Corresponding author. E-mail address: joseantonio.souza@ufabc.edu.br (J.A. Souza).

misleading interpretations of the magnetic and electrical transport properties.

## 2. Experimental details

X-ray powder diffraction (XRD) was performed on a  $\theta$ - $2\theta$  Bruker AXS D8 Focus diffractometer with Cu K $\alpha$  radiation. Structural parameters of as-prepared BiFeO<sub>3</sub> nanoparticles were refined by using Rietveld method. The space group *R*3*c* in its hexagonal representation was used as the basis, and the starting values for all Rietveld refinements were  $a_{hex} = 5.577$  Å,  $c_{hex} = 13.86$  Å, Bi (0, 0, 0.2988), Fe (0, 0, 0.197), O (0.2380, 0.3506, 1/12) [26]. The crystallite sizes ( $d_{XRD}$ ) were calculated by using the Scherrer equation corrected for instrumental peak broadening determined with an Al<sub>2</sub>O<sub>3</sub> standard. Magnetic measurements were performed by using a physical property measurement system (PPMS) from Quantum Design.

## 3. Results and discussion

BiFeO<sub>3</sub> nanoparticle samples have been obtained by wet chemical route using metal nitrates Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as starting materials. For the first set of nanoparticles, the precursors were obtained by dissolving 0.0015 mol of metal nitrate in 20 mL of deionized water with the addition of nitric acid (HNO<sub>3</sub>) to pH 1-2. Separately, maleic acid (0.03 mol) was dissolved in deionized water (3 mL). Ethylene glycol in a molar ratio to the maleic acid of 1:1 was added as a polymerizing agent. Ethylene glycol will create a membrane within which the nanoparticles are formed. The two solutions were then heated at 60°C under constantly stirring. Subsequently, the two solutions were mixed and maintained at 100°C with constant magnetic rotation. After few hours, it changed into a fluffy black/brown gel which was calcined at 600 °C in air for 2 h. X-ray diffraction measurements revealed the existence of spurious reflections belonging to Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as shown in the inset of Fig. 1(a). Thus, a leach process with HNO<sub>3</sub> (0.05 M) was done in order to remove the Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> impurity formed during the process. Fig. 1(a) shows the X-ray powder diffraction pattern along with the Rietveld refinement obtained after the wash process. The XRD of this sample, which was called as S1, suggests single-phase belonging to rhombohedral space group R3c indicating that the wash process was successful. This process has been widely used to remove impurity phases [12,13,27, 28]. The unit cell parameters found from Rietveld refinement are  $a_{hex} = 5.5698(1)$  Å,  $c_{hex} = 13.8392(4)$  Å, V = 371.81(2) Å<sup>3</sup>.

For the second sample, the precursors were obtained similarly as for S1. Thus, 0.001 mol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 0.001 mol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were initially dissolved in dilute nitric acid (20% HNO<sub>3</sub>) to form a transparent solution. In this case, we used a different polymerizing agent. Ethylenediaminetetraacetic acid (EDTA) in 1:1 molar ratio with respect to the metal nitrates (0.002 mol) was added to the solution described above. This solution was then evaporated at 130 °C under constantly stirring until the formation of a fluffy brown gel. This gel was also heat treated at 600°C for 2 h. At this point, we also observed the spurious phases  $Bi_2Fe_4O_9$ and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (see inset of Fig. 1(b)), but the amount is lower. They were removed through the same leach process with HNO<sub>3</sub> (0.05 M) used for the first sample S1. The sample prepared by this route was called as S2 and its X-ray powder diffraction data along with the Rietveld refinement obtained after the wash process is showed in Fig. 1(b). A single-phase sample belonging to rhombohedral space group R3c is also suggested. The unit cell parameters are  $a_{hex} = 5.5679(1)$  Å,  $c_{hex} = 13.819(1)$  Å, V = 371.02(3) Å<sup>3</sup>. The sample S1 has a grain size slightly larger  $(90 \pm 20 \text{ nm})$  than sample S2 ( $75 \pm 15$  nm), as determined by scanning electron microscopy.



**Fig. 1.** (Color online.) X-ray powder diffraction pattern along with Rietveld refinement after the wash process for (a) *S*1 ( $R_{WP} = 3.34$  and  $R_P = 2.43$ ) and (b) *S*2 ( $R_{WP} = 3.54$  and  $R_P = 2.66$ ). The tick marks represent the expected Bragg reflections for the rhombohedral phase. Insets show the diffraction pattern normalized (divided) to the most intense reflections where one can see the reflections belonging to Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> observed in the samples before the wash process.



**Fig. 2.** (Color online.) Temperature dependence of the ZFC and FC magnetic susceptibility at low temperatures obtained with an applied magnetic field of H = 1000 Oe for (a) S1 and (b) S2.

Fig. 2 shows the zero field cooling (ZFC) and field cooling (FC) measurements of the magnetic susceptibility as a function of temperature obtained with an applied magnetic field H = 1000 Oe for the two samples. The ZFC curves of both samples showed a prominent and broad maximum at low temperatures. This maximum takes place at  $T_{max} = 184$  K and 148 K for S1 and S2, respectively. The  $T_{max}$  temperature, which is in very good agreement with literature, has been interpreted by several authors as the freezing-like temperature of the system [20,29–31]. A spin cluster-glass-like state is suggested to be present in single crystals and nanocrystals of BiFeO<sub>3</sub> [29,32]. A careful inspection in the temperature dependence of the magnetic susceptibility reveals that the sample S1 has a larger magnetic moment than S2. Representative



Fig. 3. (Color online.) Representative curves of the magnetization as a function of applied magnetic field obtained at different temperatures for the samples S1 (a) and S2 (b).

curves of the magnetization as function of applied magnetic field obtained at different temperatures for S1 and S2 are shown in Fig. 3. A pronounced difference in the shape of hysteresis was observed when comparing both samples. For example, in the sample S1, the magnetization tends to saturate at H > 4 kOe resembling ferromagnetic character whereas in the sample S2 the magnetization increases monotonically up to high magnetic fields suggesting antiferromagnetic-like ground state. On the other hand, T.J. Park et al. [20] showed that the magnetization increases monotonically with the reduction of the nanoparticle size. Another good example of this evolution is shown by Castillo et al. [33] where the magnetic moment of the smaller sample (54 nm) is almost four times larger than the bigger one (150 nm). We have observed an increase in the value of the magnetization of our nanoparticles as compared to that of bulk compound. However, the magnetic moment measured in S2, the sample with the smaller average size, is much lower than that measured in S1. For example, at T = 350 K and H = 10 kOe, the measured value of the magnetic moment is 362 and 34 emu/mol for S1 and S2, respectively.

In order to get insight into the nature of the magnetic character of both nanoparticle samples, we have plotted the temperature dependence of the coercive field  $H_c$  and saturation magnetization

 $(M_S)$ , defined at H = 10 kOe, in Fig. 4. The measured values of  $H_C$ and  $M_S$  for S1 are larger than those for S2 which again suggests that the magnetic properties are more influenced in this sample. We have also observed that the temperature dependence of  $H_C$  is very different in both samples. Below the antiferromagnetic transition  $(T < T_N)$ , we can see that the  $H_C$  has a linear behavior for sample S1 while in the sample S2, it is not observed. On the other hand, above the antiferromagnetic transition  $(T > T_N)$ , the values of  $H_C$  tend rapidly to zero in both samples. Fig. 5(b) also shows the saturation magnetization  $(M_S)$ , defined at H = 10 kOe, as a function of the temperature for both samples. In the sample S1, the  $M_{\rm S}$  follows the trend expected for the Bloch model in the whole temperature range studied. This result suggests the presence of spin waves structure due to ferromagnetic alignment of spins. The temperature dependence of the saturation magnetization for spin waves of FM alignment is given by the well known Bloch's relation [34]  $M_{S}(T) = M_{S}(0)(1 - AT^{3/2})$ , where  $M_{S}(0)$  is the saturation magnetization in 0 K and A is Bloch's constant. One can also see in Fig. 5(b) that the sample S2 shows a completely different behavior from that expected for Bloch law. For  $T < T_N$ , a linear behavior followed by an upturn in  $M_S$  at low temperature was observed. On the boundary of the antiferromagnetic transition,  $M_S$  undergoes a sharp drop followed by linear behavior but with different slope. These combined results could confirm a scenario where magnetic state with very different spin configuration would be present in the samples. This suggestion would reflect an underlying competition between AFM and FM interactions which is consistent with the spin-glass state, considered to be present in these systems. In spin glass systems, magnetic spins are subjected to competing forces which bring about frustrated magnetic exchange interactions where the ferromagnetic and antiferromagnetic bonds randomly distributed in the system compete each other. As we shall see, the presence of very small amount of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> impurity phase, not detected by XRD, can strongly influence these magnetic properties of the system. It is very interesting that this spurious phase also affects the sharpness of the AFM transition of BiFeO3 at high temperature. The sample S2 has a sharp magnetic transition around T = 576 K whereas the transition close to T = 596 K in the sample S1 is rounded.

The temperature dependence of the magnetic susceptibility measured at high temperatures is shown in Fig. 5. Divergence between the ZFC and FC curves is clearly observed much above the Neel temperature of BiFeO<sub>3</sub> (643 K) which is unexpected for single phase compounds. The susceptibility curves of both samples along with strong irreversibility reveal two magnetic phase transitions, one below 650 K and the second one close to 750 K. The first transition is clearly related to the antiferromagnetic transition of BiFeO<sub>3</sub> and the second transition at higher temperature is a contribution from nanocrystals of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Indeed, it has been reported that the Neel temperature of this composition decreases



**Fig. 4.** (Color online.) (a) The coercive magnetic field ( $H_C$ ) and (b) the saturation magnetization ( $M_S$ ), defined at H = 10 kOe, as a function of the temperature for the two samples. The lines joining the points of sample S1 represent a linear fitting (a) and the Bloch model (b). The lines joining the points of sample S2 are guide to the eye.



**Fig. 5.** (Color online.) Temperature dependence of the magnetic susceptibility measured at high temperatures with an applied magnetic field of H = 1000 Oe for the sample (a) S1 and (b) S2.

with the reduction of the size particle [35,36]. As one can see, the presence of this impurity phase induces a complete different magnetic properties of our samples due to its weak ferromagnetic ordering. Note also that the transition temperature (defined at the peak position) corresponding to the impurity phase is lower for the smaller sample, being around 764 K (for S1) and 726 K (for S2). This result suggests that the particle size of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is smaller in S2. In this case, the increase of the magnetic moment will be less pronounced in this sample. The measured values of the magnetic moment at H = 10 kOe lies in the range 0.07–0.09  $\mu_B$ /Fe for S1 and 0.007–0.012  $\mu_B$ /Fe for S2, which is 10 times lower.

In the sequence, we have investigated the electrical properties of both samples. The ferroelectricity in the BiFeO<sub>3</sub> compound brought about by the A-site through the displacement (s) of the Bi ion from the centrosymmetric position in its oxygen surrounding [10,19,37,38]. The displacement *s* is caused by the stereochemically active 6s<sup>2</sup> lone pair. Electrical polarization at interfaces and/or grain boundary brought about by delocalized charge carriers can also contribute to the electrical properties of the system. Electrical polarization measurements (polarization hysteresis (P-E) loops) were carried out varying the amplitude of the applied voltage (V). Hysteresis P-E loops measured up to V = 50, 100, 150, and 190 Vobtained at room temperature are shown in Fig. 6 for S1 and S2, respectively. The overall magnitude of the electrical polarization, which increases with the applied voltage, is similar to both samples. However, a pronounced difference in the shape of the hysteresis loops (it becomes more elliptical) was observed in the sample S1. The remanent polarization  $P_r$  and coercive electric field  $E_c$ are important parameters for technological application and should be obtained accurately. Fig. 7(a) shows a comparative study of the remanent polarization and coercive electric field for both samples. We can see that the values of  $P_r$  and  $E_c$  for S1 are higher than that of S2. It is most pronounced at high electrical fields where the coercive field is three times higher for S1 than S2, for example. In order to check this high value of coercive electrical field we have measured leakage current for both samples.

Indeed, the behavior of  $P_r$  and  $E_c$  observed in Fig. 7(a) can be understood by performing a comparative study of the leakage current density. The leakage current density is related with an extrinsic contribution to the electrical conductivity of the system. This extrinsic contribution may come from the occurrence of charged defects (oxygen vacancies and Fe<sup>2+</sup>). The interface elec-



**Fig. 6.** (Color online.) Measurements of electrical polarization as a function of electric field obtained at room temperature for the sample (a) S1 and (b) S2.



**Fig. 7.** (Color online.) (a) Remanent polarization and coercive field, and (b) leakage current density as a function of electric field obtained at room temperature.

trode/sample may also contribute to the leakage current of the compound. Indeed, several models have been presented in order to explain the behavior of the leakage current in high temperatures such as interface-limited Schottky emission, bulk-limited Poole–Frenkel emission, and space charge limited conduction [39]. Fig. 6(b) shows the density of the leakage current (*J*) as a function of the electric field measured at room temperature. It is observed that the density leakage current is lower for the sample S2. For example, for V = 1 V (E = 0.025 kV/cm), we have measured  $J = 2.23 \times 10^{-9} \text{ A/cm}^2$  and  $7.99 \times 10^{-10} \text{ A/cm}^2$  for S1 and S2, respectively. This indicates that the carriers are more delocalized in S1 and its interfacial polarization plays an important role contributing to larger values of  $P_r$  and  $E_c$ . There are primarily two important factors that control the electrical conductivity [40]. First, the concentration of oxygen vacancies produced due to highly volatile nature of Bi [41,42]. The oxygen vacancies generate deep trap energy levels within the band gap and provide a path for thermally or electrically stimulated charge carriers to flow under applied electric field. Furthermore, the delocalization of the oxygen vacancies may also be thermally or electrically activated. Second, the mixed valence states of Fe ions ( $Fe^{2+}$  and  $Fe^{3+}$ ) [43-46]. It is known that slight oxygen deficiency in BiFeO<sub>3</sub> may also lead to the creation of  $Fe^{2+}$  ions within the iron sublattice. The coexistence of  $Fe^{2+}$  and  $Fe^{3+}$  in the octahedral sites favors the electron hopping conduction from  $Fe^{2+}$  to  $Fe^{3+}$  via oxygen ions at high electric field. As explained before, the delocalization of the charge defects (oxygen vacancies and/or  $Fe^{2+}$ ) will cause an increase of the leakage current density. We suggest that the presence of very small amount of impurity (not detected by XRD) as shown in this work can increase the leakage current influencing the values of  $P_r$  and  $E_c$ . Furthermore, the impurities are usually at the grain boundaries affecting the microstructure of the sample which in turn changes also the leakage current of the system [47,45,48,49].

# 4. Conclusions

We have performed a systematic study on the magnetization and electrical polarization of BiFeO3 nanoparticles. Two sets of BiFeO<sub>3</sub> nanoparticle samples were synthesized by employing a wet chemical method with slightly different route. Our results suggest that the presence of very small amount of magnetic impurity phase, not detected by XRD, can strongly influence the magnetic and electrical properties of this system. The presence of impurity affects the leakage current density causing an enhancement in the interfacial polarization. The delocalization character of the charge carriers, influenced by impurities, plays a major role in the electrical polarization. The interfacial polarization contribution makes the remanent polarization and coercive field seem higher. We have discussed how an apparently single phase sample can lead to misleading interpretations of general physical properties such as magnetization, electrical polarization, and magnetic/electric coercive fields which are important parameters in multiferroic systems. We emphasize that in order to study this system and to compare with others, samples must be prepared with extremely care.

#### Acknowledgement

This material is based upon work supported by the Brazilian agencies CNPq Grants Nos. 485405/2011-3 and 305772/2011-2 and Fapesp under Grants Nos. 2010/18364-0 and 2013/16172-5.

## Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.physleta.2015.03.035.

#### References

- [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, R. Ramesh, Science 299 (2003) 1719.
- [2] N. Nuraje, X. Dang, J. Qi, M.A. Allen, Y. Lei, A.M. Belcher, Adv. Mater. 24 (2012) 2885.

- [3] M. Fiebig, T. Lottermoser, D. Fröhlich, A.V. Goltsev, R.V. Pisarev, Nature 419 (2002) 818.
- [4] R. Nechache, C. Harnageab, F. Roseib, Nanoscale 4 (2012) 5588.
- [5] C.H. Yang, D. Kan, I. Takeuchi, V. Nagarajand, J. Seidel, Phys. Chem. Chem. Phys. 14 (2012) 15953.
- [6] H. Zhang, M. Richter, K. Koepernik, I. Opahle, F. Tasnãdi, H. Eschrig, New J. Phys. 11 (2009) 43007.
- [7] C.N.R. Rao, R.J. Serrao, J. Mater. Chem. 17 (2007) 4931.
- [8] R. Ramesh, A. Spaldin, Nat. Mater. 6 (2007) 21.
- [9] W. Eerenstein, N.D. Mathur, J.F. Scott, Nature 442 (2006) 759.
- [10] S.W. Cheong, M. Mostovoy, Nat. Mater. 6 (2007) 13.
  - [11] A. Sing, V. Pandey, R.K. Kotnala, D. Pandey, Phys. Rev. Lett. 101 (2008) 247602.
    [12] G. Catalan, J.F. Scott, Adv. Mater. 21 (2009) 2463.
  - [13] M.M. Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, Appl. Phys. Lett. 76
  - (2000) 2764. [14] J.D. Bucci, B.K. Robertson, W.D. James, J. Appl. Crystallogr. 5 (1972) 187.
  - [15] A. Maitre, M. Franãois, I.C. Gachon, I. Phase Equilib, 25 (2004) 59.
  - [16] J.M. Moreau, C. Miche, R. Gerson, W.J. James, J. Phys. Chem. Solids 32 (1971) 1315.
  - [17] J. Seidel, L.W. Martin, Q. He, Q. Zhan, Y.H. Chu, A. Rother, M.E. Hawkridge, P. Maksymovych, P. Yu, Nat. Mater. 8 (2009) 229.
  - [18] D.P. Dutta, O.D. Jayakumar, A.K. Tyagi, K.G. Girija, C.G.S. Pillaia, G. Sharmab, Nanoscale 2 (2010) 1149.
  - S.M. Selbach, T. Tybell, M.A. Einarsrud, T. Grande, Chem. Mater. 19 (2007) 6478.
    T.J. Park, G.C. Papaefthymiou, A.J. Viescas, A.R. Moodenbaugh, S.S. Wong, Nano
  - Lett. 7 (2007) 766.
  - [21] J. Wei, D. Xue, Mater. Res. Bull. 43 (2008) 3368.
  - [22] A.T. Raghavender, D. Pajic, K. Zadro, T. Milekovic, P.V. Rao, K.M. Jadhav, D. Ravinder, J. Magn. Magn. Mater. 316 (2007) 1.
  - [23] T.J. Park, Y. Maoa, S.S. Wong, Chem. Commun. (2004) 2808, http://dx.doi.org/ 10.1039/B409988E.
  - [24] T. Vijayanand, H.S. Potdar, P.A. Joy, Appl. Phys. Lett. (2009) 1, http://dx.doi.org/ 10.1063/1.3132586.
  - [25] P.K. Siwach, J. Singh, H.K. Singh, O.N. Srivastava, J. Appl. Phys. (2009) 916, http://dx.doi.org/10.1063/1.3072823.
  - [26] P. Fischer, M. Polomska, I. Sosnowska, M. Szymanski, J. Phys. C, Solid State Phys. 13 (1980) 1931.
  - [27] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J.F. Marucco, S. Fusil, Phys. Rev. B 76 (2007) 024116.
  - [28] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J.F. Marucco, S. Fusil, Appl. Phys. Lett. 91 (2007) 022907.
  - [29] M.K. Singh, W. Prellier, M.P. Singh, R.S. Katiyar, J.F. Scott, Phys. Rev. B 77 (2008) 144403.
  - [30] M.K. Singh, R.S. Katiyar, W. Prellier, J.F. Scott, J. Phys. Condens. Matter 21 (2009) 42202.
  - [31] C.J. Cheng, C. Lu, Z. Chen, L. You, L. Chen, J. Wang, T. Wu, Appl. Phys. Lett. 98 (2011) 242502.
  - [32] S. Dong, Y. Yao, Y. Hou, Y. Liu, Y. Tang, X. Li, Nanotechnology 22 (2011) 385701.
  - [33] M.E. Castillo, V.V. Shvartsman, D. Gobeljic, Y. Gao, J. Landers, H. Wende, D.C. Lupascu, Nanotechnology 24 (2013) 355701.
  - [34] C. Kittel, Introduction to Solid States Physics, 8th edition, John Wiley and Sons, Inc., 2005.
  - [35] H.M. Lu, X.K. Meng, J. Phys. Chem. C 114 (2010) 21291.
  - [36] L. Bao, H. Yang, X. Wang, F. Zhang, R. Shi, B. Liu, W. Lin, H. Zhao, J. Cryst. Growth 328 (2011) 62.
  - [37] R. Seshadri, N.A. Hill, Chem. Mater. 13 (2001) 2892.
  - [38] J.B. Neaton, C. Ederer, N.A. Waghmare, K.M. Rabe, Phys. Rev. B 71 (2005) 014113.
  - [39] Y. Wang, J. Wang, J. Phys. D, Appl. Phys. 42 (2009) 162001.
  - [40] A.R. Makhdoom, M.J. Akhtar, M.A. Rafic, M.M. Hassan, Ceram. Int. 38 (2012) 3829.
  - [41] B. Yu, M. Li, J. Liu, D. Guo, L. Pei, X. Zhao, J. Phys. D, Appl. Phys. 41 (2008) 065003.
  - [42] Z. Yan, K.F. Wang, Y. Qu, Y. Wang, Z. Song, S.L. Feng, Appl. Phys. Lett. 91 (2007) 082906.
  - [43] Y. Wang, C.W. Nan, Appl. Phys. Lett. 89 (2006) 052903.
  - [44] J. Liu, M. Li, L. Pei, J. Wang, Z. Hu, X. Wang, X. Zhao, Europhys. Lett. 89 (2010) 57004.
  - [45] J. Liu, L. Li, L. Pei, B. Yu, D. Guo, X. Zhao, J. Phys. D, Appl. Phys. 42 (2009) 115409.
  - [46] X. Qi, J. Dho, R. Tomov, M.G. Blamire, J.L. MacManus-Driscoll, Appl. Phys. Lett. 86 (2005) 062903.
  - [47] P. Uniyal, K.L. Yadav, Mater. Lett. 62 (2008) 2858.
  - [48] Y. Wang, C.W. Nan, J. Appl. Phys. 103 (2008) 24103.
  - [49] M. Idrees, M. Nadeem, M. Atif, M. Siddique, M. Mehmood, M.M. Hassan, Acta Mater. 59 (2011) 1338.