



Possible misleading interpretations on magnetic and transport properties in BiFeO₃ nanoparticles caused by impurity phase



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ABSTRACT

BiFeO₃ 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 BiFeO₃ and another from α -Fe₂O₃ 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.

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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 BiFeO₃ 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 BiFeO₃ 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-

sizing a pure phase of BiFeO₃ 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 γ -Fe₂O₃ or Fe₃O₄, is present in the grain boundary of BiFeO₃ nanocrystals [24,25]. However, a comprehensive understanding on the influence of α -Fe₂O₃ impurity phase on the magnetic and electrical properties of BiFeO₃ is important for future works.

In the present work, we have performed a systematic study on the magnetic and electric properties of BiFeO₃ nanoparticles. We have employed a wet chemical method to obtain two sets of apparently single-phase BiFeO₃ nanoparticles with crystallite average size of ~ 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, α -Fe₂O₃ 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

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misleading interpretations of the magnetic and electrical transport properties.

2. Experimental details

X-ray powder diffraction (XRD) was performed on a θ - 2θ Bruker AXS D8 Focus diffractometer with Cu $K\alpha$ radiation. Structural parameters of as-prepared BiFeO₃ nanoparticles were refined by using Rietveld method. The space group $R3c$ 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 Al₂O₃ standard. Magnetic measurements were performed by using a physical property measurement system (PPMS) from Quantum Design.

3. Results and discussion

BiFeO₃ nanoparticle samples have been obtained by wet chemical route using metal nitrates Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O 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 (HNO₃) 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 Bi₂Fe₄O₉ and α -Fe₂O₃ as shown in the inset of Fig. 1(a). Thus, a leach process with HNO₃ (0.05 M) was done in order to remove the Bi₂Fe₄O₉ 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, $V = 371.81(2)$ Å³.

For the second sample, the precursors were obtained similarly as for S1. Thus, 0.001 mol Bi(NO₃)₃·5H₂O and 0.001 mol Fe(NO₃)₃·9H₂O were initially dissolved in dilute nitric acid (20% HNO₃) 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 Bi₂Fe₄O₉ and α -Fe₂O₃ (see inset of Fig. 1(b)), but the amount is lower. They were removed through the same leach process with HNO₃ (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 shown 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, $V = 371.02(3)$ Å³. The sample S1 has a grain size slightly larger (90 ± 20 nm) than sample S2 (75 ± 15 nm), as determined by scanning electron microscopy.

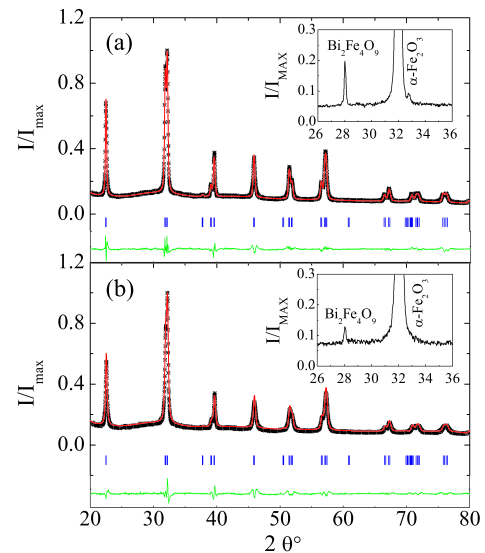


Fig. 1. (Color online.) X-ray powder diffraction pattern along with Rietveld refinement after the wash process for (a) S1 ($R_{WP} = 3.34$ and $R_p = 2.43$) and (b) S2 ($R_{WP} = 3.54$ and $R_p = 2.66$). The tick marks represent the expected Bragg reflections for the rhombohedral phase. Insets show the diffraction pattern normalized (divided) to the most intense reflections where one can see the reflections belonging to Bi₂Fe₄O₉ and α -Fe₂O₃ observed in the samples before the wash process.

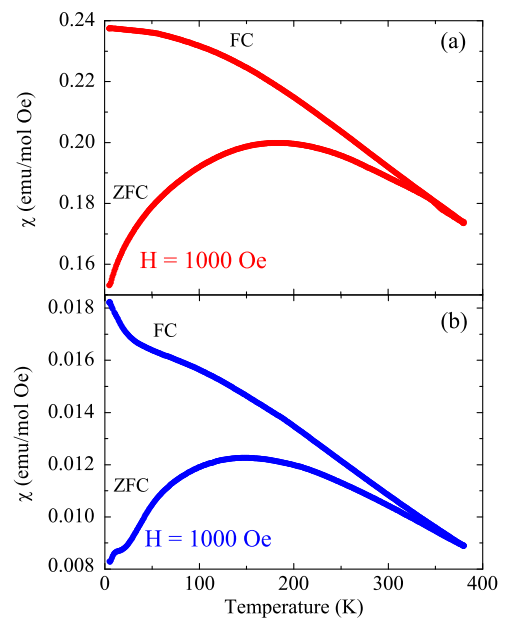


Fig. 2. (Color online.) Temperature dependence of the ZFC and FC magnetic susceptibility at low temperatures obtained with an applied magnetic field $H = 1000$ Oe for (a) S1 and (b) S2.

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 BiFeO₃ [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

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