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Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Composition-driven enhanced magnetic properties and magnetoelectric coupling in Gd substituted BiFeO₃ nanoparticles

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ARTICLE INFO

Article history:

Received 29 November 2015

Received in revised form

10 February 2016

Accepted 16 February 2016

Available online 17 February 2016

Keywords:

BiFeO₃

Oxide materials

Sol–gel processes

Magnetization

Magnetic measurements

ABSTRACT

Bi_{1-x}Gd_xFeO₃ ($x=0, 0.05$ and 0.1) samples were synthesized by modified sol–gel process. X-ray diffraction studies confirmed that the crystal structures of Gd substituted samples remain stable for $x < 0.1$, while compositional-driven structural phase transition from rhombohedral to orthorhombic was observed in the case of $x=0.1$. The average particle sizes of pure and Gd substituted BiFeO₃ nanoparticles were found to be in the range 62–46 nm. The size of the oblate spherical particles decreased with increasing Gd concentration. XPS studies revealed the trivalent oxidation states of Bi and Fe ions along with sample purity. Pure BiFeO₃ exhibited linear $M-H$ loop indicating its antiferromagnetic characteristics, whereas obvious non-linear $M-H$ loops were observed in Gd substituted samples. In contrast to the observed room temperature magnetization (0.36 emu/g) under 40 kOe for BiFeO₃, the sample with 10% Gd exhibited appreciable enhancement of magnetization (1.88 emu/g). A leaky type $P-E$ hysteresis loop was observed for the pure one, whereas concave-like ferroelectric loops were obtained for Gd substituted samples. The possible origins of enhanced multiferroic properties have been explained on the basis of substituent, its concentration, phase purity, particle size, structural distortion and the modified magnetic structure. The measurement of magnetoelectric studies at room temperature revealed the coupling between magnetic and ferroelectric ordering, which is desirable for multifunctional device applications of multiferroics.

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1. Introduction

The revival of research interest in multiferroics led to innovative architecture and fabrication of unconventional devices with multi-functionalities as they exhibit different ferroic (magnetic, electric, and elastic) ordering in a single-phase simultaneously [1]. Besides an intriguing physics in multiferroics, they also have potential for various applications in the area of nanoelectronics and spintronics such as multiple-state memory devices, magnetomechanical actuators, piezoelectric transducers, both electrically and magnetically controlled sensors, spin transistors and spin valves [2]. Multiferroics are a rare class of materials of which bismuth ferrite (BiFeO₃, BFO) is a unique room temperature single-phase multiferroic that crystallizes in a rhombohedrally distorted perovskite structure with space group $R3c$ [3]. Simultaneous ferroelectric ($T_C \sim 1103$ K) and antiferromagnetic ($T_N \sim 643$ K) properties of bulk BFO are attractive features for room

temperature applications. Despite a large ferroelectric polarization of 90–100 $\mu\text{C}/\text{cm}^2$ as predicted theoretically and achieved experimentally in a few cases, the polarization hysteresis loop and remnant polarization of BFO are disappointingly poor in many cases due to high leakage current and low resistivity caused by the formation of secondary phases and oxygen vacancies [4–7]. On the other hand, unlike ferromagnetic, antiferromagnetic nature of BFO leads to insignificant macroscopic magnetization [8]. Moreover, the superimposition of spiral spin structure on the G-type antiferromagnetic ordering inhibits spontaneous magnetization and limits the observation of linear magnetoelectric coupling [9].

The magnetic properties of BFO can be enhanced by suppressing the spin periodicity of length ~ 62 nm. However, the synthesized pure BFO nanostructures of size less than 62 nm also exhibited low magnetization values [10–12]. Thus, in order to enhance the magnetic and electrical properties of BFO, numerous research groups have carried out the substitution of either divalent or trivalent metal ions in Bi or/and Fe sites of BFO. Currently, many attempts have focused on substituting trivalent rare-earth (RE) ion (La, Sm, Eu, Tb, Dy, and Gd) at A-site or transition metal at B-site due to the remarkable enhancement of magnetic and ferroelectric

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properties [13–16]. In the list of RE ions, Gd^{3+} is chosen for the partial substitution in Bi site due to the following reasons: the first principle calculations suggest that the effective magnetic moment of Gd^{3+} is large ($8.0 \mu_B$) [17]. The ionic radius of Gd^{3+} ion (0.935 \AA) is quite smaller than that of Bi^{3+} ion (1.03 \AA) [18], so one can expect a large lattice distortion in Bi-site, which in turn would modify the properties. Further, Gd substitution would promote a possible coupling between Gd^{3+} and Fe^{3+} ions leading to weak ferromagnetism [17]. The variation in Fe–O–Fe bond angles and Fe–O bond distances due to the substitution of Gd ions would intensify the Dzyaloshinskii–Moriya (DM) interaction which eventually leads to macroscopic magnetization [19]. Therefore, it is reasonable to expect an enhanced magnetization if Gd^{3+} ions are substituted in BFO.

The primary objective of any partial substitution is to realize BFO as a potential candidate for multiferroic device applications like magnetoelectric random access memory (MERAM), wherein data can be written electrically and read out nondestructively by means of magnetic ordering [1]. For that matter, it is magneto-electric (ME) coupling ordering that needs to be significantly improved along with the ferroic ordering. Although a few indirect measurement of ME effect (magneto dielectric studies) are done previously, to the best of our knowledge, a systematic direct study of ME coupling has not been conducted in Gd substituted BFO nanoparticles or thin films to manifest the potential of Gd substituted BFO into device applications [20–22]. Moreover the results of enhanced multiferroic properties in Gd substituted BFO in the literature lack of common consensus, which requires more substantial work in this area. Therefore, the objective of the current work is to study the effect of Gd substitution on the structural, magnetic, ferroelectric properties of BFO. Further, we determine ME coefficient (α_E) in order to study the coupling parameters between magnetic and electric ordering in the synthesized pure and Gd substituted BFO samples.

2. Material and methods

2.1. Material synthesis

The samples of $Bi_{1-x}Gd_xFeO_3$ ($x=0, 0.05, \text{ and } 0.1$) were prepared by modified sol–gel process. Ultrapure bismuth (III) nitrate pentahydrate, iron (III) nitrate nonahydrate, and gadolinium (III) nitrate hydrate were taken in an appropriate ratio as starting materials and dissolved in 2-methoxyethanol to prepare the precursor solutions. Malonic acid and ethylene glycol were added to the solutions as complexants in 1:1 M ratios with respect to the cations. The mixtures were stirred continuously to obtain gels. The dried gels were ground and calcined at the temperature of $500 \text{ }^\circ\text{C}$ for 1 h in static air atmosphere to achieve single-phase perovskites. Using the similar procedure, the following samples were prepared; $BiFeO_3$ (BFO), $Bi_{0.95}Gd_{0.05}FeO_3$ (BG_5FO), and $Bi_{0.90}Gd_{0.10}FeO_3$ ($BG_{10}FO$).

2.2. Characterizations

Calcined BFO powders were structurally characterized through X-ray powder diffractometer by X'Pert Pro PANalytical with Cu K α ($\lambda=1.5406 \text{ \AA}$). Step-scanned diffraction patterns of the samples were collected between 15° and 85° in steps of 0.01° . The morphologies of the samples were investigated using a field emission scanning electron microscope (FESEM, Hitachi SU6600, Japan). Chemical state analysis was performed by using X-ray photoelectron spectroscopy (XPS, Omicron Nanotechnologies). The core level binding energies were aligned with the carbon binding energy of 284.6 eV . Magnetic measurements were performed by

using superconducting quantum interference device magnetometer (SQUID-VSM, Quantum Design, USA). Field dependent magnetizations were measured under $\pm 40 \text{ kOe}$ magnetic field with a step size of 750 Oe . Temperature dependent magnetizations were measured in ZFC and FC conditions at a constant magnetic field of 500 Oe . The calcined powders were pressed into pellets with a diameter of 13 mm under a pressure of $\sim 50 \text{ MPa}$ and subsequently sintered at $500 \text{ }^\circ\text{C}$. For electrical measurements, the opposite flat faces of the pellets were coated with silver paste to make them parallel plate capacitors. The ferroelectric hysteresis loops were obtained at room temperature by using a PE loop tracer (Marine India) based on Sawyer-Tower circuit at 50 Hz . Magneto-electric study was performed using a commercial set up manufactured by Marine India based on lock-in technique. The generated voltage was measured across each sample under the application of a static bias magnetic field in presence of an alternating magnetic field using Helmholtz coils (10 Oe at 850 Hz).

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction (XRD) patterns of pure and Gd substituted samples. It is well known that BFO is a metastable compound, so the formation of other stable impurity phases such as $Bi_{25}FeO_{40}$, $Bi_2Fe_4O_9$ and Bi_2O_3 remains inevitable during synthesis [23]. Therefore, the optimized conditions in our previous work were followed to attain single-phase compounds [24]. It is important to note that the XRD patterns of pure BFO and BG_5FO shown in Fig. 1 indicate single-phase crystal structure without any traceable amount of secondary phases. The experimental XRD pattern of pure BFO was well matched with the ICDD entry # 100-1090, which reveals that the crystal structure of the synthesized pure BFO corresponds to the rhombohedral structure with space group $R3c$ [3]. Slight variation in peaks and their shift toward higher 2θ values in the sample BG_5FO suggest that the rhombohedral structure is further distorted by Gd substitution. As the content of Gd ions increases, as in the case of $BG_{10}FO$, the shift of peaks toward higher angles is prominent. Moreover, the doubly peaks near the 2θ values of 32.0° , 39.3° , 51.7° , and 56.7° merge to appear as single peak. For instance, Fig. 1b shows the enlarged portion of the XRD patterns of 2θ region between 30.5° and 34° , where the reflections from (104) and (110) planes are evident in the pure BFO. In contrast, both the peaks in $BG_{10}FO$ merge to appear as single peak and some minor peaks rise in the vicinity of 2θ around 41° and 53° . Merging of those doubly peaks, evolution of the minor peaks and the disappearance of (006) peak in the sample signify the reduction of the rhombohedral phase and increase that of the orthorhombic phase [25,26]. The effect observed in the present case is attributed to compositional-driven structural distortion due to the inclusion of gadolinium ions. This is possible due to the mismatch between the radius of substituent ion and that of the host ion. The results are consistent with that of previous studies as well [17,25]. However our results differ from the work by Mukherjee et al. who reported that the peaks shifted toward lower angles with increasing Gd ions [21]. Generally, as observed in the present work, shifting of peaks toward higher angles indicates the reduction of unit cell parameters, which is possible to happen with the substitution of Gd ions as its radius is lower than that of Bi ions.

3.2. Microstructure analysis

Fig. 2 shows the field emission scanning electron microscopy (FESEM) images of all the synthesized samples. The FESEM images

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