Journal of Magnetism and Magnetic Materials 378 (2015) 333–339

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Magnetic hysteresis of cerium doped bismuth ferrite thin films

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A R T I C L E I N F O

Article history:
Received 1 February 2014
Received in revised form
14 November 2014
Accepted 17 November 2014
Available online 20 November 2014

Keywords:
Rietveld refinement
Raman scattering
wasp waist hysteresis loop
Hard and soft phase

A B S T R A C T

The influence of Cerium doping on the structural and magnetic properties of $BiFeO_3$ thin films have been investigated. Rietveld refinement of X-ray diffraction data and successive de-convolution of Raman scattering spectra of $Bi_{1-x}Ce_xFeO_3$ (BCFO) thin films with $x=0$–0.20 reflect the single phase rhombohedral (R3c) formation for $x<0.08$, whereas concentration-driven gradual structural phase transition from rhombohedral (R3c) to partial tetragonal (P4mm) phase follows for $x\geq 0.08$. All low wavenumber Raman modes ($<300\ cm^{-1}$) showed a noticeable shift towards higher wavenumber with increase in doping concentration, except Raman E-1 mode ($71\ cm^{-1}$), shows a minor shift. Sudden evolution of Raman mode at $668\ cm^{-1}$, manifested as A_1-tetragonal mode, accompanied by the shift to higher wavenumber with increase in doping concentration (x) affirm partial structural phase transition. Anomalous wasp waist shaped (M–H) hysteresis curves with improved saturation magnetization (M_s) for BCFO thin films is attributed to antiferromagnetic interaction/hybridization between Ce 4f and Fe 3d electronic states. The contribution of both hard and soft phase to the total coercivity is calculated. Polycrystalline $Bi_{0.88}Ce_{0.12}FeO_3$ thin film found to exhibit better magnetic properties with $M_s=15.9$ emu/g without any impure phase.

1. Introduction

Among several promising multiferroic materials, perovskite (ABO_3) structure based Bismuth Ferrite $BiFeO_3$ (BFO) has been emerged as most popular lead free and environmental friendly room temperature multiferroic material, which display concurrence of coupled ferroic order i.e. (anti)ferroelectricity, (anti) ferromagnetism, and/or ferroelasticity within a single phase in recent decades [1,2]. BFO has engrossed much attention worldwide owing to revealed signature of coupled electric and magnetic order parameters which provide an added degree of freedom for multifunctional device application in the evolving field of spintronics [1,2], multiple state memory devices [2,3], electric field controlled ferromagnetic resonance devices and magnetically modulated piezoelectric transducers [3–5]. BFO is known to exhibit ferroelectric properties with a high Curie temperature (T_c ~830 °C) and G-type antiferromagnetic behavior below Néel temperature (T_N~370 °C) with canted incommensurate spin spiral structure of period 62 nm which results into macroscopically weak ferromagnetism [4,5]. Though promising, non-ferroelectric parasite phase formation, spin modulated spiral magnetic structure, weak magneto-electric coupling coefficient and high leakage current density leading to poor electric polarization and large dielectric loss are the major hindrances in its real technological applications. However, several material engineering techniques such as oxygen ion implantation [6], epitaxial film growth [7,8], chemical leaching [9], application of large magnetic field (upto 20 T) [10], partial A-site/B-site cation substitution[11–13], preparation of particulate and laminar composites [14,15] and multilayer deposition with other perovskite families [14–16] have been rigorously employed to subdue the effect of such drawbacks. Undoubtedly, site engineering approach is widely adopted for its simplicity and controlled outcomes [17–24] and indeed, certain rare earth elements (La, Ce, Nd, Sm, Gd, Ho, Eu etc.) and alkaline earth metals (Ba, Ca, Sr etc.) substitution for Bi [11,17–20] and (3d, 4d) transitional metals (Ti, V, Cr, Mn, Co, Ni, Zn, W etc.) substitution for Fe [21–24] have been proved successful in improving the ferroelectric and magnetic performance of BFO thin film. In contrast, wasp waist shaped magnetic hysteresis loops observed for rare earth doped BFO thin films in general, have not been paid much consideration, to investigate the possible reasons and enriched physics hidden behind it [25–28]. In particular, Jeon et al. [25] have reported peculiar magnetization-field double hysteresis loop with enhanced remnant magnetization in 10% Ho doped BFO. However, no plausible description of pinch characteristics was reported. Similarly, pinched hysteresis loop has also been reported in PLD grown 10% Gd, 10% Sm and 10% Nd doped BFO thin films respectively [26]. Hu et al. have also confirmed maximum pinching

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http://dx.doi.org/10.1016/j.jmmm.2014.11.062
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behavior in hysteresis loop for PLD grown 10% Eu doped BFO thin films [27]. Not enough, pinched (*M*–*H*) hysteresis loop has also been reported for another rare earth ion Ce doped BFO thin films deposited using spin casting technique[28,29]. Moreover, such wasp waist shaped (*M*–*H*) loops has been reported in even transition metal such as (Ni, Co) substituted BFO thin films also [30]. Unfortunately, this peculiar observation has been neglected in previous literature and hence, motivated us for the present communication. In this report, we focused on synthesis of single phase $Bi_{1-x}Ce_xFeO_3$ thin films with varying dopant concentration of Ce ($x=0.0$, 0.04, 0.08, 0.12, 0.16 and 0.2) on low cost corning glass and silicon substrates using chemical solution deposition (CSD) technique. A systematic study of doping effects on the structural phase transition, vibrational dynamics and magnetic properties of BCFO thin film has been carried out. In particular, origin of the wasp waist shaped (*M*–*H*) hysteresis loop has been discussed and practical applications of such materials exhibiting pinching behavior are conferred.

2. Experimental technique

$Bi_{1-x}Ce_xFeO_3$ thin films with varying dopant concentration ($x=0$, 0.04, 0.08, 0.12, 0.16 and 0.2) were prepared on corning glass and silicon substrates by CSD technique. The BCFO precursor solutions were prepared using bismuth nitrate pentahydrate [$Bi(NO_3)_3 \bullet 5H_2O$], iron nitrate nanohydrate [$Fe(NO_3)_3 \bullet 9H_2O$] and cerium nitrate hexahydrate [$Ce(NO_3)_3 \bullet 6H_2O$] as starting material for Bi, Fe and Ce source respectively. 5 mol% of excess Bi was added to all precursors to compensate bismuth loss during the heat process [31]. All salts were dissolved in 2-methoxy ethanol [$CH_3CH_2OCH_2CH_2OH$] according to the composition formula and stirred rigorously for 30 min using magnetic stirrer. Finally, adequate amount of glacial acetic acid [CH_3COOH] and formamide [$HCONH_2$] was added to adjust the viscosity and concentration of stock solution to 0.2 M. Such homogeneous solution containing the above mentioned species was first filtered using fine filter paper (Particle retention~1.2 μm). All above stated processes were performed in an ambient atmosphere at room temperature. Fabrication of thin films was carried out by spin casting at 3500 rpm for 20 s. The as deposited wet thin films were pyrolysed at 300 °C for 5 min in air ambient and a number of coatings were deposited by spin casting to obtain required thickness of BCFO thin films. Thus, deposited BCFO thin films were annealed in temperature controlled quartz tube furnace at 575 °C, except pristine BFO thin film at 550 °C respectively in nitrogen gas (N_2) atmosphere for approximate 45 min to subdue the growth of oxygen vacancy defects and then cooled down slowly to room temperature [31]. Thickness of all deposited thin films was estimated using surface profiler (Veeco Dektak 150). High Resolution X-ray diffraction (XRD) pattern of the prepared samples were acquired using (BRUKER: D8 DISCOVER) diffractometer in Bragg–Brentano (θ–2θ) mode in range of 20–70° using CuKα (0.154 nm) radiation source operated at 40 kV and 40 mA. Variation in structural properties of BFO thin films with increasing Cerium doping concentration has been investigated by means of Rietveld refinement. Room temperature Raman spectra have been measured in back-scattering geometry using Renishaw InVia Reflex Micro Raman Spectrophotometer (polarized Ar^+ ion laser, $\lambda=514.53$ nm). Room temperature magnetic behavior of thin film samples was measured using vibrating sample magnetometer (VSM) (Microsense EV9 with sensitivity 5×10^{-5} emu) for maximum field (2.2 T) applied perpendicular to normal of the film surface. All the prepared BFO and BCFO thin films were found to be uniform, transparent and strongly adherent to the substrates. Thickness of all thin films was kept constant (350 nm) for all the employed measurements to avoid thickness dependent variation in the properties. The results obtained for prepared BFO and BCFO thin films are discussed and correlated in the subsequent sections.

3. Results and discussion

3.1. Structural properties

XRD pattern of $Bi_{1-x}Ce_xFeO_3$ thin films ($x=0$, 0.04, 0.08, 0.12, 0.16 and 0.20) deposited on corning glass substrate are shown in Fig. 1(a–f) and to determine the structural features of BCFO thin films further, experimental XRD data is analyzed by Rietveld refinement program using Bruker TOPAS 3 Software. The best theoretical fit and difference of XRD patterns are also plotted in Fig. 1 (a–f). The difference pattern in each curve indicates a perfect matching between the calculated and experimental XRD pattern and all XRD peaks observed for all prepared samples match very well with the stoichiometric phase of BFO [10,11]. Whereas, no trace of residual peak corresponding to secondary and impurity phases (e.g. $Bi_2Fe_4O_9$, Fe_2O_3, Bi_2O_3 etc) is observed in XRD pattern of pristine BFO thin film (Fig. 1(a)) affirms single phase crystallization within the limitation of XRD system [6,7]. Further, relative high intense doubly split peaks centered at around $2\theta=32°$, 40° and 56.8° corresponding to (104)/(110), (006)/(202) and (214)/(300) planes in observed XRD of pristine BFO thin film indicates characteristic rhombohedral distorted structure [(International Centre of Diffraction Data (ICDD) file no. 00-020-0169] having spatial group R3c (161) [31]. However, merging of the splitting of these characteristic XRD peaks is observed with increasing the Ce doping concentration in BFO from 0.08 to 0.2 [Fig. 1(c–f)] suggests the partial structural modification in host rhombohedral structure of BFO to the lower symmetry [11–13]. In addition, (110) diffraction peak is found to be shifting towards higher 2θ angle, indicates decrease in lattice parameters of BCFO thin films with increase in Ce dopant concentration. Such structural distortion verified to be favorable to exhibit enhanced ferroelectric behavior (shown in our earlier work) [31] and manifested to destroy the homogeneous spiral magnetic structure to release more magnetic moment compared to pristine BFO. Such structural transformations with rare earth doping have been reported earlier in literature by other fellow workers for both epitaxial or polycrystalline BFO thin films [17–20]. Also, the lattice parameters ("a" and "c"), unit cell volume (*V*) for all composition and corresponding "*R* values" along with goodness of fitting factor (GOF) which are obtained from the Rietveld refinement of XRD patterns are summarized in Table 1. The integer in the bracket next to lattice parameters is the corresponding error values in the last digit whereas the low GOF values ($S=R_{WP}/R_{exp}$) illustrates that refinement is successfully performed with all the investigated parameters close to literature data. Refined lattice parameters ($a=b=5.6141(4)$ Å, $c=13.8797(3)$ Å) and volume ($V=374.8180(3)$ Å^3) for pristine BFO thin film, are found to be in good agreement with the literature values reported for BFO thin film having rhombohedral R3c symmetry [13,14]. Similarly, Retvield refinement preformed using rhombohedral structure (R3c) results in best profile fitting of XRD pattern for $Bi_{0.96}Ce_{0.04}FeO_3$ thin film (Fig. 1b) and establish single phase formation of 4% Ce doped BFO thin film with a slight decrease in lattice parameters as illustrated from Table 1. It is important to highlight that the best profile fit for $Bi_{0.92}Ce_{0.08}FeO_3$, thin film having higher (8%) Ce doping concentration shown in Fig. 1 (c) could only be attained for non-centrosymmetric space group base model (rhombohedral (R3c)+tetragonal (P4mm)) with small *R* factors, while either tetragonal (P4mm) or rhombohedral (R3c) models resulted in the divergence of *R* factors. Thus, obtained results predicts, that crystallographic structure of 8% Ce doped BFO