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Nanoscale piezoresponse and magnetic studies of multiferroic Co and Pr co-substituted BFO thin films

Neeraj Panwar[a], Indrani Coondoo[a,*], Amit Tomar[b], A.L. Kholkin[a], Venkata S. Puli[c], Ram S. Katiyar[c]

[a] Department of Materials and Ceramics Engineering & CICECO, University of Aveiro, Aveiro 3810-193, Portugal
[b] N. A. S. College, C.C. S. University, Meerut, India
[c] Department of Physics, University of Puerto Rico, San Juan, PR 00931, USA

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ABSTRACT

Piezoresponse Force Microscopy (PFM) technique has been employed to acquire *out-of-plane* (OPP) piezoresponse images and local piezoelectric hysteresis loop in rhombohedrally distorted $Bi_{1-x}Pr_xFe_{1-y}Co_yO_3$ [$x = 0, 0.05$; $y = 0.05$] polycrystalline thin films fabricated via chemical solution deposition method. PFM images revealed that piezoelectric contrast is dependent upon the film composition. Furthermore, negative self-polarization effect was observed in the cobalt substituted BFO film. Well saturated local piezo-hysteresis loops were monitored and an increase was noticed in the piezoelectric coefficient (d_{33}) value with cobalt doping (25.1 pm/V) whereas with Pr co-substitution in BFCO film, the piezoelectric behavior was almost suppressed. Pr and cobalt co-substituted film exhibited the lowest leakage current density. Magnetic behavior (M–H curves) exhibited nearly eight times enhancement in the saturation magnetization values in the Co- and Co–Pr substituted films. The present study provides the different elements' substitution effect on the local piezoelectric and magnetic properties of $BiFeO_3$ multiferroic thin film.

1. Introduction

With an ever-increasing demand for data storage, transducers, and microelectromechanical (MEMS) systems applications, materials with superior ferroelectric and piezoelectric responses are of great interest. A number of multiferroics have been identified; however, their low transition temperatures hinder the potential applications. $BiFeO_3$ (BFO) with its high ferro-paraelectric transition temperature (T_C) ~ 1100 K and high antiferromagnetic to paramagnetic Néel temperature (T_N) ~ 643 K, stands out among all others [1,2]. Ever since, BFO has been widely studied in bulk and thin film forms [3–10]. It has been shown that the addition of dopants, affects the electrical and magnetic properties of BFO samples through structural modifications and the control over the concentration of oxygen vacancies. Consequently, several attempts have been employed to tailor the properties of BFO films by A- or B-site substitutions [2,11–15]. In order to further improve the electric and magnetic properties, co-substitutions have been attempted [16–22]. For example, Yu et al. reported enhanced dielectric, ferroelectric and anti-fatigue properties in La^{3+} and V^{5+} co-substituted $Bi_{0.85}La_{0.15}Fe_{1-x}V_xO_3$ (BLFV, $x = 0$–0.1) ceramics [16]. The leakage current density of BLFV ceramic was only 2.1×10^{-6} A cm^{-2}, several orders of magnitude lower than that for single element substituted BLF and BFV ceramics. Singh et al. studied La^{3+} and Ni^{2+} co-substituted BFO films and observed three orders of magnitude lower leakage current density than pure BFO [17]. This was even much lower than that for single ion La^{3+} or Ni^{2+} substituted films. The lower leakage current density helped in the observation of well saturated ferroelectric hysteresis loop in the co-substituted film. Zhai et al. prepared $Bi_{0.9}La_{0.1}Fe_{0.98}Nb_{0.02}O_3$ (BLFNO) polycrystalline ceramic and noticed a rhombohedral to monoclinic structural transition with Nb^{5+}-substitution in BLFO. Further, BLFNO sample showed a large coercive field and remnant magnetization ~ 1.35 T and 0.23 A m^2 kg^{-1}, respectively at room temperature [18]. The enhanced magnetic behavior was attributed to several factors including collapse of cycloid spin structure due to structural transition, destruction of magnetic balance between the antiparallel sub-lattices of Fe^{3+} ions and drastic grain size decrease with Nb^{5+} co-substitution in BLFO compound. Enhancement in these physical properties was also obtained by Cheng et al. in La^{3+} and Nb^{5+} co-substituted BFO films [19]. Hu et al. prepared pure BFO, Nd-substituted BFO (BNF), Nd and Mo co-substituted BFO (BNFM) thin films and reported minimum dielectric loss and leakage current density, well-saturated ferroelectric hysteresis loop, fatigue-free behavior and improved ferromagnetism with a saturation magnetization of ~15 emu/cm^3 in BNFM film [20]. Lan

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[*] Corresponding author. Tel.: +351 910446473; fax: +351 234 401470.
E-mail address: indrani_coondoo@yahoo.com (I. Coondoo).

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et al. investigated La^{3+} and Zr^{4+} co-substitution effect in BFO ceramics (BLFZ) and observed improved magnetic behavior and exchange bias effect [8]. The enhanced effects in BLFZ ceramics were ascribed to grain size reduction and antiferromagnetic–ferromagnetic core–shell structure formation. Liu et al. concluded that among various A-site Ce and B-site Zr co-substituted $Bi_{1-x}Ce_xFe_{1-y}Zr_yO_3$ (BCFZ) thin films, $Bi_{0.97}Ce_{0.03}Fe_{0.97}Zr_{0.03}O_3$ film showed the lowest dielectric loss and leakage current density, a well-squared P-E loop and fatigue-free characteristics as well as the strong magnetization [22]. Kawae et al. suppressed the leakage current density in the high electric field regions with co-substitution of Pr^{3+} and Mn^{4+} in BFO thin films [21]. As far as praseodymium (Pr) is concerned, it has been found more effective in enhancing the ferroelectric and magnetic properties than other rare earth ions substituted BFO films [4]. Similarly, cobalt (Co) has also been observed a suitable substituent for improving ferroelectric and magnetic properties of BFO [13]. Therefore, in this paper, we planned to investigate the simultaneous doping effect of Pr and Co on the electrical and magnetic properties of $BiFeO_3$ film. The electrical properties, e.g. local piezoelectricity, were studied by Piezoresponse Force Microscopy (PFM) technique. This technique helps to characterize the samples with higher conductivity which hampers macroscopic polarization measurement. The piezoelectric and magnetic measurements on Co- and Co–Pr-doped BFO films are discussed.

2. Experimental details

$BiFeO_3$ (BFO), $BiFe_{0.95}Co_{0.05}O_3$ (BFCO) and $Bi_{0.95}Pr_{0.05}Fe_{0.95}Co_{0.05}O_3$ (BPFCO) films were deposited on Pt(1 1 1)/Ti/SiO_2/Si substrates by chemical solution deposition technique. The precursor solutions were prepared by dissolving bismuth nitrate pentahydrate, iron nitrate nonahydrate, cobalt nitrate hexahydrate, praseodymium nitrate hexahydrate in acetic acid, and 2-methoxyethanol according to the metal ion ratios. Molarity of the resultant solutions was 0.5 M. The films were deposited onto the substrates by spin coating and pyrolysed layer by layer at 300 °C for 3 min. The process of coating and drying was repeated 15 times resulting in film thickness ~ 300 nm. Finally the films were annealed at 550 °C for 1 h in N_2 atmosphere to avoid secondary phase formation. Phase analysis of the films and investigation of their crystal structure were performed by X-ray diffraction (XRD) technique using Siemens diffractometer with Cu K_α radiation over an angular range $20^\circ \leq 2\theta \leq 60^\circ$. Local ferroelectric/piezoelectric properties of the films were investigated with PFM (simultaneously acquired with topography) using a commercial setup multimode nanoscope IIIA (Veeco) equipped with a lock-in amplifier (SR-830A, Stanford Research) and a function generator (FG-120, Yokagawa). Platinum coated silicon cantilever (force constant 42 N/m and resonance frequency 204–497 kHz) was used for this study. PFM images were obtained by applying ac voltage (5 V, peak-to-peak) with frequency of 50 kHz (*out-of-plane*) between the grounded tip and the bottom electrode. A standard ferroelectric tester (Radiant Technology) was used to measure the leakage current. The magnetization hysteresis loop (*M*–*H* loop) measurement was carried out using a vibrating sample magnetometer (VSM) (Lakeshore 7407).

3. Results and discussion

Fig. 1a shows the XRD patterns of the single phase BFO, BFCO and BPFCO films with rhombohedrally distorted $BiFeO_3$ perovskite structure. The lattice constants of both the substituted films (BFCO and BPFCO) are smaller (a = 3.961 Å and 3.956 Å) as compared to those of pristine BFO film (a = 3.977 Å) due to smaller ionic sizes of the substituents, viz. Pr^{3+} (112.6 pm) and Co^{3+} (54.5 pm) than those for Bi^{3+} (117 pm) and Fe^{2+} (61 pm)/Fe^{3+} (55 pm) ions, respectively [23]. Due to this effect, an increase in the diffraction angles of the peaks (1 0 4) and (1 1 0) of the substituted films can be noticed in Fig. 1b which represents the magnified XRD patterns from 31° to 33° of Fig. 1a. The rhombohedral distortion of the pristine BFO film is reduced toward the orthorhombic or tetragonal structure with Co/Pr substitution, as can be deduced from the broadening of (1 0 4) diffraction peak in Fig. 1b. Such effect has also been earlier reported in smaller ions substituted BFO samples [11,12].

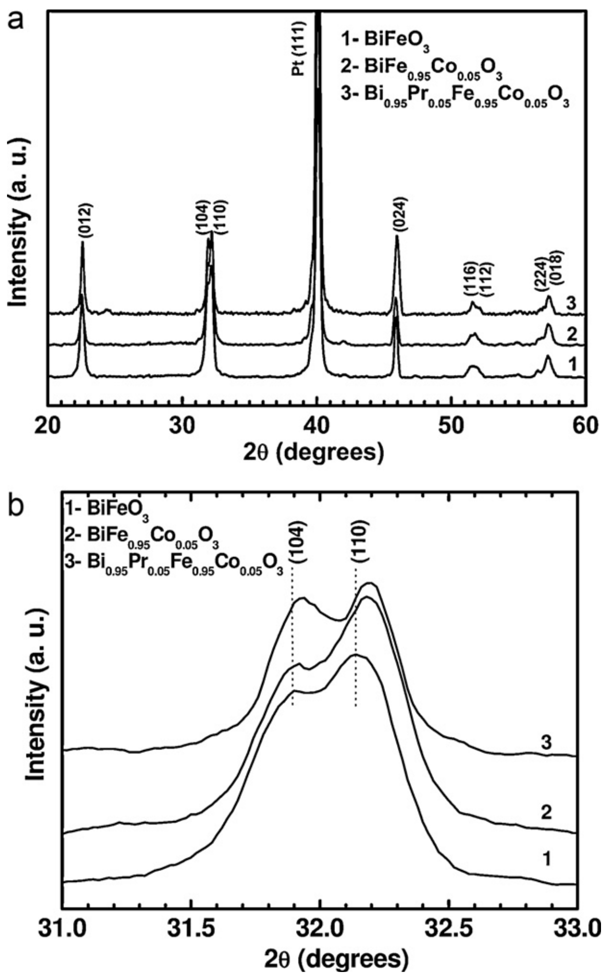

Fig. 1. (a) X-ray diffraction patterns of BFO, BFCO and BPFCO thin films; (b) magnified view of the (1 0 4) and (1 1 0) peaks (the vertical dotted lines are guidelines to the eyes).

Fig. 2a–c shows the surface topographies of the films acquired using standard AFM technique. The films present granular microstructure with root-mean-square (rms) roughness being 4.4 nm (BFO) and 3.9 nm (BFCO) and 4.8 nm (BPFCO). For the BFO and BFCO films, the average grain size is almost similar (~200 nm) whereas for the co-substituted BPFCO film, it is about 125 nm. In BPFCO film, clustering of grains can also be seen. The decrease in the grain size in the co-substituted film can be understood in terms of the decrease in the oxygen vacancies which are mobile and diffuse easily. With Pr at Bi-site in BFO, the bond strength with oxygen ion increases, since the bond dissociation energy of Pr–O bond (753 ± 17 kJ mol^{-1}) being higher than that of Bi–O bond (343 ± 6 kJ mol^{-1}), it firmly holds oxygen [4,24]. This also affirms that Bi-site substitution is more effective in oxygen vacancies suppression than Fe-site substituted BFO. Fig. 2d–f compares out-of-plane PFM images of the co-substituted films with that of pure BFO film. PFM