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Electric field induced nanoscale polarization switching and piezoresponse in Sm and Mn co-doped $BiFeO_3$ multiferroic ceramics by using piezoresponse force microscopy

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ABSTRACT

Samarium (5%Sm) and manganese (0.5%Mn) co-doped $BiFeO_3$ (B5SF0.5MO) polycrystalline multiferroic ceramics were prepared by solid-state-reaction to study the morphology, local polarization switching and piezoresponse, using atomic force microscopy (AFM) and piezoresponse force microscopy (PFM). Room temperature x-ray diffraction (XRD) and micro-Raman spectra reveal that samarium and manganese co-doping retains the parental rhombohedral *R*3*c* structure of $BiFeO_3$ (BFO). The out-of-plane (OP) PFM phase images show domains with oppositely oriented polarizations which are distinguished as domains with downward and upward polarizations with respect to the cantilever direction. Polarization switching occurs in the poled sample by locally poling the sample at negative and positive biases. Following the domain switching mechanism in BFO, it was found that 109° domain switching occurred besides the growth of 180° domains upon application of an electric field. The clockwise phase hysteresis implies the Debye model of piezoelectric relaxation effect due to defects that are both elastic and electric dipoles. The negative self-polarization in these samples is supposed to be the result of built-in internal bias field generated from excess electrons and charge defects like oxygen vacancies. The Saturated localized in-field hysteresis phase and amplitude loops from 180° domains suggest the existence of well-defined polarization along the field direction and suggests that Sm and Mn co-doped BFO can be a potential material for nanoscale piezoelectric applications.

1. Introduction

The continuous tendency towards miniaturization of electronic and optical components requires the understanding of polarization switching in dimensionally confined systems, such as thin films, nanowires and nanoparticles [1–3]. The fundamental property of ferroelectric materials that enables their applications in functional materials and heterostructures is the presence of switchable polarization and associated domain structures. Polarization switching directly underpins the functions of data storage, FeRAMs and electroresistive memories [4]. In this regard, the study of ferroelectric materials at the nanoscale level has become highly topical and of large interest in the applications involving high-sensitivity piezoelectric ceramics or thin films as transducer elements in microelectromechanical systems [5,6]. More attention has been drawn to nanostructured ceramics of several high-sensitivity piezoelectric systems, such as $Pb(Mg_{1/3}Nb_{2/3})O_3{-}PbTiO_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3PbTiO_3$, in which their morphotrophic phase boundaries and size effects studies have been reported for grain sizes down to 15 nm [7,8]. Environmental concerns, however, are presently driving the development of alternative lead-free multiferroic materials, which have great potential to offer for a wide range of applications with fascinating physical phenomena [9,10].

Bismuth ferrite (BFO) is one of the widely studied multiferroics whose ferroelectricity originates from the structural distortion of $6s^2$ lone pair electrons of Bi^{3+} ions, while its magnetic property comes from the Fe–O–Fe superexchange interactions [11–13]. In

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addition, BFO exhibits high ferroelectric Curie temperature of ~1103 K and antiferromagnetic Néel temperature of ~643 K. Many research efforts have been made to manipulate the ferroelectric polarization and the ferromagnetic behaviors using the external field, such as an electric field to tune the magnetic domain, or conversely, using a magnetic field to tune the ferroelectric polarization [14–16]. A minor dopant can significantly distort the FeO_6 octahedra, and modify the concentration of the oxygen vacancies, the spin or even the surface charge density [17]. Enhanced multiferroic properties of BFO were found after substituting it with different alkaline-earth metal ions [18–20]. A-site substitutions of alkaline earth metal elements in BFO, i.e., $(Bi_{1-x}A_x)FeO_3$ (A = Ca, Ce, Sr, Ba), have demonstrated an improvement of optical, photovoltaic, magnetic and ferroelectric properties [21–31]. Recently, it has been shown that the space-modulated spin structure of BFO can be collapsed by the A-site lanthanum (La) substitution [32,33]. Compared with La^{3+} ions, Sm^{3+} ions possess a smaller effective radius (~1.24 Å for coordination number = 12) [34] suggesting that the effect of an A-site substitution may further be enhanced if Sm^{3+} ions are substituted with Bi^{3+} ions (~1.4 Å for coordination number = 12) [34] in BFO. It was shown that the 12.5%Sm-doped BFO ceramics produced large piezoelectric d_{33} coefficient of 29 pC/N, together with a high remanent polarization of 15.09 $\mu C/cm^2$ at room temperature, suggesting the existence of long-range ferroelectric order on a macroscopic scale [35]. More recently, the composition-induced morphotrophic phase boundary (MPB) in Sm-doped BFO has become an intense research topic due to its complex structure and enhanced piezoelectric and ferroelectric properties [36–39].

Alternatively, the B-site doping with rare-earth elements or transition metals were employed to improve the multiferroic properties of BFO [40,41]. It was shown that manganese (Mn) substitution does not alter the space group of $BiFe_{1-x}Mn_xO_3$ for $x = 0.3$, but it strongly decreases the temperatures of the ferroelectric and magnetic phase transitions [42]. More recently, the co-substitution of (La, Co), (Ba, Mn) and (Eu, Co) at A- and B-sites showed an enhancement in magnetic properties of BFO [43–45]. Furthermore, the (Sm, Mn) co-doped BFO thin films [46], nanoparticles [47], single crystals [45] and ceramics [48] have shown enhanced magnetic and dielectric properties compared to the pure and single element doped BFO.

In this work, we present the study of localized domain structure, polarization switching, and electromechanical strain of (Sm, Mn) co-doped BFO ceramics using piezoresponse force microscopy (PFM). In PFM experiments, an ac electric field was applied between the conductive atomic force tip and bottom electrode. The piezoelectric response of the surface was detected as a periodic deflection of the cantilever and used to construct ferroelectric domain images. Domains with oppositely oriented polarization are distinguished by different contrast in the PFM image. Our results reveal that the ferroelastic 109° domain switching appears in the 180° ferroelectric domain matrix under an electric field. The well-defined piezoelectric phase hysteresis and classical butterfly amplitude loops from 180° domains suggest the existence of well-defined ferroelectric polarization along the field direction.

2. Experimental procedure

Polycrystalline $(Bi_{0.95}Sm_{0.05}Fe_{0.995}Mn_{0.005})O_3$ (B5SF0.5MO) ceramics were prepared by the solid-state reaction method. High-purity (>99%) powders of Bi_2O_3, Sm_2O_3, Fe_2O_3 and Mn_2O_3, were used as starting materials. Stoichiometric amounts of powders were mixed with zirconia balls in an agate mortar for more than 24 h with ethanol as a medium. The mixture was calcined at 800 °C for 3 h and a high-energy planetary ball-mill (Retsch PM100 (RETSCH, Haan, Germany) was used to reduce particle size. The powder mixture was then pressed into a 1.0 cm diameter disk for sintering at 850 °C for 3 h. The as-sintered samples were polished down to 0.2 mm and annealed at 500 °C for 30 min in order to remove residual stress. An *In situ* XRD analysis was conducted by using a Rigaku Mulitplex X-ray Diffractometer with radiations of $K\alpha_1$ (1.5444 Å) and $K\alpha_2$ (1.5406 Å). Room-temperature Raman spectra was obtained by using micro Raman instrument (Horiba micro Raman spectrometer), equipped with a green laser of $\lambda = 514$ nm. Grain morphologies were obtained using a field-emission scanning electron microscope (FE-SEM; HITACHI SU 8010) operated at 20 keV. Surface topography, domain switching behavior of out-of-plane (OP) polarization and amplitude images were obtained by using AFM (Bruker multimode 8) with PFM contact mode. The microscope was equipped with an external lock-in amplifier and a function generator which were used to apply ac and dc voltages to the sample surface for poling and imaging. Stiff-conducting silicon (Si) doped antimony (Sb) cantilevers (MESP-RC; L = 115–135 μm, k = 5 N/m) were used for the measurements performed in ambient environment. Field-dependent macroscopic polarization hysteresis (P-E) loops were obtained by using Radiant precision multiferroic tester.

3. Results and discussion

Fig. 1 shows the XRD pattern at room temperature for B5SF0.5MO. The pattern is consistent with the polycrystalline perovskite structure with small amount of parasitic non-perovskite $Bi_2Fe_4O_9$ phase as indicated by the asterisk. The second phase was known to occur as part of the diffusion-controlled reaction between Bi_2O_3 and Fe_2O_3 [49]. The inset (a) shows the doublet peaks at 31.8° and 32.1° which correspond to the (104) and (110) lattice planes of (110) pseudo cubic direction. The separation of (104) and (110) peaks is the characteristic diffraction pattern of rhombohedral BFO. This indicates that 5%Sm+0.5%Mn co-doping retains the parental rhombohedral *R*3*c* structure at room temperature. This is further evidenced by the clear splitting of the peak at (111) pseudo cubic direction as shown in inset (b).

Fig. 2 shows Raman vibration modes for BFO, 5%Sm doped BFO (B5SFO) and B5SF0.5MO at room temperature. To identify the Raman vibrational modes, the Raman spectra of BFO and B5SFO are included in this work. The group theory predicts that a rhombohedrally distorted BFO perovskite with *R*3*c* space group (Z = 2), should have 13 ($\Gamma = 4A_1 + 9E$) Raman active modes [50–52]. As shown in Fig. 2, B5SFO and B5SF0.5MO exhibit similar Raman

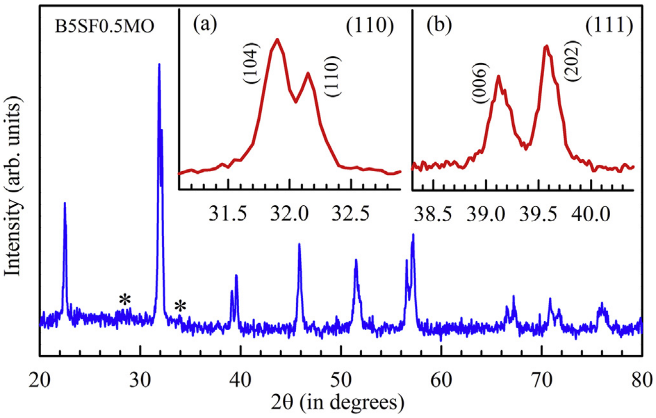

Fig. 1. XRD spectra of polished B5SF0.5MO ceramics at room temperature. Second phase $Bi_2Fe_4O_9$ is indicated by the asterisk. Insets (a) and (b) are the short angle scanned (110) and (111) diffraction peaks respectively.