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Multiferroic and in-plane magnetoelectric coupling properties of $BiFeO_3$ nano-films with substitution of rare earth ions La^{3+} and Nd^{3+}

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Abstract: Single-phase multiferroic $BiFeO_3$ and $Bi_{0.9}(La/Nd)_{0.1}FeO_3$ (doped with rare earth ions La^{3+} and Nd^{3+}) films grown on (111)-Pt/Ti/SiO_2/Si substrate were prepared via sol-gel method and a subsequent rapid thermal process. The phase composition, microstructure, ferroelectric, dielectric, ferromagnetic properties were investigated, and meanwhile, the in-plane magnetoelectric (ME) coupling effects of the films were reported and studied for the first time in this work. Structural characterization by X-ray diffraction and scanning electron microscopy showed that both $BiFeO_3$ and $Bi_{0.9}(La/Nd)_{0.1}FeO_3$ exhibited a rhombohedral structure with (111) preferred orientation. The results of the physical properties indicated that the introduction of rare earth ions improved significantly the polarization, magnetization and dielectric properties than the undoped $BiFeO_3$ crystals, and it enhanced effectively the in-plane ME coupling (the ME coupling coefficient α_E increased from 0.13 in the pure $BiFeO_3$ to 0.21 in $Bi_{0.9}La_{0.1}FeO_3$ and 0.34 V/(Oe·cm) in $Bi_{0.9}Nd_{0.1}FeO_3$). The mechanism of these phenomena was investigated systematically.

Keywords: bismuth ferrite; substitution; rare earth ions; ferroelectricity; dielectricity; ferromagnetism; magnetoelectric coupling

New multi-function materials, possessing not only many kinds of physical and chemical effects but couplings to realize mutual regulation and control, have become hotspots in academic and industrial fields nowadays. Multiferroic materials are one of the most typical multi-function materials, which own simultaneously two or more types of the ferroelectricity, the ferromagnetism, the ferroelasticity, the ferrotoroidicity, and present couplings between any two ferroic properties[1]. For this reason, they have arrested considerable attention at present. Recently, focuses of researching or investigating are all on single-phase and composite multiferroic materials with their ferroelectric, ferromagnetic and magnetoelectric (ME) properties, which are used possibly for the design of novel storage devices.

$BiFeO_3$ (BFO), owning the ferroelectricity and antiferromagnetism, is a representative single-phase multiferroic materials, which has lately received widespread attentions since that it presents an extra-high ferroelectricity while epitaxially growing on single-crystal perovskite substrates[2]. The preparation methods of BFO films primarily include pulsed laser deposition (PLD)[3, 4], hydrothermal synthesis[5] and sol-gel has been reported scarcely. But either way, BFO film in the pure phase shows large leakage current, an endogenetic fatal defect stemmed from oxygen vacancies for the fluctuations of Fe^{3+} [6]. However, its performances will ameliorate obviously by doping technique[7]. Common practices now are embracing substitutions of La^{3+}, Sm^{3+} at A-site[8–10], Ti^{4+}, Mn^{4+} [11,12], Cr^{3+} [13] at B-site in ABO_3 structures, which will improve properties of films and lays a foundation for further investigating the microcosmic mechanism of multiferroics.

Recent studies on BFO and its doping series still focus on their ferroelectricity and dielectricity, while, to the best of our knowledge, there is no documented research on the actual measured in-plane ME coupling of them due to their complexity. In this work, we synthesized BFO nano-films and the films doped with 10 mol.% La^{3+} and Nd^{3+} ions for the optimal performances than the 5 mol.%, 15 mol.% and 20 mol.% control groups on the (111)-Pt/Ti/SiO_2/Si substrate via sol-gel method and a subsequent rapid thermal treatment process. Not only the phase composition, the microstructures, the electric and magnetic effects, but also the in-plane ME coupling properties of both pure BFO and $Bi_{0.9}(La/Nd)_{0.1}FeO_3$ films were studied. And meanwhile, the influences of dopants on dielectric properties, polarization and mag-

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netization behaviors of the doped sample films were investigated in detail according to the tolerance theory and defect chemistry, providing references for further study of coupling mechanism, applications and devices design.

1 Experimental

1.1 Synthesis

Precursors of $BiFeO_3$ and $Bi_{0.9}(La/Nd)_{0.1}FeO_3$ were synthesized by sol-gel and rapid thermal process (RTP). Raw materials were $Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $La(NO_3)_3{\cdot}5H_2O$ and $Nd(NO_3)_3{\cdot}6H_2O$. Ethylene glycol monomethyl ether ($C_3H_8O_2$) and acetic anhydride ($C_4H_6O_3$) acted as the solvent and the high performance water removal agent, respectively. Note that the content of bismuthate must excess 10 mol.%–15 mol.% to supply its volatilization loss during annealing. These precursors should be preserved in a dark-brown color glass in the dark. The films were fabricated on the (111)-Pt/Ti/SiO_2/Si substrate by a spin-coating method at 4000 r/min for 30 s and dehydrated at 200 ºC for 300 s. The residual organics were removed at 450 ºC for 300 s and crystallized at 600 ºC for 420 s by RTP process. Finally, Pt electrodes were deposited by magnetron sputtering method on the surface of films using a metal mask with a diameter of 0.2 mm and heated at 500 ºC for 300 s before measurements to improve the adhesion between the substrate and ferroelectric films.

1.2 Characterization

The crystalline phases and crystal structure of the films were determined by an X-ray diffractometer (XRD, model D/max-2500 V, Rigaku Co., Japan) with Cu Kα monochromatic radiation (λ=0.154 18 nm) at a scanning speed of 2(º)/min in step of 0.02º. The microstructure of the films was obtained by a model S5500 scanning electron microscope (SEM, Hitachi Co., Japan). The ferroelectric properties of the samples were analyzed by a model multiferroic 200 V Test System (Radiant Technologies). The dielectric properties were measured by an impedance analyzer (Agilent 4294A) in the frequency range from 20 Hz to 1 MHz.

The ferromagneticity was obtained by a physical property measurement system (PPMS, Quantum Design). The ME measurement of these films was performed in an open circuit condition. The film samples were electrically connected with silver wires bonded on the top Pt electrode and the substrate. A dc bias magnetic field H_{dc} is superimposed by a small ac magnetic field δH in parallel. The magnetoelectric coupling coefficients α_E was calculated from the dielectric data using the relation[14],

$$\alpha_E = \frac{\delta E}{\delta H_{ac}} = \frac{\delta V}{t \cdot \delta H_{ac}} \tag{1}$$

where δV is the induced ME voltage signal collected by a lock-in amplifier (SRS, model SR830), t is the thickness of the films and was measured by a profilometer (BRUKER Dektak XT), and δH_{ac} is the alternating magnetic field signals collected by a Gauss/Tesla meter (REF, model F1218). All measurements were performed at room temperature.

2 Results and discussion

2.1 Phase identification and SEM analysis

Fig. 1 shows the XRD patterns of $BiFeO_3$ and $Bi_{0.9}(La/Nd)_{0.1}FeO_3$ (BLF or BNF) films according to the inorganic crystal structure database (ICSD) 72-2035. All specimens exhibit a rhombohedral structure with (111) orientation. No any other intermediate phases like $Bi_2Fe_4O_9$ has been found because the ionic radii of lanthanides are similar to that of Bi^{3+} (demonstrated in Table 1[15]). In fact, their extranuclear strucure of the outermost two layers exhibits high similarity[16]. The (111) and $(\bar{1}11)$ peaks overlap completely and the intensity remains roughly the same, while the (110) and $(\bar{1}10)$ peaks also overlap completely and the intensity is increasing gradually. Since that the dopants with different ionic radius could cause the distortion of crystal lattice to various degrees and even change their syngony[17]. All films show the (111) preferred orientation for the (111)-Pt/Ti/SiO_2/Si substrate.

The scanning electron microscopy (SEM) micrographs of the films are shown in Fig. 2. The average grain sizes calculated by Cottrell's method[18] are given in Table 2. Clearly, the lattice parameters and average grain sizes all decrease after the introduction of rare earth dopants. Fig. 2(a) shows the representative microstructure of BFO and the inset is an AFM image of BFO. The elliptic crystalline grains in the pure BFO film are legible, homogeneous and possess a superior compactness. The shapes of

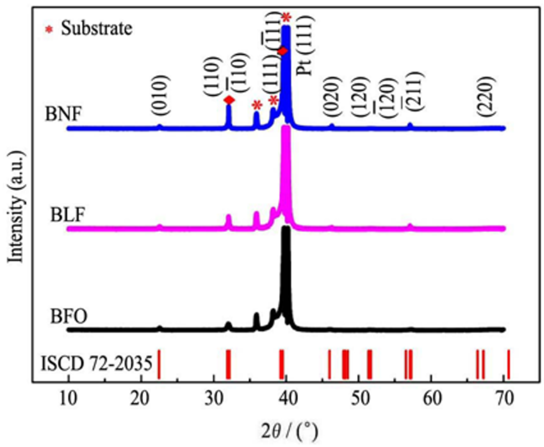

Fig. 1 XRD patterns of BFO and its doping series

Table 1 Radius of common ions quoted from Lange's Chemistry Handbook, Version 15[15]

Ion	Bi^{3+}	Fe^{3+}	O^{2-}	La^{3+}	Nd^{3+}
Radius/nm	0.096	0.065	0.132	0.112	0.106