

Improved multiferroic properties in (Ho, Mn) co-doped BiFeO₃ thin films prepared by chemical solution deposition

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Abstract

Pure BiFeO₃ (BFO), Bi_{0.92}Ho_{0.08}FeO₃ (BHFO) and Bi_{0.92}Ho_{0.08}Fe_{0.97}Mn_{0.03}O₃ (BHFMO) films were successfully deposited on FTO/glass substrates by chemical solution deposition method. X-ray diffraction, Rietveld refinement and Raman spectra results demonstrate that a structural transition from rhombohedral (R3c:H) to biphasic structure (R3c:H+R-3m:R) occurs in BHFO and BHFMO films. The improved dielectric properties, leakage current, ferroelectric properties and ferromagnetic properties are obtained by co-doping Ho and Mn. A giant remanent polarization ($2P_r \sim 231.4 \mu\text{C}/\text{cm}^2$) is observed in BHFMO film. In addition, the dramatically decreased leakage current density ($4.02 \times 10^{-4} \text{ A}/\text{cm}^2$ at 400 kV/cm) is obtained in BHFMO film, which is about two orders of magnitude lower than that of pure BFO. The superior ferroelectric properties of BHFMO film are mainly attributed to the structure transition and low leakage current. Furthermore, BHFMO film shows enhanced ferromagnetism ($M_s \sim 2.74 \text{ emu}/\text{cm}^3$), implying the collapse of space modulated spin structure by the structural transition.

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1. Introduction

Perovskite-based bismuth ferrite, BiFeO₃ (BFO), is one of the most promising multiferroic materials and receives special attention in recent years because of its simultaneous ferroelectricity and antiferromagnetism above room temperature ($T_c \sim 1103 \text{ K}$ and $T_N \sim 643 \text{ K}$) [1]. Furthermore, the intrinsic magnetoelectric effect can be caused by the prospect of controlling polarization by magnetic fields, or magnetization by an electric field [2]. These outstanding properties have aroused extensive research activities on BFO. BFO is a rhombohedral distorted perovskite structure with space group R3c [3]. In addition, magnetic ordering in BFO is G-type antiferromagnetic, and the canting of the antiferromagnetic sublattices results in a macroscopically so-called weak ferromagnetism [4].

BFO is being considered as a superior candidate for next-generation devices including non-volatile memories, spintronics, high-density microactuators, piezoelectric sensors, optoelectronic

devices, etc. [5,6]. However, the practical applications of BFO in electronic devices are limited due to the serious leakage-current problem, which will make it difficult to obtain a large remanent polarization in BFO. Therefore, many research groups have attempted to address these difficulties by chemical doping, where it can be called site-engineering concept.

In general, substitution of rare earth (RE) metal (RE=Ho, Gd, Sm, Nd, Dy, Tb, etc.) ions for the Bi-site and transition-metal (TM=Cu, Mn, Cr, Ni, Ti, Zn, etc.) ions for the Fe-site is an effective way to reduce leakage current density as well as enhance the multiferroic properties [7–13]. The doping also enhances magnetization of BFO by suppressing the cycloid spin structure [14,15]. Among different kinds of doping elements, RE and TM ions co-substitution is found to be especially attractive. These combinations not only decrease leakage current significantly, but also cause the enhanced remanent magnetization [16–18]. Ho substitution for the Bi-site is an effective way to decrease leakage current and enhance the magnetization of BFO [19]. Generally, Mn substitution for the Fe-site contributed to improving ferroelectric property [20,21]. Therefore, (Ho, Mn) co-doping is expected to enhance the ferroelectric and magnetic properties, simultaneously.

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In present work, BiFeO_3 (BFO), $\text{Bi}_{0.92}\text{Ho}_{0.08}\text{FeO}_3$ (BHFO) and $\text{Bi}_{0.92}\text{Ho}_{0.08}\text{Fe}_{0.97}\text{Mn}_{0.03}\text{O}_3$ (BHFMO) films are synthesized by chemical solution deposition method. The effects of Ho and Mn co-doping on the structure, surface morphology, dielectric, leakage current, ferroelectric properties and magnetic properties are investigated systematically.

2. Experimental

The BiFeO_3 (BFO), $\text{Bi}_{0.92}\text{Ho}_{0.08}\text{FeO}_3$ (BHFO) and $\text{Bi}_{0.92}\text{Ho}_{0.08}\text{Fe}_{0.97}\text{Mn}_{0.03}\text{O}_3$ (BHFMO) films were successfully deposited on (FTO)/glass substrates by the chemical solution deposition method and sequential-layer annealing process. The precursor solutions were prepared by $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (5 mol% of excess Bi was added to compensate for bismuth loss during the heat treatment), $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ as raw materials, which were dissolved into 2-methoxyethanol based on the compound stoichiometric ratio and solution concentration (0.3 mol/L) and stirred continuously for 30 min at room temperature until a clear solution was observed. Subsequently, the acetic anhydride with a volume ratio of one third to 2-methoxyethanol was added into the solution to dehydrate and adjust the pH value of the solution. After further constant stirring for 1.5 h at room temperature, a homogeneous and stable precursor solution was obtained. FTO/glass substrates were washed in deionized water, acetone, and alcohol sequentially.

The precursor solution was spin coated on FTO/glass substrates with a constant spinning rate of 4000 rpm for 15 s. Each layer of the films was dried on a hot plate at 200°C for 10 min, and then annealed at 550°C for 10 min in a rapid thermal process furnace. These deposition processes were repeated several times to get the desired film thickness. In order to measure the electrical behaviors, Au top electrodes (with areas of 0.502 mm^2) were sputtered on the top surface of the thin films by ions sputtering through a metal shadow mask.

The polycrystalline structure of the films was characterized by X-ray diffraction (XRD, D/MAX-2200, Rigaku) using $\text{Cu K}\alpha$ radiation ($\lambda=0.154056\text{ nm}$). The scanning range was from 15° to 70° . Raman spectra measurements were performed by a RENISHAW inVia Raman microscope equipped an excitation with 532 nm. A field emission scanning electron microscopy (FE-SEM, S4800, Hitachi) was utilized for the observation of microstructures and cross-sectional morphologies. Dielectric properties of the films were carried out on Agilent E4980A Concise LCR meter. The leakage current density of the films was measured by Agilent B2901A. The electric hysteresis loops of the films were tested by an aixACCT TF-Analyzer 2000 and the magnetic properties of the films were analyzed by the MPMS-XL-7 superconducting quantum interference magnetic measuring system.

3. Results and discussion

Fig. 1(a) shows the typical XRD patterns of BFO, BHFO and BHFMO films deposited on FTO/glass substrates at room temperature. The impurity phase appearing in the vicinity of

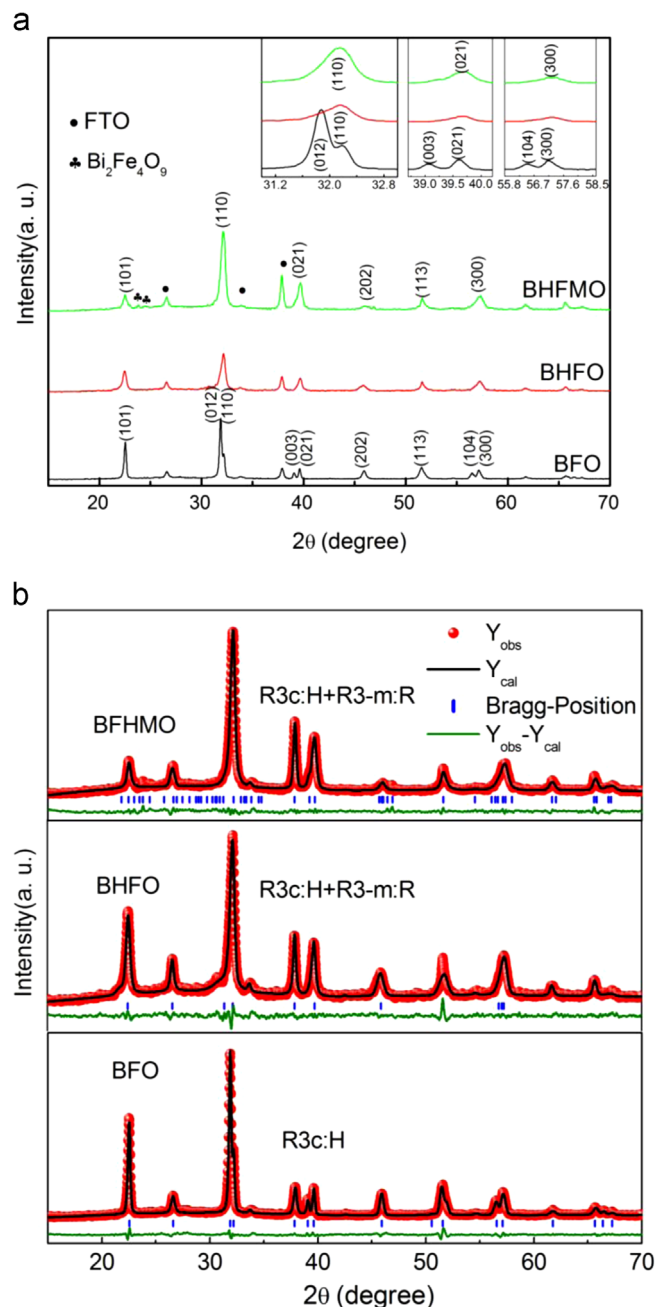


Fig. 1. (a) XRD patterns of pure BFO, BHFO and BHFMO films; the insets show the enlarged XRD patterns in the vicinities of $2\theta = 32.0^\circ$, 39.0° and 57.0° ; (b) Rietveld refined XRD patterns of the thin films.

$2\theta \approx 24^\circ$ for BHFMO film could be indexed as the $\text{Bi}_2\text{Fe}_4\text{O}_9$. The distorted rhombohedral R3c structure has been observed for pure BFO film, which matches well with the JCPDS card no. 20-0169. The insets exhibit the magnifications around 2θ values of 32.0° , 39.6° and 57.0° , respectively. As shown in the magnified XRD patterns, the (012) and (110) diffraction peaks are clearly separate in pure BFO film, but the peaks are merged into the single peak in BHFO and BHFMO films. Moreover, (003) and (104) peaks disappear completely compared with pure BFO film. All these changes of the XRD patterns suggest that Ho-doping and (Ho, Mn) co-doping give rise to the

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