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Effects of Sm and Mn co-doping on structural, optical and magnetic properties of $BiFeO_3$ films prepared by a sol–gel technique

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ABSTRACT

Multiferroic $(Bi_{1-x}Sm_x)(Fe_{0.95}Mn_{0.05})O_3$ (*x*BSFMO, $x=0.00$, 0.03, 0.06, and 0.09) films were deposited on the quartz substrates by a sol–gel technique. X-ray diffraction patterns indicate that all the films exhibit a polycrystalline perovskite structure with a high degree of (110) preferred orientation. The Sm and Mn co-doping at A- and B-site of $BiFeO_3$ (BFO) results in structural distortion, improves surface morphology and reduces the average grain size of the films. With increasing *x* from 0.00 to 0.09, the optical band gap of *x*BSFMO films increases and can be expressed by $(2.60+0.8x)$ eV, which may be due to Burstein–Moss effect. Compared with Mn-doped BFO film, the saturation magnetization (M_S) of the (Sm, Mn) co-doped BFO films are significantly enhanced, which provides potential applications in information storage.

1. Introduction

Multiferroic materials, which combine two or more of the properties of ferroelectricity, ferromagnetism and ferroelasticity [1], have attracted much attention since they potentially offer a wide range of applications on information storage process, spintronics, multiple-state memories, as well as presenting fascinating physical phenomena [2,3]. $BiFeO_3$ (BFO) with a rhombohedrically distorted perovskite structure is one of the well-known multiferroic compounds exhibiting simultaneous ferroelectric (Curie temperature $T_C \sim 1103$ K) and G-type antiferromagnetic (Neel temperature $T_N \sim 643$ K) properties above room temperature [4]. Additionally, BFO thin films exhibit remarkable ferroelectric photovoltaic effect [5]. These properties make it not only fascinating in the fundamental physics of ferroelectromagnetic materials but also interesting for potential applications in photovoltaic devices and infrared detectors. Over the past few years, great efforts have been focused on ferroelectric property, ferromagnetism, magnetoelectric effect in the BFO films, while reports about its optical properties are rare. Following the site-engineering concept proposed in previous studies [6,7], Bi-site doping with rare-earth elements and/or Fe-site doping with transition elements were often employed to improve the multiferroic properties of BFO [8,9]. Recently, Arya et al. found the significantly enhanced magnetic properties in the Sm–Mn co-substituted BFO nanoparticles [10]. This motivates us to synthesize the (Sm, Mn) co-doped BFO films and investigate their crystal structure and magnetic properties. Besides, the effects of co-doping on the optical properties of BFO are also worth studying.

In this letter, $(Bi_{1-x}Sm_x)(Fe_{0.95}Mn_{0.05})O_3$ (*x*BSFMO, $x=0.00$, 0.03, 0.06, and 0.09) films were deposited on the quartz substrates by a sol–gel technique. The microstructure, surface morphologies, optical and magnetic properties were analyzed. Especially, the optical properties of the *x*BSFMO films were first studied by transmittance spectra.

2. Experimental details

*x*BSFMO films with $x=0.00$–0.09 were deposited on the quartz substrates by a sol–gel method. The precursor solutions were prepared by using bismuth nitrate $[Bi(NO_3)_3 \cdot 5H_2O]$ (99%), samarium nitrate $[Sm(NO_3)_3 \cdot 6H_2O]$ (99.9%), iron nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ (98.5%) and manganese acetate $[Mn(CH_3COO)_2 \cdot 4H_2O]$ (99%) as starting materials and acetic acid (99.5%) as solvent. Ethylene glycol (99%) was also added as thickening agent. $Sm(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, Mn $(CH_3COO)_2 \cdot 4H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ (5 mol% of excess Bi was added to compensate for bismuth loss during the heat treatment) were dissolved in acetic acid and ethylene glycol. The concentration of the final solution was adjusted to 0.25 mol/L. The precursor solution was spin coated on the quartz glass substrate at 6000 rpm for 30 s. After

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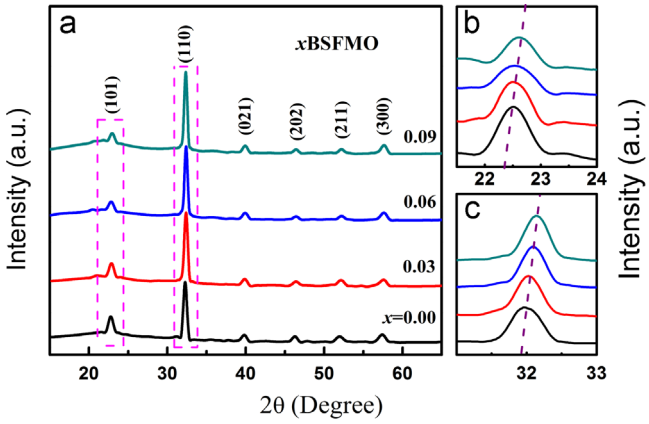

Fig. 1. (a) XRD patterns of the *x*BSFMO ($x=0.00$, 0.03, 0.06, and 0.09) films. (b) The magnified patterns of (101) peak around 22.5°. (c) The magnified patterns of (110) peak around 32°.

spun-coating, each layer was preannealed at 350 °C for 3 min. When every four layers had been coated, the films were moved to the rapid thermal annealing equipment and annealed at 600 °C for 5 min in atmosphere for crystallization. The above process was repeated several times to obtain the desired film thickness.

The crystal-structure and morphology of the *x*BSFMO films were characterized by X-ray diffraction (XRD, Bruker D8 Advance, with Cu Kα radiation) and scanning electron microscopy (SEM, Philips XL30FEG), respectively. The optical properties were characterized by transmittance spectra (PerkinElmer UV/VIS Lambda 2S). The magnetic properties of the samples were investigated by a physical property measurement system (PPMS-9, Quantum Design).

3. Results and discussion

Room-temperature XRD patterns of the *x*BSFMO ($x=0.00$, 0.03, 0.06, and 0.09) films grown on the quartz substrates are shown in

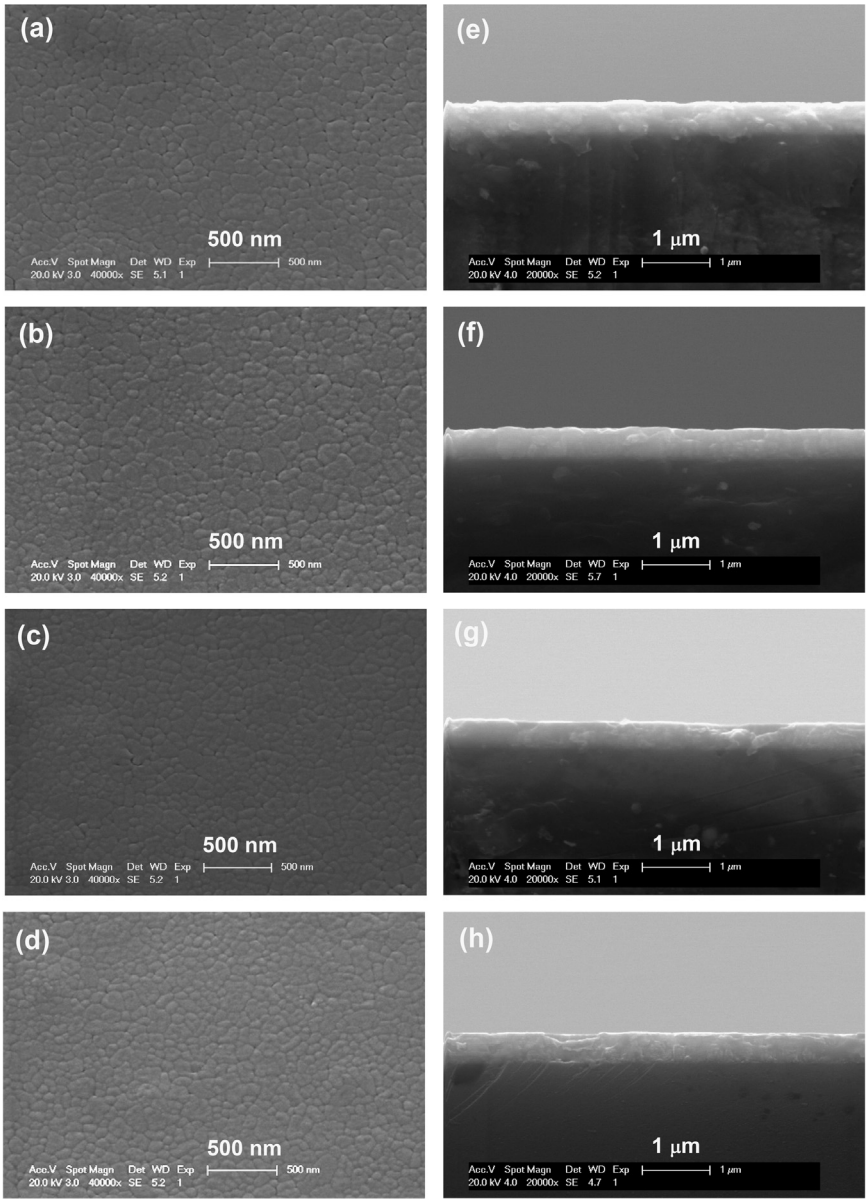

Fig. 2. SEM surface morphologies of *x*BSFMO films (a) $x=0.00$, (b) $x=0.03$, (c) $x=0.06$, and (d) $x=0.09$. Cross-section images of *x*BSFMO films (e) $x=0.00$, (f) $x=0.03$, (g) $x=0.06$, and (h) $x=0.09$.