



Structure and multiferroic properties of Sr substituted $\text{Bi}_{0.89-x}\text{Sm}_{0.11}\text{Sr}_x\text{Fe}_{0.94}(\text{Mn}_{0.04}\text{Cr}_{0.02})\text{O}_3$ thin films

Wenlong Liu, Guoqiang Tan*, Xu Xue, Guohua Dong, Huijun Ren, Ao Xia

School of Materials Science and Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China

Received 20 April 2014; received in revised form 8 May 2014; accepted 9 May 2014

Available online 16 May 2014

Abstract

Sr^{2+} substituted $\text{Bi}_{0.89-x}\text{Sm}_{0.11}\text{Sr}_x\text{Fe}_{0.94}(\text{Mn}_{0.04}\text{Cr}_{0.02})\text{O}_3$ (BSSrFMC, $x=0.00, 0.02, 0.04$ and 0.06) thin films were prepared on FTO/glass ($\text{SnO}_2:\text{F}$) substrates by using a sol–gel method. The effects of Sr^{2+} substitution on the structure, leakage current, dielectric, ferroelectric and magnetic properties of BSSrFMC thin films have been investigated. X-ray diffraction (XRD), Rietveld refinement of XRD patterns and Raman spectroscopy results indicated two space groups (P4 and P422) to coexist in the tetragonal BSSrFMC thin film when $x=0.04$. Meanwhile, the lattice constant a was increased compared with that of the non-doped BSFMC thin film, which may result in an expanded unit cell. Highly enhanced multiferroic properties were observed in the BSSrFMC thin film with $x=0.04$, i.e., large remanent polarization ($2P_r=173.43 \mu\text{C}/\text{cm}^2$), and large saturated magnetization ($M_s=2.3 \text{ emu}/\text{cm}^3$). Furthermore, a giant dielectric constant of 290 was observed in the BSSrFMC ($x=0.04$) thin film at 1 kHz. © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sol–gel processes; C. Ferroelectric properties; C. Magnetic properties; D. Ferrites

1. Introduction

As a multiferroic material, bismuth ferrite (BFO) is perhaps the only material which exhibits ferroelectric ($T_C=1103 \text{ K}$) and G-type anti-ferromagnetic ($T_N=643 \text{ K}$) properties simultaneously at room temperature [1–3]. In recent years, it has been widely studied due to fascinating fundamental physical properties and potential applications in the electronic information storage, spintronic devices and integrated microelectronic memory devices [4,5]. However, pure BFO thin film still shows high leakage currents, unsaturation P – E hysteresis loops and weak ferromagnetic properties due to the existence of oxygen vacancies and anti-ferromagnetic structures [6].

In order to reduce the leakage current and enhance the multiferroic properties of BFO thin films, several recent attempts have been made, such as by substituting appropriate ion at either A-site, B-site or both sites of A and/or B [7–9]. It is reported that the co-substitution of double transition metal

ions, or rare earth ions and transition metal ions, or alkaline earth metal ions and lanthanide rare earth ions can enhance the ferromagnetic and ferroelectric properties of BFO thin films [10–12].

Therefore, the co-substitution with four element ions of Mn, Cr, Sm and Sr could be an effective way to simultaneously improve the ferroelectric and magnetic properties of BFO thin films. So far, there have been fewer investigations on four elements co-substituted BFO thin films. In this work, Sr^{2+} -substituted $\text{Bi}_{0.89-x}\text{Sm}_{0.11}\text{Sr}_x\text{Fe}_{0.94}(\text{Mn}_{0.04}\text{Cr}_{0.02})\text{O}_3$ (BSSrFMC, $x=0.00, 0.02, 0.04$ and 0.06) thin films were prepared on FTO/glass ($\text{SnO}_2:\text{F}$) substrates by using the sol–gel method. The effects of Sr^{2+} -substitution on the structure, leakage current, dielectric and multiferroic properties of BSSrFMC thin films were investigated systematically.

2. Experiments

Sr^{2+} -substituted $\text{Bi}_{0.89-x}\text{Sm}_{0.11}\text{Sr}_x\text{Fe}_{0.94}(\text{Mn}_{0.04}\text{Cr}_{0.02})\text{O}_3$ thin films with $x=0.00, 0.02, 0.04$ and 0.06 were prepared on the FTO/glass substrates (FTO is the F-doped SnO_2

*Corresponding author. Tel.: +86 13759878391.

E-mail address: tan3114@163.com (G. Tan).

conductive film) by using the sol–gel method. The BiFeO_3 precursor solution was prepared using $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as raw materials, which were mixed together in an atomic ratio of $0.89-x:x:0.11:0.94:0.04:0.02$ ($x=0, 0.02, 0.04, 0.06$) (5 mol% of excess Bi was added to compensate for bismuth loss during the heat treatment). Then 2-methoxyethanol which served as a solvent was added into the raw materials and stirred for 1 h. Then acetic anhydride was added to dehydrate and adjust the pH value of the solution under constant stirring for 5 h (the volume ratio of 2-methoxyethanol and acetic anhydride was 3:1), and a stable precursor solution was obtained. The concentration of the solution was 0.3 mol/L. All the above processes were performed in an ambient atmosphere at room temperature. Meanwhile, the air humidity is less than 40%. FTO/glass substrates were washed in detergent, acetone, alcohol and deionized water sequentially. The precursor solution was spin coated on the FTO/glass substrates at 4000 rpm for 15 s with spin coating. After spin-coating, the wet films were dried at 240°C for 5 min immediately to remove volatile materials and subsequently annealed at 550°C for 10 min in the atmosphere for crystallization. Top Au electrodes of 0.502 mm^2 were deposited through a shadow mask on the surface of BFO films by sputtering. The films with top electrodes were annealed at 300°C for 20 min for the electrode and the film to achieve full contact.

Japan Rigaku Company D/max-2200X-ray diffractometer (with Cu target, the scanning step length was 0.02° and operated at 40 kV, 20 mA) and laser Raman spectrometer (Horiba JYHR800 Raman system equipped with an Ar ion laser excitation at 534 nm) were used to identify the structure and crystallinity of the thin films; the surface morphologies of the thin films were observed by FE-SEM (Hitachi S4800); the chemical bonding states of the films were investigated by X-ray photoelectron spectroscopy (XPS, Kratos Ltd., XSAM 800). The electric hysteresis loops of the thin films were measured by an aix ACCT TF-Analyzer 2000. The leakage current of the thin films was measured by Agilent B2901A and the ferromagnetic properties of the thin films were tested by the MPMS-XL-7 superconducting quantum interference magnetic measuring system.

3. Results and discussion

Fig. 1(a) shows XRD patterns of BSSr_xFMC thin films. An enlarged view of (110) peaks of the films is shown in Fig. 1(b). The main diffraction peaks of BSSr_xFMC thin films were successfully indexed by using PDF card no. 20-0169. All the thin films are polycrystalline BFO phases with (110) preferential orientations. No impurity phase is detected in all the thin films. The FWHM values of the BSSr_xFMC thin films are smaller than those of the non-doped BSFMC thin film, suggesting better crystallinities [13]. With increasing Sr^{2+} concentration, the (110) diffraction peaks are observed to shift towards lower 2θ value for BSSr_xFMC thin films, indicating changes in lattice parameters due to relatively large ionic

radius of Sr^{2+} ion (1.12 \AA) compared with that of Bi^{3+} ion (1.03 \AA) [14].

With regard to the better ferroelectric and ferromagnetic properties observed in the BSSr_xFMC ($x=0.04$) thin film, the detailed structural analysis of the pure BFO and BSSr_xFMC ($x=0.00$ and 0.04) thin films has been performed by Rietveld refinement [15,16] using “Maud” software [17,18]. Fig. 2(a)–(c) shows the observed, calculated and difference profiles of the studied specimens obtained after Rietveld refinements. The refinement result of the BFO thin film confirms a single trigonal phase, which belongs to $\text{R}\bar{3}\text{c}:\text{H}$ space group. However, the structure of the $x=0.00$ thin film was fitted very well to the tetragonal phase with $\text{P}4$ space group. In the case of the $x=0.04$ thin film, the contribution of the tetragonal phase with $\text{P}4$ space group is 95.34% and the tetragonal phase with $\text{P}422$ space group is 4.66%. This structural transformation will affect the multiferroic properties of the BSSr_xFMC ($x=0.04$) thin film. With Sr^{2+} -substitution, the lattice constant a increases from 3.9415 to 3.9583 compared with the BSFMC thin film, resulting in unit cell volume expansion. This volume expansion can be expected because of the small difference between the ionic radius of Sr^{2+} (1.12 \AA) ions and Bi^{3+} (1.03 \AA) ions. Furthermore, the lattice parameters and schematics of the crystal structures of the thin films are also shown in Fig. 2.

The structural evolution of the BSSr_xFMC thin films can also be expressed through Raman spectra. The Raman spectra of all thin films are shown in Fig. 3, which are fitted into individual Lorentzian components. According to the group theory, 13 Raman active modes ($4A_1+9E$) are predicted for the rhombohedrally distorted $\text{R}\bar{3}\text{c}$ space group for BFO [19]. For the pure BFO thin film, three peaks at 141.5, 169.7, and 214.9 cm^{-1} can be assigned to A_1 mode, and other peaks located at 262.0, 346.7, 467.2, 538.7 and 606.5 cm^{-1} are associated with E mode. However, three different aspects can be derived from the BSFMC thin film compared with the pure BFO. Firstly, the peak intensities decrease and increase for the A_1 and $E-7$ modes, respectively. Secondly, the A_1 and E modes greatly shift to higher frequencies. Thirdly, $E-4$ and $E-6$ modes disappear. This may be attributed to changes of Fe–O bonds with Sm-substitution at the Bi-site and (Mn, Cr) co-substitution at Fe site, which implies that a structural transition occurred in the BSFMC thin film. It shows shift of A_1 and E modes towards the high frequency side in the spectrum for BSSr_xFMC thin films due to Sr^{2+} -substitution. Meanwhile, the peak intensity of $E-7$ mode increases with the increase of Sr^{2+} content. Changes in peak intensity and peak position demonstrate a small structural transition occurring in the BSSr_xFMC thin films [20], which is consistent with the XRD data.

The FE-SEM micrographs of the BSSr_xFMC thin films are shown in Fig. 4(a)–(d). It is observed that there are some pores in all the thin films. The grain size increases with increasing Sr^{2+} -substitution concentration. Greater grains are beneficial to achieving a good electrical property [21]. The values of grain sizes estimated from SEM records for $x=0.00$, $x=0.02$, $x=0.04$ and $x=0.06$ films are 20–40, 40–70, 50–80 and 50–90 nm, respectively. This result reveals that the Sr^{2+} -substitution is in favor of the grain growth of the BSSr_xFMC

Download English Version:

<https://daneshyari.com/en/article/10625333>

Download Persian Version:

<https://daneshyari.com/article/10625333>

[Daneshyari.com](https://daneshyari.com)