Journal of Alloys and Compounds 765 (2018) 27–36

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Electrical and magnetic properties of Aurivillius phase $Bi_5Fe_{1-x}Ni_xTi_3O_{15}$ thin films prepared by chemical solution deposition

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ARTICLE INFO

Article history:
Received 20 April 2018
Received in revised form
14 June 2018
Accepted 16 June 2018
Available online 19 June 2018

Keywords:
Aurivillius phase
Electrical properties
Magnetic properties
Chemical solution deposition

ABSTRACT

The Aurivillius $Bi_5Fe_{1-x}Ni_xTi_3O_{15}$ (BFNT-x) ($0 \le x \le 0.5$) thin films were deposited by chemical solution deposition route. The microstructures, electrical and magnetic properties were systematically investigated in BFNT films. It has been found that the *c*-orientation of the films increases with the increase of Ni content. The coexistence of weak ferromagnetism and ferroelectricity at room temperature were observed in BFNT films except the $x = 0.5$ sample. The BFNT-0.1 sample exhibits a maximum remnant polarization $2P_r$ ~49.3 μC/cm^2, which is enhanced by 12.6% compared with that of the Ni-free thin film. The leakage current is decreased evidently with Ni content less than 0.3. The BFNT-0.1 film also shows the highest remnant magnetization $2M_r$ ~2.14 emu/cm^3. The origins of weak ferromagnetism in the BFNT films are attributed to the spin canting of the antiferromagnetic (AFM) coupling caused by Dzyaloshinskii-Moriya (DM) interaction based the Fe-O and Ni-O octahedral and affected by other causes as discussed. The saturation magnetization values of in-plane loops are smaller than that of the out-of-plane loops, indicating obvious anisotropic magnetism. These results demonstrate that partial substitution of Ni for Fe is an effective way for improving the multiferroic properties of Aurivillius compounds.

1. Introduction

Multiferroic materials which simultaneously exhibit ferroelectric (FE), ferromagnetic (FM) and/or ferroelastic orders have great significance in fundamental physics, as well as potential applications in spintronics, sensors, data storages and so on [1–4]. However, there are very few room-temperature (RT) single-phase multiferroic materials in nature due to the natural exclusion between ferroelectricity and magnetism. In recent years, bismuth-based layer-structured Aurrivillius compounds with the general formula $Bi_{n+1}Fe_{n-3}Ti_3O_{3n+3}$ have gained considerable attention due to their potential in obtaining unusual dielectric, magnetoelectric (ME) coupling and high ferroelectric phase transition temperature [5–11]. In this kind of system, perovskite-like units are sandwiched with fluorite-like layers $(Bi_2O_2)^{2+}$ along *c* direction, and *n* refers to an integer corresponding to the number of sandwiched perovskite-like layers. The $(Bi_2O_2)^{2+}$ layers play the key role in space-charge compensation and charge insulation, providing excellent electrical insulation. Most importantly, the multiferroic properties can be modulated by doping foreign elements or changing the number of perovskite-like units (n) [12,13].

$Bi_5FeTi_3O_{15}$ (BFTO), as a typical member of Aurrivillius family with $n = 4$, has been widely investigated. Its ferroelectric Curie temperature T_c was determined to be 1003 K with space group transformed from $A2_1am$ to $I4/mmm$, and the anti-ferromagnetic → Neel temperature is about 80 K [5,14]. However, there are some differences in the understanding about the magnetism of BFTO. Others considered its magnetic behavior to be associated with a superparamagnetic (SPM) state with local anti-ferromagnetic (AFM) interaction and even weak ferromagnetism in paramagnetic (PM) background [8,15].

In previous research, although weak ferromagnetism has been found in BFTO film, its statured magnetization is relatively small

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https://doi.org/10.1016/j.jallcom.2018.06.167
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[16]. It has been found that the coexistence of ferroelectric and ferromagnetic orders at RT can be realized by substituting partial Fe ions with Co element in BFTO [17–20]. Furthermore, the ferromagnetic Curie temperature (T_c) is significantly improved and reaches a very high value ~ 618 K. And the Co-substituted BFTO sample shows obvious magnetoelectric and magneto-dielectric effects [18,19]. Similarly, the investigation on five-layered $Bi_6Ti_3Fe_{2-x}Co_xO_{18}$ ($n = 5$) [21] and six-layered $Bi_7Fe_{3-x}Co_xTi_3O_{21}$ ($n = 6$) [22,23] also show enhanced ferromagnetism behaviors and improved ferroelectric properties. Thus Co is the most usually reported magnetic element substituted for Fe in layered Aurivillius compounds to improve the magnetic and ferroelectric properties. Except Fe and Co, Ni is also an important magnetic element. Recently, some breakthroughs have been achieved in Ni doped Aurivillius compounds, such as four-layered $Bi_4NdTi_3Fe_{0.7}Ni_{0.3}O_{15}$ [24], five-layered $Bi_6Ti_3Fe_{2-x}Ni_xO_{18}$ [25] and six-layered $Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ [12,13], all of which exhibit coexistence of ferroelectricity and ferromagnetism above RT. Moreover, the leakage current can be significantly decreased by Ni doping in $BiFeO_3$ and five-layered Aurivillius phase [25,26].

Taking into account the reports above, it suggests a good reason to use Ni substitution for Fe in Aurivillius phase. For BFTO, previous study referring to the doping effect mostly focused on Co/Mn/Cr doping or codoping with magnetic ions and rare-earth elements [17–19,27–29]. Although the magnetic and dielectric properties in Ni-doped $Bi_4NdTi_3FeO_{15}$ ceramics were reported, its leaky ferroelectric hysteresis loop showed poor ferroelectricity [24]. Until now, the magnetic and ferroelectric properties of the Ni-doped BFTO thin films have not been reported.

In this work, we fabricated Ni-substituted four-layered BFTO: $Bi_5Fe_{1-x}Ni_xTi_3O_{15}$ (BFNT-x) ($0 \le x \le 0.5$: $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5) thin films, and systematically investigated their microstructures, magnetic properties, ferroelectricity, and leakage currents. We found that the Ni content has a great effect on ferroelectricity, leakage currents and magnetic properties in this kind of materials. Our results provide a basis for further optimization of the multiferric properties in layer-structured Aurivillius compounds.

2. Experiment

$Bi_5Fe_{1-x}Ni_xTi_3O_{15}$ (BFNT-x) ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5) thin films were deposited on (111) $Pt/Ti/SiO_2/Si$ substrates by the chemical solution route. The precursor solution was prepared using Bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$], iron acetylacetonate [$Fe(C_{15}H_{21}O_6)$], nickel acetylacetonate [$Ni(C_{10}H_{14}O_4)$] and titanium n-butoxide [$Ti(C_4H_9O_4)$] as the staring materials. 10% excess of $Bi(NO_3)_3 \cdot 5H_2O$ was added to compensate the volatilization of Bi. Acetic acid [CH_3COOH] and n-propanol [$CH_3(CH_2)_2OH$] were used as solvent, and acetylacetone [$CH_3COCH_2COCH_3$] was used as a stable agent. Thin films were spin coated at 3500 rpm for 30 s, and a two-step baking procedure was employed at the baking temperature of 200 °C and 350 °C for 2 min respectively. Then the films were annealed at 750 °C for 4 min in oxygen atmosphere. The above process from spin coating, baking to annealing was repeated five times to obtain the ultimate thickness. To measure the electrical properties, Pt dot were sputtered on the surface of the films as top electrodes through a shadow mask.

The crystal microstructures of the films were analyzed by X-ray diffraction (Bruker D8) with Cu K_α radiation and by Raman scattering spectra (Renishaw inVia Raman Microscope). The surface morphology was investigated with scanning electron microscopy (FESEM: Hitachi, S-4800). X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo Fisher Scientific, USA) spectra were measured to obtain information on the valence state of the Fe and Ni ions. The ferroelectric responses, including hysteresis loops, leakage current were carried out using the TF 3000E standard ferroelectric test unit. The magnetization hysteresis measurements were carried out using a magnetic property measurement system (SQUID VSM, Quantum Design).

3. Result and discussion

Fig. 1 shows the X-ray diffraction patterns of the BFNT-x films deposited on platinum coated silicon substrates. The XRD patterns can be indexed by using the powder data of $Bi_5FeTi_3O_{15}$ (JCPDS card No.89-8545). All the samples possess single layered-perovskite phase with no detectable secondary phase or impurity phase, consistent with those reported previously [18,19,28–30]. With the increase of Ni content, the intensity of (00l) peak increases while that of (119) peak decreases, indicating that c-orientation of the films is enhanced substantially with Ni substitution. The degree of c orientation can be represented by the equation $\alpha = \frac{I(0010)}{I(0010)+I(119)}$, where $I(119)$ and $I(0010)$ denote the intensities of (119) and (0010) peaks respectively. According to the above equation, we can get $\alpha_0 = 7.8\%$ for $x = 0$, $\alpha_1 = 51.1\%$ for $x = 0.1$, $\alpha_2 = 42.7\%$ for $x = 0.2$, $\alpha_3 = 64.6\%$ for $x = 0.3$, $\alpha_4 = 89.6\%$ for $x = 0.4$, and $\alpha_5 = 96.6\%$ for $x = 0.5$ samples respectively. The enlarged diffraction peaks are indicated in Fig. 1 (b) and (c). The peak (200)/(020) shifts toward the lower angle with the increase of Ni content, indicating an increase in the cell constants of a or b. While the (00l) peaks, *i. e.* (008) and (0010) shift to the higher angle with the increase of x, implying

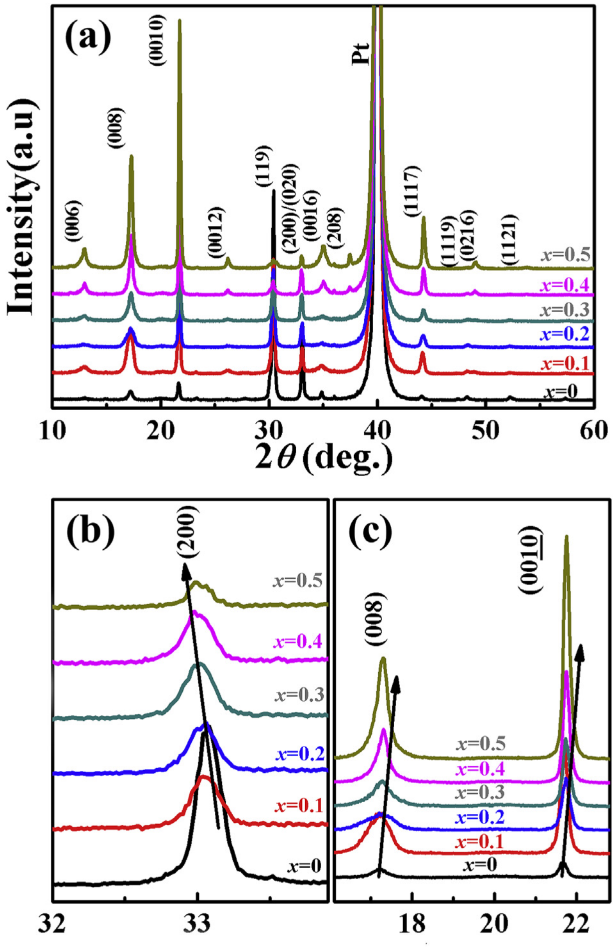

Fig. 1. (a) XRD patterns of $Bi_5Fe_{1-x}Ni_xTi_3O_{15}$ ($0 \le x \le 0.5$) films. (b)–(c) The amplified plots of the diffraction peak (200), (008) and (0010) respectively.