



Structural, optical and magnetic studies of (Y, Co) co-substituted BiFeO₃ thin films



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ABSTRACT

Polycrystalline BiFeO₃ (BFO) and Bi_{0.9}Y_{0.1}Fe_{1-x}Co_xO₃ (x = 0, 0.03, 0.05, and 0.10) thin films were prepared on quartz and Pt(111)/Ti/SiO₂/Si(100) substrates using a sol-gel method. X-ray diffraction and micro-Raman measurements demonstrated that the phase of all films was a perovskite-type rhombohedral structure. Bi_{0.9}Y_{0.1}Fe_{1-x}Co_xO₃ thin films exhibited a merging of (104) and (110) peaks, which indicated obvious distorted deformation of FeO₆ octahedra. UV–visible absorption spectra confirmed that the substitutions of Y and Co ions in Bi and Fe sites caused an increase in the optical band gap of BFO thin film, suggesting their potential application as UV and blue-green-driven photocatalysts. The magnetic test indicated that the ferromagnetic behavior was enhanced with the increase of Co ion concentration for (Y, Co) co-substituted BFO films, which could be attributed to the different magnetic moments of Co³⁺ and Fe³⁺. The saturation magnetization at room temperature for x = 0.10 sample was 132 memu/cm³. The results revealed that the (Y, Co) co-substitution played an important role for the improved ferromagnetic properties of BFO thin films. The mechanisms of (Y, Co) co-substitution effects on structural, optical and magnetic characteristics of BFO films were discussed.

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1. Introduction

Multiferroic materials exhibiting simultaneous coupled electric, magnetic, and elastic order parameters at room temperature (RT) are of high interest for the development of next generation micro-electromechanical devices such as magnetic recording media, multiple-state information storage, spintronics, and magneto-electric sensor devices [1–6]. BiFeO₃ (BFO) with a rhombohedrally distorted perovskite structure (space group *R3c*) is being extensively studied and exhibits ferroelectric, ferroelastic, and weakly ferromagnetic properties [7–10]. BFO has a high Curie temperature (*T*_C ~1103 K) and a G-type antiferromagnetic transition temperature (*T*_N ~643 K) [11], which are important for practical applications. In particular, doped BFO thin films have shown greatly enhanced ferroelectricity and new phenomena, such as photo-controlled exchange bias [12,13]. Ferroelectricity of BFO materials originates from the hybridization of stereochemically active Bi 6s²

lone pair electrons with the empty 6p⁰ orbital of Bi³⁺ and 2p⁶ orbital of O²⁻ and the relative displacements of Bi³⁺ and Fe–O octahedron along the (111) orientation [7,14]. On the other hand, the spin moments of Fe³⁺ are arranged in G-type antiferromagnetic order superimposed with a long range space modulated spin structure of incommensurate wavelength of 620 Å [14]. The incommensurate cycloid spin structure in BFO shows a small spontaneous magnetization at macroscopic level [11]. However, the potential of BFO in device applications is greatly hindered mainly due to the presence of leakage current, weak ferromagnetism. It is a valid approach to tune BFO multiferroic properties by co-substitution at the A and the B sites, because A-site and B-site are mainly responsible for ferroelectric and magnetic properties of BFO, respectively. Similar techniques have been explored in other oxides for photovoltaic applications. For example, Choi et al. have reported that La and Co co-substituted Bi₄Ti₃O₁₂ films can narrow the band-gap of the bismuth titanate and remain strongly ferroelectric [15]. Katiyar et al. have reported the ferroelectric photovoltaic properties in doubly substituted Bi_{0.9}La_{0.1}Fe_{0.97}Ta_{0.03}O₃ thin films [16]. Comes et al. have reported the band-gap reduction and dopant interaction in epitaxial La, Cr co-doped SrTiO₃ thin films

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[17]. Grinberg et al. have reported that Ba and Ni co-doping KNbO₃ samples can absorb three to six times more solar energy than the current ferroelectric materials [18]. Some literatures [19–21] have also reported the property of BFO thin films by optical second harmonic generation. Recently, enhanced magnetization, reduced leakage current, and improved ferroelectric properties were observed in (Y, Zr) [22], and (Y, Mn) co-substituted BFO [23]. In previous works, our group had reported the preparation of Y-doped BFO thin films [24]. A structural transition from the main *R3c* to the single phase *R-3m* was obtained for Bi_{0.9}Y_{0.1}FeO₃ thin film, which induced the distorted deformation of FeO₆ octahedra and thereby enhanced the ferroelectric property. Although the ferroelectric property of BFO thin film is enhanced by Y doping, the magnetic property of BYFO thin film still need to be improved. Naganuma et al. have reported ferroelectric, electrical and magnetic properties of Cr, Mn, Co, Ni, Cu added polycrystalline BFO films [25]. It was revealed that Co addition could preferably induce spontaneous magnetization in the polycrystalline BFO films. On the basis of Y doped BFO, Co dopant was introduced to improve the magnetic property of BYFO thin film. Moreover, the multiferroic properties of (Y, Co) co-substitution BFO films fabricated by a sol-gel method have not yet been reported. Thus, the effects of (Y, Co) co-substitution on the multiferroic properties of BFO thin film are ambiguous. Our aim in the present study is to enhance magnetic property by (Y, Co) co-substitution BFO, due to the difference between magnetic moments of Co³⁺ and Fe³⁺, which has a possibility to induce a local ferromagnetic spin configuration or a change in the gradient of spin canting [25].

In this work, BiFeO₃ (BFO), Bi_{0.9}Y_{0.1}FeO₃ (BYFO), Bi_{0.9}Y_{0.1}Fe_{0.97}-Co_{0.03}O₃ (BYFC3), Bi_{0.9}Y_{0.1}Fe_{0.95}Co_{0.05}O₃ (BYFC5) and Bi_{0.9}Y_{0.1}Fe_{0.9}-Co_{0.1}O₃ (BYFC10) thin film samples were prepared on quartz and Pt(111)/Ti/SiO₂/Si(100) substrates by a sol-gel method. The structural, optical and magnetic properties of pure and (Y, Co) co-substitution BFO thin films are reported. It was observed from our exploration that the (Y, Co) co-substitution enhanced the RT magnetization of BFO thin film. The remanent and saturation magnetization of BYFC10 sample are 39.94 and 132 memu/cm³, respectively, which is much larger than those of literatures with single cobalt doping [26,27]. The mechanisms of (Y, Co) co-substitution effects on structure, optical and magnetic properties of BFO thin films were discussed in detail.

2. Experimental details

BFO, BYFO, BYFC3, BYFC5 and BYFC10 precursor solutions were prepared using Fe(NO₃)₃·9H₂O, Bi(NO₃)₃·5H₂O, Y(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O as raw materials by a sol-gel process. Fe(NO₃)₃·9H₂O, Bi(NO₃)₃·5H₂O, Y(NO₃)₃·6H₂O and Co(NO₃)₂·6H₂O were firstly dissolved in the 2-methoxyethanol. To compensate Bi loss during the high-temperature process, excess 5 mol% of bismuth nitrate pentahydrate was added. The solutions were stirred for 2 h at RT and then a small amount of acetic anhydride used as dehydrating agent was added to the solution. The solution concentration was 0.1 mol/L. The solutions were again stirred for 1 h at RT and dissolved to form the coating solutions.

The solutions were spread on quartz and Pt(111)/Ti/SiO₂/Si(100) substrates using spin coating. The thin film deposition was carried out with a rotation speed of 3500 rpm and a time of 20 s. After spin coating of each layer, the films were pre-fired at 350 °C for 10 min to decompose remaining organic compounds. The spin coating and pyrolysis process were repeated for 15 times until the desired thickness. Finally, the dried films were annealed at 600 °C by a rapid thermal process for 15 min in an ambient atmosphere.

The structure and Raman spectroscopy of pure and doped BFO thin films were analyzed by an x-ray diffractometer (XRD) (D-MAX

2200 VPC, RIGAKU) with Cu K α radiation and a Confocal Micro-Raman Spectrometer (inVia Reflex, Renishaw) with 514 nm excitation source, respectively. The absorption spectra of all films were measured by ultraviolet–visible spectrophotometer (UV-3150, Shimadzu). The surface images of pure and doped BFO thin films were measured by thermal FE Environment scanning electron microscope (SEM: Quanta 400, Dutch Philips). The XPS spectra of the films were measured by X-ray Photoelectron Spectroscopy (XPS) device (ESCALAB 250, Thermo Fisher Scientific). Magnetic property of the films was measured by a magnetic measurement system (MPMS XL-7, quantum design).

3. Results and discussion

Fig. 1(a) shows XRD patterns of BFO, BYFO, BYFC3, BYFC5 and BYFC10 films prepared on quartz substrates. Fig. 1(b) shows the magnified XRD patterns of all samples in the vicinity of $2\theta = 32^\circ$. From Fig. 1(a), it can be seen that BFO thin film exhibited diffraction peaks of (012), (104), (110), (006), (202), (024), (116), (122), (018), (214) and (300), which was indexed as a perovskite-type rhombohedral structure with space group *R3c*. From Fig. 1(b), the magnified XRD pattern of BYFO film exhibited a merging of (104) and (110) peaks compared to that of BFO film, which indicated a structural transition from the main *R3c* to the single phase *R-3m*. The result was reported in our previous work [24]. The structural transition results from the relatively smaller ionic radius of Y³⁺ (0.90 Å) compared to that of Bi³⁺ (1.03 Å), which induced the distorted deformation of FeO₆ octahedra. This is consistent with other reports [28,29]. The structure of (Y, Co) co-substitution BFO thin films is consistent to that of BYFO. A small amount of impurity phase corresponding to orthorhombic Bi₂Fe₄O₉ marked by asterisk can be observed in XRD patterns. The impurity phase was reported in the literatures [26,30], which indicated that un-doping and rare-earth doping couldn't eliminate the impurity phase in BFO. Impurity phase is obvious because of its chemical kinetics of formation in meta-stable BFO [31] and the volatilization of Bi in the crystallized process [32].

The structures of BFO, BYFO, BYFC3, BYFC5 and BYFC10 films are further studied by Raman spectroscopy. Fig. 2(a) shows the Raman spectra of pure and co-substituted BFO thin films measured at RT. Raman spectra of all the samples have been fitted by Lorentzian components, which are shown in Fig. 2(b)–(f). The fitted results of pure and co-substituted BFO thin films are listed in Table 1. It is clear that most of A₁ and E modes for all samples can be clearly seen, which are well correlated with those of rhombohedral perovskite BFO. Compared with pure BFO film, the blue shift of A₁-1

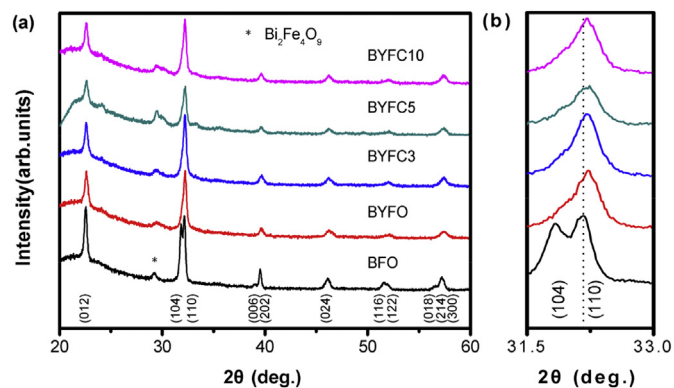


Fig. 1. (a) XRD patterns of pure and doped BFO thin films on quartz substrates in the range of 2θ from 20° to 60° and (b) the magnified XRD patterns in the range of 2θ from 31.5° to 33° .

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