



Tailoring the magnetic and optical characteristics of BiFeO₃ ceramics by doping with La and Co



Xingquan Zhang*, Chunmei Zhang, Nian Ran

Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, China

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ABSTRACT

Single-phase Bi_{0.95}La_{0.05}Fe_{1-x}Co_xO₃ ceramics with $x=0, 0.1$, and 0.2 were prepared by high pressure synthesis. X-ray diffraction patterns demonstrated rhombohedral structure for all samples. Ferroelectric transition temperature was found to decrease with increasing cobalt content. La and Co co-doping favors weak ferromagnetism ordering with evident magnetic hysteresis loop and enhances magnetization values at room temperature, which is attributed to the change in the spin structure from a cycloidal space modulated spin structure to a collinear G-type antiferromagnetic structure. Optical properties of the samples, as studied by diffuse reflectance spectroscopy, showed low optical band gap that decreases with increasing cobalt content, which provides potential applications in photocatalytic activity and optoelectronic devices.

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1. Introduction

Single phase multiferroic BiFeO₃ (BFO) has received considerable attention recently because of its very interesting magneto-electric properties for spintronic applications [1]. However, it is quite difficult to obtain ferromagnetic and ferroelectric ordering simultaneously at room temperature (RT) for BFO owing to its incommensurate cycloid magnetic spin structure [2]. The modification of the spin structure is therefore the key issue for the realization of BFO-based multiferroics. Many attempts to add ferromagnetic properties to BFO compound by both A and B site substitutions were made [3–6]. However, the spatially modulated magnetic structure in these doped BFO materials remains.

Recently, Baettig and Spaldin, using ab-initio first-principles density functional theory, reported the design and properties of BFO-BiCoO₃ solid solutions, which present large electric-field-driven phase change effects of various types, including piezoelectric, electric, and magnetoelectric ones [7]. In addition, recent neutron diffraction studies on Co doped BFO revealed that the magnetic structure of BFO can be changed due to Co doping [8,9]. Therefore, Co doped rhombohedral BFO is promising as a multiferroic material and it is of interest to investigate the effect of the substitution of Co for Fe on the physical properties of BFO. However, most studies on Co doped BFO were focus on BiFe_{1-x}Co_xO₃ nanoparticles or films with low concentration of Co ($x < 0.08$) due to the difficulty for preparation of such compounds through

normal solid state reaction [9–11].

It is reported that high-pressure synthesis is an effective method to prepare those unstable Bi based perovskites. Indeed, several groups have synthesized BiFe_{1-x}Co_xO₃ ceramics under high pressure successfully [12,13]. However, these investigations mainly focused on aspects related to doping-induced structural transformations in the BiFe_{1-x}Co_xO₃ series. There are rarely any reports on magnetic and optical properties of Co doped BFO bulk ceramics. This triggered us to synthesize Bi_{0.95}La_{0.05}Fe_{1-x}Co_xO₃ ceramics and study its structural, magnetic and optical properties. A small amount of lanthanum is added to stabilize the perovskite BFO phase as reported by Palkar et al. [14].

2. Experimental procedure

Bi_{0.95}La_{0.05}Fe_{1-x}Co_xO₃ ($x=0, 0.1$ and 0.2) ceramics were prepared by using solid state reaction at high pressure [8]. The starting materials of Bi₂O₃, La₂O₃, Fe₂O₃, and Co₃O₄ were carefully weighed in stoichiometric ratio and mixed by ball milling in anhydrous alcohol for 24 h, and sintered isothermally for 30 min under 5 GPa at 1000 °C.

Crystallographic structure analysis was performed by using Bede D1 XRD diffractometer with Ni filtered Cu K_α ($\lambda=0.15406$ nm) radiation. Calorimetric properties were measured by using differential thermal analysis (DTA) (TA SDT Q600). Magnetic properties of the samples were obtained by using the physical properties measurement system (PPMS) of Quantum Design. Optical properties were determined using a Shimadzu UV-3150 spectrophotometer.

* Corresponding author.

E-mail address: zxqli@163.com (X. Zhang).

3. Results and discussion

Fig. 1(a) shows XRD patterns of $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) ceramics. It can be seen that all samples exhibit single-phase characteristics with no trace of other impurity phases (e.g. Bi_2O_3 , CO_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, etc.) within the uncertainty of XRD. All the diffraction peaks in each pattern can be indexed based on the polycrystalline rhombohedrally distorted perovskite structure, which indicates that the ground-state space group does not change within the range of Co substitution.

The existence of ferroelectricity and the corresponding Curie temperature (T_c) for these samples were determined using DTA. Fig. 1(b) shows DTA curves of the $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ceramics for heating cycles in the $600\text{ }^\circ\text{C}$ to $880\text{ }^\circ\text{C}$ temperature interval. Endothermic peaks signifying the first-order phase transition could be identified. For $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$, The T_c is obtained to be $827.2\text{ }^\circ\text{C}$, which is in agreement with previous reports [6]. As the doping contents of Co increase, the T_c decreases significantly from $815.1\text{ }^\circ\text{C}$ ($x=0.1$) to $802.7\text{ }^\circ\text{C}$ ($x=0.2$). The decrease in ferroelectric transition temperature of co-doped samples may be attributed to site disorder and defects generated due to substitution.

Fig. 2(a) shows RT magnetization - magnetic field (M - H) curves of the $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) ceramics. $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$ displays a low level of spontaneous magnetization, which is attributed to the fact that the spiral spin order is partially destroyed due to the La doped effect. In comparison, the samples with $x=0.1$ and $x=0.2$ show clear hysteresis. It can be concluded herein that Co doping is an effective way to modulate the magnetic properties BFO. However, it should be noted that there is no obvious difference between the remanent magnetization values of the $x=0.1$ and 0.2 samples. This indicates that the ferromagnetic moment was not coming from the ferrimagnetism or double-exchange mechanism dominantly [8]. Generally, the superimposed spiral spin structure of the rhombohedral BFO based samples hinders the net magnetization being observed. The weak ferromagnetic in $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ceramics with $x=0.1$ and 0.2 maybe results from the change of the spin structure, which allows canted weak ferromagnetism.

Fig. 2(b) shows zero field cooled (ZFC) and field cooled (FC) magnetization measurements of the $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) ceramics, measured at a magnetic field of 1000 Oe in the temperature range of $10\text{--}390\text{ K}$. For the $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$ samples, the ZFC and FC magnetization values decrease with

decreasing the temperature in the temperature range $390\text{--}150\text{ K}$, which is consistent with conventional antiferromagnetic material. As the temperature decreases below 150 K , both the ZFC and FC magnetization values increase gradually with decreasing temperature, which indicate that a change in spin ordering at low temperature may be due to spin reorientation in $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$ like other orthoferrites. For the samples with $x=0.1$ and 0.2 , the ZFC and FC magnetization values decrease with decreasing the temperature in the whole temperature range, which is a confirmation of the antiferromagnetic exchange interaction of the spins in these samples. In addition, it can be found that both the ZFC and FC magnetization curves show a large drop in the magnetization in the temperature range $150\text{--}100\text{ K}$. This should relate to phase transition from the cycloidal space modulated spin structure to a collinear G-type antiferromagnetic structure, as indicated by the neutron diffraction measurements on BFO samples [8,9]. The substitution of Co^{3+} for Fe^{3+} not only changes the local lattice and increases the Fe-O bond anisotropy in the FeO_6 -octahedron cage but also induces anharmonic effect, which is reflected in some bunching of the spin magnetic moments and results in the magnetic phase transition. In addition, the substitution of Co^{3+} results in more spin canting. Thus, the observed enhanced magnetization at RT in the samples with $x=0.1$ and 0.2 can be attributed to the magnetic phase transition and the variation of the spin-canting angle induced by Co doping. On decreasing the temperature, the degree of magnetic anharmonicity decreases and the cycloidal space modulated spin structure revives [9].

Absorption spectra of the $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) ceramics transformed from diffuse reflection spectra based on Kubelka-Munk theory were presented in Fig. 3(a). Two absorption bands can be observed. The broad absorption band in the wavelength range of $500\text{--}600\text{ nm}$ is attributed to the overlapping of electronic transition from ${}^6\text{A}_1$ state to ${}^4\text{T}_1(4\text{G})$ state and ${}^6\text{A}_1$ to ${}^4\text{E}$, ${}^4\text{A}_1(4\text{G})$ ligand field transitions and the weak absorption band around 660 nm may be attributed to the crystal field transition [5]. In addition, I can be found that the absorption cut-off wavelength increases with increasing Co content, which indicated that Co addition cause an obvious change in the band structure. Because Co doping is electron doping, the Fermi level of Co doped $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$ samples should be moved up-ward, and its band gap is smaller than that of $\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$. The optical band gap of the samples were calculated by Tauc formula: $ah\nu = A(h\nu - E_g)^{1/2}$,

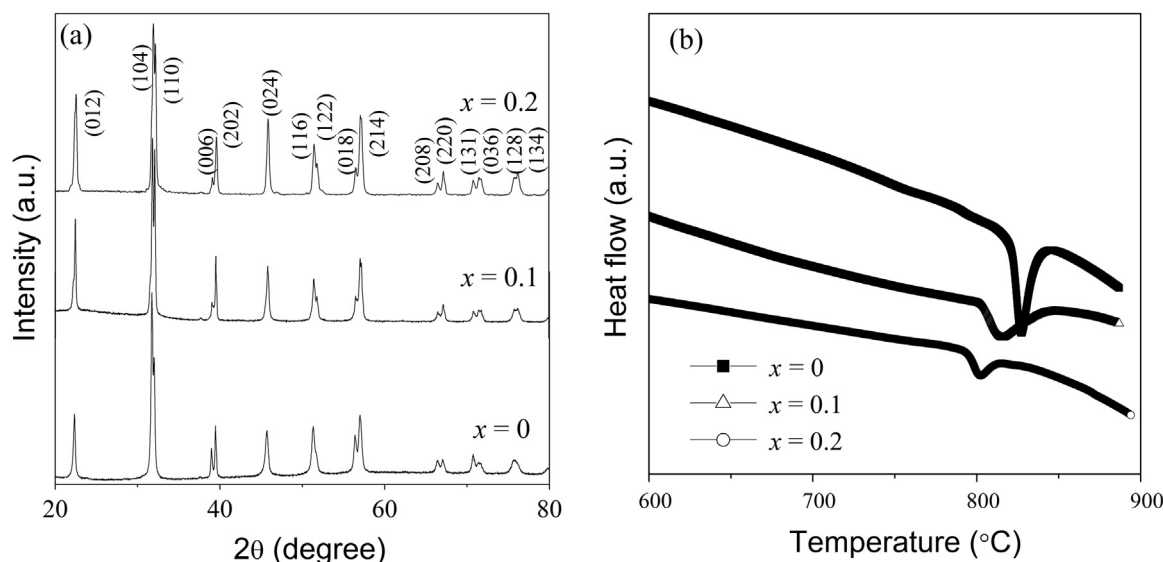


Fig. 1. (a) XRD patterns and (b) DTA traces of the $\text{Bi}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ ($x=0, 0.1$ and 0.2) ceramics.

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