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Substitution driven reverse distorted FeO_6 octahedral structure, magnetic properties and hyperfine interaction studies in $Bi_{1\text{-}x}La_xFeO_3$ powder

RenZheng Xiao [a, b, *], Tao Hu [a, b], XiaoQiang Ma [a, b], XianBao Yuan [a, b], JianJun Zhou [a, b], DeJun Fu [c]

[a] College of Mechanical & Power Engineering, China Three Gorges University, Yichang 443002, China
[b] Hubei Key Laboratory of Hydroelectric Machinery Design & Maintenance, China Three Gorges University, Yichang 443002, China
[c] Key Laboratory of Artificial Micro- and Nano-Materials of Ministry of Education School of Physics and Technology, Wuhan University, Wuhan 430072, China

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ABSTRACT

The $Bi_{1\text{-}x}La_xFeO_3$ ($x = 0$, 0.05, 0.10, and 0.15) powders were prepared by the hydrothermal method. The X-ray diffraction revealed an increase of lattice constants of the doped samples evidencing substitution of Bi by La ions. The morphology of the samples was investigated by the Scanning Electron Microscopy. The magnetic properties of the films were studied by vibrating sample magnetometry at room temperature. The evidence of reverse distorted FeO_6 octahedral structure in the La doped samples was revealed by the Mössbauer spectra parameters: Is, Qs, H, Γ, χ^2 and area ratio (A_1/A_2) of two-sextet.

1. Introduction

During last ten years, perovskite-type oxide $BiFeO_3$ (BFO) has attracted great interest due to the potential applications in spintronics devices, various sensors and multiple-state memories [1–3] which benefit by its crystal structure of a distorted rhombohedral perovskite (space group R3c) [4,5]. Such symmetry allows the coexistence of two orders: ferroelectricity and antiferromagnetism with rather high ordering temperatures of 1143 and 643 K, respectively [6,7]. More important is the coupling behavior between the multiferroic properties in BFO, which makes it more attractive [8]. The magnetoelectric coupling, especially Dzyaloshinskii-Moriya interaction (DM), which is connected with the exchange interaction and spin orbit coupling, plays important role in spin cycloid structure modulation [8]. The spin cycloid with an extremely long period of 620 Å, which arises from competition between the usual symmetric exchange interaction and the DM interaction, can be destroyed by rare earth doping [3]. BFO possesses G-type antiferromagnetism or weak ferromagnetism with spontaneous magnetization in cubic (111) plane [9] and a long-range cycloidal spiral, which is incommensurate with the lattice parameters [10]. The rotation of magnetization vector over cycloid period yields zero magnetization in magnetic sub-lattices in average. This potential magnetization can be released by applying high magnetic field [11].

The multiferroic and magnetoelectric coupling coefficients of BFO can be effectively improved by rare earth doping in A site (Bi^{3+}) or B site (Fe^{3+}), which is generally attributed to the distortion of the structure and led to the destroying or modulation of the spiral spin structure. Srivastav et al. have found that the observed enhancement in magnetic properties of $BiFeO_3$ with Pr doping is mainly due to the suppression of the modulated spiral spin structure [12]. Sakar et al. have proved that Dy substitution in BFO induces suppression of the spin cycloid [13]. Nayek et al. have studied the origin of enhanced magnetization in rare earth doped multiferroic bismuth ferrite and found that the spin canting is induced by structural distortion [14]. Lazenka et al. have found that the Gd-doped $BiFeO_3$ strongly enhances magnetization and magnetoelectric coefficient

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* Corresponding author. College of Mechanical & Power Engineering, China Three Gorges University, Yichang 443002, China.
E-mail address: rzxiao@whu.edu.cn (R. Xiao).

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at room temperature due to the structural change and the spiral modulated spin structure collapses [15].

The Mössbauer spectrometry is a vital nuclear technique with a high energy resolution about 10^{-8} eV and has a unique advantage in the study of hyperfine interactions, it can be extensively used in the field of research of the hyperfine structure of BFO and further revealed the mechanism of the modulation of the spiral spin structure. Sando et al. using Mössbauer and Raman spectroscopies combined with Landau–Ginzburg theory and effective Hamiltonian calculations show that the bulk-like cycloidal spin modulation, which exists at low compressive strain is driven towards pseudo-collinear anti-ferromagnetic structure at high strain, both for tensile and compressive deformation [16]. Landers et al. studied the effects of different temperatures and particle sizes on the anharmonic cycloidal spin structure in $BiFeO_3$ nanoparticles [17]. Srivastav et al. using ^{57}Fe Mössbauer spectroscopy revealed that the observed enhancement in magnetic properties of $BiFeO_3$ with Pr doping is mainly due to suppression of modulated spiral spin structure [12]. Kothari et al. unambiguously showed that the observed magnetic properties in $BiFeO_3$ with chemical substitution (Eu) are mainly due to the structural distortions [18].

In our previous work, the BPFO thin film was investigated by means of magnetometry and conversion-electron Mössbauer spectroscopy (CEMS), and we have found an evidence of the spin cycloid destruction due to Pr doping [19]. Based on the report, here we study the substitution driven reverse distorted FeO_6 octahedral structure, magnetic properties and hyperfine interaction in $Bi_{1-x}La_xFeO_3$ powder, and try to find the characteristics of the FeO_6 octahedral structure distortion in BFO caused by La doping and to explore the mechanism of the magnetic changes.

2. Experimental details

$Bi_xLa_{1-x}FeO_3$ ($x = 0$, 0.05, 0.10, and 0.15) (BLFO) powder were prepared by hydrothermal route using $Fe(NO_3)_3 \cdot 9H_2O$, $Bi(NO_3)_3 \cdot 5H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ as precursors, deionized water and nitric acid as solvent, KOH as a mineralizer. The stoichiometric La/Bi/Fe ratio in the solution was x:(1-x):1, where $x = 0$, 0.05, 0.10, and 0.15. The hydrothermal route was carried out in the reactor inside the oven at 200 °C over 12 h, finally BLFO powder was obtained, then cleaned by deionized water and dried in the oven at 100 °C for 1 h. The crystal structure was characterized by Bruker AXS D8 Advance X-ray diffractometer. The morphology of the samples was investigated by SIRION 200 Field Emission Gun Scanning Electron Microscope System. The magnetic properties were detected by vibrating sample magnetometry (VSM) using PPMS-9T Physical Properties Measurement System. The Mössbauer hyperfine structure of the samples was revealed at room temperature by MS-500 Mössbauer spectrometer, which used a proportional counter and a ^{57}Co in Rh matrix source with activity of 25 mCi relative to *a*-Fe foil with a thickness of 10 μm standard absorber with effective thickness of 10 mg Fe/cm^2 [20,21].

3. Results and discussion

Fig. 1 shows XRD spectra of $Bi_{1-x}La_xFeO_3$ samples with $x = 0$, 0.05, 0.10, and 0.15. The crystal structure of all samples has been defined as rhombohedral perovskite (R3c space group, ICSD 86-1518). Cell refinement of the XRD patterns was obtained by Rietveld method and gave the crystal parameters: a = b = 5.575 Å, c = 13.859 Å; a = b = 5.580 Å, c = 13.860 Å; a = b = 5.580 Å, c = 13.863 Å; a = b = 5.582 Å, c = 13.876 Å for $x = 0$, 0.05, 0.10 and 0.15, respectively. Increasing of the crystal parameters in the doped samples is evidence of substitution of Bi ions by La, and corresponds to slightly bigger ionic radius of La^{3+} (1.032 Å) as compared to Bi^{3+} (1.030 Å) [22,23].

The morphology images of the $Bi_{1-x}La_xFeO_3$ powder ($x = 0$, 0.05, 0.10 and 0.15) observed by SEM is shown in Fig. 2. The SEM image shows that the particle size of BFO powder is about 90–110 μm, whereas the particle size of $Bi_{1-x}La_xFeO_3$ powder ($x = 0.05$, 0.10 and 0.15) is about 22 μm, 20 μm and 16 μm, respectively. It can be concluded that the particle size of BLFO decreases with La doping, and that the particle growth of BLFO was suppressed by La doping. This phenomenon is consistent with the results of research of Gd-doped $BiFeO_3$ nanoparticles by Lotey et al. [24]. It should be noted that the preparation of the large size particle BLFO powder is to avoid the impact of such finite size effects as, interparticle interactions, a random distribution of anisotropy axes, and the superparamagnetism appeared in Mössbauer spectrum when measuring nanostructured samples [25].

The magnetization of the $Bi_{1-x}La_xFeO_3$ powder ($x = 0$, 0.05, 0.10 and 0.15) as a function of external magnetic field in the range of −20–20 kOe at room temperature is shown in Fig. 3. The magnetization versus field (M-H) presented in Fig. 3 shows that the samples have weak ferromagnetism. The saturation magnetizations are 0.0141, 0.0122, 0.0102, and 0.0093 emu/g, the remnant magnetizations are 1.2×10^{-4}, 2.0×10^{-4}, 3.1×10^{-4}, and 5.9×10^{-4} emu/g, and the coercive field are 434.9, 35.3, 115.0, and 220.4 Oe for the $Bi_{1-x}La_xFeO_3$ powder with $x = 0$, 0.05, 0.10 and 0.15, respectively. The smaller saturation magnetization of BLFO is consistent with the results obtained by Lin et al. [26] and Gautam et al. [27]. The decrease of the saturation magnetization in the doped samples can be explained by suppression of the formation of the secondary phases by La doping. The result is consistent with Pr doped BFO ceramic studied by Kumar et al. [28]. However, these secondary phases cannot be found in XRD patterns. The possible reason is that the grain size of the impurities was too small and appeared x-ray amorphous behaviors. Therefore, them cannot be revealed by XRD techniques. Concerning Mössbauer spectroscopy, certainly, it is powerful means to study iron secondary phases, but not in the case of relatively pure BFO. As it is known this material is difficult to be studied by Mössbauer spectroscopy due to high mass absorption coefficient of Bi (123 cm^2/g for 14.4 keV γ-ray). If the content of the impurities in the samples is too small, its Mössbauer spectra signal was covered by the noise signal. Therefore, the impurities would be hard to detected by Mössbauer techniques too.

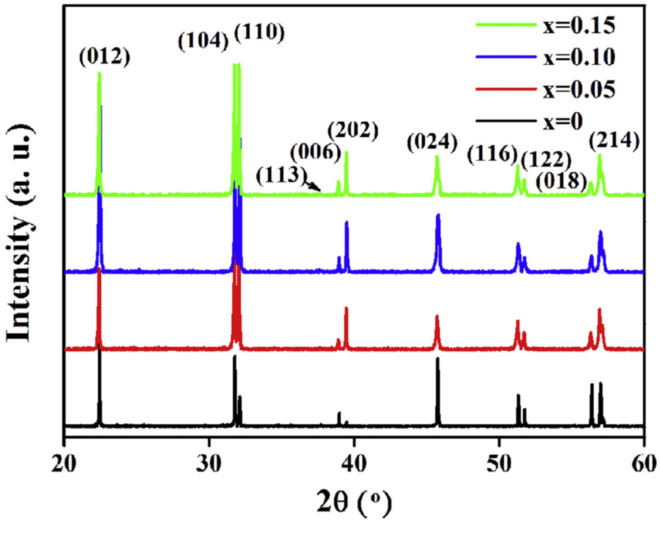

Fig. 1. X-ray diffraction spectra of $Bi_{1-x}La_xFeO_3$ powder ($x = 0$, 0.05, 0.1 and 0.15).