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# Origin of enhanced magnetization in (La,Co) codoped BiFeO3 at the morphotropic phase boundary

T.H. Le<sup>a</sup>, N.V. Hao<sup>b</sup>, N.H. Thoan<sup>c</sup>, N.T.M. Hong<sup>d</sup>, P.V. Hai<sup>e</sup>, N.V. Thang<sup>c</sup>, P.D. Thang<sup>d</sup>, L.V. Nam<sup>d</sup>, P.T. Tho<sup>b</sup>, N.V. Dang<sup>b</sup>, X.C. Nguyen<sup>f,g,\*</sup>

<sup>a</sup> Institute of Research and Development, Duy Tan University, Da Nang, 550000, Viet Nam

<sup>b</sup> Department of Physics and Technology, Thai Nguyen University of Sciences, Thai Nguyen, Viet Nam

<sup>c</sup> School of Engineering Physics, Hanoi University of Science and Technology, Viet Nam

<sup>d</sup> Faculty of Engineering Physics and Nanotechnology, VNU University of Engineering and Technology, Hanoi, Viet Nam

e Department of Physics, Hanoi National University of Education, 136 Xuan Thuy, Hanoi, Viet Nam

<sup>f</sup> Laboratory of Advanced Materials Chemistry, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

<sup>8</sup> Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

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#### ABSTRACT

In this work, we studied the effect of Co doping on the crystal structure and magnetic properties of  $Bi_{0.84}La_{0.16}FeO_3$  polycrystalline ceramics. The analysis of X-ray diffraction patterns (XRD) demonstrates the coexistence of the *R3c* rhombohedral and *Imma* orthorhombic structures, along with small  $Bi_{25}FeO_{40}$  and  $CoFe_2O_4$  parasitic impurities in the samples. The study of phonon vibration with different excitation wavelengths identifies an individual contribution of two structures on the Raman spectra. Scanning electron micrographs identify small and large grains in the *Imma* and *R3c* phases, respectively. The magnetic impurity strongly impacted the magnetic properties of the compounds, while La and Co substitution for BiFeO<sub>3</sub> at the polymorphs induces the phase boundary ferromagnetism. The variation in magnetization confirms a formation of phase boundary spins, and distinguishes the individual contributions of the coexisting phases and  $CoFe_2O_4$  on the magnetic properties of the compounds.

# 1. Introduction

Multiferroic materials possess a magneto-electric coupling which allows magnetic field control of ferroelectric polarization and manipulation of magnetization by an electric field [1]. This coupling has enormous potential applications in data storage, spintronics, and sensors [2,3]. Single-phase BiFeO<sub>3</sub> (BFO) is a well-known multiferroic material possessing both antiferromagnetism and ferroelectricity above room temperature [4]. However, it is difficult to obtain ferromagnetism for BFO because the cycloidal modulation spin structure cancels an intrinsic and weak ferromagnetic moment driven by the Dzyaloshinskii–Moriya interactions [5]. The weak ferromagnetism of BFO can be revealed by controlling the particle size to less than a cycloidal modulation period (62–64 nm) [6], and substituting elements on the Bisite and Fe-site to suppress or destroy the cycloidal spin [7]. Among transition element doped BFO, cobalt doping and codoping with rareearth elements are quite effective in enhancing magnetization with an appearance of weak ferromagnetism [8-11]. Most researchers believe the origin of ferromagnetic-like behavior in Co doped BFO is due to a destruction of the spatially modulated cycloidal spin to the collinear spin structures with or without structural transition [9,12–16]. The change in spin structure can be confirmed by either neutron diffraction or low energy Raman spectroscopy [17]. However, several reports propose that some magnetic impurities, e.g.,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, CoFe<sub>2</sub>O<sub>4</sub>, can be presented in a sample during high temperature sintering at ambient pressure, and thus contribute to the enhanced magnetization [8,18,19]. Moreover, it is difficult to detect a small amount of impurity by XRD and Raman spectroscopy. The impurity phase CoFe<sub>2</sub>O<sub>4</sub> (CFO) is normally formed together with sillenite phases, e.g., Bi<sub>25</sub>FeO<sub>40</sub>, Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, in Co doped BFO compounds, and the XRD peak position of CFO  $(2\theta \sim 35.5^{\circ})$  is also closed to that of  $Bi_{25}FeO_{40}$  ( $2\theta \sim 35.2^{\circ}$ ) [10,16,20]. The enhanced magnetization of Co doped BFO-based compounds

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<sup>\*</sup> Corresponding author. Laboratory of Advanced Materials Chemistry, Advanced Institute of Materials Science, Ton Duc Thang University, Ho Chi Minh City, Viet Nam.

E-mail address: nguyenxuanca@tdtu.edu.vn (X.C. Nguyen).

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therefore remains confusing [10,16,20]. Generally, the destruction of the cycloidal spin structure can enhance the saturation magnetization  $(M_s)$  up to 0.5 emu/g for bulk ceramics [7,9,14,21,22], while a composite of CFO-BFO (10:90) can show an  $M_s$  value in the range of 3–5 emu/g [11,23,24]. Consequently, the  $M_s$  value higher than 1 emu/g could originate from the magnetic impurities. Although in most cases high magnetization possibly relates to the magnetic impurities, a very large saturation magnetization is continuously reported as an intrinsic suppression of the cycloidal spin and the superexchange interaction of Co and Fe without the elimination of the magnetic impurity [16,20,25]. In this paper, we report on the crystal structure and magnetic properties of  $Bi_{0.84}La_{0.16}Fe_{1-x}Co_xO_3$  (0.02  $\leq x \leq 0.1$ ) compounds at the polymorphs of the R3c rhombohedral and Imma orthorhombic structures. The analysis of XRD patterns and Raman spectra reveal the magnetic impurities of CFO parasitic in the samples, and thus it greatly enhances magnetization of Bi<sub>0.84</sub>La<sub>0.16</sub>Fe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> (BLFCO) compounds. We also studied variation of magnetization with time, which revealed reduced magnetization in all samples. The self-change in magnetization is believed to originate from a reconstruction of the spin structure at the boundary of two crystal structures, and from the isothermal structural transformation. Thanks to the variation of magnetization, we are able to identify the intrinsic/extrinsic magnetization of BLFCO compounds.

# 2. Experimental details

Polycrystalline Bi<sub>0.84</sub>La<sub>0.16</sub>Fe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> compounds with x = 0.02-0.1 were prepared by solid-state reaction, using high-purity oxides of Bi<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> as precursors. These powders were thoroughly mixed in nominally stoichiometric amounts by using an agate mortar and pestle, and then pressed into disc-shaped pellets. After several iterations of a pre-annealing process at 810 °C in air for 12 h, the pellets were finally annealed at 900 °C for 10 h. The crystalline structure and phonon characteristics of the fabricated samples were studied by using an X-ray diffractometer (Miniflex Rigaku) equipped with a Cu- $K_{\alpha}$  radiation source ( $\lambda = 1.5405$  Å), and Raman scattering spectroscopy with excitation wavelengths of 532 nm (LabRam HR evolution, Horiba) and 635 nm (Renishaw, UK). The morphology and composition of the samples were examined by scanning electron microscope (Hitachi S – 4800). Magnetization measurements were performed on a VSM Lake-Shore 7400. All investigations were carried out at room temperature.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the BLFCO compounds. The diffraction peaks of all the samples are well identified according to the rhombohedral symmetry with space group R3c of the BFO. In addition, a small impurity phase is observed in the compounds marked by a diamond symbol  $(\blacklozenge)$  in Fig. 1. This phase can be assigned to the cubic structure of sillenite Bi<sub>25</sub>FeO<sub>40</sub> with space group I23 [9]. Although the sillenite phase can be suppressed well by La doping and codoping with Ti (or Mn) [8,26], it is however difficult to prevent its formation for synthesizing La and Co codoped BFO at ambient pressure [7,9,10]. As shown in the insert of Fig. 1, the diffraction peaks have an obvious shift toward a high angle. This can be ascribed to the smaller ion radius of  $Co^{3+}$  (0.61 Å) compared to that of Fe<sup>3+</sup> (0.65 Å), which clearly confirms an incorporation of Co ions into the lattice of the BLFCO compounds. A careful analysis of the XRD patterns reveals a splitting of the diffraction peak at around  $2\theta = 22.5^{\circ}$  and  $46.1^{\circ}$ , indicating a structural transition towards the orthorhombic structure, such as the Pbam, Imma, Pbnm, and Pnma symmetries [27-31]. The structural transformation can also be revealed by an emergence of a new peak around  $2\theta = 32^{\circ}$ , as seen in the inset of Fig. 1. Among these orthorhombic structures, the Imma symmetry fits well to the peak positions of our samples [31]. Therefore, besides an impurity phase, all samples show a coexistence of the major R3c rhombohedral and minor Imma orthorhombic structures. This result is in good agreement with previous reports on Mn (or Ti)

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Fig. 1. XRD patterns of BLFCO samples. The inset shows a magnified view of the highest intensity peak.

doped Bi<sub>1-y</sub>La<sub>y</sub>FeO<sub>3</sub> compounds [4,27,29,31]. It is interesting to observe a preservation of the intrinsic *R3c* symmetry of BFO at high Co concentration compared to the other elements doped at the Fe-site [4,32,33], and thus the intrinsic ferroelectric properties arising from the 6s<sup>2</sup> lone pair of Bi<sup>3+</sup> electrons can remain [12]. The maintenance of the ferroelectric phase up to 10 wt% of Co-doping possibly originates from the small ion radius of Co substitution for Fe [12]. In order to clarify the presence of the CFO impurity, we show an enlarged portion of the XRD patterns of samples x = 0.02, 0.1, along with the simulated patterns of CFO (*Fd3m* symmetry) and Bi<sub>25</sub>FeO<sub>40</sub> (*I23* symmetry) in the 20 range 32.5–36.5°, as seen in Fig. 2. The main peak of CFO at 20 = 35.5 shows a good fit to the XRD patterns of the BLFCO samples compared to that of Bi<sub>25</sub>FeO<sub>40</sub>. We therefore conclude that the BLFCO compounds contain a small amount of magnetic impurity of CFO.



Fig. 2. Comparison of XRD patterns of BLFCO samples (x = 0.02, and 0.1) with the simulated patterns of CoFe<sub>2</sub>O<sub>4</sub> and Bi<sub>25</sub>FeO<sub>40</sub>.



Fig. 3. Rietveld-refined XRD patterns of two typical samples x = 0.02 and 0.1.

# Table 1

The crystal symmetry and lattice parameters of  $^{\rm Bi0.84La0.16Fe1-xCoxO3}$  compounds. The *I23* and *Fd-3m* space groups correspond to  $\rm Bi_{25}FeO_{40}$  and  $\rm CoFe_2O_4$  impurities, respectively.

| Composition     | Space group | a (Å)   | b (Å)   | c (Å)   | $V(\text{\AA})^3$ |
|-----------------|-------------|---------|---------|---------|-------------------|
| <i>x</i> = 0.02 | R3c (~90%)  | 5.5775  | 5.5775  | 13.8189 | 372.29            |
|                 | Imma (~10%) | 5.5488  | 7.8908  | 5.5689  | 243.83            |
|                 | I23 (%)     | -       | -       | -       | -                 |
|                 | Fd3m (%)    | -       | -       | -       | -                 |
| <i>x</i> = 0.04 | R3c (80%)   | 5.5772  | 5.5772  | 13.8067 | 371.92            |
|                 | Imma (12%)  | 5.5582  | 7.8490  | 5.5707  | 243.03            |
|                 | I23 (5%)    | 10.1557 | 10.1557 | 10.1557 | 1047.45           |
|                 | Fd3m (3%)   | 8.3865  | 8.3865  | 8.3865  | 589.86            |
| x = 0.06        | R3c (73%)   | 5.5764  | 5.5764  | 13.8059 | 371.79            |
|                 | Imma (14%)  | 5.5425  | 7.8761  | 5.5687  | 243.09            |
|                 | I23 (8%)    | 10.1487 | 10.1487 | 10.1487 | 1045.27           |
|                 | Fd3m (5%)   | 8.3832  | 8.3832  | 8.3832  | 589.15            |
| x = 0.08        | R3c (62%)   | 5.5770  | 5.5770  | 13.7986 | 371.67            |
|                 | Imma (18%)  | 5.5785  | 7.8521  | 5.5481  | 243.03            |
|                 | I23 (14%)   | 10.1597 | 10.1597 | 10.1597 | 1048.66           |
|                 | Fd3m (6%)   | 8.3816  | 8.3816  | 8.3816  | 588.82            |
| x = 0.1         | R3c (55%)   | 5.5769  | 5.5769  | 13.7922 | 371.49            |
|                 | Imma (20%)  | 5.5663  | 7.9429  | 5.5389  | 244.89            |
|                 | I23 (17%)   | 10.1579 | 10.1579 | 10.1579 | 1048.13           |
|                 | Fd3m (8%)   | 8.3801  | 8.3801  | 8.3801  | 588.49            |
|                 |             |         |         |         |                   |

Sample x = 0.02 does not show the diffraction patterns of CFO due to a limitation of the XRD technique in detecting the impurity phase at low concentrations (< 3 wt%). A gradual increase in peak intensity observed in samples x = 0.02-0.1 indicates that the concentration of CFO increases with increasing Co concentration. Although CFO is an unexpected magnetic impurity, its presence can be enhanced by both the magnetic and ferroelectric properties of BLFCO compounds [8,24,34]. The Rietveld refined XRD patterns of two typical samples x = 0.02 and 0.1 are shown in Fig. 3. All the diffraction peaks are well fitted to the suggested phase models as discussed above, which are the *R*3*c* and *Imma*, *Fd*3*m*, and *I*23 for BLFCO, CFO, and Bi<sub>25</sub>FeO<sub>40</sub>, respectively. The refined lattice parameters and phase ratios of all samples are given in Table 1. According to the refinement results, the *R*3*c* phase gradually





Fig. 4. Raman spectra of BLFCO samples excited by a 635 nm wavelength and deconvoluted RS of sample x = 0.02.

decreases from 90% for x = 0.02-55% for x = 0.1 while the *Imma* phase increases from 10% for x = 0.02-20% for x = 0.1.

In order to derive more detailed structural information, we measured the Raman scattering (RS) spectra at different excitation wavelengths ( $\lambda = 635$  nm and 532 nm) to examine the vibrational modes of BLFCO compounds. According to group theory, it is possible to distinguish the individual contribution of Raman active modes for different crystal structures. Unfortunately, in practice, the coexisting phase displays an overlap of Raman peaks and the spectra is governed by a major phase in the compounds. To date, this problem rarely takes into account solving a single contribution of each symmetry to the RS spectra of BFO-based compounds at the morphotropic phase boundary. We expect that measuring RS at different excitation wavelengths may clarify a distinction between the R3c and Imma symmetries. Due to a dominance of the R3c phase in BLFCO compounds, the RS spectra of all samples are similar to that of BFO, as seen in Figs. 4 and 5. The spectra shown in Fig. 4 reveals eleven phonon modes, among which the peaks at around 133, 168, 220, 266, 310, 374, 479, 526, 614 cm<sup>-1</sup> can be assigned to the E-2 (TO), E-2 (LO), A<sub>1</sub>-2 (TO), E-4 (TO), A<sub>1</sub>-3 (TO), E-7 (TO), E-8 (LO), E-9 (TO), and E-9 (LO), respectively [35,36]. Two phonon vibrations below  $200 \text{ cm}^{-1}$  are related to the Bi–O bond vibration, while the other modes at higher frequency are caused by the stretching and bending of the FeO<sub>6</sub> octahedral [4]. Fig. 4 shows that the frequencies of E-2 (TO) remain almost unchanged, while the frequencies of the E-2 (LO) mode slightly increases with increasing Co concentration. Therefore, the ferroelectric properties arising from the R3c ferroelectric phase do not undergo a rigorous modification [8,12,37]. The tilt mode A<sub>1</sub>-2 (TO) is related to the oxygen octahedral tilts in the R3c phase [36]. Basically, the shift in tilt mode can be used to evaluate the effect of Co-doping on the magnetic properties [4,36]. Unfortunately, it shows very weak intensity in BLFCO compounds. The high frequency-shift of the E-4 (TO) and E-9 (TO) modes, which is marked by arrows in Fig. 4, reveals a modification of the crystal structure by substituting Co at the Fe-site. Besides the night phonon modes of the R3c phase, we observe two modes at around 200 and  $419 \text{ cm}^{-1}$ . The mode at 200 cm<sup>-1</sup> can be assigned to the phonon vibration of CFO [38], while the phonon vibration of the I23 cubic symmetry of Bi25FeO40 or lattice defect can contribute to the peak at



Fig. 5. Raman spectra of BLFCO compounds excited by a 532 nm wavelength. The insert shows deconvoluted Raman spectra for x = 0.1 in the region of 200–350 cm<sup>-1</sup>.

419 cm<sup>-1</sup>. Fig. 5 shows the Raman spectra of BLFCO compounds excited by a 532-nm wavelength. All samples clearly show eleven phonon modes with a great enhancement in intensity of the two modes at 253, and  $520 \text{ cm}^{-1}$ . Among these modes, we assign two modes that peaked at 125 and 253 cm<sup>-1</sup> to the vibrational modes of the Imma symmetry [36], which were not clearly observed in Fig. 4. The excitation laser energy affects not only the intensity but also the position of Raman modes, as seen by comparing the RS spectra in Figs. 4 and 5. The influence of excitation energy on the Raman spectra has rarely been reported for BFO-based compounds. In fact, the enhanced intensity (resonance) originates from the electronic transition when the laser energy closes to the band gap of the sample [39,40]. Besides, the resonant effect is only observed in some modes located at high frequency concerning the electronic transition in the FeO<sub>6</sub> octahedral [4]. In the case of the resonant mode at  $520 \text{ cm}^{-1}$ , it only shows the resonant effect at high Co concentration ( $x \ge 0.06$ ), implying the gradual decrease of the band gap with x. It has been reported that the band gap of Co doped Bi<sub>1</sub>.  $_{v}Re_{v}FeO_{3}$  (Re = La, Nd) is gradually decreased with increasing cobalt concentration [7,41], and its band gap energy is smaller than the laser energy of 2.33 eV (532 nm), but higher than that of 1.96 eV (635 nm). The resonant mode at 253 cm<sup>-1</sup> observed in all samples arises from the vibration of the FeO<sub>6</sub> octahedral of the Imma symmetry. This indicates that the Imma phase has a smaller band gap than the R3c phase.

Fig. 6 shows a typical EDX spectra and SEM images of sample x = 0.1. The microstructures represent two types of grain which are mainly related to the two major phase presences in BLFCO compounds, as discussed above (Tab. 1). A small grain region is routinely observed in samples where the *Imma* phase is dominant. According to the previous report of Walker et al. [42], the separation of two grains may relate to Bi-rich (Bi<sub>1-y</sub>La<sub>y</sub>Fe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub>) and La-rich (La<sub>1-y</sub>Bi<sub>y</sub>Fe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub>) isolated grains. However, the La-rich compounds prefer to stabilize in the *Pnma* orthorhombic instead of the *Imma* structure, and the Bi-rich compounds can crystalize in both the *R*3c and *Imma* structures [43]. We believe that the large and small grains are respectively related to the *R*3c and *Imma* symmetries of (La,Co) doping on BFO rather than the La-rich compounds. In addition, the fine grains are seldomly observed in all samples. The fine grains could be reflected in the minor phases

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**Fig. 6.** Typical EDX spectra and SEM images of sample x = 0.1.

#### Table 2

Elemental composition of BLFCO samples determined by the semiquantitative analysis of EDX spectra.

| Sample                                      | Experimental atomic % Bi   La   Fe<br>  Co  O   | Theoretical atomic % Bi   La   Fe<br>  Co  O           |
|---|---|--|
| x = 0.02 x = 0.04 x = 0.06 x = 0.08 x = 0.1 | 17.36       2.78       17.93       0.19       61.74         17.22       2.76       18.04       0.63       61.35         16.61       3.42       19.08       1.41       59.48         16.63       2.95       18.18       1.67       60.57         16.94       3.40       17.89       2.31       59.46 | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

(impurities) in the compounds. The SEM data confirms the presence well of both the *R*3*c* and *Imma* phases in all samples, consistent with the results of the XRD analysis (Figs. 1 and 3). The elemental compositions of all samples are listed in Table 2. The experimental results are consistent with the expected stoichiometry.

The influence of the coexisting phases and CFO ferrimagnetic impurity on the magnetic properties of BLFCO compounds are shown in Fig. 7. As expected, the saturation magnetization of the samples that contain the parasitic magnetic impurity is proportional to the CFO concentration. For instance, the  $M_s$  is gradually increased from 0.51 emu/g for x = 0.02-4.00 emu/g for x = 0.1. The coercivity (H<sub>c</sub>) of samples x = 0.02-0.1 remains around 0.3 (  $\pm 0.05$ ) kOe, implying that the ferromagnetism of BLFCO compounds may mainly relate to the CFO impurity because the change in Imma/R3c phase ratio and increase in Co concentration are expected to vary the coercivity of the intrinsic magnetic properties of the R3c and Imma phases. It is widely known that the R3c symmetry has a cycloidal modulation spin superimposed on the G-type antiferromagnetic structure, and the Imma symmetry has a collinear G-type antiferromagnetic structure with a small spin canting angle [29,30]. The cycloidal modulation spin cancels a macroscopic magnetization [5], and hence the R3c phase generally shows a linear magnetic field-dependent magnetization. According to previous reports, cobalt doping and codoping with rare-earth elements can reveal a weak ferromagnetism in the R3c symmetry due to the destruction of the cycloidal spin structure [9,12]. However, the cycloidal spin structure can be destroyed, or extend the modulation period dependent on La concentration [7,44]. The destruction of cycloidal spin in the R3c symmetry can provide the  $M_s$  up to 0.03  $\mu_{\rm B}/{\rm f.}$  u. (~0.53 emu/g) for bulk BiFe\_{0.8}Co\_{0.2}O\_3 [12,14], and 0.06  $\mu_B/f$ . u. (~1.07 emu/g) for the  $BiFe_{0.85}Co_{0.15}O_3$  thin film [12]. Yet, the canted spin structures in the



Fig. 7. Magnetic-field dependence of magnetization of BLFCO samples. The inset shows the variation of  $M_r$  as a function of Co concentration.

orthorhombic symmetries, e.g., Imma, Pbam, Pbnm, have been shown with  $M_s$  less than 0.5 emu/g in various BFO-based compounds [30,33,37,45]. The magnetization of BLFCO compounds are comparable to the magnetization of composite CFO:BFO (10:90) [11,23,24,46]. Therefore, it is clear that the magnetic properties of our samples are primarily related to the magnetic impurity. It is worth mentioning that the high  $M_s$  is frequently reported as an intrinsic suppression of the cycloidal spin of Co doping compounds [16,20,25], and a carefully analysis of the XRD patterns and RS spectra are still lacking so far as seeing whether CFO is parasitic in compounds. In general, the enhancement of magnetization possibly originates from: i) the suppression of the cycloidal modulation spin structure; ii) the contribution of the collinear antiferromagnetic structure of the minor phase (Imma symmetry) in BLFCO compounds; and iii) the phase boundary ferromagnetism [4,27]. Due to the paramagnetic behavior at room temperature of sillenite Bi25FeO40, it does not take into account the magnetic properties of BLFCO samples. Unlike the Co doped BFO, La and Co codoping may be less effective in suppressing cycloidal spin due the extension of the modulation period [14]. In fact, the previous work of Xu et al. observes a reduction in magnetization in Bi<sub>1-v</sub>La<sub>v</sub>Fe<sub>0.95</sub>Co<sub>0.05</sub>O<sub>3</sub>  $(y \ge 0.1)$  compared to BiFe<sub>0.95</sub>Co<sub>0.05</sub>O<sub>3</sub> samples [44]. The increase in the modulation period has previously been observed in BFO doping with La [14], Sm [47], and Mn [48], and is believed to originate as an opened hysteresis loop of the R3c phase of doped BFO compared with BFO [47,49,50].

In order to shed light on the intrinsic/extrinsic magnetic properties of BLFCO compounds, we studied the variation of magnetization with time. The change of magnetic properties of BLFCO compounds after 16 months synthesis are shown in Fig. 8. The hysteresis loop of all samples shows a drastic reduction of magnetization. The decrease of magnetization in compounds is strongly dependent on the coexisting phases and the *R3c/Imma* phase ratio. For instance, the remanent magnetization ( $M_r$ ) slightly decreases from 0.08 emu/g (as-prepared) to 0.05 emu/g (after 16 months) for sample x = 0.02, but it shows a drastic decrease from 0.93 emu/g (as-prepared) to 0.50 emu/g (after 16 months) for sample x = 0.1. The variation in magnetization with time implies that the self-transformation of the crystal structure and/or the reconstruction of the spin structure at the interface of the two crystal structures could be the origin of this effect [51,52]. Due to the different spin structures of each symmetry, a disordered spin can form in the



**Fig. 8.** M(H) loops of BLFCO samples measured after 16 months synthesis. The inset shows the variation of  $M_r$  as a function of Co concentration.

ferromagnetic or antiferromagnetic orders, namely the phase boundary ferromagnetism. Unfortunately, the phase boundary ferromagnetism varies over time because of the spin frustration at the phase boundary [51]. Therefore, the variation in magnetization observed in BLFCO compounds should originate from the reconstruction of the spin structure at the phase boundary. Obviously, the change in magnetization in our samples cannot relate to a decomposition of CFO or BLFCO. Due to the variation of magnetization, we can clearly conclude that the enhancement of magnetization observed in Fig. 7 mainly comes from the CFO impurity and phase boundary ferromagnetism. The suppression of the cycloidal modulation spin in the R3c phase and the collinear antiferromagnetic structure in the Imma phase play a minor role in the enhancement of magnetic properties of BLFCO compounds. Recently, several reports revealed that the interfacial ferromagnetism in polycrystalline ceramics plays a crucial role in the magnetic coupling between the R3c and Imma phases [27], the spontaneous exchange bias at the interface of BiFeO3-Bi2Fe4O9 or BiFeO3-CoFe2O4 composites [53,54], and the irreversible ferromagnetic transition in the Bi-FeO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub> composite [55]. The spin frustration is lacking so far in the research on the interfacial magnetic coupling and the magnetic properties of materials at the morphotropic phase boundary. The phase boundary spins can provide several interesting effects, such as the spontaneous exchange bias, the abnormal hysteresis loop, and the fieldstep dependent hysteresis loop. In this work, we observed both the twisted hysteresis loop and the field-step dependent hysteresis loop after 16 months synthesis, as seen in Fig. 9(b); whereas, the hysteresis loop measured after 3 months does not show any change in comparison with the as-prepared sample, as shown in Fig. 9(a). The implication is that the contribution of phase boundary ferromagnetism can only be revealed with the help of spin frustration at the phase boundary. The dependence of the hysteresis loop on the field-step originates from the magnetic coupling between the phase boundary spins and the intrinsic antiferromagnetic structure of the two phases [27].

In summary, we studied the crystal structure and magnetic properties of Co doped  $Bi_{0.84}La_{0.16}Fe_{1-x}Co_xO_3$  (0.02  $\leq x \leq$  0.1). Analysis of the crystal structure reveals the polymorphs of the *R3c* rhombohedral and *Imma* orthorhombic symmetries, along with CFO and  $Bi_{25}FeO_{40}$  impurities. The study of phonon vibration at different excitation wavelengths identifies the individual contribution of each symmetry. Scanning electron micrographs reveal the small and large grain regions

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Fig. 9. M(H) loops of sample x = 0.1 measured after 3 months and 16 months synthesis at different field-steps.

of the *Imma* and *R*3*c* phases, respectively. The enhancement of magnetic properties mainly originates from the magnetic impurity and the phase boundary ferromagnetism. The spin frustration at the interface of the *Imma* and *R*3*c* phases reveals the twisted hysteresis loop and the field-step dependent hysteresis loop. Our research suggests that manipulation of the interfacial spin in polycrystalline composites is the key to improving the magnetic properties of BFO-based compounds and to obtaining the exchange bias effect.

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