

# Hydrothermal synthesis and characterization of multiferroic $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ crystallites

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## Abstract

$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$  (BLFO,  $x=0.0-0.2$ ) crystallites were synthesized by the hydrothermal route. X-ray diffraction results indicate that pure BLFO crystallites could be obtained for  $x \leq 0.1$ , and the phase purity was sensitive to the PH value of precursor solutions. Transmission electron microscope observation reveals that needle like BLFO crystallites were formed for  $x=0.1$ . The coexistence of ferroelectric and magnetic transition is detected by using differential thermal analysis, indicating the multiferroic characteristics of BLFO crystallites. The Néel temperature of BLFO crystallites for  $x=0.1$  shifts upwards, whereas the Curie temperature shifts downwards, compared with those of BFO crystallites without La substitution. Weak ferromagnetic property of BLFO crystallites was induced and enhanced with increasing the La content.

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## 1. Introduction

Multiferroic materials that exhibit ferroelectric and ferromagnetic properties simultaneously have attracted much attention. These materials could offer potential applications in the next generation information storage, sensors and spintronics devices.<sup>1,2</sup> Most of single phase multiferroic materials reveal such properties well below room temperature, such as  $\text{RMnO}_3$  and  $\text{RMn}_2\text{O}_5$ , where R represents rare earth elements.<sup>3-5</sup> Perovskite  $\text{BiFeO}_3$  (BFO) is the most unique one with Curie and Néel temperature of 830 and 340 °C, respectively, being a kind of high temperature multiferroics.<sup>6,7</sup> However, it is hard to fabricate bulk BFO avoiding non-ferroelectric impurities, such as  $\text{Bi}_{25}\text{FeO}_{40}$  and  $\text{Bi}_2\text{Fe}_4\text{O}_9$ ,<sup>8,9</sup> by using the conventional solid state reaction method. Moreover, the antiferromagnetic BFO has a spiral modulated spin structure (SMSS) in the period of 62 nm, resulting in the vanish of the overall magnetization.<sup>10</sup> It has been reported that the morphology and grain size of BFO crystallites had great effects on the magnetic enhancement. BFO crystallites with smaller grain size would exhibit the enhanced magnetic properties.<sup>11,12</sup> Furthermore, various substitutions of  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Mn}^{3+}$ ,  $\text{La}^{3+}$  etc. for  $\text{Bi}^{3+}$  and  $\text{Fe}^{3+}$  ions have been

utilized to stabilize the perovskite structure and to induce the latent magnetic properties of BFO.<sup>13-16</sup> Upon using the cation substitution, the SMSS in BFO could be partially destroyed, and the spatial homogenization of spin arrangement could be realized causing the magnetic property of BFO to increase.

The hydrothermal route is usually utilized to synthesize crystalline particles at a lower temperature range of about 100–250 °C without an additional annealing treatment.<sup>17</sup> The single-phase perovskite BFO crystallites were previously obtained in our group by using the hydrothermal method at 200 °C for 6 h, with grain size of about 200 nm and the antiferromagnetic characteristics.<sup>18</sup> In this study, La-modified BFO was fabricated by using the hydrothermal method. The structure, morphology and magnetic properties of BLFO crystallites were investigated for different La contents and PH values of precursor solutions. The objective of this study was to further reduce the grain size and induce the latent magnetic properties of BFO-based materials.

## 2. Experimental procedure

Analytical grade  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were used as starting reagent. The iron, bismuth and lanthanum nitrates were dissolved in the mixed solutions of HCl and de-ionized water in the stoichiometric proportion according to the molecular formula of  $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$

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( $x=0.0-0.2$ ). KOH aqueous solution of 4M was employed as mineralizer. The PH value of precursor solutions was also adjusted by KOH. The mixture was ultrasonically dispersed for 15 min, and then transferred into teflon-lined autoclaves. Autoclaves were sealed and displaced in an oven at 200 °C for 6 h. The reaction temperature and time were chosen according to our previous investigation.<sup>18</sup> After the hydrothermal reaction, autoclaves were quenched to room temperature. The products were filtered and washed by de-ionized water several times to remove all soluble salts, and then dried at 90 °C in air. We found that the quenching process was an efficient way to prepare phase pure BFO crystallites with reduced grain size. The related work has been submitted to another journal.<sup>19</sup>

The phase structure of BLFO crystallites was characterized by X-ray diffraction (XRD, Rigaku D/MAX-3C) with graphite monochromatized CuK $\alpha$  radiation ( $\lambda=0.154$  nm). The particle morphology and size were observed with transmission electron microscope (TEM, JEM-2010F). The composition of BLFO was roughly examined by energy dispersive spectroscopy (EDS) attached with field emission scanning electron microscopy (FE-SEM, LEO1530VP, Germany). Differential thermal analysis (DTA, STD Q600) of BLFO crystallites was carried out in nitrogen ambient at a scan rate of 20 °C/min. The magnetic property of BLFO was measured at  $T=27$  °C using a quantum design physical property measurement system (6700 magnet controller).

### 3. Results and discussion

Fig. 1 shows XRD patterns of Bi<sub>0.9</sub>La<sub>0.1</sub>FeO<sub>3</sub> crystallites for different PH values of precursor solutions. It can be seen that BLFO could not be synthesized from the precursor solution with the PH value of 13.1. By increasing the PH value to 13.5, the perovskite BFO could be formed, however, the existence of non-perovskite Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> phase was also detected at around  $2\theta$  of 14.5°. Diffraction peaks that come from BLFO powders for the PH value of 14 can be indexed as only perovskite BLFO, according to the powder data of JCPDS card no. 86-1518. It indicates that higher PH value of precursor solution was neces-

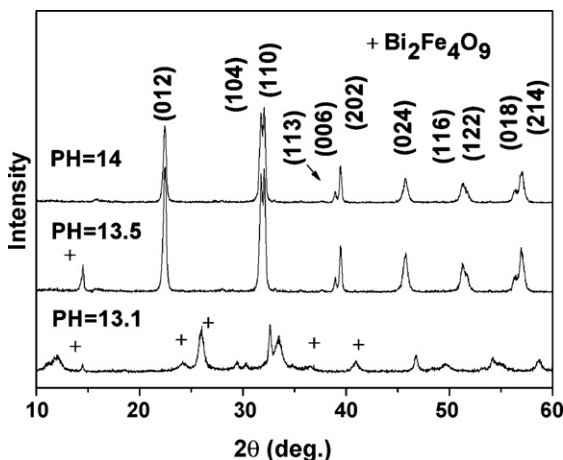


Fig. 1. XRD patterns of Bi<sub>0.9</sub>La<sub>0.1</sub>FeO<sub>3</sub> crystallites for different PH values of precursor solution.

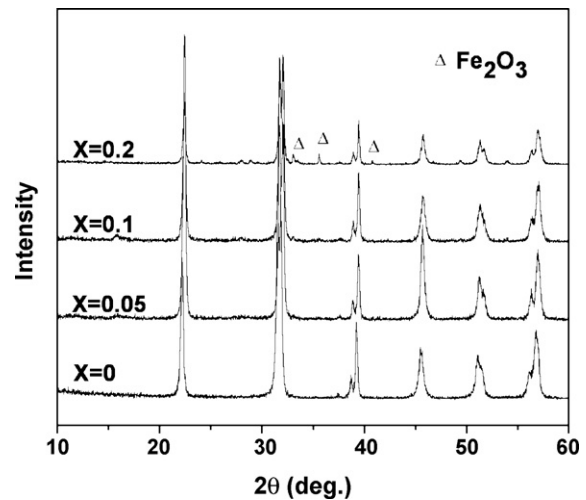


Fig. 2. XRD patterns of BLFO crystallites for  $x=0, 0.05, 0.1$  and  $0.2$  synthesized from the precursor solution with the PH value of 14.

sary for synthesizing source materials into perovskite BLFO and could restrain the formation of second phases effectively. In the process of hydrothermal reaction, precursor solutions with high PH value have more OH<sup>-</sup> ions, which provide necessary alkali condition and driving force for the crystallization of BLFO crystallites. Moreover, high alkalinity could increase the solubility of reactants and hydroxide products avoiding the over-saturation of reactants and the formation of second phases.

Fig. 2 shows XRD patterns of BLFO crystallites for  $x=0, 0.05, 0.1$  and  $0.2$  synthesized from the precursor solution with the PH value of 14. Single-phase BLFO crystallites have been obtained for  $x \leq 0.1$ . The diffraction peaks of BLFO for  $x=0.05, 0.1$  and  $0.2$  have a slight shift compared with those of BFO without La, indicating the lattice change caused by the La substitution. This may result from the difference in atom radii between Bi<sup>3+</sup> and La<sup>3+</sup> ions. However, the phase structure of BLFO crystallites does not change with increasing the La content. It has been reported that BLFO ceramics prepared by the solid state reaction method usually had a structure change from rhombohedral to orthorhombic phase for  $x=0.2$ .<sup>20,21</sup> The differences between BLFO crystallites and ceramics may result from their different internal stress conditions and their different preparation processes. It is noticed that the Fe<sub>2</sub>O<sub>3</sub> rather than Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub> phase appear with perovskite BLFO for  $x=0.2$ . Upon using the cation substitution, the hydrothermal reaction became more complicated than that for synthesizing single BFO crystallites. In order to further examine the existence of La element in BLFO crystallites, the energy dispersive spectroscopy (EDS) analysis of our specimen was performed. Fig. 3 shows the EDS pattern of BLFO crystallites for  $x=0.05$ . The La element could be detected from the EDS curve, though the calculated atom ratio of Bi to La was away from the stoichiometry. It has been known that lanthanum oxides or La contained compounds could not be detected from XRD patterns. Thus, the La element has occupied the lattice position in BLFO crystallites.

Fig. 4(a) and (b) shows TEM images of BLFO crystallites for  $x=0$  and  $0.1$ . It can be seen that the La substitution has great effects on the morphology of BLFO crystallites. Without La,

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