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Hydrothermal synthesis and characterization of multiferroic $Bi_{1-x}La_xFeO_3$ crystallites

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Abstract

$Bi_{1-x}La_xFeO_3$ (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.

Keywords: Powders-chemical preparation; Electron microscopy; Magnetic properties; Ferrites; Multiferroics

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.[1,2] Most of single phase multiferroic materials reveal such properties well below room temperature, such as $RMnO_3$ and RMn_2O_5, where R represents rare earth elements.[3–5]. Perovskite $BiFeO_3$ (BFO) is the most unique one with Curie and Néel temperature of 830 and 340 °C, respectively, being a kind of high temperature multiferroics.[6,7] However, it is hard to fabricate bulk BFO avoiding non-ferroelectric impurities, such as $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$,[8,9] 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.[10] 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. [11,12] Furthermore, various substitutions of Cr^{3+}, Ti^{4+}, Mn^{3+}, La^{3+} etc. for Bi^{3+} and Fe^{3+} ions have been utilized to stablize the perovskite structure and to induce the latent magnetic properties of BFO.[13–16] 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.[17] 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.[18] 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 $Fe(NO_3)_3{\cdot}9H_2O$, $Bi(NO_3)_3{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}6H_2O$ 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 $Bi_{1-x}La_xFeO_3$

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($x = 0.0$–0.2). KOH aqueous solution of 4 M 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.[18] 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.[19]

The phase structure of BLFO crystallites was characterized by X-ray diffraction (XRD, Rigaku D/MAX-3C) with graphite monochromatozed CuKα 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 $Bi_{0.9}La_{0.1}FeO_3$ 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 $Bi_2Fe_4O_9$ phase was also detected at around 2θ 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 necessary 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^- irons, 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.

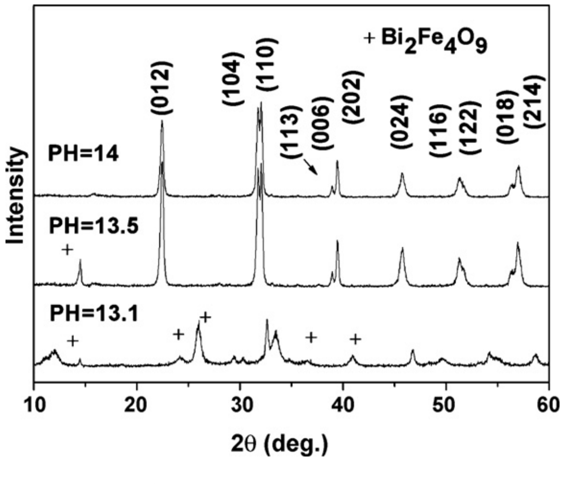

Fig. 1. XRD patterns of $Bi_{0.9}La_{0.1}FeO_3$ crystallites for different PH values of precursor solution.

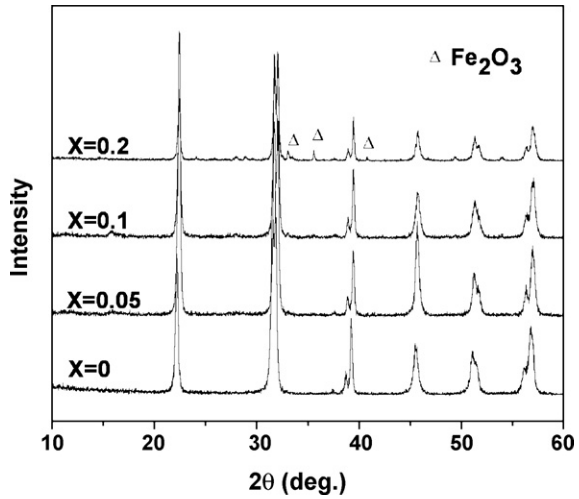

Fig. 2. XRD patterns of BLFO crystallites for $x = 0$, 0.05, 0.1 and 0.2 synthesized from the precusor solution with the PH value of 14.

Fig. 2 shows XRD patterns of BLFO crystallites for $x = 0$, 0.05, 0.1 and 0.2 synthesized from the precusor 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^{3+} and La^{3+} 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 $x = 0.2$.[20,21] 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_2O_3 rather $Bi_2Fe_4O_9$ 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,

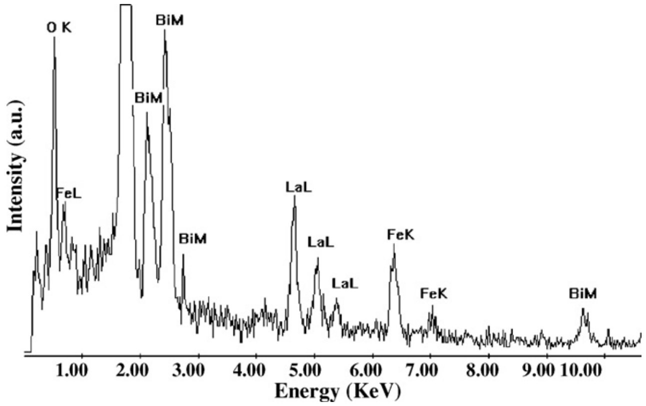

Fig. 3. EDS pattern of BLFO crystallites for $x = 0.05$.

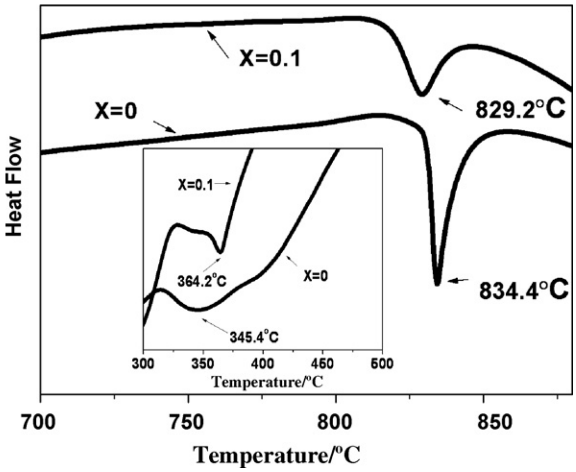

Fig. 5. DTA curves of BLFO crystallites for $x = 0$ and 0.1.

BFO crystallites consist of rectangle or cubic particles as shown in Fig. 4(a), with size of 50–60 nm. However, needle like BLFO particles were formed upon using the La substitution. The short edge of BLFO is about 50–60 nm, and the length and aspect ratio (length over diameter) are in the ranges of 300–500 nm and 6–10, respectively. The crystal size of BFO in this study was significantly reduced compared with that of about 200 nm in our previous work,[18] due to the application of a quick cooling after the hydrothermal reaction. The formation mechanism of needle like BLFO could be understood based on a “dissolution and crystallization” hydrothermal process, in which Bi^{3+}, La^{3+} and Fe^{3+} hydroxides dissolved in alkali solution under the high temperature and pressure. The formation of BLFO crystallites underwent the nucleation, precipitation, dehydration and growth between the ions and ion groups on the interfaces of the nuclei. An anisotropy of grain growth in the homogeneous hydrothermal condition could be favored, making grain grow along a preferential orientation. La entered into the BFO lattice offering additional energy for a certain crystal plane to grow fast. As a result, the morphology of BLFO crystallites became needle like.

Differential thermal analysis was carried out to trace the thermal evolution of hydrothermal BLFO crystallites. Fig. 5 presents DTA curves of BFO crystallites and BLFO for $x = 0.1$. It is found that two endothermic peaks appear with the rise of measuring temperature for each specimen, corresponding to the magnetic and ferroelectric transition, respectively. BLFO for $x = 0.1$ has a more sharp magnetic transition peak than that of BFO, which may imply the stronger magnetic response caused by La substitution. The temperatures at peaks were determined to be the Néel and Curie temperature (T_N and T_c), respectively. The T_N and T_c are about 345.4 and 834.4 °C for BFO without La, whereas they are 364.2 and 829. °C for BLFO of $x = 0.1$. These temperatures are in agreement with reports in literatures for BFO-based materials.[6,7] It reveals that the magnetic transition of BLFO was shifted to higher temperature, however the ferroelectric transition was shifted to a lower temperature with La substitution. The increase of T_N for BLFO of $x = 0.1$ may be due to the higher Néel temperature of $LaFeO_3$, which is a kind of G-type antiferromagnetic materials with T_N of 465 °C.[22] The decrease of T_c with La has also been found in La-substituted BLFO films.[23] Perovskite materials have high T_c values when the tolerance factor, t, is small. The substitution of larger La^{3+} for Bi^{3+} ions in BFO lattice would increase t, which might be an explanation of the reduction of T_c for La-modified compounds.[24]

It has been reported that the reduction of particle size could induce the magnetic response of BFO crystallites.[11] Combined with TEM and DTA results, the magnetic behavior was expected

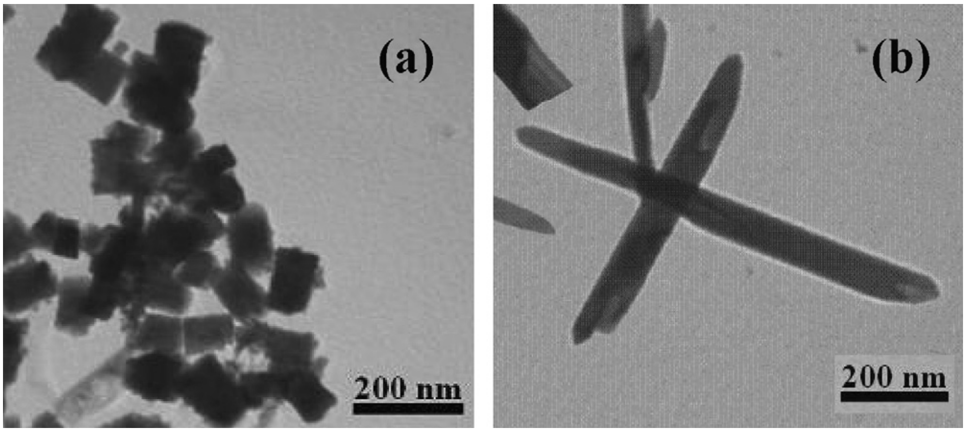

Fig. 4. TEM images of BLFO crystallites for (a) $x = 0$ and (b) $x = 0.1$.

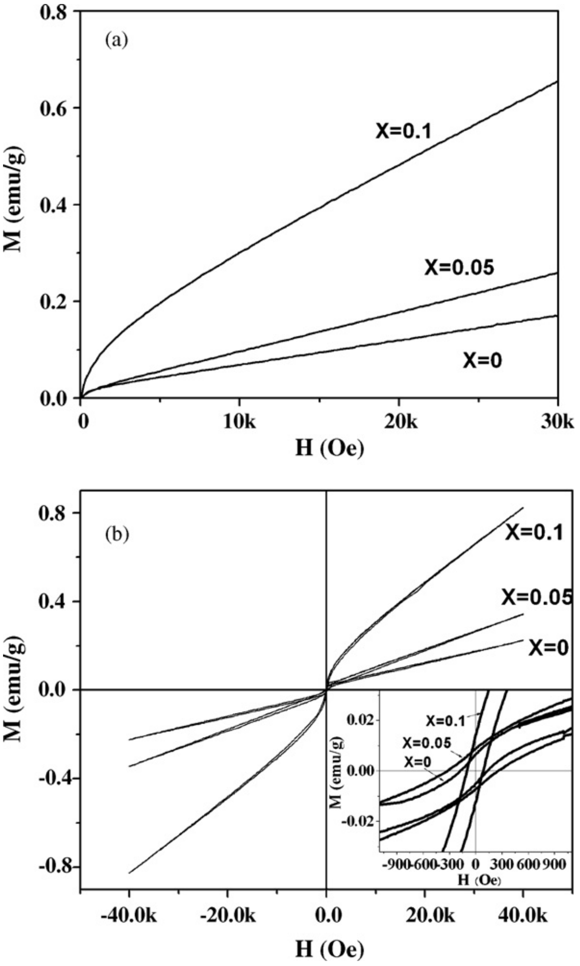

Fig. 6. Initial *M–H* curves (a) and ferromagnetic hysteresis loops (b) of BLFO crystallites for different La contents.

in our hydrothermal BLFO crystallites. Fig. 6 shows the magnetization (M) of BLFO crystallites for different La contents as a function of applied field (H). According to Fig. 6(a), the non-linear *M–H* relationship is observed in the field of lower than 10 kOe, reflecting the contribution of the spontaneous magnetization to the total magnetization. The magnetization linearly increases with the further increase of H field, reflecting the basic antiferromagnetic nature of our specimens. The spontaneous magnetization M_s were obtained by extrapolating the linear portion of *M–H* curve to $H = 0$. The M_s of BLFO increases with the increase of La content, achieving of 0.1381 emu/g for $x = 0.1$, which is about one order of magnitude higher than that of 0.0207 emu/g for $x = 0$. The symmetric magnetic hysteresis loops shown in Fig. 6(b) indicate that BLFO crystallites are of magnetic ordered materials. An induced (net) magnetization was observed at much lower field compared with that for $BiFeO_3$ single crystals.[25] The remanent magnetization of BLFO for $x = 0$, 0.05 and 0.1 achieved around 0.0066, 0.0091 and 0.0141 emu/g, respectively, showing a rise with the increase of La. The enhancement of magnetic response of BLFO for $x = 0.1$ under field is in agreement with the stronger magnetic transition peak observed from the above DTA pattern. It is well known that $BiFeO_3$ is an antiferromagnet. The $BiFeO_3$ single crystal exhibited a near linear *M–H* relationship for $H < 70$ kOe due to the presence of cycloidal spin structure in unmodified crystals.[25] Remnant magnetizations observed in this investigation reveal ferromagnetism, but very weak compared to typical ferromagnetic compounds. However, the magnetic response have been induced at much low field for our BLFO crystallites and the enhancements of net magnetization in the La modified $BiFeO_3$ crystallites are enormous. The enhancement of magnetic properties of BLFO crystallites might result from the size and morphology variation caused by La substitution. The latent magnetic behavior could be induced when the particle size of BFO was less than the wavelength period of 62 nm. In addition, La substitution in BFO have been investigated to destroy the SMSS of BFO favoring a collinear antiferromagnetic spin configuration.[26] Moreover, the incorporation of La^{3+} in BFO might also cause a large off-centre movement of Fe^{3+} ions in the octahedra giving a rise of spontaneous electric polarizations. Thus, the La modified BFO crystallites might be potential multiferroic materials with the enhanced magnetic and ferroelectric properties well above room temperature.

4. Conclusions

Perovskite BLFO crystallites for $x \leq 0.1$ have been synthesized by a hydrothermal route, from precusor solutions with the PH value of 14. BLFO crystallites for $x = 0.1$ has a needle like grain morphology due to an anisotropic grain growth caused by the La substitution. The coexistence of magnetic and ferroelectric transition indicates the multiferroic characteristics of BLFO. The T_N of 364.2 °C and T_c of 829.2 °C were obtained for BLFO of $x = 0.1$. The magnetic responses of BLFO crystallites could be induced under a much low field, achieving a M_S of 0.1381 emu/g for $x = 0.1$.

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