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Crystal structure and magnetic behavior of the $La_{0.1}Bi_{0.9}FeO_3$ compound

YAO Qingrong (姚青荣)[1,2,3], SHEN Yihao (沈逸豪)[2], ZHOU Huaiying (周怀营)[1,2,*], RAO Guanghui (饶光辉)[2], DENG Jiangqiu (邓健秋)[2], PAN Shunkang (潘顺康)[2]

(1. School of Materials Science and Engineering, Central South University, Changsha 410083, China; 2. School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China; 3. Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China)

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Abstract: The nano-crystalline $La_{0.1}Bi_{0.9}FeO_3$ compound was successfully synthesized by starch-based combustion method. The crystal structure and magnetic behavior were studied by temperature-dependent X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and magnetic measurements. The $La_{0.1}Bi_{0.9}FeO_3$ compounds crystallized in a rhombohedrally distorted perovskite structure with space group $R3c$. The substitution of La for Bi reduced the rhombohedral distortion. The structural phase transitions in $La_{0.1}Bi_{0.9}FeO_3$ driven by temperature showed that the extraordinary two-phase coexistence state of $BiFeO_3$ and $LaFeO_3$ was observed in a narrow temperature range of 630–700 ºC. The magnetization of the $La_{0.1}Bi_{0.9}FeO_3$ sample was improved by heat treatment in the temperature range. When the heat treatment temperatures rose from 25 to 600 ºC, the remanence (M_r) and coercivity (H_c) of the $La_{0.1}Bi_{0.9}FeO_3$ compound almost remained the same, and increased rapidly to 0.134 emu/g and 7.1 KOe on further increasing the heat treatment temperature to 650 ºC.

Keywords: X-ray diffraction; phase transition; La-doped $BiFeO_3$; magnetism; rare earths

Among various multi-ferroic materials, $BiFeO_3$ (BFO)-based compounds have been widely studied. Pure BFO manifests both the ferro-electricity with Curie temperature of 830 ºC and the anti-ferromagnetism with Neel temperature 370 ºC[1–3]. In addition to multi-ferroic properties, BFO can also be used in variety of devices because of its interesting optical and photocatalytic properties[4–7]. The $6s^2$ lone pair electrons of Bi^{3+} are responsible for the ferromagnetic (FE) while the magnetic properties are generated from the partially filled *d* orbitals of Fe^{3+} [8]. Spin-canting in the G-type anti-ferromagnetic structure with long wavelength (62 nm) leads to a cancellation of macroscopic magnetization in BFO and hence inhibits the observation of the liner magnetoelectric effect[9]. So far the small coercivity (H_c) and poor magnetoelectric (ME) seem to limit its usage in multiple state memory devices. It is found that rare-earth (RE) doping in BFO stabilizes the single phase and breaks the spiral antiferromagnetic (AFM) configuration of rhombohedral bismuth ferrite[10,11]. Bismuth ferrite-based multiferroics with the compositions near doping-induced phase transitions attract renewed interest in the last years due to their physical properties[12–16]. In spite of a large number of studies, the mechanism of the structural transitions of $BiFeO_3$-based compounds is still ambiguous and is the subject of the intensive discussions[17–19].

The present study aimed at further clarification of the thermal stability, driving forces for temperature-induced structural transitions and magnetic behaviors of La-doped $BiFeO_3$ nano-crystalline. The study focused on the temperature evolution of the crystal structure of $La_{0.1}Bi_{0.9}FeO_3$ ceramic characterized by the coexistence of the structural phase. Understanding the exact crystal structure and structural stability of the $BiFeO_3$-based compounds is of fundamental interest and will bring forward practical perspectives of using functional materials with controlled physical properties.

1 Experimental

The sample of $La_{0.1}Bi_{0.9}FeO_3$ nano-crystalline was synthesized by starch-based combustion method. High-purity $Bi(NO_3)_3·5H_2O$ and $La(NO_3)_3·6H_2O$ of Sigma-Aldrich taken in a stoichiometric molar ratio were dissolved in 2 g acetic acid and 5 mL deionized water. $Fe(NO_3)_3·9H_2O$ was added together with further 5 mL deionized water. After addition of 6.0 g soluble starch the resulting turbid solution was continuously stirred until it became a high viscous gel. The viscous gel was dried to xerogel at 80 ºC and ground to powders in an agate pot. After being calcined at 500 ºC for 2 h, the final powder samples were prepared.

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* **Corresponding author:** ZHOU Huaiying (**E-mail:** zhy@guet.edu.cn; **Tel.:** +86-773-2291434)

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The sample was carried out by *situ* X-ray diffraction using a PANalytical PIXcel^{3D} high-resolution diffractometer with Cu Kα radiation operated at 45 kV, 40 mA. For *in-situ* high temperature X-ray diffraction (HTXRD) measurements, attachment (HTK-1200N) to the PANalytical X'pert PRO diffractometer was used. The HTXRD experiments were performed in air and the temperature range was from 300 to 1023 K. A heating rate of 10 K/min and a soaking time of 5 min were employed. The analysis of the XRD data was performed using Rietveld crystal structure refinement software (FULLPROF)[20]. The chemical composition and microstructure of the ceramic sample was examined by scanning electron microscopy (SEM) using a HITACHI S-4700 microscope equipped with energy dispersive spectroscopy (EDS) microanalysis. Differential scanning calorimetry (DSC) was performed on a TA-Q600 calorimeter at a heating rate of 10 ºC/min. The sample was heated at a constant rate of 10 ºC/min from ambient temperature to 1000 ºC after being isothermal at 50 ºC for 20 min. High-purity N_2 was used as purging gas at a constant flowing rate.

The prepared samples were sealed silica tubes and annealed at 500, 600, 650 and 700 ºC for 48 h, respectively. Then the samples were quenched into liquid nitrogen. In order to investigate the magnetic properties, room temperature magnetization hysteresis (*M-H*) measurements were carried out on a physical property measurement system (PPMS).

2 Results and discussion

2.1 Crystal structure at room temperature

The XRD investigation was performed to identify the phase formation and phase transformation in $La_{0.1}Bi_{0.9}FeO_3$ nano-crystalline. X-ray patterns reveal that the powder sample of $La_{0.1}Bi_{0.9}FeO_3$ is pure BFO phase and crystallizes in rhombohedrally distorted pervoskite structure with space group $R3c$. The experimental and calculated XRD patterns of the $La_{0.1}Bi_{0.9}FeO_3$ compound are shown in Fig. 1, in which the solid crosses stand for observed intensities and the solid lines is the calculated pattern. Vertical lines show reflection positions. Differences between the observed and the calculated intensities are shown at the bottom of the figure. Based on the R-factors (R_{wp}=10.9, R_p=5.61) and the goodness of fitting (χ^2=3.78), the calculated patterns agree well with the experimental ones. The hexagonal cell metric was calculated as $a=b$=0.55723 (2) nm, c=1.37760 (5) nm and V= 0.379 nm^3. Compared to BFO, the peaks in XRD pattern are found to shift to higher angle. The lattice parameters and unit-cell volume become smaller than that of pure BFO. The smaller ionic radius of La^{3+} (0.103 nm) than that of Bi^{3+} (0.117 nm) may be responsible for decrease in lattice parameters. The magnified XRD pattern between 30°–36° is presented in the inset of Fig. 1, which shows that the split reflections of (104) and (110), (006) and (202), (116) and (122), (018) and (214) begin to merge into a single peak with a shift towards higher 2θ value. The appreciable mergence of the double splitting Bragg peaks indicates that the rhombohedral distortion reduces as the La content increases, in agreement with Zalesskii and Yao et al.[21,22]. The crystallite size of nano-particles $La_{0.1}Bi_{0.9}FeO_3$ was calculated from the broadening of the XRD peaks by using the Scherrer's formula[23] given by the following equation:

$$D = \frac{K\lambda}{\beta_{\rm hkl}\cos\theta} \tag{1}$$

where D is crystallite size, K is shape factor (0.95), λ is wavelength of Cu Kα radiation, $\beta_{\rm hkl}$ is width of peak at half maximum in radians and θ is peak position. The calculated crystallite size is about 34.5 nm.

2.2 Evolution of crystal structure with temperature

Fig. 2 shows the XRD pattern of the $La_{0.1}Bi_{0.9}FeO_3$ compound at different temperatures. Compared to the room temperature, the peaks in XRD pattern are found to shift to lower angle with the temperature increasing. The analysis of the XRD temperature data reveals a progressive increase of the lattice parameters up to 360 ºC (as seen in Fig. 3). At about 360 ºC, an appreciable turning point of the unit cell parameters indicates the phase transition from antiferromagnetic phase to paramagnetic phase. The 370 ºC value can be considered as the end of phase transition temperature, which is well consistent with the antiferromagnetic Neel temperature (373 ºC) of the $BiFeO_3$ compounds[23]. With temperature rising to 630 ºC, the diffraction peaks (111) and (210) of the $LaFeO_3$ phase emerge. The magnified XRD pattern between 23°–28° is presented in the inset of Fig. 2. The $La_{0.1}Bi_{0.9}FeO_3$ compound presents two phases coexis-

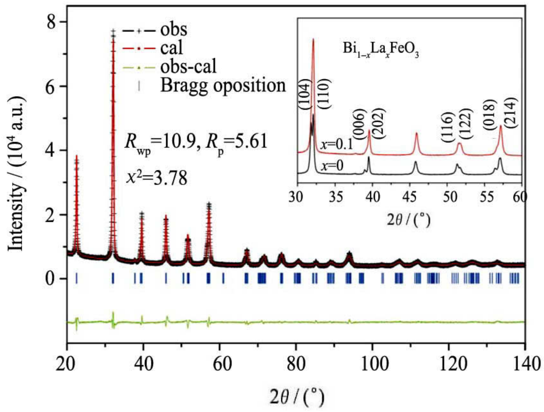

Fig. 1 XRD pattern of the nano-crystalline $La_{0.1}Bi_{0.9}FeO_3$ compound at room temperature (Crosses are experimental data, lines are calculated ones. Bragg positions are indicated by vertical ticks. The insets show component evolution of the structural peaks specific for different compounds)