

Influence of pyrolysis temperature on ferroelectric properties of La and Mn co-doped BiFeO₃ thin films

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Abstract: Bi_{0.9}La_{0.1}Fe_{0.95}Mn_{0.05}O₃ (BLFMO) ferroelectric thin films were fabricated on Pt/Ti/SiO₂/Si/ substrates by the sol-gel process at different pyrolysis temperatures. The mass loss of BLFMO powder was investigated by thermo gravimetry analyser (TGA), and the polycrystalline structure and smooth surface of BLFMO thin films were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. The remnant polarization (P_r) of the BLFMO films pyrolyzed at 420 °C is 21.2 $\mu\text{C}/\text{cm}^2$ at the coercive field (E_c) of 99 kV/cm and the leakage current density is $7.1 \times 10^{-3} \text{ A}/\text{cm}^2$, which indicates that the BLFMO thin films display relatively good ferroelectric property at this temperature.

Key words: BLFMO thin films; thermogravimetry analysis; pyrolysis temperature; ferroelectrics

1 Introduction

Lead-free BiFeO₃ (BFO) ferroelectric thin film, with a rhombohedral distorted perovskite structure, is the only thin film material that exhibits both ferroelectricity and G-type antiferromagnetism at room temperature, and possesses a giant remanent polarization and high Curie temperature ($T_C=1103 \text{ K}$), which makes itself a candidate material for high-density nonvolatile ferroelectric random access memory and other potential interesting applications [1–3]. Besides pulsed-laser deposition (PLD) and RF sputtering [4,5], large remnant polarization (P_r) in BFO thin films has also been reported in previous literatures by sol-gel preparation which has many advantages [6,7], such as easy control of stoichiometry, low processing temperature, and low cost. However, pure BFO thin films are confronted with a serious high leakage current problem resulting from poor sample quality, the charge defects such as oxygen vacancies, and the switching valence of Fe³⁺ between Fe²⁺, which

hinders its practical applications. To reduce the leakage current and improve the remanent polarization of BFO [8,9], A-site is substituted by La³⁺, Ce³⁺ and Eu³⁺, and B-site is substituted by Mn³⁺, Ti⁴⁺ and Zr⁴⁺ [8–11]. Additionally, co-doping on both sites can also diminish the leakage current, even in two or three orders of magnitude [12,13].

First-principle calculation predicts that the BiFeO₃ films possess a large spontaneous polarization (P_s) of $\sim 100 \mu\text{C}/\text{cm}^2$ for rhombohedral structure and $\sim 150 \mu\text{C}/\text{cm}^2$ for tetragonal structure [14]. SINGH et al [9] reported that Mn-doped BFO films can increase P_r value due to the increasing of the tetragonality phase transition. Their successive researches indicated that a better saturated polarization-electric field (P — E) hysteresis loop with a larger remanent polarization of $100 \mu\text{C}/\text{cm}^2$ can be obtained in 5% Mn-doped BFO film using sol-gel process [15,16].

So far, much attention has been paid to the process conditions of the BFO thin film, such as the doping, annealing temperature, annealing atmosphere, thickness,

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the bottom electrode and solution configuration. However, little attention is paid to the pyrolysis temperatures. Therefore, we try to obtain preferable pyrolysis temperature by TGA, and analyze the influence of different pyrolysis temperatures on the electrical properties of thin films. In this study, in order to enhance ferroelectricity and reduce leakage current, $\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ films were fabricated on Pt/Ti/SiO₂/Si substrates by sol-gel process, using sequential layer annealing (SLA) process and pyrolysis at different temperatures. Crystalline structure, surface morphology and electrical properties were investigated, respectively.

2 Experimental

To prepare $\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ (BLFMO) precursor solution, bismuth nitrate, lanthanum nitrate, iron nitrate and manganese acetate were dissolved into 2-methoxyethanol, ethylene glycol and acetic anhydride, stirred at 110 °C for 1 h, and then adjusted solution to 0.2 mol/L BLFMO. After ageing for 48 h, the solution was filtered by pinhole membrane filter of 0.22 μm in diameter, and was spin-coated on the Pt/Ti/SiO₂/Si substrates at 4000 r/min, pyrolyzed at 350, 400 and 420 °C, and annealed at 550 °C for 5 min. These processes were repeated 9 times until the thickness of the film approached about 300 nm, and then the final annealing was conducted at 550 °C for 20 min in O₂.

The mass loss of BLFMO powder was estimated by TGA, the crystalline structure and surface morphology of BLFMO thin films were investigated by XRD and AFM, respectively. For the measurement of electrical properties, Pt top electrodes were deposited through a shadow mask by RF sputtering. The ferroelectric property and leakage current behavior of the films were measured using a Radiant technologies precision workstation ferroelectric test system. All measurements were implemented at room temperature.

3 Results and discussion

Figure 1(a) shows the TG curve of $\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ power at a heating rate of 10 °C/min. There is a fall in sample mass of ~23% between 180 °C and 240 °C, due to the volatile substances. Another fall in sample mass of ~28% appears between 360 °C and 420 °C because of the precursor decomposition. We recognize that pyrolysis temperature may be determined by volatile organic compounds. If the sample is pyrolyzed below the temperature of the precursor decomposition, some organic compositions in the films were volatile in the annealing process, resulting in inferior quality films. Therefore, based on the analysis

of the TG curves, we intended to choose three temperatures (350 °C, 400 °C and 420 °C) as the pyrolysis temperatures, among which, 350 °C is usually adopted as a pyrolysis temperature in other papers [9,13,14]. Figure 1(b) exhibits the XRD patterns of BLFMO thin films pyrolyzed at various temperatures, and indicates that BLFMO thin films are polycrystalline and crystallized. Besides the relatively strong (012), (024) and (104/110) diffraction peaks, there are also (202), (116/122) and (018) peaks. As the pyrolysis temperature grows, crystallinity of films overall increases, especially the (012) diffraction peaks enhance significantly, while (104/110) diffraction peaks decline. Due to the release of other elements before annealing, the density of the thin films ascends, and the activation energy of crystallization of thin films lessens [17]. We can choose a suitable temperature to pyrolyze the films to get the crystallization enhanced while the annealing temperature unchanged.

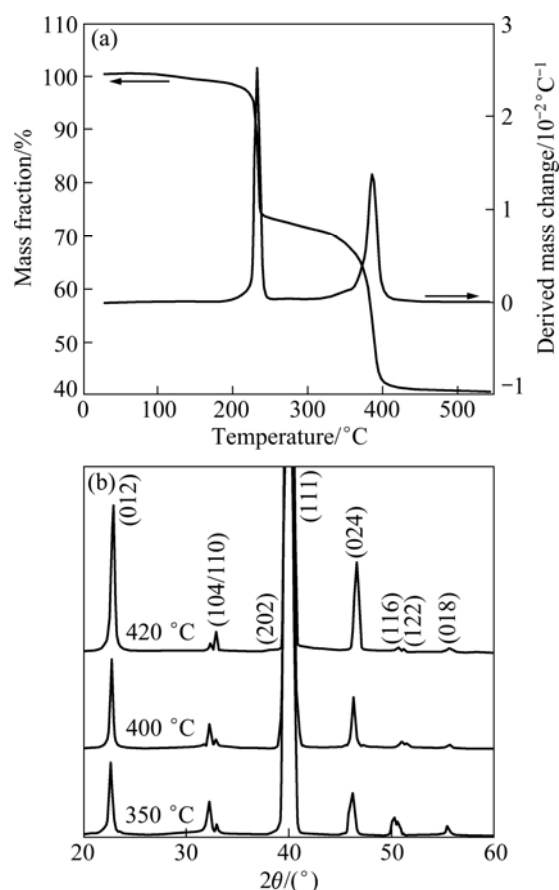


Fig. 1 TG curve of BLFMO powder (a) and XRD patterns of BLFMO thin films (b)

Figure 2 shows the surface morphology of the BLFMO thin films characterized using atomic force microscopy (AFM). BLFMO thin film pyrolyzed at 350 °C (Fig. 2(a)) has larger grain size with a few tiny interstices, while the thin film pyrolyzed at 420 °C (Fig. 2(b)) presents dense, crack-free and smooth surface

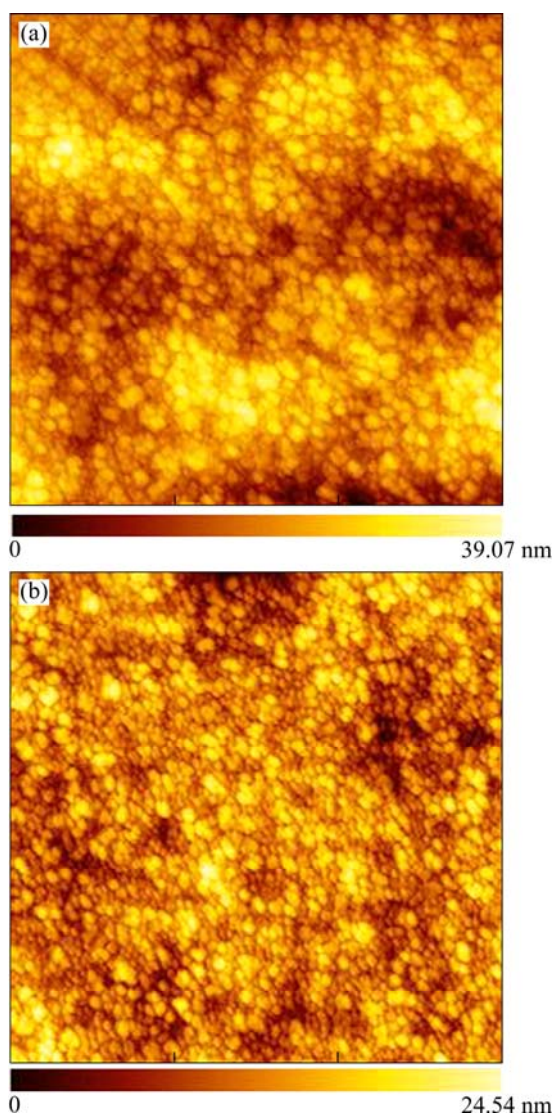


Fig. 2 AFM images of BLFMO thin films under pyrolysis temperature: (a) 350 °C; (b) 420 °C

and small grain size. With the increase of pyrolysis temperature, the interstices of BLFMO thin films diminish, and the density, smoothness and crystallization improve as well. We predict that the dense and crack-free microstructure contributes much more to improving ferroelectric performance.

Figure 3(a) displays the typical P — E hysteresis loops of BLFMO thin films at different pyrolysis temperatures. One can see that the ferroelectric properties (the remanent polarization and the coercive electric field) become better as the pyrolysis temperature increases. The sample pyrolyzed at 350 °C is not well saturated under the coercive field (E_c) of 63 kV/cm and the ferroelectric performance is not obvious, due to its high leakage current and low crystallization. When the pyrolysis temperature goes up to 420 °C, the P_r is 12 $\mu\text{C}/\text{cm}^2$ and the E_c is 42 kV/cm. LI et al [18] reported that different preferred orientations have different

spontaneous polarizations (P_s), and the P_s value of (012) peak is theoretically smaller than that of (104/110) peak. In our study, due to the higher crystallization and relatively good film quality, the film pyrolyzed at 420 °C with (012) preferred orientation gets higher P_r value than the one pyrolyzed at 350 °C with (104/110) preferred orientation. Figure 3(b) shows the P — E loops with different operation electric fields at the pyrolysis temperature of 420 °C. Under the condition of 267 kV/cm electric field and 10 kHz frequency, the largest P_r value comes to be 21.2 $\mu\text{C}/\text{cm}^2$ with a low coercive field ($E_c=99$ kV/cm).

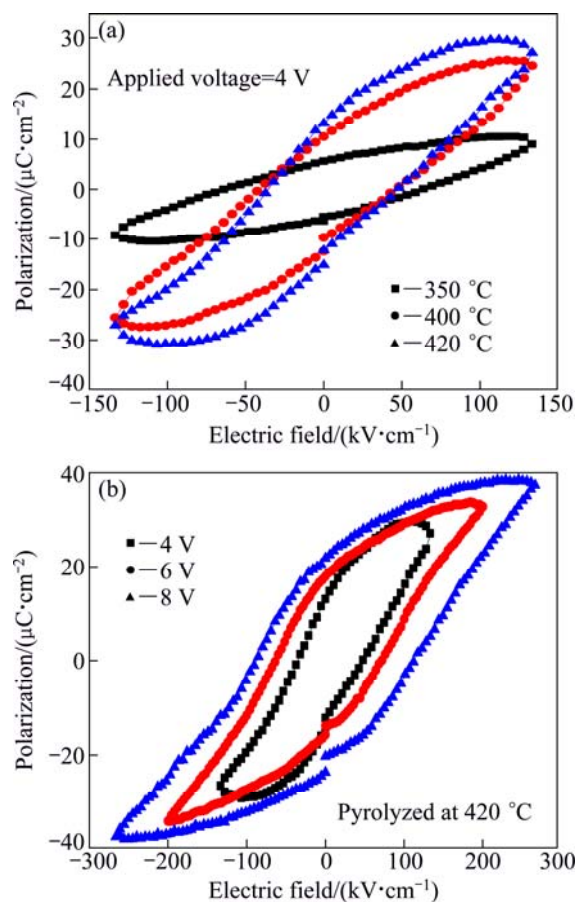


Fig. 3 P — E loops of BLFMO thin films at different pyrolysis temperatures (a) and at different operating electric fields pyrolyzed at 420 °C (b)

Figure 4(a) illustrates the leakage current density—voltage (J — V) curves of BLFMO thin films. One can see that the current density value decreases as the pyrolysis temperature increases. The leakage current density of the sample pyrolyzed at 420 °C is less than 7.1 mA/cm^2 at the maximum applied electric field of 200 kV/cm. Large leakage current mainly results from the oxygen vacancies and iron valence (Fe^{2+} , Fe^{3+}), as well as from various defects such as stoichiometry, pores, cracks and interstices in films. In this work, besides by means of substitution and annealing in O_2 , we try to decrease the

leakage current by improving the quality of thin films and reducing its defects. We can see from the XRD patterns that the enhancement of crystallinity is one of the improvements for the thin film quality. And a higher pyrolysis temperature can reduce unwanted content of thin films before annealing, and make thin films lessen the cracks and pores, etc.

Figure 4(b) shows the double logarithmic plots of the leakage current curve of BLFMO films pyrolyzed at different temperatures. In all samples, the leakage current density was in proportion to the electric field. The slope 1.21 under a low electric field for the films pyrolyzed at 350 °C is transitional region. The slopes of films pyrolyzed at 400 and 420 °C are approximately 1 under a low electric field, and turn to 2 when electric field increases, indicating that the leakage current predominantly depends on Ohmic conduction.

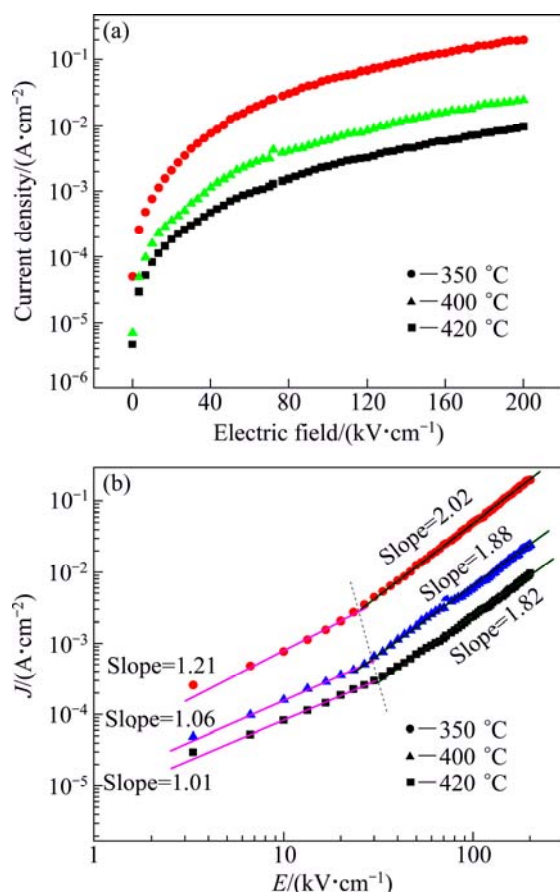


Fig. 4 J — V curves of BLFMO thin films pyrolyzed at various temperatures (a) and double logarithmic plots of leakage current curve for BLMO films at various temperatures (b)

4 Conclusions

BLFMO ferroelectric thin films were fabricated at different pyrolysis temperatures. When the pyrolysis temperature was increased, relatively high quality thin films with higher crystallization, better density and smoothness, larger remnant polarization, and lower

leakage current density were obtained. At the electric field of 133 kV/cm, the P_r ranges from 6.2 $\mu C/cm^2$ to 12 $\mu C/cm^2$ with coercive electric field varying from 63 kV/cm to 42 kV/cm at various temperatures in the range of 350–420 °C. At the electric field of 267 kV/cm, thin film pyrolyzed at 420 °C exhibits a saturate ferroelectric hysteresis loop with the remanent polarization of 21.2 $\mu C/cm^2$ at coercive electric field of 99 kV/cm and leakage current density of 7.1 mA/cm².

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热解温度对镧、锰共掺杂铁酸铋薄膜铁电性能的影响

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摘要: 在不同热解温度下, 采用溶胶-凝胶法在 $\text{Pt/Ti/SiO}_2/\text{Si}$ 衬底上制备镧、锰共掺杂铁酸铋铁电薄膜 $\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$ (BLFMO)。利用热失重仪(TGA)分析 BLFMO 原粉的质量损失, 用 X 射线衍射仪(XRD)和原子力显微镜(AFM)分析 BLFMO 薄膜的晶体结构和表面形貌。在热解温度为 420 °C 时, 得到 BLFMO 薄膜的剩余极化值为 $21.2 \mu\text{C}/\text{cm}^2$, 矫顽场为 99 kV/cm, 漏电流密度为 $7.1 \times 10^{-3} \text{ A}/\text{cm}^2$, 说明薄膜在此热解温度下具有较好的铁电性能。

关键词: BLFMO 薄膜; 热重分析; 热解温度; 铁电

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