



# Effect of oxygen annealing on magnetic, electric and magnetodielectric properties of Ba-doped BiFeO<sub>3</sub>

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## ABSTRACT

We investigate the effect of oxygen annealing on magnetic, electric and magnetodielectric properties of Ba-doped BiFeO<sub>3</sub>, Bi<sub>0.75</sub>Ba<sub>0.25</sub>FeO<sub>3</sub> (BBFO) bulk. Magnetization, resistivity, polarization and magnetodielectric measurements reveal that as-grown BBFO shows weak ferromagnetism, leaky dielectric behavior with activation energy of 0.40 eV and 0.06% change of dielectric constant at 60 kOe. However, oxygen-annealed BBFO at 850 °C shows antiferromagnetism, leaky dielectric behavior with activation energy of 0.73 eV and 0.04% change of dielectric constant at 60 kOe. These differences are discussed by the formation of Fe<sup>3+</sup> valence with oxygen vacancy in as-grown BBFO, and the formation of mixed Fe<sup>3+</sup> and Fe<sup>4+</sup> valences without oxygen vacancy for oxygen-annealed BBFO.

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## 1. Introduction

The prospective of mutual control of magnetism and electricity in a multiferroic, where two order parameters (such as antiferromagnetism and ferroelectricity) coexist and couple, has drawn much attention due to scientific interest as well as technological application [1–4]. Among multiferroics, BiFeO<sub>3</sub> (BFO) is a unique material, in which antiferromagnetic and ferroelectric transition temperatures are located above room temperature [5,6]. However, the technological application of the coupling between magnetism and electricity in BFO is hindered due to the spiral antiferromagnetic spin order and large leakage current [7–9]. Therefore, there have been a lot of efforts to modify the magnetic and electric properties of BFO through an epitaxial strain, a rare-earth ion substitution and so on [10–12].

On the other hand, there have been several reports on the modification of magnetic and electric properties of BFO through the doping of divalent ions such as Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> for Bi<sup>3+</sup> [13–15]. For example, Wang et al. reported the observation of ferromagnetism, ferroelectricity and magnetoelectric coupling in a Ba-doped BFO bulk [14]. And, Khomchenko et al. reported the correlation between ionic radius and magnetization, i.e., ferromagnetism in a Ba<sup>2+</sup> doped BFO and antiferromagnetism in a Ca<sup>2+</sup> doped BFO at room temperature [15]. It has been suggested that

the doping-induced oxygen vacancy and/or mixed Fe valence could suppress the spiral antiferromagnetic spin configuration of BFO and result in weak ferromagnetism [13–15]. However, the role of oxygen vacancy and mixed Fe valence on observed weak ferromagnetism is not clearly understood yet.

In this paper, we attempt to investigate the role of oxygen vacancy and mixed Fe valence for the weak ferromagnetism in Ba-doped BFO, Bi<sub>0.75</sub>Ba<sub>0.25</sub>FeO<sub>3</sub> (BBFO). As-grown BBFO, in which oxygen vacancy seems to form, shows weak ferromagnetism, whereas oxygen-annealed BBFO, in which mixed Fe valence seems to form, shows antiferromagnetism. The change of dielectric constant upon external magnetic field is larger for as-grown BBFO than that for oxygen-annealed BBFO, probably due to the weak ferromagnetism for the former.

## 2. Experiments

Polycrystalline Ba-doped BiFeO<sub>3</sub>, i.e., Bi<sub>0.75</sub>Ba<sub>0.25</sub>FeO<sub>3</sub> (BBFO) samples were prepared by the conventional solid state reaction method. High purity Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and BaCO<sub>3</sub> powders were thoroughly mixed and calcined at 850 °C for 24 h. After calcination, the powders were pressed into pellets and sintered at 875 °C for 36 h. Hereafter, we call the as-grown BBFO sintered sample as BBFO-AG. The BBFO-AG was annealed in the presence of oxygen at different temperatures varying from 650 to 850 °C. Hereafter, we call the annealed BBFO at different temperatures as BBFO-temperature.

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The phase and crystalline quality were characterized by X-ray diffraction (XRD) in a Phillips X'pert PRO MRD diffractometer using  $\text{Cu K}\alpha$  radiation. A vibrating sample magnetometer (VSM) option in a physical property measurement system (PPMS) was used to measure the magnetic hysteresis loops ( $M-H$ ) and temperature dependence magnetization curves ( $M-T$ ). Resistivity and ferroelectric hysteresis loops ( $P-E$ ) were measured by using a Keithley 236 source measure unit and a Sawyer-Tower circuit, respectively. The magnetic field dependent dielectric constant  $\Delta\varepsilon/\varepsilon = [(\varepsilon(H) - \varepsilon(0))/\varepsilon(0)]$  was obtained by the combination of a LCR meter and a superconducting magnet.

### 3. Results and discussion

Fig. 1 shows the XRD patterns of BBFO-AG and annealed BBFO at different temperatures. Main diffraction peaks of BBFO-AG are well-indexed by a rhombohedral structure like BFO. As the annealing temperature increases, the crystalline quality becomes better as evidenced by the narrow full width at half maximum (FWHM). However, impurity phases like  $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  start to appear for BBFO-650 and BBFO-750. At more elevated annealing temperature like BBFO-850, the impurities disappear again. This XRD result may imply that there are two stable BBFO phases with different oxygen contents and impurities form to compensate the charge of extra/deficient oxygen for BBFO at in-between the two stable phases.

Depending on the oxygen contents, the magnetic properties of BBFO are drastically modified. Fig. 2 shows the magnetic hysteresis loops ( $M-H$  curves) for BBFO at room temperature. All samples show quite small saturation magnetization, i.e.,  $< 1$  emu/g. However, clearly BBFO-AG shows a small hysteresis, whereas BBFO-850 shows a linear behavior without any hysteresis. On the other hand, the BBFO-650 shows a more clear and enhanced hysteresis loop. As evident from the XRD result in Fig. 1, the observed hysteresis loop for BBFO-650 should come from small amount of magnetic impurities like  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Fe}_2\text{O}_3$ .

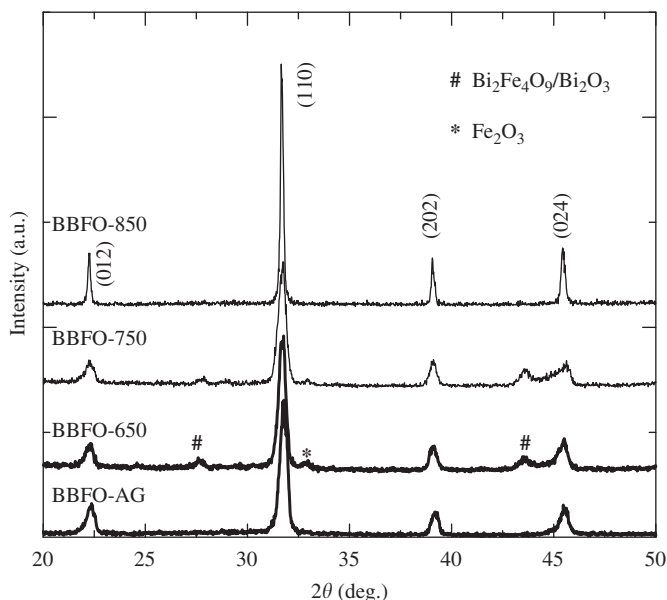


Fig. 1. XRD patterns of as-grown BBFO and annealed BBFO at different temperatures. The symbols of # and \* represent the impurity phase of  $\text{Bi}_2\text{Fe}_4\text{O}_9/\text{Bi}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , respectively.

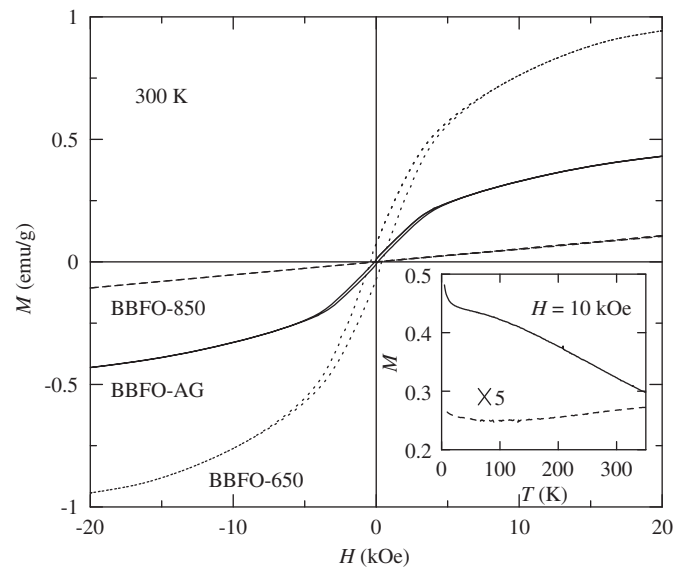


Fig. 2.  $M-H$  hysteresis loops of BBFO-AG (solid line), BBFO-650 (dot line) and BBFO-850 (dashed line) at 300 K. In the inset, we show the temperature dependent magnetization ( $M-T$ ) curves of BBFO-AG and BBFO-850. For clarity, the magnetization of BBFO-850 is multiplied by a factor of five.

To elucidate the magnetic properties of BBFO-AG and BBFO-850 in detail, we show the temperature dependent magnetization ( $M-T$  curves) in the inset of Fig. 2. The magnetization of BBFO-AG increases with lowering the temperature, whereas that of BBFO-850 slightly decreases with lowering the temperature. These  $M-H$  and  $M-T$  results clearly suggest that magnetic states for BBFO-AG and BBFO-850 should be ferromagnet and antiferromagnet, respectively. (Although we could not measure the Neel temperature of BBFO-850 to clearly confirm the antiferromagnetism due to the limited maximum temperature in our PPMS, i.e., 350 K, we can understand the  $M-T$  curves through the fact that the antiferromagnetically ordered spins are fluctuated by thermal energy, hence the increase of  $M$  with  $T$ .)

Previous Mössbauer spectroscopy results showed that oxygen vacancy rather than mixed Fe valence should be formed in as-grown divalent ion doped BFO [16]. When we anneal the as-grown divalent ion doped BFO in oxygen environment; however, mixed valence could be formed. Therefore, we can roughly consider that BBFO-AG should have  $\text{Fe}^{3+}$  with oxygen vacancy, and BBFO-850 should have  $\text{Fe}^{3+}$  and  $\text{Fe}^{4+}$  without oxygen vacancy (or very little oxygen vacancy).

Due to the ionic radius differences between  $\text{Ba}^{2+}$  (1.36 Å) and  $\text{Bi}^{3+}$  (1.17 Å) [17], the  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$  bond angle of BBFO-AG and the  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$  bond angle of BBFO-850 should be modified as compared with that of BFO. In addition, due to the ionic size difference between  $\text{Fe}^{3+}$  (0.65 Å) and  $\text{Fe}^{4+}$  (0.59 Å) [17], the bond distance for  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$  should be smaller than that for  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$ . The super-exchange interaction and reduced bond distance for  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{4+}$  will result in the antiferromagnetism in BBFO-850. Recent local spin-density approximation predicts that the weak ferromagnetism could be appeared in BFO with  $\text{Fe}^{3+}-\text{O}-\text{Fe}^{3+}$  bond, if the spiral antiferromagnetism is suppressed [9]. Since the spiral antiferromagnetism in BFO can be suppressed by local lattice distortion like oxygen vacancy as well as bond angle change [9], BBFO-AG seems to show weak ferromagnetism at room temperature.

Due to the existence of oxygen vacancy in BBFO-AG and mixed Fe valence in BBFO-850, both BBFO do not show any clear ferroelectricity. The inset of Fig. 3 shows the electric polarization

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