



Multiferroic properties and converse magnetoelectric effect in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ ceramics

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ABSTRACT

Multiferroic $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ was prepared by sol–gel method with the rapid thermal process. Ferroelectric and magnetic properties of the samples were studied at room temperature. The remanent polarization and magnetization of $\text{Bi}_{0.7}\text{Ca}_{0.3}\text{FeO}_3$ ceramics are $4 \mu\text{C}/\text{cm}^2$ and 0.153 emu/g , respectively. Moreover, converse magnetoelectric effect characterized as electric field-induced magnetization was investigated in $\text{Bi}_{0.7}\text{Ca}_{0.3}\text{FeO}_3$ ceramics.

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1. Introduction

BiFeO_3 (BFO) has been extensively investigated in the forms of bulk ceramics, single crystal and thin film owing to its high phase transition temperature and good multiferroic properties [1–5]. It is a G-type antiferromagnet with cycloidal spin magnetic structure permitting weak ferromagnetism [6]. The Bi 6s lone pair electrons are believed to be responsible for the ferroelectricity of BFO [5,7]. Actually, it is difficult to observe the ferroelectric loops in BFO ceramic due to the relatively high leakage current, which is caused by impurity and low resistivity [3]. Many methods have been attempted to enhance ferroelectric and magnetic properties in bulk BFO ceramic [3,8–15]. Among these alternatives, doping other cations in the A site of BFO ceramic is proved to be an effective way to enhance the magnetism [8,11–15]. The most used substituted ions are rare-earth trivalent ions (La^{3+} , Tb^{3+} , Nd^{3+} , etc.) [11,12] and diamagnetic bivalent ions (Ba^{2+} , Pb^{2+} , Ca^{2+} , etc.) [8,13–15]. It is reported that the value of magnetization in $\text{Bi}_{0.75}\text{Ba}_{0.25}\text{FeO}_3$ is up to 6 emu/g under $H = 15 \text{ kOe}$ [8]. In addition, the rapid thermal process (RTP) is reported to synthesize the single-phase BFO ceramic successfully, in which the spontaneous polarization is $8.9 \mu\text{C}/\text{cm}^2$ under the applied electric field of $100 \text{ kV}/\text{cm}$ [3].

The magnetoelectric (ME) coupling between magnetic and ferroelectric orders is an unique feature of multiferroic materials,

which is of great importance for physical mechanism and potential applications for next-generation devices [1,16]. The ME can be classified as direct magnetoelectric (DME) and converse magnetoelectric (CME), which are characterized as magnetic field-induced polarization and electric field-induced magnetization, respectively [17]. As it is reported, electrical control of antiferromagnetic domains [18] and electric field-induced spin flop [19] have been observed in BiFeO_3 thin film [18] and single crystal [19,20], respectively. As far as we know, there are few papers about the CME effect in doped BFO ceramics. Very recently, electric modulation of conduction and robust antiferromagnetism have been well studied in $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ (BCFO) film [21] and bulk ceramic [22], indicating that this material is of great potential for further investigation. In the present paper, we prepared single-phase BCFO samples and investigated their multiferroic properties and CME effect.

2. Experiment

Some $\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ ($x = 0.1$ and 0.3) (abbreviated to BCFO-1 and BCFO-3, respectively) fine powders were first prepared by sol–gel method. Then, the calcined powders without any organic compounds were pressed into a bar and sintered at $700\text{--}750^\circ\text{C}$ for 450 s with a high heating rate of about $100^\circ\text{C}/\text{s}$, then cooled rapidly to room temperature. The crystal structure of the samples was examined by X-ray diffraction (XRD). Capacitive structure with silver electrode was prepared for ferroelectric and CME effect measurements. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) (Lakeshore 7407) and ferroelectric properties of the samples were measured using a ferroelectric tester (Radiant Technology, USA). The CME measurement was performed by an induction method [23].

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3. Results and discussion

Fig. 1 shows the XRD patterns for BCFO ceramics. These samples have a single-phase perovskite structure with no trace of other impurity phases within the uncertainty of XRD. It is reported that both rapid sintering process and low synthesis temperature are beneficial to minimize Bi-loss and suppress the formation of impurity phases [3]. Compared with the XRD pattern of BFO ceramic, the doubly split peaks in the 2θ ranges of $31\text{--}33^\circ$ merge gradually to form a broad peak in these BCFO samples with the increasing doping content of Ca (as shown in the inset of Fig. 1), suggesting the structural distortion between the BCFO and BFO ceramics, which agrees with the results in Nd-doped BiFeO₃ [12].

The ferroelectric behavior for BCFO ceramics is presented in Fig. 2. Unlike the BCFO sample prepared by solid-state method [13,14], in which the ferroelectric loop is difficult to obtain due to the high leakage current, distinct hysteresis characteristics can be observed in these BCFO ceramics. Owing to the different breakdown fields for different samples, various drive fields are applied to the samples. For BCFO-1 and BCFO-3, the values of remnant polarization (P_r) were 0.8 and $4\ \mu\text{C}/\text{cm}^2$ at 5 and 26 kV/cm, respectively.

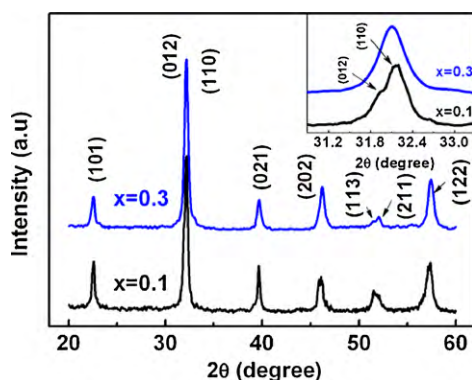


Fig. 1. The XRD patterns for BCFO ceramics.

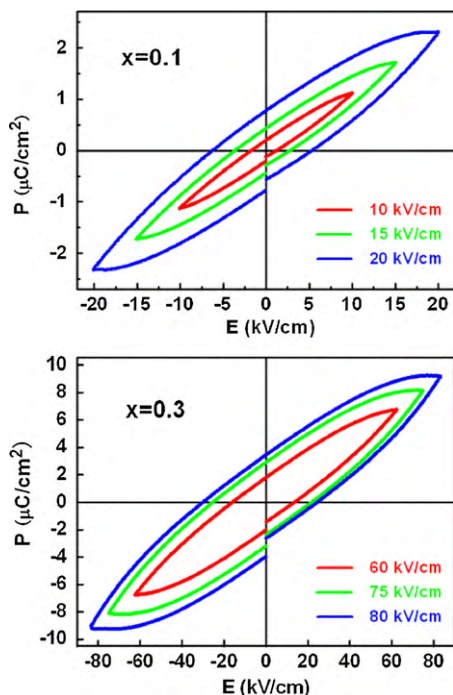


Fig. 2. The ferroelectric hysteresis loops for BCFO ceramics at room temperature.

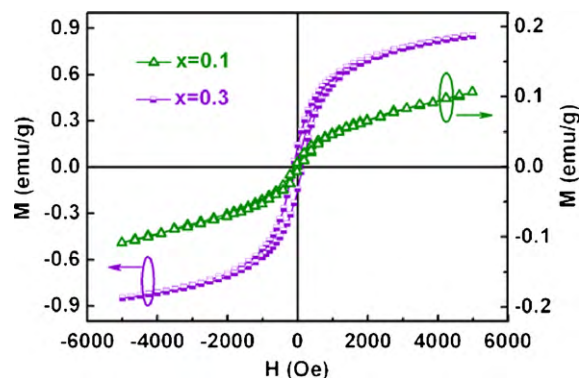


Fig. 3. The magnetic hysteresis loops for BCFO ceramics at room temperature.

The P_r value for BCFO-3 is larger than that of Ba doped BFO ceramics [8]. This result indicates that doping Ca²⁺ cation in BFO is helpful to enhance ferroelectricity and increase breakdown field. Actually, the resistivity values are up to 4×10^9 and $3 \times 10^{10}\ \Omega\ \text{cm}$ for BCFO-1 and BCFO-3, respectively, which is comparable with that of high-pressure prepared BFO ceramic [9]. It seems that the sol-gel with RTP preparing method is helpful for the high resistivity and suppression of the charged defects in our BCFO ceramics, which are responsible for the ferroelectric properties [3].

The magnetic hysteresis loops for BCFO ceramics at room temperature are shown in Fig. 3. Two well-developed M–H loops can be observed in the samples. The remnant magnetization (M_r) values are 0.007 and 0.153 emu/g, for $x=0.1$ and 0.3, respectively, which is much larger than these of BCFO ceramic prepared by solid-state reaction and some other doped BFO compounds [14,24]. As we know, the Fe magnetic moments in pure BFO are coupled ferromagnetically within the pseudocubic (111) planes and antiferromagnetically between adjacent planes, showing G-type antiferromagnetic order. If the magnetic moments are oriented perpendicular to the [111] direction, the symmetry also permits a canting of the antiferromagnetic sublattices, resulting in weak ferromagnetism [25]. Owing to charge compensation, doping bivalent cations (such as Ca²⁺, Pb²⁺, and Ba²⁺) would give rise to the formation of Fe⁴⁺ or oxygen vacancies [8,15]. As we know, the exchange interaction between Fe⁴⁺ and Fe³⁺ may result in net magnetization. But this possibility has been ruled out by the study of Mössbauer spectroscopy of bivalent cations doped BFO ceramics [15,24]. On the other hand, theoretical calculation has shown that the presence of oxygen vacancies would not affect the canting of the magnetic moments, and consequently no increase in the macroscopic magnetization due to oxygen vacancies could be found [26]. According to the recent work about the magnetic properties of A-site doped BFO ceramic, the weak ferromagnetism is proved to be attributed to the canting of the antiferromagnetic sublattices induced by structural distortion [8,11,13,15,27,28]. In the case of BCFO, the introduction of Ca²⁺ cations leads to the change of the structure, resulting in the suppression of the spiral spin structure and the appearance of the weak ferromagnetism [13,15,29,30].

For further understanding the coupling between electric and magnetic properties, the magnetoelectric effects in doped BFO are necessary to be studied. Here the CME effect of BCFO was investigated by measuring the induced magnetic induction (B_{induced}) in response to an applied ac voltage. The measurement scheme is shown in Fig. 4. The sample is polarized along thick direction and is placed in a dc magnetic field (H_{bias}). A sine voltage along the thickness direction is applied on the sample by a signal generator and the sign of ac B_{induced} is picked up by using a search double-coils according to the Faraday effect [23]. The longitudinal (transverse) B_{induced} was obtained as the polarization direction

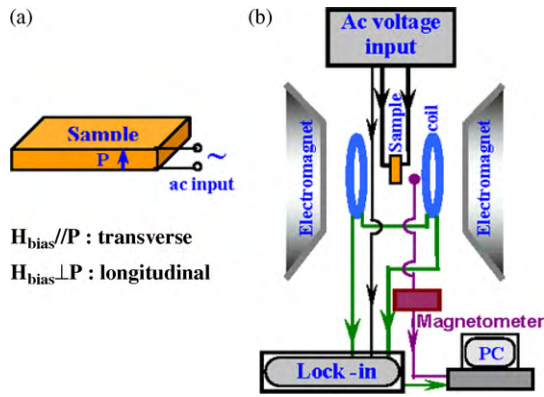


Fig. 4. The schematic illustration of (a) the directions of polarization and H_{bias} and (b) the measurements of CME effect.

was parallel (perpendicular) to B_{induced} . Since the ferroelectricity and magnetism of BFO (prepared in this work) and BCFO-1 are relatively weak, only CME effect of BCFO-3 is shown here. Fig. 5 presents H_{bias} dependence of B_{induced} in BCFO-3 at an optimized ac electric field of 160 V with $f=1.8$ kHz at room temperature. It is obvious that B_{induced} increases with increasing H_{bias} , showing a quadratic relationship. At 4.6 kOe, the values of longitudinal and transverse B_{induced} are 4.5 and 10.2 A/m and the corresponding CME coefficients ($\alpha = \mu_0 (\partial M / \partial E)_H$) are 2.83×10^{-11} and 6.47×10^{-11} s/m, respectively. The CME coupling strength α in BCFO-3 is about an order higher than that in Cr_2O_3 single crystal (4.1×10^{-12} s/m near the Neel temperature of 307 K) [31,32]. It seems that the difference between the two values of B_{induced} is attributed to the different demagnetization field in longitudinal and transverse direction [10].

Fig. 6 presents the applied ac voltage (V_{ac}) dependence of transverse B_{induced} in BCFO-3 with $H_{\text{bias}} = 2.5$ and 4.5 kOe at the frequency of 1.8 kHz at room temperature. It is obvious that B_{induced} responds almost linearly to applied ac voltage and the calculated CME coefficient α is determined to be 3.46×10^{-11} and 6.48×10^{-11} s/m for $H_{\text{bias}} = 2.5$ and 4.5 kOe, respectively. It is reported that the antiferromagnetic and ferroelectric parameters in BFO are intimately coupled and the coupling between these two orders is argued to be stronger in the bulk than in thin film [19]. When an ac electric field is applied on BCFO, an inner mechanical force (strain) is produced owing to the reverse piezoelectric effect, i.e., electric field induced the shift of ferroelectric domains. Owing to the coupling between antiferromagnetic and ferroelectric domains [18], the strain is then applied on the magnetic domains and generates the change of the magnetic moments due to the piezomagnetic effect [33].

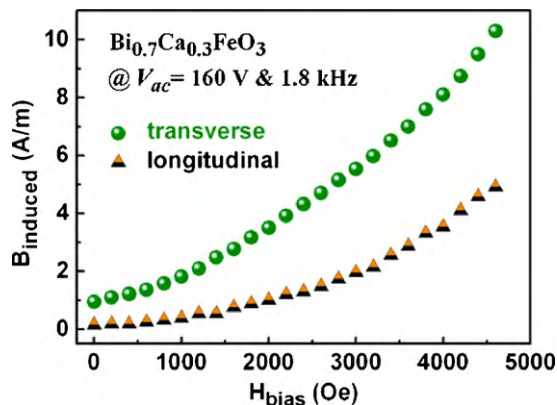


Fig. 5. The magnetic bias field (H_{bias}) dependence of the induced magnetic flux density (B_{induced}) in BCFO-3 ceramics at $V_{\text{ac}} = 160$ V.

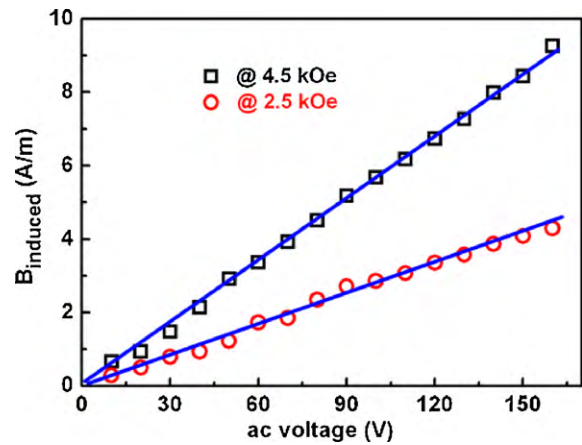


Fig. 6. The V_{ac} dependence of the transverse B_{induced} of BCFO-3 ceramics at $H_{\text{bias}} = 2.5$ and 4.5 kOe. The solid line is a guide to the eyes.

4. Conclusion

The multiferroic properties have been investigated in BCFO ceramics prepared by the sol-gel with RTP preparing method. The ferroelectric loops of these samples are observed at room temperature owing to high resistivity and suppression of the charged defects. The enhanced magnetic properties were attributed to the suppression of the space spin-modulated magnetic structure in BCFO ceramics. The CME effect of BCFO-3 ceramic has been investigated by measuring B_{induced} under different H_{bias} and ac electric field. The CME coefficient of BCFO-3 ceramic is 6.48×10^{-11} s/m, which is about an order higher than that in Cr_2O_3 single crystal.

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