The magnetoelectric coupling in rhombohedral–tetragonal phases coexisted Bi$_{0.84}$Ba$_{0.20}$FeO$_3$

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ABSTRACT

Ba doped Bi$_{1.04-x}$Ba$_x$FeO$_3$ ceramics with x up to 0.30 have been prepared by the tartaric acid modified sol–gel method. The X ray diffraction patterns show that the structure transforms from rhombohedral to tetragonal with increasing the Ba substitution concentration from 10% to 30% and the coexistence of distorted rhombohedral and tetragonal phases in 20% Ba substituted BiFeO$_3$, which was further confirmed by the Raman spectra. Bi$_{0.84}$Ba$_{0.20}$FeO$_3$ exhibits the highest magnetization (1.6 emu/g under magnetic field of 12 kOe) compared with the other samples of different Ba substitution concentration. Significant enhancement of the ferroelectricity has been observed in 20% and 30% Ba substituted BiFeO$_3$ with saturate polarization close to 6.6 μC/cm$^2$ for Bi$_{0.74}$Ba$_{0.30}$FeO$_3$. The magnetoelectric coupling of Bi$_{0.84}$Ba$_{0.20}$FeO$_3$ has been measured and the maximum decrease of magnetization under magnetic field of 9.8 kOe was about 0.06 emu/g with increasing applied electric field to 11 kV/cm, and the magnetoelectric coefficient is $1.5 \times 10^{-12}$ s/m.

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1. Introduction

Multiferroic materials have simultaneous ferroelectric and magnetic ordering, which enables a coupling interaction between them [1]. This coupling interaction, called the magnetoelectric (ME) effect, produces various possibilities for the realization of the mutual control between ferroelectric and magnetic ordering which opens the new opportunities in magnetic recording, spintronics, etc. [1]. Among the rare multiferroic materials, BiFeO$_3$ has received much attention due to that both the ferroelectric and magnetic ordering, which enables a coupling interaction between them, have received much attention due to the partial filled d orbital of Fe$^{3+}$ ion [3], thus the coupling between the ferroelectric and magnetic ordering is usually considered to be rather weak [4]. Furthermore, a cycloid spin structure with a period of about 62 nm in the BiFeO$_3$ cancels the net spins due to the small canting between the antiparallel aligned spins of the neighboring Fe$^{3+}$ ions, which averages the net macroscopic magnetization to zero and inhibits the observation of the linear ME effect [5].

Much work has been done to enhance the ferromagnetism to improve the ME effect in BiFeO$_3$. For example, with 20% Dy doping on Bi sites, sizable ME effect has been observed [6]. It has reported that Ba or other ions doping on Bi sites in BiFeO$_3$ can significantly enhance the magnetic moment of BiFeO$_3$ by suppressing the cycloid spin structure [1,7–11]. However, the ME effect has not yet been explored. In this paper, we prepared Bi$_{1.04-x}$Ba$_x$FeO$_3$ (x=0.10, 0.20, 0.30) ceramic samples and systematically studied the structural, magnetic, ferroelectric and ME properties.

2. Experimental

Bi$_{1.04-x}$Ba$_x$FeO$_3$ (x=0.10, 0.20, 0.30) ceramics were prepared by tartaric acid modified sol–gel technique [12]. Excess 0.04 Bi has been added to compensate the loss of Bi during the sample preparation. The starting materials were Bi(NO$_3$)$_3$, 5H$_2$O, Fe(NO$_3$)$_3$, 9H$_2$O, and Ba(NO$_3$)$_2$, 5H$_2$O, which were of analytical grade and used without further purification. Bi(NO$_3$)$_3$, 5H$_2$O, Fe(NO$_3$)$_3$, 9H$_2$O and Ba(NO$_3$)$_2$, 5H$_2$O were dissolved in distilled water in proper stoichiometric proportions. Tartaric acid was added to this solution and then heated at 150 °C to form a dry gel. The preheated powder was annealed at...
600 °C for 2 h. The obtained powders were grinded and pressed into 1 mm thick disks in diameter of 13 mm. The disks were directly put into an 850 °C (Bi0.74Ba0.30FeO3) and 800 °C (Bi0.98Ba0.10FeO3) oven and sintered in air for 30 min. Phase analysis of the samples and structural determination were performed by the powder X-ray diffraction (XRD) technique with Cu Kα radiation. Raman measurements were carried out on a Horiba Jobin Yvon LabRAM HR 800 micro-Raman spectrometer with 785 nm excitation source under air ambient condition at room temperature. The laser focused on the sample surface in diameter of 1 μm. Magnetic properties and the ME coupling analysis of Bi1.04- xBaFeO3 were measured using a vibrating sample magnetometer (VSM) at room temperature. Ferroelectric measurements were conducted using a Radiant Ferroelectric tester (Radiant Technologies, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of Bi1.04- xBaFeO3 ceramics samples at room temperature. No peak of impurity phases such as Bi2FeO4 or Bi25FeO39 can be observed, indicating the purity of our samples. In Fig. 1(a), the Bi0.98Ba0.10FeO3 diffraction peaks can be indexed to the rhombohedral (R3c) structure similar to BiFeO3. With increasing Ba substituting concentration, the diffraction peaks shift to the low angles, as can be seen clearly in the inset of Fig. 1, indicating the expansion of the lattice. This is due to the larger ion radius of Ba2+ (1.49 Å) than that of Bi3+ (1.17 Å) [13]. Furthermore, the peaks of (0 1 8), (2 1 4) and (3 0 0) merge to one peak, the peaks (0 0 6) and (2 0 2) merge to one peak, and the peak of (0 2 4) splits to two peaks. This is a clear indication of the transition from rhombohedral to tetragonal structure [14–17]. For Bi0.84Ba0.20FeO3, the diffraction peaks of (0 1 8), (2 1 4) and (3 0 0) merge to one peak, the peaks (0 0 6) and (2 0 2) merge to one peak, but the peak of (0 2 4) does not split to two peaks, especially the peak of (1 0 4) and (1 1 0) coalescence, indicating the coexistence of rhombohedral and tetragonal phases which induce strong lattice distortions.

Raman spectroscopy is sensitive to the symmetry of crystalline structures and is thus used to study the structural transition of Bi1.04- xBaFeO3 with increasing Ba substitution concentration [15]. As shown in Fig. 2, there are seven modes observed in the spectrum of Bi0.94Ba0.10FeO3 at 73, 137, 166, 220, 260, 480 and 625 cm−1, which are the typical vibration modes of E1-1, E1-2, A1-3, E7, E9 and E-7 and E-9 modes for BiFeO3 with R3c structure, respectively [8]. With further increasing Ba substitution concentration, it is found that the intensity of A1-2 mode decreases with increasing Ba concentration, and A1-1 and A1-2 finally merges together in Bi0.74Ba0.30FeO3, indicating the transition to the tetragonal phase [18]. A new mode at around 270 cm−1, when x = 0.30, further suggests the structural transition from rhombohedral to tetragonal [15]. The A1-1 mode shifts to 145 cm−1 and almost merge together with A1-2 for Bi0.84Ba0.20FeO3, implying the coexistence of rhombohedral and tetragonal phases. Thus the Raman results clearly confirm the structural transition from rhombohedral to tetragonal with x = 0.10 to 0.30 and the phase coexistence in Bi0.84Ba0.20FeO3, determined from the XRD patterns. It should be noted that two strong and wide peaks can be observed at about 490 cm−1 and 640 cm−1, which have been assigned to the Jahn–Teller distortion of FeO6 octahedra [18]. This is in contrast to the recent report that these two modes were only observed with Mn substitution on Fe sites but cannot be observed in Ca substitution on Bi sites [18]. This might be due to much larger ion radius of Ba2+ (1.49 Å) than that of Bi3+ (1.17 Å) and Ca2+ (1.14 Å) [13], which needs further study.

Fig. 3 shows the M–H hysteresis loops of Bi1.04- xBaFeO3 at room temperature. Bi0.94Ba0.10FeO3 exhibits weak ferromagnetism with magnetization at 10 kOe is about 0.05 emu/g, which is comparable to that of the pure BiFeO3 prepared under similar conditions [19]. This can be understood since Bi0.94Ba0.10FeO3 is in R3c structure, the cycloidal spin structure cancels the net spin due to the small canting between antiparallel aligned spins of neighboring Fe3+ ions [5,20]. A drastic increase of the ferromagnetism has been observed in Bi0.84Ba0.20FeO3. Clear magnetic hysteresis loop can be observed with magnetization of about 1.6 emu/g under magnetic field of 12 kOe, which is about 2 orders larger than that of Bi0.59Ba0.40FeO3. With further increasing x, the magnetization drastically drops to 0.35 emu/g, though the magnetic hysteresis loop can still be observed.

The drastic enhancement of the magnetization for Bi0.84Ba0.20FeO3 is due to the coexistence of two phase (rhombohedral and tetragonal), and the strong lattice distortion in the R3c phase,
which may suppress the cycloidal spin structure, and enhance the magnetization [2]. Compared with the previous study on the magnetic properties of Ba substituted BiFeO$_3$ [7,21], two distinct features in our samples can be observed. In our case, the Bi$_{0.84}$Ba$_{0.20}$FeO$_3$ exhibits the highest magnetization and the magnetization of Bi$_{1.04}$Ba$_{0.30}$FeO$_3$ drops abruptly. However, in the previous report, a continuous increase of magnetization with increasing Ba substitution concentration up to 0.30 which is in tetragonal structure has been observed [7,21]. The second is that the coercivity of our samples is much smaller than that in the previous reports [7,21,22]. Ba$^{2+}$ is nonmagnetic ions, and no extra exchange interaction will be induced by Ba$^{2+}$ substitution. Furthermore, the perovskite in tetragonal structure tends to have collinear antiferromagnetic spin structure, like BiCoO$_3$ [23]. And also recent neutron powder diffraction studies on xBiFeO$_3$–(1–x)PbTiO$_3$ show the collinear antiferromagnetic ordering when the sample is in the tetragonal structure [24,25]. With increasing Ba substitution to 0.30, the structure has changed to tetragonal structure, and the sudden drop of the magnetization can be explained by the collinear antiferromagnetic ordering. The remaining magnetization might be due the small portion of the residual lattice distorted R3c phase in Bi$_{1.04}$Ba$_{0.30}$FeO$_3$. And also in our case, the excess 0.04 Bi addition during sample preparation may compensate the Bi loss, and prevent the formation of Ba ferrites. This needs more experiments for further clarification.

Though large polarization has been reported in BiFeO$_3$ [26–28], the large leakage is still main obstacles to observe the clear ferroelectric hysteresis loop, especially in the bulk ceramics. As can be seen in Fig. 4, in Bi$_{0.94}$Ba$_{0.10}$FeO$_3$, the leakage is so large that the electric field can only be applied up to 10 kV/cm. And the loop has a rounded shape, which is due to the leakage current [14]. The leaky features of these bulk samples can be related to anion vacancies or valence fluctuation of the transition metal ion leading to electronic conduction [22]. With increasing Ba substitution concentration, the leakage current was significantly suppressed and much higher electric field of more than 50 kV/cm can be applied. And also the ferroelectric hysteresis show much better shape, instead of the round shape for Bi$_{0.94}$Ba$_{0.10}$FeO$_3$. The values of the saturate polarization $P_s$ for Bi$_{1.04}$Ba$_{0.30}$FeO$_3$ are 2 $\mu$C/cm$^2$ ($x=0.10$), 5.6 $\mu$C/cm$^2$ ($x=0.20$) and 6.6 $\mu$C/cm$^2$ ($x=0.30$). Our Mössbauer spectroscopy study has clearly confirmed the only Fe$^{3+}$ in Sr-doped BiFeO$_3$ with Sr doping concentration up to 0.3 [29]. Thus, the suppression of the leakage current and improvement of the ferroelectric properties might be related to the structural modification by Ba doping. Recently, Zhang has experimentally confirmed the polarization of 150 $\mu$C/cm$^2$ for tetragonal BiFeO$_3$, which is much higher than that of 60 $\mu$C/cm$^2$ for (0 0 1) oriented rhombohedral BiFeO$_3$ film [30]. We believe that the enhancement of the polarization with increasing Ba substitution concentration might be related to increasing concentration of the tetragonal phase.

Recent calculation further indicated that the significant contribution to the ferroelectric polarization from Fe$^{3+}$ ions (22 $\mu$C/cm$^2$ from the totally 88 $\mu$C/cm$^2$ for rhombohedral BiFeO$_3$, and 55 $\mu$C/cm$^2$ from 135 $\mu$C/cm$^2$ for tetragonal BiFeO$_3$) [30]. With the excellent magnetic and ferroelectric properties of Bi$_{1.04}$Ba$_{0.30}$FeO$_3$, an improved ME effect is expected, similar to Dy substituted Bi$_{0.7}$Dy$_{0.3}$FeO$_3$ [31]. We adopted the static method, which is the magnetization response on the applied dc electric field. Fig. 5 shows the magnetic hysteresis loops of Bi$_{1.04}$Ba$_{0.30}$FeO$_3$ under different applied electric field. The electric field was applied perpendicular to sample plate, while the magnetic field was applied parallel to the sample plate. Apparently, the magnetization decreases with increasing applied electric field, similar to the recent report on Bi$_{0.95}$Sm$_{0.10}$Fe$_{0.95}$Co$_{0.05}$O$_3$ [32]. The magnetization decreases with increasing
4. Conclusion

Pure phase Ba substituted Bi$_{1.04-x}$Ba$_x$FeO$_3$ have been prepared by tartaric acid modified sol–gel method. With increasing $x$, the structure changed from rhombohedral ($x=0.10$) to tetragonal ($x=0.30$), and the rhombohedral and tetragonal phases coexist in Bi$_{0.84}$Ba$_{0.20}$FeO$_3$, which was confirmed by the XRD and Raman measurements. A drastic enhancement of magnetization was observed with increasing $x$ from 0.10 to 0.20, and drops abruptly with further increasing $x$ to 0.30. The enhancement of magnetization was attributed to the strong lattice distortion which suppresses the cycloidal spin structure, while the decrease of magnetization with further increasing $x$ to 0.30 was attributed to the collinear antiferromagnetic spin structure in tetragonal structure. The ferroelectricity was significantly improved by substitution Ba to $x=0.20$ and 0.30. Clear converse ME coupling of $1.5 \times 10^{-12}$ s/m was found in Bi$_{0.84}$Ba$_{0.20}$FeO$_3$, which was attributed to simultaneous improvement of magnetic and ferroelectric properties.

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