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Short communication

Multiferroic and piezoelectric properties of $0.65BiFeO_3–0.35BaTiO_3$ ceramic with pseudo-cubic symmetry

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Abstract

Perovskite solid solution ceramic of $0.65BiFeO_3–0.35BaTiO_3$ (0.65BF–0.35BT) with high resistivity was prepared by conventional solid-state reaction method. At room temperature, the XRD pattern of the ceramic could be indexed as pseudo-cubic symmetry. The ceramic displays a typical ferroelectric loop, with remnant polarization P_r of 30.6 μC/cm^2. The piezoelectric coefficient d_{33} is 104 pC/N. The temperature dependence of dielectric constant $\varepsilon(T)$ exhibits a broad anomaly, with the temperature T_m for maximum dielectric constant ε_m of 414 °C at 1 MHz. The ceramic shows ferrimagnetism at room temperature, with remnant magnetization M_r of 0.07 emu/g and ferrimagnetic transition temperature T_N of ~420 °C, respectively. The appearance of pseudo-cubic phase was supposed to be related to the suppression of rhombohedral distortion by Ba ions.
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Keywords: C. Dielectric properties; C. Magnetic properties; Ferroelectrics; Structure

1. Introduction

Perovskite $BiFeO_3$ is the best candidate for multiferroic materials due to its high antiferromagnetic Neel temperature ($T_N = 370$ °C) and ferroelectric Curie temperatures ($T_c = 825$ °C) [1,2]. To achieve strong magnetoelectric coefficients, large ferroelectric and ferromagnetic ordering parameters could be requested [3]. However, the difficulty of the synthesis for high-quality $BiFeO_3$ ceramic with single phase and low leakage current hinders the observation of large polarization [4]. Besides, the $BiFeO_3$ ceramic does not show macro-magnetization at room temperature [5].

Chemical substitution is an effective way to increase the resistivity and enhance magnetic property in $BiFeO_3$ based ceramics simultaneously [6–8]. $(1 - x)BiFeO_3–xBaTiO_3$ ($(1 - x)$BF–xBT) solid solution ceramics are intensively researched for this purpose [9–13]. At room temperature, $(1 - x)$BF–xBT undergoes phase transitions from rhombohedral ($x = 0–0.33$) to cubic ($x = 0.33–0.925$), and to tetragonal ($x = 0.925–1$) [9]. The enhancement of magnetic property has been confirmed [10–12].

Still, the lack of good dielectric and ferroelectric data for $(1 - x)$BF–xBT solid solution ceramics prevented researchers from understanding the relative properties. For example, there is not an agreement toward the structure of the solid solutions with the content of $BaTiO_3$ more than 33 mole% [9,11,13]. To understand the intrinsic dielectric and ferroelectric properties, $(1 - x)$BF–xBT solid solution ceramics with good insulation must be supplied. Recently, we successfully synthesized $(1 - x)$BF–xBT ($x = 0.20–0.40$) ceramics with high resistivity, ferroelectric loops were observed for all the compositions. In this paper, we mainly report our investigation on 0.65BF–0.35BT ceramic with pseudo-cubic phase, which shows both large polarization and weak magnetization at room temperature.

2. Experimental

0.65BF–0.35BT ceramic samples were prepared by mixed oxide method. The starting reagents of Bi_2O_3, Fe_2O_3, $BaCO_3$, TiO_2 were carefully weighed in stoichiometric proportion and wet mixed thoroughly by ball milling for 10 h. After drying, the mixture was presintered at 800 °C for 2 h in a covered corundum crucible to prevent the volatilization of bismuth oxide. The presintered powder was ball milled and dried. Pellets with 12 mm in diameter and 1–2 mm in thickness were

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pressed using 10% polyvinyl alcohol binder. The pellets were sintered in a covered corundum crucible at 1050 °C for 3 h.

Crystal structure was examined by an X-ray diffractometer (XRD, Bruker AXS D8 ADVAMDMCE, German) at room temperature. The dc resistivity was measured by high resistance meter. To measure the ferroelectric hysteresis loop, a sinusoidal signal of 10 Hz, generated by a personal computer with a PCI6221 Data Acquisition (DAQ) card, was amplified through a Trek 610E high-voltage supply/amplifier/controller and applied to the sample. Current through the sample was collected by the DAQ card, and converted to a digital signal. The ferroelectric hysteresis loop was obtained through charge integration. The sample was poled in an oil bath at room temperature for 10 min. The piezoelectric coefficient constant d_{33} was measured by a Berlincount (ZJ-3, China) d_{33} meter. The planar electromechanical coupling factor k_p was calculated based on the resonance method using an impedance analyzer (Wayne Kerr 6500B, England). The dielectric measurement was accomplished on an automated system, within a temperature control sample chamber and an Agilent 4284A LCR meter were controlled by a personal computer. The magnetic hysteresis loop and temperature dependence of magnetization M under 0.4 T were measured using Vibrating Sample Magnetometer (VSM, Lakeshore7300, USA).

3. Results and discussion

Fig. 1a shows the XRD pattern for 0.65BF–0.35BT ceramic at room temperature. The ceramic exhibits a pure perovskite structure without the observation of impurity phase such as $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ [14]. Besides, no peak splitting of (1 1 1) pseudo-cubic reflection for symbol of rhombohedral symmetry, or of (2 0 0) for tetragonal symmetry was detected, as shown in Fig. 1b. It seems that the reflection peaks of 0.65BF–0.35BT ceramic could be indexed as cubic symmetry. SEM micrograph of fracture surface of 0.65BF–0.35BT ceramic is shown in Fig. 1c. The ceramic has dense and homogeneous microstructure, and the grain size is in the range of 4–7 μm.

High resistivity of pure $BiFeO_3$ ceramic synthesized by conventional solid-state reaction is usually difficult. The low resistivity could be ascribed to the mix valance of Fe ions and O vacancies, which is easy to induce large leakage current and unfavorable for the observation of saturated polarization [4]. For 0.65BF–0.35BT ceramic, the order of the magnitude for resistivity ρ_{dc} is about 10^{10} Ω cm under dc field of 10 kV/cm. That is, the co-substitution of Bi^{3+} and Fe^{3+} ions using Ba^{2+} and Ti^{4+} ions could enhance resistivity effectively.

Fig. 2 plots loops of polarization current density j and the corresponding polarization P versus electric field E under different ac maximum electric field E_m for 0.65BF–0.35BT ceramic at room temperature. The polarization current shows an abrupt increase and $j(E)$ charge peak appears when E_m increases from 10 kV/cm to 20 kV/cm, which indicates the reversion of the ferroelectric domains for 0.65BF–0.35BT. The remnant polarization P_r and coercive field E_c are both dependent on the E_m. Under E_m of 50 kV/cm, P_r and E_c are 30.6 μC/cm^2 and 27.9 kV/cm, respectively. The value of P_r for 0.65BF–0.35BT ceramic is very large in $BiFeO_3$ based ceramics, which is comparable to that for BF–BT solutions reported by Ozaki et al. [13].

The poling field E_p dependence of the piezoelectric coefficient constant d_{33} for 0.65BF–0.35BT ceramic is plotted in Fig. 3. d_{33} increases quickly with the dc poling field E_p larger

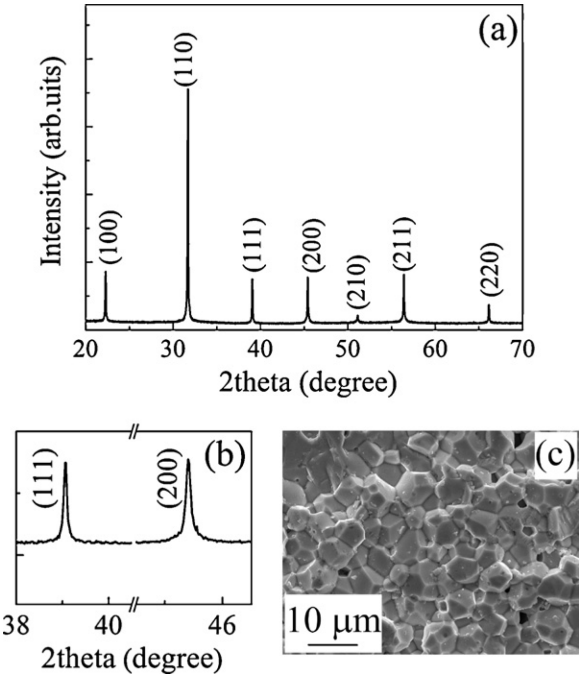

Fig. 1. (a) XRD pattern for 0.65BF–0.35BT ceramic at room temperature, (b) the magnified pattern for (1 1 1) and (2 0 0) pseudo cubic reflections, (c) SEM micrograph of fracture surface of 0.65BF–0.35BT ceramic.

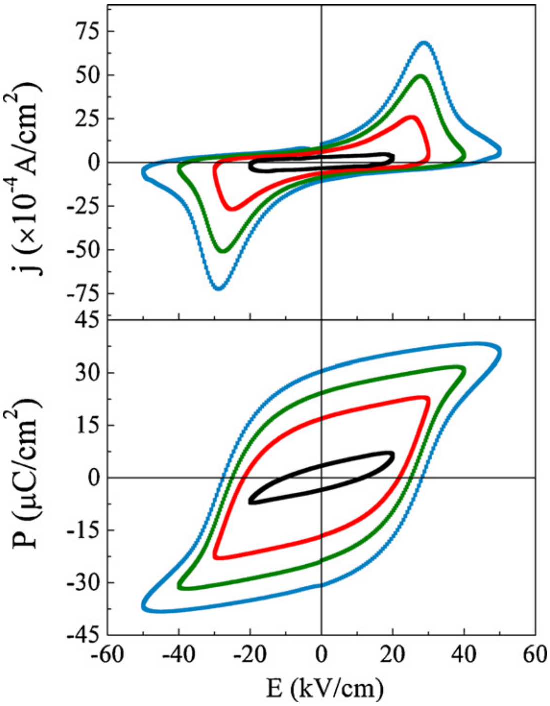

Fig. 2. Loops of polarization current j and polarization P versus external electric field E for 0.65BF–0.35BT ceramic.

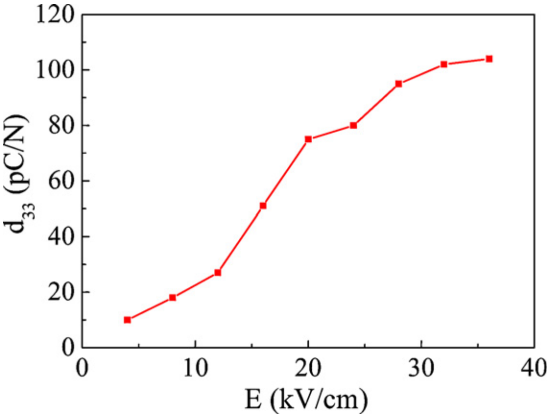

Fig. 3. The poling field E_p dependence of the piezoelectric coefficient constant d_{33} for 0.65BF–0.35BT ceramic.

than 12 kV/cm. After poled under E_p of 36 kV/cm, d_{33} increases to 104 pC/N. The planar electromechanical coupling factor k_p is about 0.19. The ceramic shows a remarkable piezoelectric enhancement compared with pure $BiFeO_3$ (26 pC/N) [15].

Temperature dependences of dielectric constant ε and dielectric loss tan δ at various frequencies for 0.65BF–0.35BT ceramic are shown in Fig. 4. The dielectric constant ε and dielectric loss tan δ at 1 kHz and 20 °C are 722 and 0.09, respectively. The ε(T) curves of 0.65BF–0.35BT ceramic show relaxation behavior. With frequency increasing from 1 kHz to 1 MHz, maximum ε_m decreases from 28,700 to 20,800 and the temperature of ε_m shifts from 386 °C to 414 °C, respectively.

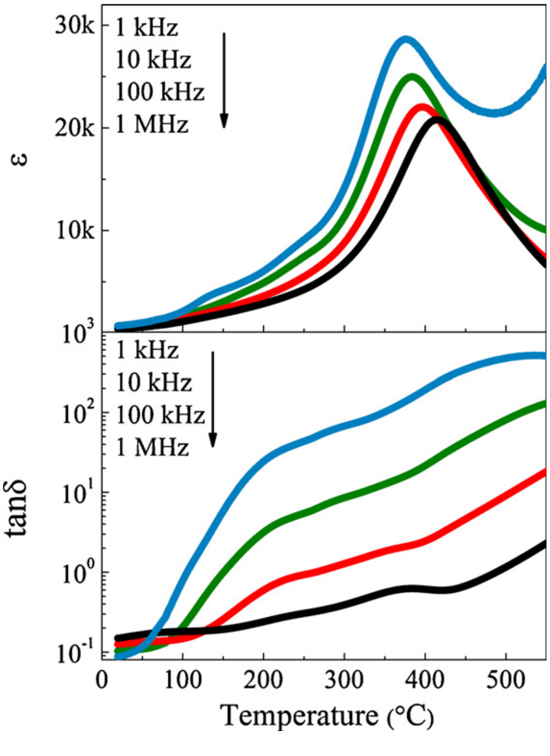

Fig. 4. Temperature dependences of dielectric constant ε and dielectric loss tan δ at various frequencies for 0.65BF–0.35BT ceramic.

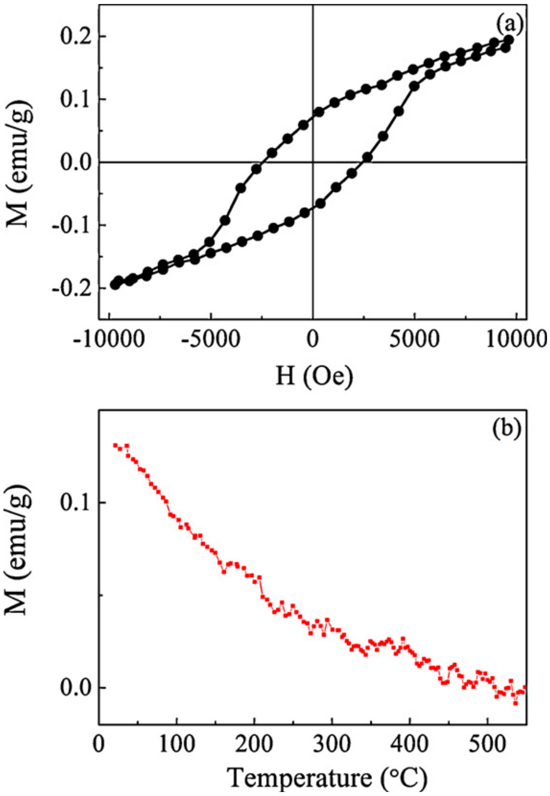

Fig. 5. (a) Loop of magnetization M versus magnetic field H at room temperature and (b) temperature dependence of M for 0.65BF–0.35BT ceramic.

The ferroelectric loop and the dielectric anomaly around T_m of 0.65BF–0.35BT ceramic indicate that the XRD reflection peaks could be indexed as pseudo cubic symmetry rather than cubic symmetry. The appearance of pseudo-cubic phase for $(1-x)$BF–xBT solid solutions is distinct to the structure evolution for $(1-x)BiFeO_3$–$xPbTiO_3$ ($(1-x)$BF–xPT) solid solutions, which show a morphotropic phase boundary (MPB) region when $x = 0.17$–0.31, with the coexistence of rhombohedral and tetragonal phases [16]. The differences are focused on the substituted ions in the A-site, with Ba^{2+} ions for BF–xBT and Pb^{2+} ions for BF–xPT. Ba^{2+} and Pb^{2+} ions are both larger than Bi^{2+} ions, which is suspected to be helpful to stable $BiFeO_3$ phase [14]. However, Pb^{2+} ions are ferroelectric active [17]. Even the content of $PbTiO_3$ is less than 35 mole%, $(1-x)$BF–xPT could have large tetragonal distortions [16]. The experimental and theoretical evidence demonstrates the hybridization between (Bi,Pb)(6s,6p) and O(2p) orbitals [18]. Contrarily, Ba^{2+} ions are not ferroelectric active, the tetragonal distortions for $BaTiO_3$ are mainly related to Ti^{4+} ions [17]. The Ba^{2+} ions in the A-site could suppress the rhombohedral distortions due to the large radius and induce the appearance of pseudo-cubic phase. The pseudo-cubic phase might appear in two situations: (1) the small rhombohedral distortion like $Pb(Zn_{1/3}Nb_{2/3})O_3$ [19], (2) the coexistence of rhombohedral and cubic phases [13].

The magnetic field H dependence of magnetization M for 0.65BF–0.35BT ceramic is plotted in Fig. 5a. The ferromagnetic hysteresis loop suggests the ferrimagnetic ordering in 0.65BF–0.35BT ceramic. The remnant magnetization M_r and coercive field H_c are 0.07 emu/g and 2.4 kOe, respectively. Our magnetic result is different to the research by Kumar et al. [10], but is consistent with the study by Kim et al. [11]. The enhancement mechanism of magnetic property in $(1-x)$BF–xBT is complicate. Both the structure moderation by Ba^{2+} ions and the influence on the Fe^{3+} spins arrangement by part of Ti^{4+} ions could be helpful to introduce weak magnetization [10]. However, the structure and the arrangement of B-site ions are both sensitive to the composition inhomogeneity due to different thermal processing. That may be one reason for the different reported M_r of $(1-x)$BF–xBT solid solution even in the same composition [10–12].

Fig. 5b shows the temperature dependence of M. $M(T)$ curve shows a gradual decrease with increasing temperature. Due to the rather weak magnetization and the complicate chemical compositions, no sharp decrease of M around ferrimagnetic transition Neel temperature T_N is observed for 0.65BF–0.35BT ceramic. The temperature at which M is about zero is around 420 °C, which could be taken as T_N. Interestingly, T_N for 0.65BF–0.35BT ceramic is rather close to its T_m.

4. Conclusion

0.65BF–0.35BT ceramic with high resistivity was successfully synthesized by solid-state reaction method. The symmetry of the ceramic could be indexed as pseudo-cubic. The ceramic shows the coexistence of ferroelectric, piezoelectric and ferrimagnetic properties. The temperature dependence of dielectric property indicates its relaxation behavior.

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