Multiferroic properties of $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics prepared by spark plasma sintering

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Multiferroic properties of $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics prepared by spark plasma sintering

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Dense $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics were prepared by spark plasma sintering. The sample showed stable dielectric constant and low dielectric loss (~5%), and a saturation ferroelectric loop with remnant polarization of 17 $\mu C/cm^2$ and saturation polarization of 19 $\mu C/cm^2$, as well as good ferromagnetism with saturation magnetization of 0.71 emu/g, at room temperature. After the sample was poled, its piezoelectric constant was measured as 12.8 pC/N, and, in particular, an obvious magnetoelectric coupling was observed. © *2007 American Institute of Physics*.

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Multiferroic magnetoelectric (ME) materials have simultaneous ferroelectric and magnetic orders.[1] In these multiferroic materials, the coupling interaction between ferroelectric and magnetic orders produces ME effect, including the direct ME effect (i.e., the appearance of an electric polarization or voltage upon applying a magnetic field) and reverse ME effect (i.e., the appearance of magnetization upon applying an electric field). ME materials have great potential for practical applications in data storage, sensors, and so on.[1] Aside from the potential applications, the fundamental physics of multiferroic ME materials is rich and fascinating. In single-phase multiferroics, $BiFeO_3$ is the most interesting compound because of its high phase transition temperatures (i.e., Curie temperature of ~1083 K, and Néel temperature of ~657 K).[2]

$BiFeO_3$ is known to have a rhombohedrally distord perovskite structure assigned to the space group $R3c$. The magnetic structure of $BiFeO_3$ is antiferromagnetic with G-type magnetic ordering, which is modified by subjecting it to a long-range modulation in a cycloidal spiral of $\lambda = 620$ Å length with [110] as the spiral propagation direction and spin rotation within (110).[3] $BiFeO_3$ only shows weak ferromagnetism. At the same time, the research on ferroelectric properties of $BiFeO_3$ was cumbered because the valence fluctuation of iron ions (from 3+ to 2+) and defects lead to leakage problem. All these make the study of the ME behavior of $BiFeO_3$ rare.

The fabrication of $BiFeO_3$ film[4] could greatly enhance ferroelectric and ferromagnetic properties of BiFeO, but it is still very hard to directly measure the ME effect in this system. Recently, rapid liquid sintering[5] has been used for the fabrication of $BiFeO_3$ ceramics with good ferroelectricity, and also the doping of various elements [e.g., Ba,[6] Nd,[7] La,[8] Tb (Ref. 9)] has been used to improve the ferromagnetism of $BiFeO_3$. Some magnetoelectric behaviors were found. For example, it was reported that the dielectric constant ε of $Bi_{0.75}Ba_{0.25}FeO_3$ increases with increasing applied magnetic field, i.e., $\Delta\varepsilon = [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0) = 1\%$ (a positive magnetodielectric coefficient) at 300 K and 0.8 T.[6] Similarly, Palkar *et al.*[10] reported an increasing dielectric constant and polarization with the magnetic field in $Bi_{0.9-x}Tb_xLa_{0.1}FeO_3$ ceramics. The origin of these magnetoelectric behaviors was not given clearly then, which may be prone to misinterpretation if a leakage current exists in these samples.[11] Kamba *et al.*[12] observed a slow temporal relaxation of the capacitance and conductance in $BiFeO_3$ ceramics prepared by rapid liquid sintering and proposed that this kind of magnetoelectric behavior is not caused by a coupling of polarization and magnetization as expected. Instead, it is caused by a combination of the magnetoresistance and Maxwell-Wagner polarization effect, which is called an improper magnetodielectric effect.[11]

In our previous work, $Bi_{0.95-x}La_{0.05}Tb_xFeO_3$ ceramics were prepared by hot-press sintering method,[9] and the results showed that $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics had better ferromagnetic and ferroelectric properties simultaneously. However, the relative density of the ceramics is a bit low (~90%). In this work, we report highly dense $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ (BLTFO) ceramics prepared by spark plasma sintering. Its high insulation rules out the improper magnetodielectric effect,[11] and thus a direct magnetoelectric effect is firsthand measured in this $BiFeO_3$-based ceramics.

$Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ precursor powders were prepared by a modified Pechini method.[13] $Fe(NO_3)_39H_2O$, $La(NO_3)_36H_2O$, $Tb(NO_3)_36H_2O$, and citric acid ($C_6H_8O_7$) were used as starting materials. Powders rapidly calcined at 860 °C for 3 min were proved to be a well-crystallized single $BiFeO_3$ phase with a D8-Advanced x-ray diffractometer.[9] The powders were firstly pressed to the pellet with the diameter of 12 mm and thickness of 1.5 mm under 60 MPa. Then the pellet was compacted in a cylindrical graphite die. The sintering process was accomplished in

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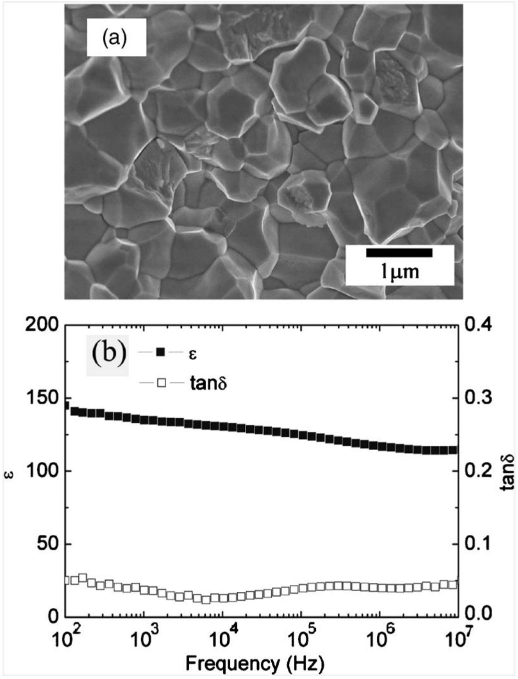

FIG. 1. (a) Typical SEM micrograph of the fractured surface and (b) frequency dependence of the dielectric constant ε and loss tan δ of the $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics.

the spark plasma sintering apparatus (SPS-1050). The samples were sintered at 750 °C for 10 min under a uniaxial pressure of 50 MPa. The relative bulk density of the BLTFO ceramic was measured as 99.9% according to Archimedes' principle. The scanning electron microscopy (SEM) observation of the fractured surface of the ceramic sample clearly demonstrates such highly dense ceramics with fine microstructure, as shown in Fig. 1(a).

For electrical measurements, the samples with a thickness of 0.2 mm were electroded by a silver paint. Dielectric measurement was performed by using Agilent HP4194A and ferroelectric loop measurement at 20 Hz was done by using a RT6000VHS ferroelectric test system with the fast mode (50 ms). All electric measurements were performed at room temperature. Magnetization measurement was carried out by using superconducting quantum interference device (MPMS-7).

As shown in Fig. 1(b), the dense BLTFO ceramics [Fig. 1(a)] exhibit a stable dielectric constant (~120–140) and, in particular, quite low dielectric loss (~5%) in the measured frequency range, which indicates high insulation and no Maxwell-Wagner polarization effect in the sample. Different from the previous report[6] that $\Delta\varepsilon$ of $BiFeO_3$-based system is positive (about 1%) due to the Maxwell-Wagner polarization effect, similar to the magnetoresistance materials (for example, $LaCaMnO_3$), our measurement shows that the dielectric constant of the BLTFO ceramic slightly decreases with the applied magnetic bias and $\Delta\varepsilon$ is about −0.5% at 0.6 T, which is larger than that observed in some other single-phase multiferroics[14,15] at phase transition temperature [e.g., $\Delta\varepsilon = 0.1\%$ for $BiMnO_3$ under 0.6 T at 100 K (Ref. 14)].

Figure 2 shows the ferroelectric hysteresis loop of the BLTFO ceramics at different applied fields. The remnant polarization of the BLTFO ceramics is measured as $2P_r = 3.8$, 7.4, 16, and 34 $\mu C/cm^2$ at an applied field of 120, 140, 160, and 180 kV/cm, respectively. A good saturation ferroelectric loop is observed at 180 kV/cm, and the coercive field of the BLTFO is about 180 kV/cm. Thus $P_r = 17$ $\mu C/cm^2$ and a saturation polarization $P_s = 19$ $\mu C/cm^2$ are measured at 20 Hz for the BLTFO ceramics.

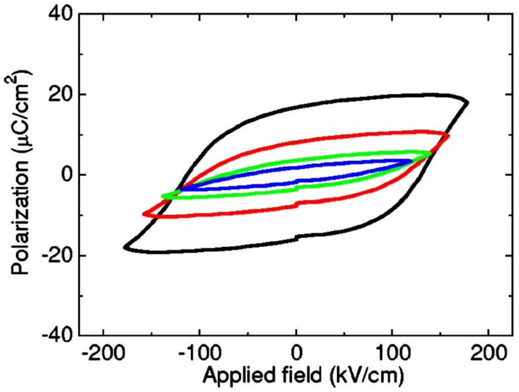

FIG. 2. (Color online) Ferroelectric loops of the $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics.

$BiFeO_3$ is *G*-type antiferromagnetic, and the magnetization for pure $BiFeO_3$ is small and varies linearly with the field. This magnetic structure may be collapsed by Tb element doping.[9] Figure 3 shows the ferromagnetic loop of the BLTFO ceramics. As seen from Fig. 3(a), an enhancement in magnetization can be observed, and M_s of the BLTFO ceramics is 0.71 emu/g at 300 K. Since Néel temperature (T_N) for $BiFeO_3$ system is above room temperature (380 °C), at lower temperatures no transition is expected in the *M-T* curves and the magnetization of the BLTFO decreases slowly with increasing temperature, as shown in Fig. 3(b).

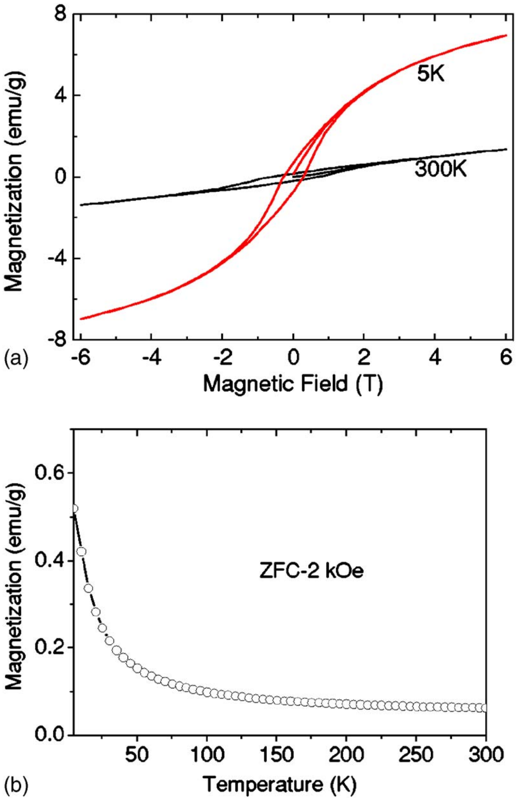

FIG. 3. (Color online) (a) Ferromagnetic loops at 5 and 300 K and (b) temperature dependent magnetization for the $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics.

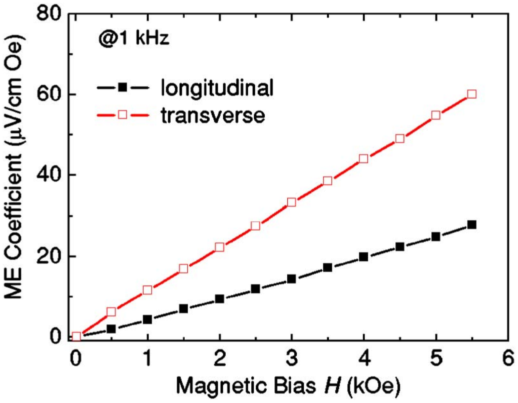

FIG. 4. (Color online) Bias magnetic field H dependence of the longitudinal and transverse ME voltage coefficients for the $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$.

To study the piezoelectric and ME properties, the BLTFO ceramics were polarized by using a dc electric field of 40 kV/cm for 20 min at room temperature. The measurement shows that its piezoelectric constant d_{33} value is 12.8 pC/N. The ME effect was measured in terms of the variation of the ME coefficient as a function of dc magnetic bias H. The sample was put into the dc magnetic field up to 0.55 T superimposed by a small ac magnetic field δH in parallel. The induced ME voltage signal δE in the sample was collected by a lock-in amplifier (EG&G 5210). When the polarization direction (out of plane) was parallel to the magnetic field, the longitudinal ME sensitivity was obtained, while the transverse ME sensitivity was measured when the polarization direction was perpendicular to the magnetic field. The magnetic field dependence of the ME coefficients $\alpha_E=(\delta E/\delta H)$ of the BLTFO is shown in Fig. 4. The ME coefficients increase linearly with the magnetic bias field. At 0.55 T, the longitudinal and transverse ME coefficients are 28 and 60 μV/cm Oe, respectively. These values are much smaller than those recently observed in the ME composites,[16] where the elastic coupling interaction between piezoelectric and magnetostrictive phases produces large ME response.[17] The longitudinal ME coefficient is smaller than the transverse ME coefficient, which is because of a larger depolarization field in the longitudinal mode than in the transverse mode. This direct ME effect observed in the BLTFO ceramics could originate from two aspects: (1) the strain effect from the piezoelectric and piezomagnetic behavior of the BLTFO as in the ME composites[17] and (2) the coupling of the ferroelectric and ferromagnetic ordering.[18]

In conclusion, highly dense $Bi_{0.87}La_{0.05}Tb_{0.08}FeO_3$ ceramics have been prepared by spark plasma sintering method. Low dielectric loss and thus high insulation of the sample ensure observation of good ferroelectric and piezoelectric behavior and rule out magnetoresistance and Maxwell-Wagner polarization effect. In particular, the BLTFO ceramics obviously present a direct magnetoelectric effect with a ME coefficient in the order of magnitude of tens of μV/cm Oe.

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