

# Multiferroicity in polarized single-phase $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$ ceramics

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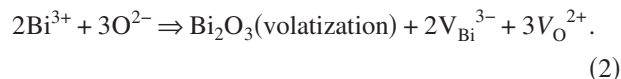
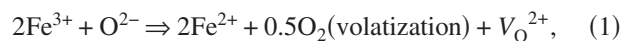
Single-phase  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  ceramics were prepared, and their crystal structure and multiferroic properties were studied. The triclinic structure with  $P1$  space group was confirmed in the ceramics by refining the x-ray diffraction data. Large piezoelectric  $d_{33}$  coefficient of 29 pC/N, together with high remnant polarization of  $15.09 \mu\text{C}/\text{cm}^2$ , was measured at room temperature, suggesting the existence of long-range ferroelectric order on a macroscopic scale. The observed small remnant magnetization of 0.071 emu/g at room temperature as a result of the collapse of the space-modulated spin structure indicated the presence of long-range canted antiferromagnetic order on a macroscopic scale. The coexistence of the long-range ferroelectric and canted antiferromagnetic orders allowed the magnetoelectric effect below the antiferromagnetic Néel temperature of 265 °C near which magnetoelectric coupling was obvious. © 2006 American Institute of Physics. [DOI: 10.1063/1.2220642]

## I. INTRODUCTION

Multiferroic materials show both (anti)ferroelectric order and (anti)ferromagnetic order in the same phase. Thus they are prime candidates for displaying magnetoelectric (ME) effect defined as an induction of magnetization by means of an electric field or an induction of polarization by means of a magnetic field.<sup>1</sup> As an interesting candidate of multiferroic materials, single-phase  $\text{BiFeO}_3$  possesses a high ferroelectric Curie temperature ( $T_{\text{C-FE}}$ ) of  $\sim 830$  °C and a high antiferromagnetic Néel temperature ( $T_{\text{N-AFM}}$ ) of  $\sim 370$  °C. These bring hope to community that ME effect may be observed at room temperature.<sup>1-4</sup> In fact, single-phase bulk  $\text{BiFeO}_3$  exhibits a rhombohedral structure with space group  $R3c$ , where all ions along the  $(111)_c$  direction are displaced relative to the ideal centrosymmetric positions and the oxygen octahedrons surrounding the transition-metal cations rotate alternately clockwise and counterclockwise about this  $(111)_c$  direction.<sup>5</sup> Besides, it has canted  $G$ -type antiferromagnetic order combined with space-modulated spin structure on a long wavelength of 620 Å. However, the possible nonzero remnant magnetization ( $M_r$ ) permitted by the canted  $G$ -type antiferromagnetic order is cancelled by the space-modulated spin structure on the 620 Å wavelength,<sup>5-7</sup> constraining the release and measurements of potential ME effect in the ceramic.<sup>1</sup>

In practice, two preconditions are required to enable potential ME effect in single-phase  $\text{BiFeO}_3$  and its modified compositions. Precondition (1) states that samples should exhibit low-leakage ferroelectric behavior with reasonably large piezoelectric properties or, in general, long-range ferroelectric order.<sup>1</sup> Precondition (2) states that samples should display large  $M_r$  (or at least nonzero  $M_r$ ) or, in general, long-range ferromagnetic order (or at least long-range canted antiferromagnetic order).<sup>1</sup> To meet precondition (1), single-phase samples with sufficiently low leakage current density

(i.e.,  $<30 \text{ mA}/\text{m}^2$  at 150 kV/cm field) have to be prepared to avoid dielectric breakdown during poling. Unfortunately, this is not the usual case in bulk  $\text{BiFeO}_3$  and its modified compositions since there exist considerable amounts of charged defects governed by  $\text{Fe}^{2+}$  ion, oxygen vacancy ( $\text{V}_{\text{O}}^{2+}$ ), and/or bismuth vacancy ( $\text{V}_{\text{Bi}}^{3-}$ ) in the bulk samples, due to the transformation of  $\text{Fe}^{3+}$  ion to  $\text{Fe}^{2+}$  ion and/or volatilization of  $\text{Bi}^{3+}$  ion, according to the following reaction mechanisms:<sup>8,9</sup>



Importantly, the presence of  $\text{V}_{\text{O}}^{2+}$  vacancy as stated in Eqs. (1) and (2) has the predominant effect on the reduction of the electrical resistivity of the bulk samples, giving rise to high leakage currents in the samples.<sup>8,9</sup> To meet precondition (2), either the canted antiferromagnetic order or the space-modulated spin structure has to be destroyed. However, effective ways to destroy canted antiferromagnetic order without weakening ferroelectric order in multiferroic materials have not yet been found. Although it is possible to collapse the space-modulated spin structure using a superhigh magnetic field of  $>10 \text{ T}$ ,<sup>5</sup> the most convenient and economical way is to modify the crystal structure of  $\text{BiFeO}_3$  by A-site substitution (e.g.,  $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ,  $\text{A}=\text{La}, \text{Sm}$ , etc.).<sup>6,7</sup> Recently, it has been shown that the space-modulated spin structure of  $\text{BiFeO}_3$  can be collapsed by the A-site La substitution, resulting in a uniform canted antiferromagnetic order in the  $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$  system.<sup>6,7</sup>

Compared with  $\text{La}^{3+}$  ion (radius=1.032 Å),  $\text{Sm}^{3+}$  ion (radius=0.958 Å) possesses a much smaller radius. This suggests that the effect of A-site substitution may further be enhanced if  $\text{Sm}^{3+}$  ion is used in substitution for  $\text{Bi}^{3+}$  ion (radius=1.030 Å) in the ordinary  $\text{BiFeO}_3$  composition. In  $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$  system,  $M_r$  may be enhanced by increasing the A-site Sm substitution, yet too much substitution may

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weaken the effect of ferroelectricity. Moreover, it is of great interest to know whether both the space-modulated spin structure can be collapsed by the A-site Sm substitution and  $T_{N\text{-AFM}}$  can be decreased towards room temperature (since ME coupling is much larger at temperatures slightly below  $T_{N\text{-AFM}}$ ). In this paper, we aim to prepare single-phase multiferroic  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples and investigate their structural, ferroelectric, piezoelectric, canted antiferromagnetic, and magnetoelectric properties. Single-phase multiferroic  $\text{BiFeO}_3$  samples are also prepared and characterized for comparison. The specific composition  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  ( $x=0.125$ ) is chosen because this composition satisfies preconditions (1) and (2) for the maximization of both remnant polarization ( $P_r$ ) and  $M_r$ .<sup>1</sup>

## II. EXPERIMENTAL DETAILS

A rapid liquid-phase sintering method with a high heating rate of 100 °C/s was applied to prepare single-phase  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  ceramics.<sup>8–10</sup> High-purity (>99%) oxide powders were weighted according to the nominal compositions of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$ . Each type of powder was finely milled into sizes of <1  $\mu\text{m}$ . After drying, the powders were mixed thoroughly with water and pressed uniaxially into disks of 3 mm diameter and 1 mm thickness. The disk samples were dehydrated at 150 °C for 10 h in a vacuum chamber before being sintered at a relatively high temperature of 855 °C for a short time of 20 min. All the preparation procedures were optimized in terms of single phase and low-leakage current density so as to meet precondition (1). Further details about the sample preparation can be found elsewhere.<sup>8–10</sup>

The crystal structure of the sintered samples was examined by an x-ray diffractometer (Bruker D8 Advance System) with a  $2\theta$  step size of 0.02° and at a scan rate of one step every 4 s. Simulation of crystal structure based on the measured x-ray diffraction (XRD) data was carried out using a Rietveld structure refinement software (FULLPROF 2000). The samples were then thinned down to 0.4 mm thick, and silver paste was applied on their two major surfaces as electrodes for subsequent measurements and poling. The relative dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) of the samples were measured from 0.01 Hz to 1 MHz using a broadband dielectric spectrometer (Novocontrol Concept80). The polarization hysteresis ( $P$ - $E$ ) loop at 100 Hz was evaluated with a standard Sawyer-Tower circuit. The leakage current density versus electric field ( $J$ - $E$ ) curve was acquired using a multimeter (Keithley 2000) and a high-voltage amplifier (Trek P0621P). Based on the measured  $P$ - $E$  loop and  $J$ - $E$  curve, an optimal dc electric field of 150 kV/cm was applied to polarize the samples at room temperature in a silicon oil bath for 1 h. The piezoelectric  $d_{33}$  coefficient was measured at 60 Hz using a piezo- $d_{33}$  meter (IAAS ZJ-30). The planar and thickness electromechanical coupling coefficients ( $k_p$  and  $k_t$ ) and their associated mechanical quality factors ( $Q_{m,kp}$  and  $Q_{m,kt}$ ) were determined using an impedance analyzer (Agilent 4294A) according to the resonance method stated in the IEEE standard on piezoelectricity. The magnetization hysteresis ( $M$ - $H$ ) loop was evaluated using a superconducting

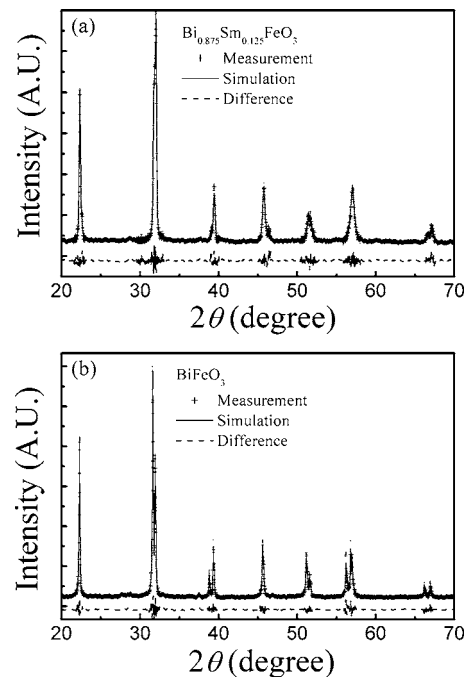


FIG. 1. Comparisons between the measured and simulated XRD patterns of (a)  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and (b)  $\text{BiFeO}_3$  samples.

quantum interference device (SQUID) (Quantum Design XL7d). The temperature dependence of both  $\epsilon$  and  $\tan \delta$  was obtained at 1 MHz using the impedance analyzer. The heat flow versus temperature curve was recorded using a differential thermal analyzer (DTA) (Netzsch STA449C Jupiter).

## III. RESULTS AND DISCUSSION

Figure 1 shows the comparisons between the measured and simulated XRD patterns of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  [Fig. 1(a)] and  $\text{BiFeO}_3$  [Fig. 1(b)] samples. From the measured XRD patterns (the + symbol), it is clear that  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  all have a single-phase perovskite structure with no trace of other impurity phases (e.g.,  $\text{Fe}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{Fe}_4\text{O}_9$ , etc.) within the uncertainty of XRD. Compared to  $\text{BiFeO}_3$ , some peaks of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  undergo a shift in  $2\theta$  and/or a combination of neighboring peaks, especially in the  $2\theta$  ranges of 31°–33° and 38.5°–40.5°. This indicates the existence of structural transformation between  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$ .

In order to further analyze such transformation, the measured XRD patterns of both  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples were used in Rietveld refinement of crystal structures based on a triclinic structure with  $P1$  space group. In more detail, the crystal structure of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  was taken to be a triclinic structure with  $P1$  space group, while the rhombohedral structure with  $R3C$  space group that was previously reported in single-phase  $\text{BiFeO}_3$  was considered as a special triclinic structure with  $P1$  space group in the refinement process for ease of comparison of the refinement results.<sup>10,11</sup> As shown in Fig. 1, the simulated XRD patterns (the solid line) agree well with the measured XRD patterns, though they show slight variations (the dashed line) between each other. From the refined structural parameters tabulated in Table I, the generally small  $R$  values of Rietveld structure

TABLE I. The refined structural parameters of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples based on the measured XRD patterns shown in Fig. 1 and according to a triclinic structure with  $P1$  space group.

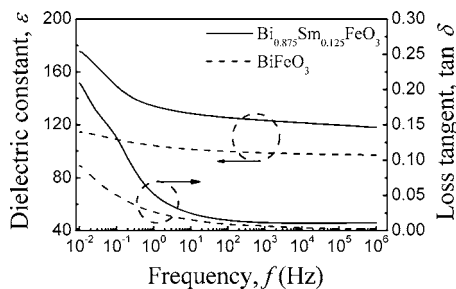
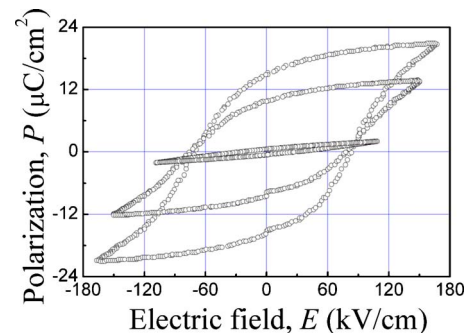
Material	Crystal structure	Lattice parameters	Atomic positions and volume	$R$ values of Rietveld structure refinement
$\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$	Triclinic structure	$a=3.943 \text{ \AA}$ $b=3.957 \text{ \AA}$ $c=3.915 \text{ \AA}$ $\alpha=89.63^\circ$ $\beta=89.82^\circ$ $\gamma=89.72^\circ$	Bi (0,0,0) Fe (0.5198,0.5566,0.5011) O-1 (0.0960,0.5632,0.6754) O-2 (0.5091,-0.0937,0.4868) O-3 (0.6216,0.1345,-0.0524) Volume= $61.073 \text{ \AA}^3$	$R_{\text{wp}}=7.19\%$ $R_p=4.96\%$
$\text{BiFeO}_3$	Rhombohedral structure	$a=3.942 \text{ \AA}$ $b=3.942 \text{ \AA}$ $c=3.942 \text{ \AA}$ $\alpha=89.43^\circ$ $\beta=89.43^\circ$ $\gamma=89.43^\circ$	Bi (0,0,0) Fe (0.5967, 0.5045, 0.5724) O-1 (0.0404,0.5999,0.6513) O-2 (0.6114,0.0326,0.6116) O-3 (0.5638,0.6477,0.1456) Volume= $61.247 \text{ \AA}^3$	$R_{\text{wp}}=6.36\%$ $R_p=4.72\%$

refinement (i.e.,  $R_{\text{wp}}=7.19$  and  $R_p=4.96$  for  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$ ;  $R_{\text{wp}}=6.48$  and  $R_p=4.76$  for  $\text{BiFeO}_3$ ) confirm that our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples have a single-phase triclinic structure with  $P1$  space group, whereas our  $\text{BiFeO}_3$  samples that show a single-phase rhombohedral structure with  $R3c$  space group can be treated as a special triclinic structure with  $P1$  space group. Nevertheless, the typical triclinic structure of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  (i.e.,  $a=3.943 \text{ \AA}$ ,  $b=3.957 \text{ \AA}$ ,  $c=3.915 \text{ \AA}$ ,  $\alpha=89.63^\circ$ ,  $\beta=89.82^\circ$ , and  $\gamma=89.72^\circ$ ) possesses comparatively larger  $a$ ,  $b$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  values, besides a relatively smaller  $c$  value, than the rhombohedral structure of  $\text{BiFeO}_3$  (i.e.,  $a=b=c=3.942 \text{ \AA}$  and  $\alpha=\beta=\gamma=89.43^\circ$ ) owing to the partial substitution of smaller  $\text{Sm}^{3+}$  ion for larger  $\text{Bi}^{3+}$  ion in  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples.

Figure 2 illustrates the frequency ( $f$ ) dependence of relative dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) for  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples. Both  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  show decreasing trends in  $\epsilon$  and  $\tan \delta$  with increasing  $f$  from 0.01 Hz to 1 MHz. At sufficiently low  $f$  of  $<10$  Hz, charged defects ( $\text{V}_{\text{O}}^{2+}$ ,  $\text{V}_{\text{Bi}}^{3-}$ , and  $\text{Fe}^{2+}$ ) are able to follow the applied electric field, resulting in increased  $\epsilon$  and  $\tan \delta$  values. At elevated  $f$  of  $>10$  Hz, the weak dependence of  $\epsilon$  and  $\tan \delta$  on  $f$ , along with the generally low  $\tan \delta$  values of  $<0.03$ , implies that electrons/domains rather than dipoles of the charged defects mainly

contribute to the characteristics of  $\epsilon$  and  $\tan \delta$  above 10 Hz.  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples possess larger  $\epsilon$  and  $\tan \delta$  in the whole  $f$  range of measurement when compared with the  $\text{BiFeO}_3$  samples. This may be attributed to the formation of relatively stronger dipoles in the triclinic structure.

Figure 3 plots the polarization hysteresis ( $P$ - $E$ ) loops of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples measured at 100 Hz for three maximum electric fields ( $E_m$ ) of 108, 150, and 167 kV/cm. The correspondingly measured remnant polarizations ( $P_r$ ) are 0.52, 9.80, and  $15.09 \mu\text{C}/\text{cm}^2$ , respectively. Although  $\text{Bi}^{3+}$  ion has been partially substituted by  $\text{Sm}^{3+}$  ion, the obvious ferroelectricity in our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples may be explained by what was found in  $\text{BiRO}_3$  ( $R=\text{Fe, Mn, Cr, etc.}$ ) systems that a lone  $s^2$  pair of electrons of a  $\text{Bi}^{3+}$  ion may hybridize with an empty  $p$  orbital of a  $\text{Bi}^{3+}$  ion or an  $\text{O}^{2-}$  ion to form a localized lobe, giving rise to noncentrosymmetrically distorted structure and hence ferroelectricity.<sup>1,12</sup> It should be noted that our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples exhibit the largest maximum polarization ( $P_m$ ) of  $20.78 \mu\text{C}/\text{cm}^2$ , in addition to the largest  $P_r$  of  $15.09 \mu\text{C}/\text{cm}^2$ , at the maximally allowed  $E_m$  of 167 kV/cm without being subjected to dielectric breakdown. Importantly, these  $P_m$  and  $P_r$  values are significantly larger than the largest reported  $P_m$  of  $8.9 \mu\text{C}/\text{cm}^2$  and  $P_r$  of  $4 \mu\text{C}/\text{cm}^2$  at the maximally allowed  $E_m$  of

FIG. 2. Frequency ( $f$ ) dependence of relative dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) for  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples.FIG. 3. Polarization hysteresis ( $P$ - $E$ ) loops of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples measured at 100 Hz for three maximum electric fields of 108, 150, and 167 kV/cm.

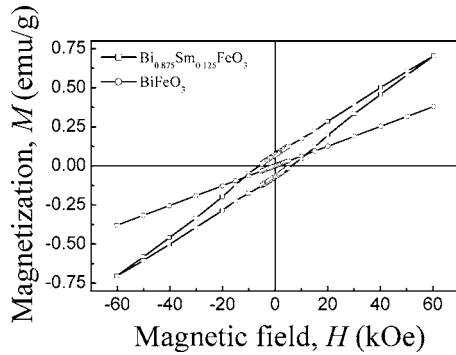


FIG. 4. Magnetization hysteresis ( $M$ - $H$ ) loops of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples for the maximum magnetic field of 60 kOe.

100 kV/cm in single-phase bulk  $\text{BiFeO}_3$ .<sup>10</sup> In agreement with our  $\text{BiFeO}_3$  samples, the  $P$ - $E$  loop of  $\text{BiFeO}_3$  may not technically saturate at its maximally allowed  $E_m$  ( $=100$  kV/cm) due to the presence of much charged defects (and hence a larger leakage current density) in  $\text{BiFeO}_3$  samples.<sup>13–15</sup> This also implies that the increased  $E_m$  in our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples should be one of the main factors in the increased  $P_m$  and  $P_r$ . In addition, the use of the optimized preparation procedures described in Sec. II is beneficial to the suppression of the charged defects.<sup>8</sup>

To enable measurements of the piezoelectric properties,  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples were polarized using an optimal dc electric field of 150 kV/cm at room temperature for an hour. The *in situ* measurement of the electric field dependence of leakage current density ( $J$ - $E$ ) revealed a gradual increase in  $J$  with increasing  $E$ , and a sufficiently low  $J$  of  $\sim 28$  mA/m<sup>2</sup> at  $E=150$  kV/m was achieved in the polarization process. This measured  $J$  should be the real  $J$  rather than the contribution of domain switching. Also, it is generally considered to be small enough to enable an effective polarization of multiferroic ceramics.<sup>9</sup> Thereafter, some important piezoelectric coefficients were measured according to the procedures mentioned in Sec. II. These piezoelectric coefficients include piezoelectric  $d_{33}$  coefficient ( $=29.2$  pC/N), planar electromechanical coupling coefficient ( $k_p=0.154$ ), thickness electromechanical coupling coefficient ( $k_t=0.283$ ), planar mechanical quality factor ( $Q_{m,kp}=251.9$ ), and thickness mechanical quality factor ( $Q_{m,kt}=42.4$ ). The success in polarizing the samples and measuring the favorable ferroelectric behavior and piezoelectric properties suggest that the required long-range ferroelectric order as described by precondition (1) has been achieved in our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples.<sup>1</sup>

Figure 4 shows the magnetization hysteresis ( $M$ - $H$ ) loops of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  and  $\text{BiFeO}_3$  samples for the maximum magnetic field ( $H_m$ ) of 60 kOe. It is obvious that a small but nonzero remnant magnetization ( $M_r$ ) of 0.071 emu/g, together with a coercive field ( $H_c$ ) of 6.12 kOe, is achieved in  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples, reflecting the presence of the required long-range canted antiferromagnetic order as stated in precondition (2). By contrast, both  $M_r$  and  $H_c$  vanish in  $\text{BiFeO}_3$  samples because of the cancellation effect of the space-modulated spin structure.<sup>5–7</sup> Nevertheless, it is necessary to clarify whether the observed

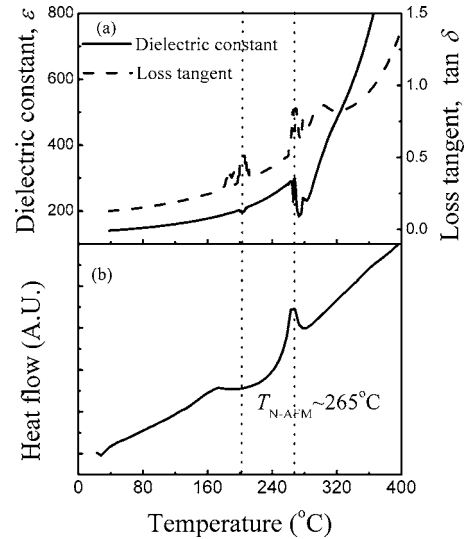


FIG. 5. (a) Temperature dependence of relative dielectric constant ( $\epsilon$ ) and loss tangent ( $\tan \delta$ ) at 1 MHz for  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples and (b) heat flow vs temperature curve for the samples.

$M_r$  (and  $H_c$ ) in  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  truly originates from the collapse of the space-modulated spin structure or it is caused by other factors such as the presence of  $\text{Fe}_2\text{O}_3$  and/or  $\text{Bi}_2\text{Fe}_4\text{O}_9$  impurity phases, the contribution of charged defects, and the change from canted antiferromagnetic order to ferromagnetic order. The clarification is as follows: First, our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples have a larger  $H_c$  ( $=6.12$  kOe) than ferromagnetic  $\text{Fe}_2\text{O}_3$  impurity ( $<100$  Oe); it is impossible that the observed  $M_r$  is a result of the small amount of  $\text{Fe}_2\text{O}_3$  impurity left in the samples. Second, as the Curie temperature of  $\text{Bi}_2\text{Fe}_4\text{O}_9$  impurity is much lower than the room temperature,  $\text{Bi}_2\text{Fe}_4\text{O}_9$  should have null effect on  $M_r$  at room temperature.<sup>16</sup> Third, since reduced charged defects have been evidenced in our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples by the significantly large  $P_m$  ( $=20.78$   $\mu\text{C}/\text{cm}^2$ ) and  $P_r$  ( $=15.09$   $\mu\text{C}/\text{cm}^2$ ) for the maximally allowed  $E_m$  ( $=167$  kV/m) and the sufficiently low  $J$  ( $\sim 28$  mA/m<sup>2</sup>) even at a high  $E$  ( $=150$  kV/cm), these limited charged defects may not be able to produce an influential effect on crystal structure and  $M_r$ . Finally, the change from canted antiferromagnetic order to ferromagnetic order can also be excluded because such change should accompany a large  $M_r$ . Therefore, the observed  $M_r$  in our  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples is likely due to the collapse of the space-modulated spin structure. Indeed, the transformation from the rhombohedral structure with space group  $R3c$  in  $\text{BiFeO}_3$  to typical triclinic structure with  $P1$  space group in  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  leads to the collapse of the space-modulated spin structure.

Figure 5(a) shows the temperature dependence of  $\epsilon$  and  $\tan \delta$  at 1 MHz of  $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$  samples. It is found that dielectric anomalies take place at  $\sim 265$  and  $\sim 202$  °C. Since ferroelectric order and canted antiferromagnetic order have been confirmed in the samples at room temperature, these dielectric anomalies may result from paraelectric-ferroelectric (PE-FE) transition and/or magnetoelectric coupling. To obtain an insight into these anomalies, the heat flow versus temperature curve of the samples is also plotted in Fig. 5(b), in which two combined endothermic peaks are



observed at  $\sim 265$  and  $\sim 790$  °C (not shown). It is known that single-phase bulk BiFeO<sub>3</sub> samples not only have a dielectric anomaly and an endothermic peak at  $T_{N-AFM} \sim 370$  °C, but also possess an endothermic peak at  $T_{C-FE} \sim 830$  °C.<sup>17</sup> Considering these facts, it is believed that the endothermic peak of our Bi<sub>0.875</sub>Sm<sub>0.125</sub>FeO<sub>3</sub> at  $\sim 790$  °C is caused by the PE-FE transition (i.e.,  $T_{C-FE} \sim 790$  °C), while the dielectric anomaly and endothermic peak at  $\sim 265$  °C originate from the magnetoelectric coupling (i.e.,  $T_{N-AFM} \sim 265$  °C). With regard to the dielectric anomaly at  $\sim 202$  °C, it may be due to magnetoelectric coupling when either the canting angle of canted antiferromagnetic order decreases to zero or the space-modulated spin structure disappears. Nevertheless, magnetoelectric coupling is observed below  $T_{N-AFM} \sim 265$  °C in our samples. This observed ME coupling and hence potential ME effect can be explained by the differentiation of free energy ( $F$ ) in Eqs. (3) and (4) shown below:<sup>1,18</sup>

$$P_i(\mathbf{E}, \mathbf{H}) = -\partial F / \partial E_i = P_i^S + \varepsilon_0 \varepsilon_{ij} E_j + \alpha_{ij} H_j + (1/2) \beta_{ijk} H_j H_k + \gamma_{ijk} H_i H_j - \dots, \quad (3)$$

$$M_i(\mathbf{E}, \mathbf{H}) = -\partial F / \partial H_i = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_i + \beta_{ijk} E_i H_j + (1/2) \gamma_{ijk} E_j E_k - \dots, \quad (4)$$

where  $\mathbf{E}$ ,  $\mathbf{H}$ ,  $P_i^S$ ,  $M_i^S$ ,  $\alpha_{ij}$ ,  $\beta_{ijk}$ , and  $\gamma_{ijk}$  are the electric field, magnetic field, spontaneous polarization along the  $i$  axis, spontaneous magnetization along the  $i$  axis, ME coefficient, higher-order ME coefficient according to  $E_i H_j H_k$ , and higher-order ME coefficient according to  $H_i E_j E_k$ , respectively. Disappearance of antiferromagnetic order can strongly impact ferroelectric order through  $\alpha_{ij}$  and/or  $\beta_{ijk}/\gamma_{ijk}$  near  $T_{N-AFM}$ ,<sup>1</sup> resulting in dielectric anomalies, i.e., ME coupling. When either the canting angle of canted antiferromagnetic order decreases to zero or the space-modulated spin structure disappears at temperatures below  $T_{N-AFM}$ , the vibration of antiferromagnetic order can also impact ferroelectric order through  $\alpha_{ij}$  and/or  $\beta_{ijk}/\gamma_{ijk}$ , leading to dielectric anomalies.  $\alpha_{ij}$  of single-phase bulk BiFeO<sub>3</sub> becomes zero in the absence of either long-range ferromagnetic order or long-range canted antiferromagnetic order, while both  $\beta_{ijk}$  and  $\gamma_{ijk}$  can still take effect.<sup>1</sup> Since obvious long-range ferromagnetic and canted antiferromagnetic orders have been verified in our Bi<sub>0.875</sub>Sm<sub>0.125</sub>FeO<sub>3</sub> samples at room temperature,  $\alpha_{ij}$  should not be zero in our case. As ME coupling is commonly enhanced near  $T_{N-AFM}$ , the decrease in  $T_{N-AFM}$  from  $\sim 370$  °C of BiFeO<sub>3</sub> to  $\sim 265$  °C of Bi<sub>0.875</sub>Sm<sub>0.125</sub>FeO<sub>3</sub> is favorable to enable large ME effect at room temperature.

## IV. CONCLUSION

In conclusion, we have shown experimentally and simulationally that single-phase bulk Bi<sub>0.875</sub>Sm<sub>0.125</sub>FeO<sub>3</sub> multiferroic ceramics have a triclinic structure with  $P1$  space group rather than the rhombohedral structure with  $R3C$  space group in single-phase bulk BiFeO<sub>3</sub>. Favorable piezoelectric properties and strong ferroelectric behavior have been measured in the ceramics at room temperature, confirming the presence of macroscopic long-range ferroelectric order. By collapsing the space-modulated spin structure, obvious canted antiferromagnetic behavior has been observed at room temperature, proving the existence of macroscopic long-range canted antiferromagnetic order. As a result, large ME coupling has been realized slightly below  $T_{N-AFM} \sim 265$  °C, allowing great prospect of measuring ME coefficients for device applications.

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