

Combinatorial discovery of a lead-free morphotropic phase boundary in a thin-film piezoelectric perovskite

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We report on the discovery of a lead-free morphotropic phase boundary (MPB) in Sm doped BiFeO₃ with a simple perovskite structure using the combinatorial thin film strategy. The boundary is a rhombohedral to pseudo-orthorhombic structural transition which exhibits a ferroelectric to antiferroelectric transition at approximately Bi_{0.86}Sm_{0.14}FeO₃ with dielectric constant and out-of-plane piezoelectric coefficient comparable to those of epitaxial (001) oriented PbZr_{0.52}Ti_{0.48}O₃ (PZT) thin films at the MPB. The discovered composition may be a strong candidate of a Pb-free piezoelectric replacement of PZT. © 2008 American Institute of Physics. [DOI: 10.1063/1.2931706]

BiFeO₃ (BFO) is a multiferroic with rich and intricate physical properties.¹ Given the need for environmentally friendly lead-free piezoelectrics,² doped BFO is being investigated for improved properties,^{3–5} so that they may emulate the performance of Pb-based piezoelectrics^{6,7} at morphotropic phase boundaries (MPBs). However, neither an increase in electromechanical constants as a function of dopant concentration or domain structures indicative of a MPB has been reported to date in BFO-based lead-free systems. There are some guidelines which predict the presence of MPBs (Refs. 8–10), and one can explore novel compositions by systematically searching for similar structural transitions. We have applied the combinatorial strategy in the form of composition spreads.¹¹

A series of pseudobinary composition spread epitaxial thin-film libraries (200 nm thick) were fabricated on SrTiO₃ (STO) (100) substrates 6 mm long by the combinatorial pulsed laser deposition system (Pascal, Inc.) at 600 °C, where a pseudobinary compositional phase diagram of Bi_{1-x}(RE)_xFeO₃ or BiFe_{1-y}(TM)_yO₃ was continuously mapped on each chip. RE and TM denote rare-earth and transition metal cations, respectively. Composition variation across the spreads were confirmed by an electron probe (JEOL JXA-8900), and the uncertainty in the composition at each point on the spread is $\pm 1.5\%$. Scanning x-ray microdiffraction (Bruker D8 Discover) was performed with a 0.5 mm diameter aperture. For electrical characterization, an epitaxial SrRuO₃ (SRO) layer (50 nm) was used as the bottom electrode, and a sputter-deposited top Pd layer (50 nm) was patterned into 50 μ m capacitor dots. Ferroelectric (FE) polarization hysteresis loops were obtained using the Radiant Precision LC at 5 kHz. Quantitative piezoresponse force microscopy was used to measure the out-of-plane piezoresponse. A number of interesting compounds were identified from our initial screening. Here, we focus on results from the Bi_{1-x}Sm_xFeO₃ (BSFO) spread.

Initial piezoforce microscopy scans of a BSFO spread indicated significant enhancement of piezoresponse near Bi_{0.8–0.85}Sm_{0.2–0.15}FeO₃, where the structure undergoes substantial change in the out-of-plane lattice constant as detected by x-ray diffraction (XRD) mapping. A series of two-dimensional XRD images of this composition region revealed the appearance of extra diffraction spots for $x \geq 0.13$ (Fig. 1), indicating a cell doubling structural transition to a lower symmetry phase identified to be triclinic (below). High temperature XRD of the same spread showed that the structural transition starts at approximately the same

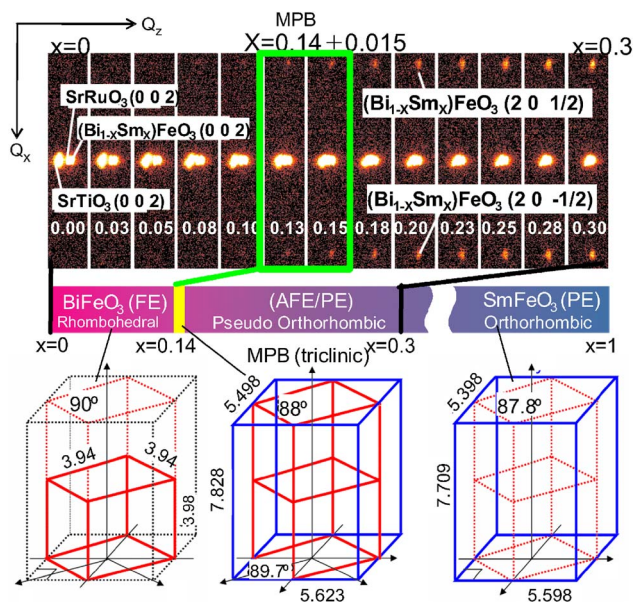


FIG. 1. (Color online) Two-dimensional diffraction images (Q_z - Q_x) taken from $x=0$ to $x=0.3$ in Bi_{1-x}Sm_xFeO₃ composition spread. The indexes are assigned using the perovskite (rhombohedral) structure. Beyond $x \approx 0.13$, the Bi_{1-x}Sm_xFeO₃ (002) spot is a mixture of (002), (020), and (200) spots due to twinning. The $(2\ 0\ \frac{1}{2})$ and $(2\ 0\ -\frac{1}{2})$ spots starting at $x \approx 0.14$ indicate cell doubling. Bi_{1-x}Sm_xFeO₃ goes from rhombohedral BiFeO₃ (unit cell in red) to orthorhombic SmFeO₃ (unit cell in blue). Beyond $x \approx 0.27$, the compound is paraelectric.

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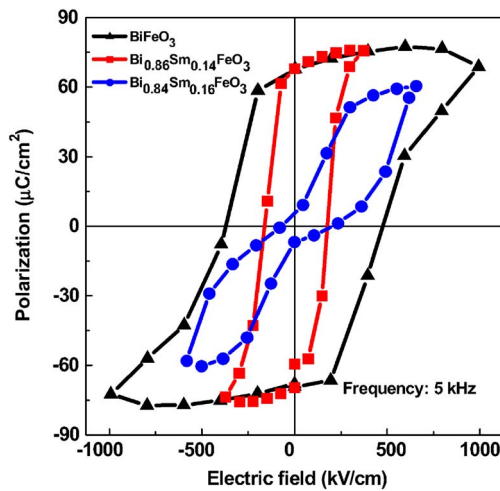


FIG. 2. (Color online) Polarization hysteresis loops for three selected compositions. The relatively high polarization of $\approx 70 \mu\text{C}/\text{cm}^2$ is maintained for $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$. Beyond MPB and until $x \approx 0.27$, AFE characteristics are observed (as seen for $x=0.16$ here).

composition of $x \approx 0.14$, with no additional structural transitions up to the highest measured temperature of 400°C .

High resolution planar transmission electron microscopy (A JEOL 2100 F operating at 200 kV) of an individual composition sample at $x \approx 0.14$ revealed the presence of unusual nanoscale twinned triclinic domains 20–50 nm in size displaying three different epitaxial orientations. The lattice parameters of this composition were determined to be $a = 5.62 \text{ \AA}$, $b = 7.83 \text{ \AA}$, $c = 5.50 \text{ \AA}$, $\alpha = \gamma = 89.8^\circ$, and $\beta = 89.7^\circ$. The occurrence of nanosized twins and concomitant stress accommodation have been previously identified as fingerprints of an adaptive FE phase at the MPB, which could result in a high piezoelectric coefficient and narrow hysteresis loops.¹² These nanodomains are observed only at this composition, and for x outside of 0.14 ± 0.015 , the domains were found to be much larger in size ($\sim 100 \text{ nm}$).

Square-shaped FE hysteresis loops with good saturation and robust switchable polarization are obtained for compositions from $x=0$ up to $x \approx 0.14$. Figure 2 plots hysteresis loops at room temperature for three compositions (BFO , $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$, and $\text{Bi}_{0.84}\text{Sm}_{0.16}\text{FeO}_3$) selected for displaying the most prominent features. While increasing the Sm concentration induces a large drop in the coercive field, a high switchable polarization ($\approx 70 \mu\text{C}/\text{cm}^2$) is maintained. For $x \geq 0.15$, we observe double hysteresis loops, indicative of an antiferroelectric (AFE) behavior.¹³ It is important to note that the AFE composition at $x \approx 0.16$ still maintains a relatively high polarization once electric-field induced switch to FE takes place. These hysteresis curves do not change their shapes with time (over 6 months) or the number of measurement cycles (tens of cycles for each measurement), indicating that the double hysteresis loops are not from domain-wall pinning.

In Fig. 3, we plot the zero-bias out-of-plane dielectric constant (ϵ_{33}) and loss tangent measured at 10 kHz as a function of increasing Sm concentration. The dielectric constant reaches a maximum at $x=0.14$ in agreement with the structural transition taking place at the composition. The loss tangent at this composition is relatively low (~ 0.01).

Figure 4(a) shows the piezoelectric behavior of BSFO with $x=0.12$ and 0.14 measured via quantitative piezoforce microscopy, which was performed on Pt/BSFO/SRO/STO.

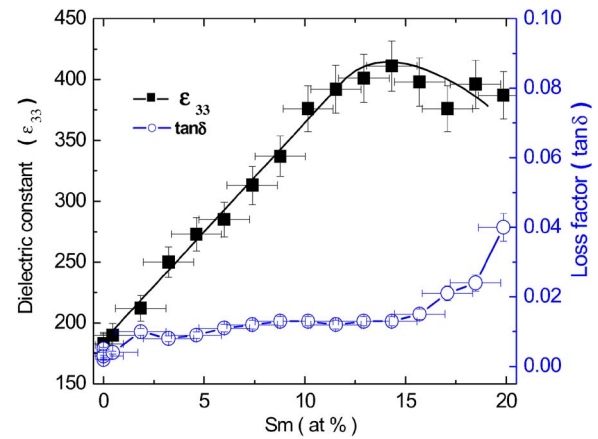


FIG. 3. (Color online) Dielectric constant (ϵ_{33}) and $\tan \delta$ measured at 1 MHz (zero bias). The curve is a guide to the eye.

structures using Pt–Ir coated contact mode tips.¹⁴ The measured d_{33} values are effective values due to the constraint imposed by the underlying substrate. The composition right near the MPB possesses a substantially higher remanent out-of-plane d_{33} ($\sim 95 \text{ pm}/\text{V}$) together with much reduced coercive field compared to that for $x=0.12$. The remanent d_{33} for a (001) oriented epitaxial $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin film with the same nominal thickness (200 nm) is $100 \text{ pm}/\text{V}$.¹⁴

Figure 4(b) plots the high-field d_{33} as a function of Sm doping. Around $x=0.13 \sim 0.15$, the effective d_{33} displays a rapid increase peaking at $x=0.14$ with $110 \text{ pm}/\text{V}$. Beyond this value, it rapidly decreases to $\approx 55 \text{ pm}/\text{V}$ for $\text{Bi}_{0.83}\text{Sm}_{0.17}\text{FeO}_3$. We have performed the Rayleigh analysis¹⁵ of the out-of-plane piezoelectric response for the MPB composition sample and confirmed that the signal is not due to any non- 180° domain wall motion.

The measured remanent and high field d_{33} here are comparable to values previously reported for epitaxial thin films of Pb-based compounds such as PZT and $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – PbTiO_3 . Domain engineered single crystals are known to exhibit enhanced electromechanical properties, but this is due to extrinsic mechanisms, which are generally absent in thin films.¹⁵ Thus, in comparing nominally similar thin-film samples of the same thickness, the MPB discovered here exhibits intrinsic piezoelectric properties which are among the best. The added advantage of the present system is a simpler crystal chemistry than some of the reported Pb-free compounds as well as ease of processing.²

There is a distinct and abrupt change in the d_{33} loop shape as one crosses from the FE to AFE composition. Figure 4(c) shows the d_{33} loop taken for $\text{Bi}_{0.84}\text{Sm}_{0.16}\text{FeO}_3$. We can relate the dependence of d_{33} on the applied electric field due to intrinsic domain reversal (i.e., no contributions such as ferroelastic motion or field-induced phase transitions) along the [001] direction of the film using¹⁴

$$d_{33}(E) = 2\bar{Q}P(E)\epsilon_{33}(E), \quad (1)$$

where $P(=P_3)$ is the polarization and ϵ_{33} is the relative dielectric constant. $\bar{Q}$ is an effective electrostrictive coefficient that accounts for the clamping effect of the substrate. This phenomenological relation states that the field dependence of the d_{33} coefficient is principally governed by the field dependence of the polarization as well as the dielectric susceptibility. The main features of the AFE d_{33} loop are consistent with

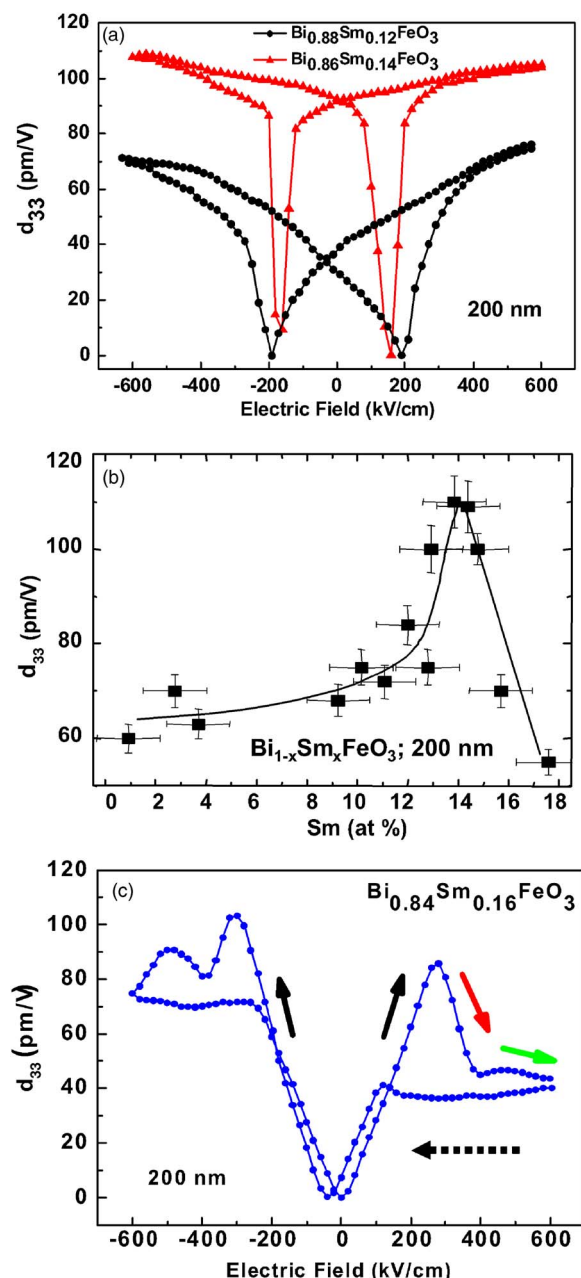


FIG. 4. (Color online) Piezoelectric properties of $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ (a) d_{33} loops for $\text{Bi}_{0.87}\text{Sm}_{0.13}\text{FeO}_3$ and $\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$. (b) High-field d_{33} determined from the piezoelectric hysteresis loops measured as a function of composition. The curve is a guide to the eye. (c) AFE d_{33} loop observed for $\text{Bi}_{0.84}\text{Sm}_{0.16}\text{FeO}_3$.

the P - E loop (Fig. 2 and the ϵ_{33} - E curve (not shown). The black arrow marks the region where electric-field induced transition from the AFE to FE state is taking place. The eventual maximum in the d_{33} loop is a consequence of the increase in the switching polarization in the FE state with a sharp positive change of the slope of the P - E loop and increase in the dielectric susceptibility at that point. As the applied electric field increases further, an inflection point is reached beyond which the net increment in switchable polarization for given increase in applied field begins to decrease. As a consequence, the dielectric susceptibility begins to decrease, and hence, also brings down the d_{33} value (the red arrow). At higher electric field, the polarization is fully switched and now similar to a “fully saturated state” in a

standard FE. Here, the drop in the dielectric susceptibility with increasing electric field dominates the shape of the d_{33} loop, which shows a downward slope (the green arrow).

The present results show that Sm^{+3} substituted BFO has unique properties compared to more popular La (Ref. 16) or Nd (Refs. 3 and 4) doped BFO. Sm^{+3} (1.24 Å) has a much smaller ionic size than La^{+3} (1.36 Å). The Goldschmidt tolerance factor¹⁰ for the Sm^{+3} doped BFO is less than 1, and lower symmetry structures such as triclinic are more likely at the MPB. The presence of a low symmetry phase at the MPB is expected to enhance the piezoelectric properties as the polarization vector is no longer constrained to lie along a symmetry axis but instead can rotate within a suitable plane.^{7,17}

Ravindran *et al.*¹⁸ have recently shown through density functional calculations that BFO undergoes a rhombohedral ($R3c$) to orthorhombic (Pnma) structural transition under pressure. Because of the small ionic radius, chemical pressure due to the continuous Sm^{+3} doping can perhaps be viewed as resulting from the similar lattice instabilities.

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