Structure, ferroelectric and piezoelectric properties of multiferroic Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ ceramics

Xiaomin Chen$^{a,b}$, Junling Wang$^c$, Guoliang Yuan$^{a,b,*}$, Di Wu$^b$, Junming Liu$^b$, Jiang Yin$^b$, Zhiguo Liu$^b$

$^a$School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
$^b$Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
$^c$School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

**Abstract**

With a rhombohedral-like structure, the Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ ceramics show much-improved ferroelectric and piezoelectric properties: a saturated ferroelectric polarization of 40 μC/cm$^2$ and a piezoelectric $d_{33}$ of 45 pC/N at 20°C. After the polarized sample was annealed at 600°C, its $d_{33}$ decreases to ~20 pC/N. Besides, Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ shows dielectric or impedance resonances at 20–550°C, suggesting that the ferroelectric component with high Curie temperature still partially remained at 550°C. However, the impedance and the resistance decrease so fast with temperature increasing that both of them are below 1000 ohm above 420°C. Even so, this piezoelectric resonance method can explore leaky ferroelectrics at high temperature.

© 2012 Elsevier B.V. All rights reserved.

---

**1. Introduction**

Although the outstanding piezoelectric properties of Pb$_{1-x}$Zr$_x$TiO$_3$ (PZT) ceramics have drawn extensive attention, their lead content is currently facing global restrictions due to its toxicity. Thus, there is an urgent need to develop such a non-Pb substitute as Bi$_1$-Sm$_x$FeO$_3$ [1] to make up for this weakness. Pb-free BiFeO$_3$ with rhombohedral R3c structure has ferroelectric order below Curie temperature ($T_{C-Fe}$) of ~800°C and G-type canted antiferromagnetic order below Neel temperature ($T_{N-HT}$) of ~370°C [2–4]. Recently, Zeches et al. have reported that the strain-driven epitaxial BiFeO$_3$ film on (110) YAlO$_3$ substrate exhibited a large piezoelectric $d_{33}$ of ~120 pm/V and a reversible electric-field-induced strain of over 5% [5]. Besides, the Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ epitaxial film also allows an enhanced $d_{33}$ of ~120 pm/V at 500 kV/cm, because the Sm$^{3+}$ ion with a smaller radius of 0.958 Å partially replaces Bi$^{3+}$ ion with a radius of 1.030 Å [6,7]. It is reported that Bi$_1$-Sm$_x$FeO$_3$ films change from rhombohedral R3c phase to PbZrO$_3$-like anti-ferroelectric orthorhombic Pbam phase at $x \sim 0.12$ and finally to SmFeO$_3$-like paraelectric orthorhombic Pnma phase at higher $x$ [6,7]. These results demonstrate the potential of Bi$_1$-Sm$_x$FeO$_3$ family as a substitute for lead-based materials in future piezoelectric applications.

First, it is necessary to study the dependence of electric properties of Bi$_1$-Sm$_x$FeO$_3$ ceramics on temperature. BiFeO$_3$ with rhombohedral R3c phase commonly keep higher $T_{C-Fe}$ [4], however it is not clear whether Bi$_1$-Sm$_x$FeO$_3$ can be used as high-temperature piezoelectric materials. As is known, bismuth layered high-temperature piezoelectric materials own wider band gap to allow higher resistivity at high temperature. For example, the CaBi$_4$Ti$_4$O$_{15}$ with $T_{C-Fe}$ of 790°C permits room-temperature $d_{33}$ of 14 pC/N and 10$^7$ ohm cm at 500°C [8]. On the contrary, BiFeO$_3$ with the band gap of ~2.8 eV usually changes from a room-temperature ferroelectric insulator to a conductor when above 400°C due to electron thermal excitation. As a result, it’s difficult to apply a high electrical field larger than coercive field ($E_c$) to leaky ceramics to polarize them before large leakage current breaks down samples at high temperature. Despite this, it is still valuable to study piezoelectric properties of leaky Bi$_1$-Sm$_x$FeO$_3$ at high temperature.

Although extensive researches, especially magnetic properties, have been down in doped BiFeO$_3$ ceramics [1–4,9,10], there are few reports on piezoelectric properties of Bi$_1$-Sm$_x$FeO$_3$ ceramics at high temperature. Piezoelectric ceramics can be applied in many sensors, actuators and so on, which cannot be replaced by the devices with films, and furthermore, their crystal structure, ferroelectric and piezoelectric properties may be different from the corresponding epitaxial films in many cases. Therefore, Bi$_1$-Sm$_x$FeO$_3$ ceramics should be studied systematically.

Here we prepare Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ ceramics and then prove that their piezoelectric responses can be observed up to 600°C though the ceramics have already become seriously leaky and the ferroelectric component only survived partially.
2. Experimental details

A rapid liquid-phase sintering method with a high heating rate of \(-100 \, ^\circ\text{C/s}\) was applied to prepare single-phase Bi\(_{1-x}\)Sm\(_x\)FeO\(_3\) ceramics [4]. High-purity 99.95\% oxide powders were weighed according to the nominal compositions of Bi\(_{0.875}\)Sm\(_{0.125}\)FeO\(_3\). Each type of powder was finely milled into sizes of \(<1 \, \mu\text{m}\). After being dried, the powders were mixed thoroughly with water and pressed into disks with 0.8 mm thickness [4]. Then, these disks were dehydrated at 400 \, ^\circ\text{C} for 10 h before being sintered at a relatively high temperature of 855 \, ^\circ\text{C} for a short time of 40 min [4].

The crystal structure of the sintered samples was examined by an X-ray diffractometer (XRD, Bruker D8 Advance System). Simulation of the crystal structure was carried out with Rietveld method. The ceramics were thinned down to \(-0.35 \, \text{mm}\) thick and then a Pt film was deposited on each of its up and down surfaces as electrodes. The polarization versus electric field (P-E) loops was measured at 5 Hz with a Radiant multiferroic tester. A dc electric field of 200 kV/cm was applied to polarize the samples for 30 min. The polarization process was paused for 2 min to lower the sample’s temperature when leakage current was over 0.1 mA. The piezoelectric coefficient was measured at 60 Hz by using a piezo-electric force microscopy under 500 kV/cm.

3. Results and discussion

The XRD patterns of Bi\(_{0.95}\)Sm\(_{0.05}\)FeO\(_3\), Bi\(_{0.875}\)Sm\(_{0.125}\)FeO\(_3\) and Bi\(_{0.85}\)Sm\(_{0.15}\)FeO\(_3\) are shown in Fig. 1. The XRD patterns of Bi\(_{0.95}\)Sm\(_{0.05}\)FeO\(_3\) and Bi\(_{0.875}\)Sm\(_{0.125}\)FeO\(_3\) agree well with a trirhombic R\(_3\)c phase and (c) orthorhombic P\(_{\text{bam}}\) phase, where red arrows represent local ferroelectric polarization.

Fig. 1. The measured XRD patterns and Rietveld fitting data of Bi\(_{1-x}\)Sm\(_x\)FeO\(_3\) ceramics, where the two insets are two local amplifications. The unit cells of (b) rhombohedral R\(_3\)c phase and (c) orthorhombic P\(_{\text{bam}}\) phase, where red arrows represent local ferroelectric polarization.

Fig. 2. (a) The P–E loops of Bi\(_{0.875}\)Sm\(_{0.125}\)FeO\(_3\) at \(E_{\text{max}} = 140, 160, 180, 200 \, \text{kV/cm}\), respectively, and (b) room-temperature \(d_{33}\) measured after the sample was annealed at various temperatures.
shows much larger $P_e$ and piezoelectric $d_{33}$ value than those of $\text{Bi}_{0.30}\text{Sm}_{0.05}\text{FeO}_3$ and $\text{Bi}_{0.85}\text{Sm}_{0.15}\text{FeO}_3$, which is consistent with previous reports [15].

Fig. 3 shows the dependence of relative dielectric constant ($\varepsilon_r = \varepsilon'_r / \varepsilon_0$) and dielectric loss (tanh = $\varepsilon''_r / \varepsilon'_r$) on temperature. The $\varepsilon_r$ varies slightly at different frequencies below 240 °C, however it strongly depends on frequency at 240–480 °C, e.g., $\varepsilon_r$ of 657 at 100 kHz, 408 at 500 kHz and 246 at 2 MHz for measurement at 360 °C (Fig. 3a). Then, the $\varepsilon_r$ becomes negative at 480–770 °C. The fast drop of $\varepsilon_r$ is due to the partial decomposition of $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$ above 780 °C. The tanh = $\varepsilon''_r / \varepsilon'_r$ reaches strong peaks at ~480, ~670 and 780 °C because $\varepsilon'_r$ is close to zero (Fig. 3b). This phenomenon is similar to the $\varepsilon_r$ frequency dispersion of ferroelectric relaxors [16], however, their origins should be different. The parasitic series inductance and resistance modifies the measured capacitance values as the sample resistance decreases with increasing temperature, which can lead to a relaxor-like artifact, negative capacitance and super large dielectric loss in Figs. 3 and 4 [17,18].

Correspondingly, the capacitance peaks are observed at <550 °C in C–F curves of $\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$ ceramics in Fig. 4, confirming the piezoelectric response to the 0.5 V AC measurement signal. At first, the C–F curve is measured by Agilent standard clamp compared with that measured at 20 °C in a temperature-control oven. There is no obvious difference between these two curves. With the temperature increasing from 20 to 420 °C, the capacitance at low frequency (e.g., 1 kHz) increases fast because more and more dipoles are activated or produced by thermal excitation and can follow the frequency of 0.5 V AC measurement signal. The capacitance peaks from planar and thickness resonance can be differentiated at ~287 kHz and ~3.76 MHz though their intensity weakens a lot with the temperature increasing from 20 to 480 °C. The dielectric loss (i.e., tanh = $\varepsilon''_r / \varepsilon'_r$) also shows a peak at ~3.76 MHz below 480 °C, however, zero $\varepsilon'_r$ introduces a very strong peak at 480 °C which was marked with red squares in Fig. 4b. Besides, the negative capacitance is observed at 500–600 °C [17,18]. Although capacitance peaks from planar resonance cannot be differentiated at ~287 kHz above 480 °C, the capacitance peaks from planar resonance still remain at ~3.76 MHz and at <550 °C, respectively. Then, this capacitance peak completely disappears at 600 °C, which suggests that the peak at 550 °C arises from piezoelectric thickness resonance rather than parasitic inductance and resistance [18].

After the polarized ceramics were measured at 600 °C and then cooled down to 20 °C, the capacitance is close to that of as-polarized ceramics (Top inset of Fig. 4a). The capacitance and dielectric loss of annealed ceramics still have peaks at ~325 kHz from piezoelectric planar resonances and at ~4.5 MHz from piezoelectric thickness resonances. Their resonance frequencies become a little larger and the intensity becomes much weaker compared with those of as-polarized ceramics. In addition to this, other resonance frequencies also shift slightly at different temperatures, because resonance can be influenced by polarization and vibrating speed of ceramics, which also slightly depends on temperature. This suggests that the polarized ceramics did not completely depolarize at 600 °C, being consistent with the room-temperature $d_{33}$ of 20.1 pC/N after the sample was annealed at 600 °C.

Piezoelectric coefficients (i.e., $k_p$, $k_t$, $Q_{mn}$ and $Q_{0mn}$) were derived from dielectric resonance in capacitance–frequency (C–F) curve, which can be conveniently measured at high temperature in Fig. 4a. Both capacitance and dielectric loss reach several peaks because of piezoelectric resonance. The first and the second planar resonances/anti-resonances at room temperature occur at 287.2/
292.6 and 762.2/774.5 kHz, respectively, which corresponds to the $k_p$ of 0.6 and the $Q_{33-kp}$ of 14.23 according to the formula in IEEE Standard on Piezoelectricity [11]. Besides, the first thickness resonance/anti-resonance at 3.763/3.914 MHz corresponds to the $k_t$ of 0.84 and the $Q_{33-kt}$ of 64.95 at room temperature [11]. With temperature increasing to 200 °C, the $k_p$ and $k_t$ remain unchanged while $Q_{33-kp}$ and $Q_{33-kt}$ drop to 8.03 and 33.47, respectively. The second planar resonance becomes blurred above 200 °C, however, it is unable to calculate its mechanical coupling factors. During C–F curve measurement, the polarized ceramics can be deformed while being applied 0.5 V AC field along thickness direction due to planar resonance and $k_p$ of 64.95 at room temperature [11]. With temperature increasing to 200 °C, the $k_p$ and $k_t$ remain unchanged.

The impedance and the resistance decrease fast with temperature increasing to 600 °C. Impedance peaks also occur at ~287 kHz due to thick-electric thickness resonance and planar resonance contribute to capacitance peaks and impedance peaks at ~550 °C, respectively, though samples’ resistance has already decreased to ~10 ohm at 500 °C.

4. Conclusions

The Bi$_{0.875}$Sm$_{0.125}$FeO$_3$ ceramic with rhombohedral R3c structure has a ferroelectric polarization of 40 μC/cm$^2$ at room-temperature. The as-polarized ceramics show an enhanced piezoelectric $d_{33}$ of 45 pC/cm at 20 °C, however, it decreases to 20 pC/N after the ceramic was annealed at 600 °C. This suggests the existence of ferroelectric component with high Curie temperature. Both piezoelectric thickness resonance and planar resonance contribute to capacitance peaks and impedance peaks at 600 °C, respectively, though samples’ resistance has already decreased to <100 ohm at 500 °C.

Acknowledgments

This work was supported by the National Key Project for Basic Research of China (2012CB619406), the National Natural Science Foundation of China (11134004 and 51072081) and the Natural Science Foundation of Jiangsu Province (SBK201123822).

References