Processing and properties of Yb-doped BiFeO₃ ceramics

Z. Yan, K. F. Wang, J. F. Qu, and Y. Wang[a)]
Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong Special Administrative Region, China and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong Special Administrative Region China

Z. T. Song and S. L. Feng
Laboratory of Nano-Technology, Shanghai Institute of Microsystems and Information Technology, The Chinese Academy of Sciences, Shanghai 200000, China

The authors prepared Yb-doped bismuth iron oxide ceramics ($Bi_{1-x}Yb_xFeO_3$, with $0 \leq x \leq 0.20$) by rapid liquid phase sintering method and investigated the material's structures and electrical properties. The x-ray diffraction measurements showed that the doping of Yb has induced noticeable lattice distortion in the ceramics, and a largest distortion was observed when the concentration of Yb was 15%. By doping electrical resistivity, ferroelectric and dielectric properties of the ceramics were improved. Among all samples, $BiFeO_3$ doped with 15% Yb was found to have the smallest leakage current density ($< 10^{-7}$ A/cm²) and the largest remnant polarization (8.5 μC/cm²). © 2007 American Institute of Physics. [DOI: 10.1063/1.2775034]

The compound $BiFeO_3$ (abbreviated as BFO) was first synthesized in the late 1950s.[1] Research in the early stage, which mainly focused on ceramics, revealed that BFO possesses a rhombohedrally distorted perovskite structure (lattice parameters $a = b = c = 0.563$ nm and $\alpha = \beta = \gamma = 59.4°$) in addition to coupled ferroelectric (Curie temperature $T_C \sim 1103$ K) and antiferromagnetic (Neel temperature $T_N \sim 643$ K) behaviors at room temperature. Despite a high Curie temperature, the bulk BFO exhibits very weak ferroelectric behavior (e.g., the spontaneous polarization P_s, is only $\sim 3.5 \mu$C/cm²).[2–5] BFO thin films have been studied since the late 1980s.[6] In 2003, Wang *et al.* reported that a very large ferroelectric polarization (remnant polarization $P_r \sim 60 \mu$C/cm²) has been achieved in a BFO thin film epitaxially grown on $SrRuO_3/SrTiO_3$.[7] The significantly enhanced polarization was interpreted as the result of a compressive stress imposed by the $SrRuO_3$ electrode, which has an in-plane lattice parameter smaller than that of BFO. Because of the compressive stress, the epitaxial BFO film has a tetragonal-like crystal structure ($a = 0.394$ nm, $c = 0.400$ nm, and $\alpha = 89.5°$) rather than the rhombohedral symmetry in bulk materials and therefore leads to large polarization. Since then more studies have reported with successful development of BFO thin films with polarizations ranging from 50 to 150 μm/cm².[2,8–10] Theoretical work has also been conducted to interpret the extraordinarily large ferroelectric polarization in BFO films.[11]

The success in the thin film studies has in turn stimulated interest to produce bulk ceramics with improved properties. New processing techniques, such as rapid liquid phase sintering, have been developed to synthesize single-phase BFO ceramics.[12,13] The effect of compositional modification, either by forming of solid solution (e.g., with $Pb(Zr_{1-x},Ti_x)O_3$)[14] or by doping, has also been extensively studied. Quite a number of transition metal elements (e.g., Ni, Ti, Cr, and Mn)[15–18] and rare-earth elements (e.g., La and

Nd)[19,20] have been employed as dopants. The authors are more interested in the doping of rare-earth elements because this may significantly change both the ferroelectric properties and magnetic behaviors of BFO which could possibly lead to enhanced magnetoelectric effect.[21,22] In this work, we report the synthesis and characterization of ytterbium (Yb)-doped $BiFeO_3$ ceramics. Yb was chosen as dopant mainly because it has small atomic and ionic radii and thus, the doping could lead to large lattice distortion to BFO and, consequently, giving rise to enhanced ferroelectric polarization.

In this study, $Bi_{1-x}Yb_xFeO_3$ ($x = 0-0.2$) ceramics were prepared by the rapid liquid phase sintering method.[12] High purity powders of Bi_2O_3, Fe_2O_3, and Yb_2O_3 were used as starting materials. After weighing, ball milling, and drying, the mixed powders were dry pressed (a very small amount of water was used as "binder" in the dry pressing) into small cylindrical pellets with a diameter of ~ 10 mm and thickness of ~ 0.5 mm. After being dehydrated in a vacuum chamber at 150 °C for 12 h, the samples were put into a furnace for sintering. During the sintering, the furnace temperature was quickly raised to 855 °C and kept at this value for 20 min before it was lowered to room temperature. The heat up and cooling rates were ~ 100 and 10 °C/s respectively. The crystal structures of the sintered samples were examined by x-ray diffraction (XRD) on an x-ray diffractometer (Brucker D8 Discover) using Cu $K\alpha$ radiation with a wavelength of 0.15408 nm. The polarization hysteresis (P-E) loop was measured with a standard Sawyer-Tower circuit at a frequency of 100 Hz and the dielectric properties were determined by using an impedance analyzer (Agilent 4294A).

Figure 1 shows the XRD patterns of the $\theta/2\theta$ scan on our ceramic samples. All peaks can be indexed based on the pervoskite-type structure. A noticeable lattice distortion can be observed in the Yb-doped samples. For example, the peak position of (110) planes for the undoped BFO is 31.67°. When the amounts of doping increased from 0.05, 0.1, 0.15, and 0.2, the peak positions changed to 31.50°, 31.25°, 31.50°, and 31.60°, respectively. This means that doping of lattice expansion in the doped ceramics with the largest distortion occurs at $x = 0.15$. This result is analogous to that in

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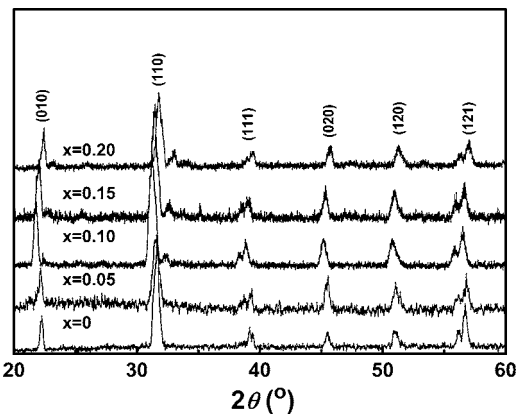[a)]Author to whom correspondence should be addressed; FAX: +852-23337629; electronic mail: apywang@inet.polyu.edu.hk

FIG. 1. X-ray diffraction patterns of $Bi_{1-x}Yb_xFeO_3$ ceramics with $x=0$, 0.05, 0.1, 0.15, and 0.2, respectively.

the Nd-doped BFO ceramics reported in the literature.[19]

Electrical properties of the ceramics were determined. Figure 2 shows the electric field dependence of leakage current density (J-E) at room temperature. Under a same test voltage, the Yb-doped BFO has a smaller leakage current density than the undoped and the smallest leakage current density was obtained in the sample with 15% Yb. When test voltage is equal to 6 V, for example, the leakage current densities of BFO-15%Yb and pure BFO are 2×10^{-7} and 5×10^{-5} A/cm^2, respectively.

The mechanism for the leakage current reduction in the doped samples is complicated. According to recent literature, the leakage current mechanism in $BiFeO_3$ is dominated by Poole-Frenkel emission, which is analogous to that in some other ferroelectric perovskites such as $Pb(Zr,Ti)O_3$.[23–25] This conduction mechanism involves the consecutive hopping of charges between defect trap centers. In undoped BFO, the oxygen vacancies rather than Fe^{2+} ions are the main cause of high conductivity and the likely trap center is the oxygen vacancy.[15] Therefore, the Yb-doping effect on the electrical conductivity in our samples is very likely a result of changes of oxygen vacancy concentration. To better understand the conduction mechanism, we have assessed the samples' electrical conductivity at elevated temperatures. The measurement results shown in the inset of Fig. 2 are found to conform to Arrhenius' law and follow the equation σ
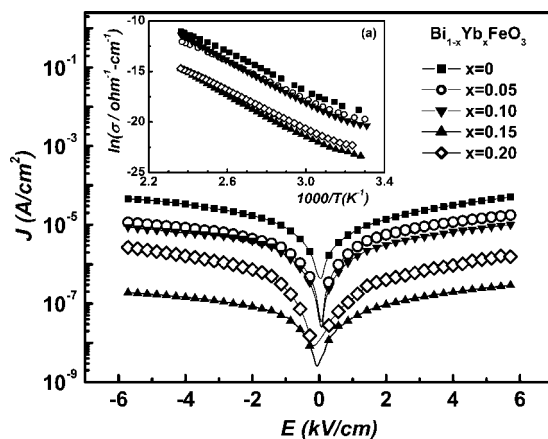

FIG. 2. Leakage current as a function of applied electrical field in $Bi_{1-x}Yb_xFeO_3$ ceramics with $x=0$, 0.05, 0.1, 0.15, and 0.2, respectively. The inset shows the temperature dependence of electrical conductivity of the samples.
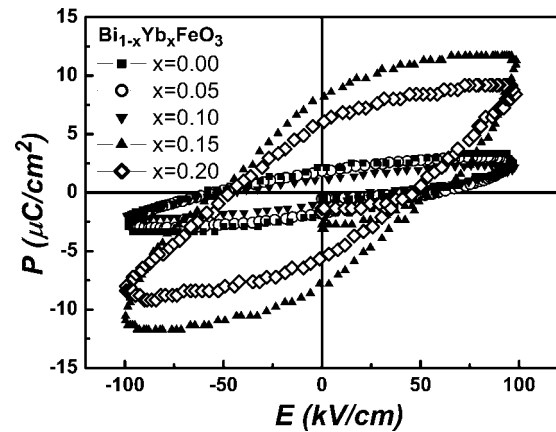

FIG. 3. Ferroelectric hysteresis loops of $Bi_{1-x}Yb_xFeO_3$ ceramics with $x=0$, 0.05, 0.1, 0.15, and 0.2, respectively.

$= \sigma_0 \exp(-E_a/kT)$, where σ_0 is the preexponential coefficient, E_a is the activation energy of conduction or the Poole-Frenkel trap ionization energy, k is Boltzmann's constant, and T is the absolute temperature. The values of E_a for all five compositions were found to be 0.815, 0.807, 0.912, 0.929, and 0.837 eV, respectively, all falling in the typical range (0.9–1.4 eV) of activation energy for oxygen vacancies in some typical materials.[26] This implies that the conduction of all samples is dominated by oxygen vacancy motion and the different oxygen vacancy concentrations have led to significant difference in room temperature resistivity between samples.

Figure 3 shows the ferroelectric properties of the ceramics measured at room temperature. Under a maximum test field of 100 kV/cm, the saturated polarization (P_s) and remnant polarization (P_r) of the undoped $BiFeO_3$ were found to be 3.3 and 2.1 $\mu C/cm^2$, respectively, which are consistent with the literature. All doped samples have exhibited improved polarization and the largest polarizations in all samples were observed in BFO with 15%Yb—under 100 kV/cm, $P_s=11.7$ $\mu C/cm^2$, and $P_r=8.5$ $\mu C/cm^2$. These results are comparable to the enhanced polarizations of modified BFO bulk ceramics reported in the literature.[12,13,20,27] (For example, in Ref. 13, a P_s of 17 $\mu C/cm^2$ was found in a quenched BFO ceramic tested under 155 kV/cm and in Ref. 27, a P_s of 20 $\mu C/cm^2$ was obtained in La-doped BFO ceramics measured under 200 kV/cm.) It is believed that the enhancement in the ferroelectric polarization of the doped ceramics is due to both lattice distortion and leakage current reduction.[7,12,13]

Associated with the change of ferroelectric properties, the dielectric properties of the samples were also found to be dependent on the doping level. Figure 4 illustrates the frequency (f) dependence of relative dielectric constant (ε) for the $Bi_{1-x}Yb_xFeO_3$ ($x=0$, 0.05, 0.1, 0.15, and 0.2) ceramics. All samples display a decreasing trend in ε with increasing f from 1000 Hz to 4 MHz and Yb-doped $BiFeO_3$ possesses a larger ε from 57 of pure $BiFeO_3$ to 98 of $x=0.15$ Yb-doping content.

In summary, $BiFeO_3$ ceramic samples with different amounts of Yb doping have been synthesized and characterized. It was found that the doping of Yb has caused noticeable lattice distortion of the ceramics. Large electrical resistance and higher ferroelectric polarizations have been
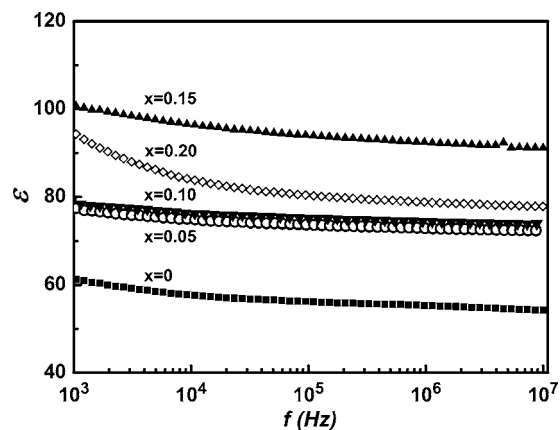
FIG. 4. Dielectric constant as a function of frequency in $Bi_{1-x}Yb_xFeO_3$ ceramics with $x=0$, 0.05, 0.1, 0.15, and 0.2, respectively.

observed in the doped ceramics and the best properties were obtained in $BiFeO_3$ doped with 15% Yb.

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