Structural transformation and ferroelectromagnetic behavior in single-phase Bi$_{1-x}$Nd$_x$FeO$_3$ multiferroic ceramics

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(Received 18 April 2006; accepted 16 June 2006; published online 4 August 2006)

Single-phase Bi$_{1-x}$Nd$_x$FeO$_3$ (BNFO) ($x$=0–0.2) multiferroic ceramics were prepared to study the effects of Nd substitution on their crystal structure and ferroelectromagnetic behavior. Rietveld refinement of x-ray diffraction data showed a continual transformation of crystal structure from the rhombohedral structure of BNFO$_{x=0}$ (BiFeO$_3$) to a triclinic structure in BNFO$_{x=0.05-0.15}$ and a pseudotetragonal structure in BNFO$_{x=0.175-0.2}$. Ferroelectromagnetic measurements revealed the existence of ferroelectricity with remnant polarization of $\sim$9 $\mu$C/cm$^2$ in BNFO$_{x=0.0-0.175}$, paraelectricity in BNFO$_{x=0.2}$, and weak ferromagnetism with remnant magnetizations of 0.07–0.227 emu/g in BNFO$_{x=0.15-0.2}$. Magnetoelectric coupling was obvious in BNFO$_{x=0.15-0.175}$ near the Néel temperature of $\sim$380 °C. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2266992]

Single-phase BiFeO$_3$ is one of very important multiferroic materials characterized by the high Curie ($T_C$ $\sim$ 830 °C) and Néel ($T_N$ $\sim$ 370 °C) temperatures. Extensive studies have been put on this bulk ceramic in recent years, yet three crucial problems have limited the release and studies have been put on this bulk ceramic in recent years, yet three crucial problems have limited the release and realization weak ferromagnetism-antiferromagnetism interaction, and magnetoelectric coupling. The specific synthesis technique that was adopted to prepare single-phase BNFO$_{x=0.15}$ samples was used to prepare BNFO$_{x=0.15}$ disk samples with diameter of 5 mm and thickness of 1 mm. This technique involved the use of high-purity ($>$99%) Bi$_2$O$_3$, Fe$_2$O$_3$, and Nd$_2$O$_3$ powders of $<$1 $\mu$m size and a rapid liquid-phase sintering process of 855 °C for 20 min at high heating and cooling rate of 100 and 10 °C/s, respectively.

Figure 1 shows the comparison between the measured and simulated XRD patterns of BNFO$_{x=0.15}$ and BNFO$_{x=0.2}$. The crystal structure of the sintered samples was examined by an x-ray diffractometer (Brucker D8) with a 2$\theta$ step size of 0.02° and at a scan rate of 1 step per 4 s. Simulation of crystal structure based on the measured x-ray diffraction (XRD) data was performed using a Rietveld crystal structure refinement software (FULLPROF 2000). The polarization hysteresis ($P$-$E$) loop was measured with a standard Sawyer-Tower circuit at 100 Hz. The magnetization hysteresis ($M$-$H$) loop was evaluated using a superconducting quantum interference device (Quantum Design XL7d). The temperature dependence of the relative dielectric constant ($\varepsilon$) and loss tangent (tan $\delta$) was determined at 10 kHz using an impedance analyzer (Agilent 4294A).

Recently, we have shown that problems 1 and 2 can be solved using a specific synthesis technique. To practically realize weak ferromagnetism (problem 3), Mathe et al. proposed to suppress the space-modulated spin structure of BiFeO$_3$ by A-site substitution of a smaller Nd$_{3+}$ ion for Bi$_{3+}$ ion. While structural, dielectric, and electrical properties of Bi$_{1-x}$Nd$_x$FeO$_3$ (BNFO) were obtained for various Nd concentration $x$ of 0.2–1, the effects of ferroelectricity and weak ferromagnetism were not addressed at all due to the extremely low resistivity and paraelectric nature of their samples. In this letter, we prepared single-phase BNFO$_{x=0}$ bulk samples with $x$ slightly varying in the ferroelectric-ferroelectric transition region of 0–0.2 (where BNFO$_{x=0}$ is BiFeO$_3$) and reported their crystal structure parameter changes, ferroelectricity-ferroelectricity transition, weak magnetism-antiferromagnetism interaction, and magnetoelectric coupling.

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In order to further analyze such transformation, the measured XRD patterns of the samples were used in Rietveld refinement of crystal structures based on a triclinic structure, P1 space group, and a single cell with A-site Bi/Nd mixed atoms rather than a supercell. In more detail, since single-phase BiFeO$_3$ has a rhombohedral structure with R3c space group at room temperature, this highly symmetric structure can be treated as a special triclinic structure with comparatively lower symmetry. As a result, all the BNFO$_{x=0-0.2}$ samples were considered to have a triclinic structure in the refinement for ease of comparison of the refinement results. As shown in Fig. 1, the simulated XRD patterns coincide well with the measured XRD patterns with generally small $R_w$ values (i.e., $\leq 8.84\%$ for $R_w$ and $\leq 6.32\%$ for $R_p$). Thus, our BNFO$_{x=0-0.2}$ samples should have a single-phase triclinic structure with P1 space group by nature, and BNFO$_{x=0}$ that possess a single-phase rhombohedral structure with R3c space group in specific can be regarded as a special triclinic structure with P1 space group.

Figure 2 illustrates the refined crystal structure parameters as a function of $x$. The rhombohedral structure of BNFO$_{x=0}$ with crystal axes $a=b=c=3.942$ Å and crystal axial angles $\alpha=\beta=\gamma=89.43^\circ$ is confirmed again in this study. A distortion of crystal structure from the rhombohedral structure of BNFO$_{x=0}$ to a triclinic structure (i.e., $a \neq b \neq c; \alpha \approx \beta \approx \gamma$) with larger crystal structure parameters occurs in BNFO$_{x=0.05}$. BNFO$_{x=0.1}$ also shows a triclinic structure even though its crystal structure parameters are subtle different from those of BNFO$_{x=0.05}$. BNFO$_{x=0.15}$ displays comparatively larger $a$, $b$, $\alpha$, $\beta$, and $\gamma$ values, besides a relatively smaller $c$ value, than the rhombohedral structure of BNFO$_{x=0}$. This indicates that while BNFO$_{x=0.15}$ can be described by a triclinic structure, there is a tendency for it to transform to a pseudotetragonal structure with $a=b>c$ and $\alpha=\beta=\gamma=90^\circ$. Both BNFO$_{x=0.175}$ and BNFO$_{x=0.2}$ demonstrate a pseudotetragonal-like structure with $a=b>c$ and $\alpha=\beta=\gamma=90^\circ$ as a result of a primary tetragonal distortion plus a possible small triclinic distortion. Consequently, BNFO$_{x=0-0.2}$ transforms from rhombohedral structure at $x=0$ to triclinic structure at $x=0.05–0.15$ and finally to pseudotetragonal structure at $x=0.175–0.2$.

Figure 3 plots the polarization hysteresis ($P-E$) loops of BNFO$_{x=0}$, BNFO$_{x=0.1}$, BNFO$_{x=0.175}$, and BNFO$_{x=0.2}$ samples measured at 100 Hz. Obvious ferroelectric behavior with a large remnant polarization ($P_r$) of $\sim 9 \mu C/cm^2$ is observed in BNFO$_{x=0}$, BNFO$_{x=0.1}$, and BNFO$_{x=0.175}$. While paraelectric behavior is seen in BNFO$_{x=0.2}$. For the ferroelectric BNFO$_{x=0}$, BNFO$_{x=0.1}$, and BNFO$_{x=0.175}$, the maximum polarization ($P_m$) and electric field ($E_m$) are 17.9 $\mu C/cm^2$ at 137 kV/cm, 18.1 $\mu C/cm^2$ at 139 kV/cm, and 19.1 $\mu C/cm^2$ at 143 kV/cm, respectively. These ferroelectric $P_m$ values are significantly larger than the paraelectric $P_m$ of 1.9 $\mu C/cm^2$ even at a higher $E_m$ of 145 kV/cm in BNFO$_{x=0.2}$. The results suggest that the stereochemical activ-
ity of the Bi lone electron pair plays an important role in the transition from ferroelectricity to paraelectricity at 0.175 < x < 0.2.\textsuperscript{1,3} In conventional ferroelectric perovskites, the ferroelectric distortion is stabilized by charge transfer from the oxygen to the unoccupied transition metal d orbitals. Although Bi\textsuperscript{3+} ion has been partially substituted by Nd\textsuperscript{3+} ion in our BNFO\textsubscript{x} samples, a lone \textsuperscript{5}p pair of electrons of a Bi\textsuperscript{3+} ion may hybridize with an empty p orbital of Bi\textsuperscript{3+} or an O\textsuperscript{2−} ion to form a localized lobe, resulting in the non-centrosymmetric distortion and hence ferroelectricity.\textsuperscript{1,2} Further increase in x towards 0.175 tends to weaken the stereochemical activity of the Bi lone electron pair, leading to a ferroelectric-paraelectric transition at 0.175 < x < 0.2. As the crystal structure parameters only change slowly in the range of 0.175–0.2, the stereochemical activity should have the predominant effect on the observed ferroelectric-paraelectric transition.

Figure 4 shows the magnetization hysteresis (M-H) loops of BNFO\textsubscript{x=0.2} samples for the maximum magnetic field (H\textsubscript{m}) of 60 kOe. It is evident that the antiferromagnetism intrinsic in BNFO\textsubscript{x=0} becomes weak ferromagnetism with a small but nonzero M\textsubscript{r} of \approx 0.0227 emu/g in BNFO\textsubscript{x=0.1–0.2}. From the inset of Fig. 4, M\textsubscript{r} essentially vanishes in BNFO\textsubscript{x=0}; it exhibits a slow increasing trend from zero for x \approx 0.1 before displaying a relatively rapid rise from 0.015 to 0.227 emu/g when x is increased from 0.1 to 0.2. In fact, the crystal structure parameters change dramatically in the x range of 0.1–0.175, as evidenced in Fig. 2. The continuing increase in M\textsubscript{r} in our samples is likely due to the continuing collapse of the space-modulated spin structure of BNFO\textsubscript{x=0}.\textsuperscript{4,6,12} Indeed, the transformation from the rhombohedral structure in BNFO\textsubscript{x=0} to triclinic structure in BNFO\textsubscript{x=0.05–0.15} and then to pseudotetragonal structure in BNFO\textsubscript{x=0.175–0.2} gives rise to the continuing collapse of the space-modulated spin structure.\textsuperscript{4,6,12}

Figure 5 shows the temperature dependence of relative dielectric constant (\varepsilon) and loss tangent (tan \delta) at 10 kHz for BNFO\textsubscript{x=0.175} and BNFO\textsubscript{x=0.2} samples. It is found that BNFO\textsubscript{x=0.175} has dielectric anomalies at T\textsubscript{N} of \approx 380 °C, which is similar to those of BNFO\textsubscript{x=0} at T\textsubscript{N} of \approx 370 °C and suggests the presence of magnetoelectric coupling in BNFO\textsubscript{x=0.175} for temperatures below \approx 380 °C.\textsuperscript{1,3–13} However, dielectric anomalies are not detected in BNFO\textsubscript{x=0.2} in the whole temperature range of 40–450 °C.\textsuperscript{9} As found in Fig. 3, BNFO\textsubscript{x=0.2} is paraelectric rather than ferroelectric; it should not display any magnetoelectric coupling, i.e., the origin of dielectric anomalies near T\textsubscript{N}.

In conclusion, we have found that single-phase BNFO\textsubscript{x} multiferroic ceramics have a rhombohedral structure at x = 0, a triclinic structure at x = 0.05–0.15, and a pseudotetragonal structure at x = 0.175–0.2. The ferroelectric-paraelectric transition occurred at 0.175 < x < 0.2 mainly results from the weakening of the stereochemical activity of the Bi lone electron pair. Due to the transformation of crystal structure, the space-modulated spin structure in BNFO\textsubscript{x=0} collapses continuously with increasing x and eventually releases weak ferromagnetism at x = 0.15–0.2. The coexistence of ferromagnetism and weak ferromagnetism in BNFO\textsubscript{x=0.15–0.175} allows significant magnetoelectric coupling near the Néel temperature of \approx 380 °C.

This work was supported by the Hong Kong Research Grants Council (PolyU 5255/03E) and the National Natural Science Foundation of China (10374048 and 50502018).