Enhanced piezoelectric and pyroelectric effects in single-phase multiferroic Bi$_{1−x}$Nd$_x$FeO$_3$ (*x*=0−0.15) ceramics

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Single-phase multiferroic Bi$_{1−x}$Nd$_x$FeO$_3$ (*x*=0−0.15) ceramics are polarized and their piezoelectric and pyroelectric effects are reported. The success in polarizing the ceramics originates from low electrical conductivities controlled predominantly by the Poole-Frenkel conduction mechanism. Limited internal traps due to reduced oxygen vacancies in the ceramics result in sufficiently low leakage current densities of <30 mA/m^2 even at a high electric field of 145 kV/cm. The piezoelectric d_{33} coefficients of the ceramics before and after annealing at 550 °C for 4 h are measured to be $\sim$28 and $\sim$24 pC/N, respectively. These values are higher than those of most major lead-free high-temperature piezoelectric ceramics. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2169905]

Multiferroic materials possess both ferroelectric order and ferromagnetic (or antiferromagnetic) order in the same phase. As a result, they have a spontaneous polarization that can be switched by an applied electric field, a spontaneous magnetization that can be switched by an applied magnetic field, and often some coupling between the two.[1]

Single-phase BiFeO$_3$ ceramic, which has ferroelectric order below a high Curie temperature ($T_C \sim 830$ °C) and antiferromagnetic order below a high Néel temperature ($T_N \sim 370$ °C), is one of the most widely studied multiferroic materials.[1–3] However, BiFeO$_3$ becomes unsuitable for applications owing to its high leakage current (i.e., subject to dielectric breakdown at fields <100 kV/cm) besides exhibiting a spatial nonuniformity of magnetic structure and a quadratic ferromagnetoelectric behavior.[1,3,4]

By using smaller Nd^{3+} ions (radius=0.983 Å) in substitution for larger Bi^{3+} ions (radius=1.03 Å) in the BiFeO$_3$ composition, it is possible to create single-phase multiferroic Bi$_{1−x}$Nd$_x$FeO$_3$ (*x*=0−0.15) ceramics possessing an improved spatial uniformity of magnetic structure, and a rather linear ferromagnetoelectric behavior.[5,6] Nevertheless, it still remains a significant challenge to prepare such single-phase ceramics with sufficiently low leakage current densities (i.e., $J < 30$ mA/m^2 at 145 kV/cm). Accordingly, effectively polarized samples demonstrating favorable piezoelectric and pyroelectric effects are not yet found.

The challenge can further be described by the reaction mechanisms shown in Eqs. (1)–(7). Equations (1)–(5) indicate that if Bi$_2$O$_3$, Fe$_2$O$_3$, and Nd$_2$O$_3$ powders do not react with each other during the sintering process due to some specific reasons such as the volatilization of Bi$_2$O$_3$, insufficient mixing of powders, or inadequate sintering conditions, it will be difficult to keep the stoichiometry of Bi$_{1−x}$Nd$_x$FeO$_3$ and hence to form single-phase ceramics.[3,7] The reaction mechanisms are as follows:

$$\mathrm{Bi_2O_3 + Fe_2O_3 \Rightarrow (1-x)BiFeO_3 + (x/2)(Bi_2O_3}$$
$$\mathrm{+ Fe_2O_3) \ [no \ reaction],} \tag{1}$$

$$\mathrm{(1-x)Bi_2O_3 + xNd_2O_3 + Fe_2O_3 \Rightarrow 2(1-x)BiFeO_3}$$
$$\mathrm{+ x(Nd_2O_3 + Fe_2O_3) \ [no \ reaction],} \tag{2}$$

$$\mathrm{Bi_2O_3 + Fe_2O_3 \Rightarrow (4/25)Bi_{12}(Bi_{1/2}Fe_{1/2})O_{19}}$$
$$\mathrm{+ (24/25)Fe_2O_3 \ [no \ reaction],} \tag{3}$$

$$\mathrm{Bi_2O_3 + Fe_2O_3 \Rightarrow (1/18)Bi_{36}Fe_2O_{57}}$$
$$\mathrm{+ (17/18)Fe_2O_3 \ [no \ reaction],} \tag{4}$$

$$\mathrm{Bi_2O_3 + Fe_2O_3 \Rightarrow (1/2)Bi_2Fe_4O_9}$$
$$\mathrm{+ (1/2)Bi_2O_3 \ [volatilization \ or \ no \ reaction].} \tag{5}$$
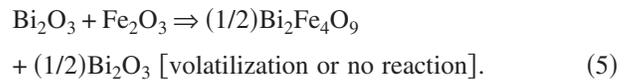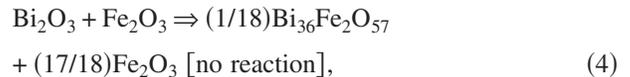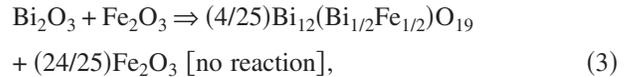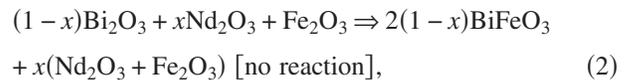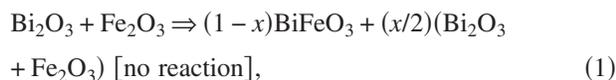
In addition, Eqs. (6) and (7) suggest that if Fe^{3+} ions partially transfer to Fe^{2+} ions, or if Bi^{3+} ions volatilize in single-phase Bi$_{1−x}$Nd$_x$FeO$_3$, it will be hard to reduce oxygen vacancies (V$_O^{2+}$) or bismuth vacancies (V$_{Bi}^{3−}$), leading to highly conductive samples:[5,6,8]

$$\mathrm{2Fe^{3+} + O^{2-} \Rightarrow 2Fe^{2+} + (1/2)O_2 \ [volatization] + V_O^{2+},} \tag{6}$$

$$\mathrm{2Bi^{3+} + 3O^{2-} \Rightarrow Bi_2O_3 + 2V_{Bi}^{3-} + 3V_O^{2+}.} \tag{7}$$
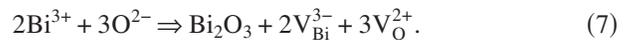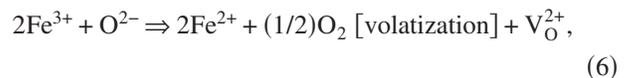
Therefore, it is our aim in the present work to study the preparation and polarization of low-conductive single-phase multiferroic Bi$_{1−x}$Nd$_x$FeO$_3$ (*x*=0−0.15) ceramics as well as measurements of their piezoelectric and pyroelectric properties. The possible conduction mechanism that governs low leakage currents in the ceramics (i.e., the precondition of polarizing the ceramics) is also investigated.

Bi$_{1−x}$Nd$_x$FeO$_3$ ceramics with *x* varying from 0 to 0.15 in steps of 0.05 were prepared by an improved rapid liquid-phase sintering method.[3,7] Stoichiometric amounts of Bi$_2$O$_3$ (99.9%), Fe$_2$O$_3$ (99.0%), and Nd$_2$O$_3$ (99.9%) were weighed, and each type of powder was milled into an average size of 1 μm. After drying, the powders were mixed thoroughly with water and pressed uniaxially into disk samples of 5 mm diameter and 1.5 mm thickness. The disk samples were dehydrated at 200 °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 with a high heating rate of 100 °C/s.

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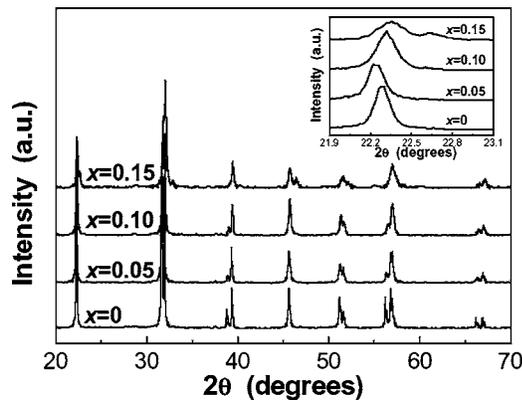
FIG. 1. XRD patterns of $Bi_{1-x}Nd_xFeO_3$ ceramics with $x=0$, 0.05, 0.1, and 0.15.

FIG. 2. The electric field dependence of leakage current density (J-E). The insets show the plots of J-E^2, $\ln J$-$E^{1/2}$, and $\ln(J/E)$-$E^{1/2}$ for the SCLC, Schottky, and Poole-Frenkel conduction mechanisms, respectively, where the symbols are the experimental data converted from the major J-E curves.

The crystalline structure of the sintered samples was examined using an x-ray diffractometer at a scan rate of 0.02° per 4 s (Brucker D8 Advance System).

The samples were then thinned down to 0.35 mm thickness, and silver paste was applied on their two major surfaces as electrodes for subsequent poling and measurements. The electric field dependence of leakage current density (J-E) of the samples was measured using a multimeter (Keithley 2000) and a high-voltage amplifier (Trek P0621P). Based on the measured J-E curves, an optimal electric field of 145 kV/cm was applied to polarize the samples at room temperature in a silicon oil bath for 1 h. The piezoelectric coefficient (d_{33}) of the polarized samples was measured at 60 Hz using a piezo-d_{33} meter (IAAS ZJ-30). The dielectric constant ($\varepsilon_{33}^T/\varepsilon_0$) was obtained at 1 kHz using an impedance analyzer (HP 4294A). The planar (k_p) and thickness (k_t) electromechanical coupling coefficients and their associated mechanical quality factors ($Q_{m,kp}$ and $Q_{m,kt}$) were determined using the impedance analyzer according to the resonance method.[9] The pyroelectric coefficient (p) and pyroelectric figure of merit (R_V) were measured at 0.01 Hz with an in-house pyroelectric coefficient measurement system.

Figure 1 shows the x-ray diffraction (XRD) patterns of $Bi_{1-x}Nd_xFeO_3$ samples with $x=0$, 0.05, 0.1, and 0.15. Besides the peaks associated with single-phase ABO_3-type perovskite structure, no other peaks are detected within the uncertainty of XRD. It has been reported that single-phase $BiFeO_3$ sample has a rhombohedral structure with $R3C$ space group at room temperature.[3,4] From the inset of Fig. 1, the $(001)_c$ peak according to pseudocubic lattice type undergoes a shift in 2θ and a split into two peaks when x is changed from 0 to 0.15. This reveals a continual change of lattice constant of monoclinic structure with $P1$ space group as a result of replacing the larger Bi^{3+} ions (radius =1.03 Å) by the smaller Nd^{3+} ions (radius=0.983 Å).[5,10] Therefore, our samples essentially have a single-phase rhombohedral ($x=0$) or monoclinic ($x=0.05-0.15$) perovskite structure with all constituent components forming a solid solution rather than a mixture of Bi_2O_3, Fe_2O_3, Nd_2O_3, and other impurity phases as stated in Eqs. (1)–(5).

Figure 2 illustrates the measured electric field dependence of leakage current density (J-E) for samples with $x=0$ and $x=0.15$. It is clear that J increases essentially linearly with E at the low end of E (<17 kV/cm), elucidating an ohmic conduction mechanism in this region. Thereafter,
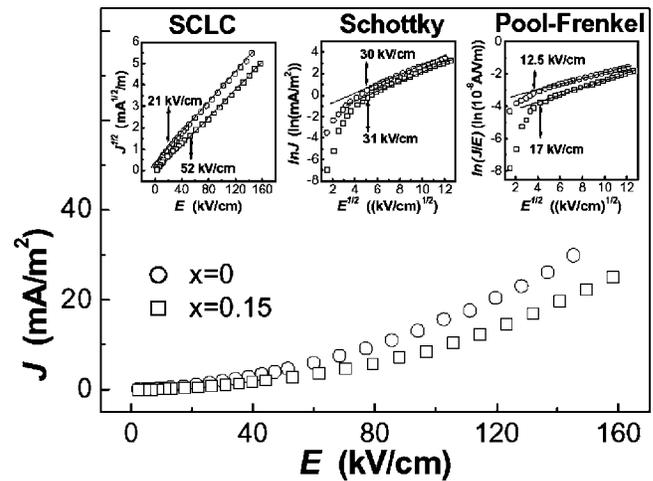
J exhibits an increasing trend faster than linear with E, implying the existence of a different conduction mechanism other than the ohmic in the high-E region. Since the presence of Fe^{2+} ions, V_{Bi}^{2+} vacancies, and V_O^{2+} vacancies is believed to be the main cause of high leakage current in $BiFeO_3$ ceramic,[3,6,8,11] and as polarity reversal of E does not produce Schottky effect (e.g., asymmetric J-E curves),[12] the most probable conduction mechanism for the high-E region should be due to the thermal excitation of inner charged defects, such as the Poole-Frenkel conduction mechanism with an electric-field-enhanced thermal excitation of charge carriers from internal traps. To obtain physical insights into the conduction above the ohmic region, three most important conduction mechanisms, namely, the space-charge-limited current (SCLC), Schottky, and Poole-Frenkel conduction mechanisms, are considered. Recalling that the J-E characteristics of the SCLC, Schottky, and Poole-Frenkel conduction mechanisms are characterized by the linear relationships of J-E^2, $\ln J$-$E^{1/2}$, and $\ln(J/E)$-$E^{1/2}$, respectively.[12–14] These three relationships are thus plotted as the three insets of Fig. 2 along with the measured J-E data shown in Fig. 2. It is found that the $\ln(J/E)$-$E^{1/2}$ plot controlled by the Poole-Frenkel conduction mechanism provides the most satisfactory description to the samples, suggesting that the electrical conduction above the ohmic region is mainly attributed to the Poole-Frenkel conduction mechanism with current density J_{PF} expressed as follows:

$$J_{PF} \propto E \exp\left(-\frac{q}{kT}\phi_{PF} + \beta_{PF}E\right), \qquad (8)$$

where q is the electron charge, k is the Boltzmann constant, T is the temperature, ϕ_{PF} is the barrier height, and β_{PF} is the temperature-dependent slope of the $\ln(J/E)$-$E^{1/2}$ plot. It is important to note that while J has been elevated in the Poole-Frenkel conduction region, it remains low enough (<30 mA/m²) that the samples are subject to a high poling field of 145 kV/cm. The observed low J in the Poole-Frenkel conduction region gives important evidence of minimizing the contributions of Fe^{2+}, V_{Bi}^{2+}, and V_O^{2+} to our samples.[3,6,8,11] This is partially attributed to the use of a high heating rate (100 °C/s) and a high sintering temperature
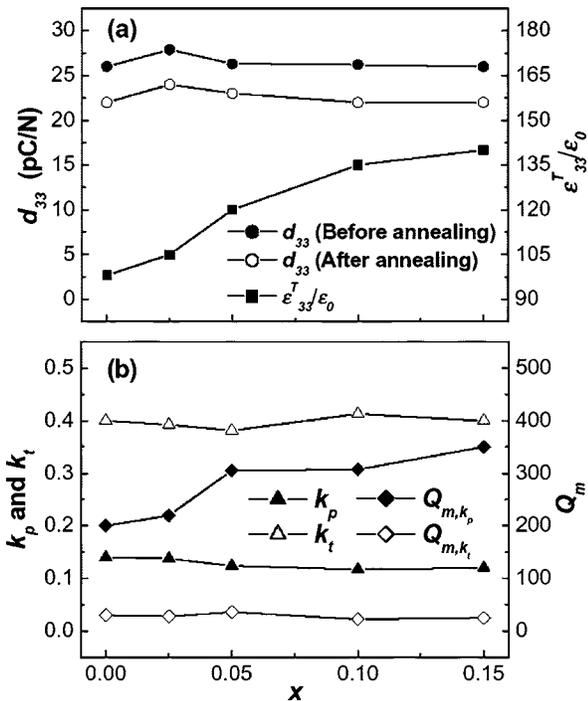
FIG. 3. Dielectric ($\varepsilon_{33}^T/\varepsilon_0$) and piezoelectric ($d_{33}$, k_p, k_t, $Q_{m,kp}$, and $Q_{m,kt}$) properties of $Bi_{1-x}Nd_xFeO_3$ ($x=0-0.15$) ceramics as functions of x.

FIG. 4. Pyroelectric coefficient (p) and figure of merit (R_V) of $Bi_{1-x}Nd_xFeO_3$ ($x=0-0.15$) ceramics as a function of x.

(855 °C) in the sintering process so that the relatively low melting Bi_2O_3 (817 °C) is immediately transformed into liquid phase and reacted with other constituent powders (Fe_2O_3 and Nd_2O_3). In other words, these specific sintering conditions lead to suppressing the reactions of Eqs. (1)–(5) and maintaining the theoretical stoichiometric amounts. Moreover, the use of a short sintering time (20 min) is a key factor to mitigate the charged defects related to the formation of Fe^{2+}, V_O^{2+}, and V_{Bi}^{3-} in the samples [Eqs. (6) and (7)]. Comparing to V_{Bi}^{3-}, V_O^{2+} has a smaller radius and a larger density so that V_O^{2+} vacancies are comparatively easy to migrate.[8,15] Although the exchange action of $Fe^{2+}-O^{2-}-Fe^{3+}$ also leads to leakage currents, it can be neglected due to limited amount of Fe^{2+} in our low conductive samples.[8] Therefore, V_O^{2+} vacancies act mainly as the internal traps in the samples, causing the Poole-Frenkel conduction in the high-E region.

Figure 3 shows the measured dielectric ($\varepsilon_{33}^T/\varepsilon_0$) and piezoelectric ($d_{33}$, k_p, k_t, $Q_{m,kp}$, and $Q_{m,kt}$) properties of the ceramics as functions of x. A small increase in $\varepsilon_{33}^T/\varepsilon_0$ from 100 to 140 when x is increased from 0 to 0.15 may be due to the formation of relatively strong dipoles in the monoclinically distorted perovskite structure. For the same range of x, d_{33} (before annealing) varies slightly between 26 and 28 pC/N, k_p and k_t show small fluctuations about 0.13 and 0.4, respectively, and their associated $Q_{m,kp}$ and $Q_{m,kt}$ change in the ranges of 200–350 and 22.6–30, respectively. The fact that the dependence of piezoelectric properties on x is generally weak in the measured x range may be explained by the combined effects of the different degrees of polarization in the ceramics and property variations in x. Due to their significantly high $T_C \sim 830$ °C,[2,3,5] it is of special interest to evaluate the practical viability of deploying the ceramics in high-temperature environment. Apart from the d_{33} measured before annealing, the ceramics' d_{33} after annealing at 550 °C for 4 h is also included in Fig. 3 for comparison. Only a $\sim 14\%$ drop in d_{33} after annealing (i.e., 22–24 pC/N) sug-

gests potential applications of the ceramics at high temperatures. It is interesting to note that these values are higher than those of most major lead-free high-temperature piezoelectric ceramics such as $Ca_xBi_4Ti_{3+x}O_{12+3x}$ ($x=1,2$) with $T_C=700-800$ °C and $d_{33}=10-20$ pC/N.[16]
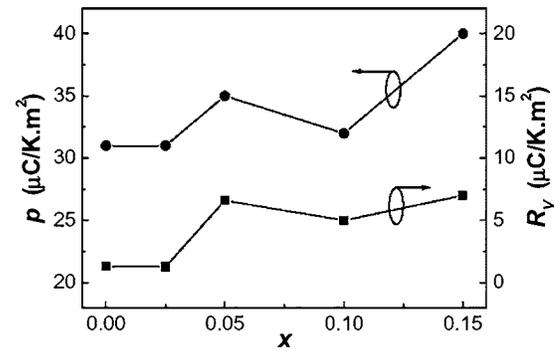
Figure 4 plots the pyroelectric properties (p and R_V) of the ceramics as a function of x. It is found that both p and R_V display similar property trends with relatively small variations of 30–50 and 1.3–6.6 μC/Km^2, respectively.

In conclusion, favorable piezoelectric and pyroelectric properties have been reported in polarized single-phase multiferroic $Bi_{1-x}Nd_xFeO_3$ ($x=0-0.15$) ceramics. Reduced oxygen vacancies result in limited internal traps in the ceramics, leading to sufficiently low leakage current densities. The electrical conduction in ceramics has been found to be controlled by the Poole-Frenkel conduction mechanism at E of $17-145$ kV/cm. The large d_{33} of 26–28 and 22–24 pC/N observed in the ceramics before and after annealing at 550 °C shows promising applications of the ceramics at high temperatures.

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