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

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Single-phase multiferroic \( \text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3 \) \((x=0\text{–}0.15)\) 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 \(<30\,\text{mA/m}^2\) even at a high electric field of \(145\,\text{kV/cm}\). The piezoelectric \(d_{33}\) coefficients of the ceramics before and after annealing at \(550\,\text{°C}\) for 4 h are measured to be \(\sim28\) and \(\sim24\,\text{pC/N}\), respectively. These values are higher than those of most major lead-free high-temperature piezoelectric ceramics.

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.1–3

Single-phase \(\text{BiFeO}_3\) ceramic, which has ferroelectric order below a high Curie temperature \((T_C\sim830\,\text{°C})\) and antiferromagnetic order below a high Néel temperature \((T_N\sim370\,\text{°C})\), is one of the most widely studied multiferroic materials.1–3 However, \(\text{BiFeO}_3\) becomes unsuitable for applications owing to its high leakage current density, subject to dielectric breakdown at fields \(<100\,\text{kV/cm}\) besides exhibiting a spatial nonuniformity of magnetic structure and a quadratic ferromagnetoelectric behavior.1–3

By using smaller \(\text{Nd}^{3+}\) ions \((\text{radius}=0.983\,\text{Å})\) in substitution for larger \(\text{Bi}^{3+}\) ions \((\text{radius}=1.03\,\text{Å})\) in the \(\text{BiFeO}_3\) composition, it is possible to create single-phase multiferroic \(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3 \) \((x=0\text{–}0.15)\) 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 \((J<30\,\text{mA/m}^2\) at \(145\,\text{kV/cm}\)). 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 \(\text{Bi}_3\text{O}_5\), \(\text{Fe}_2\text{O}_3\), and \(\text{Nd}_2\text{O}_3\) powders do not react with each other during the sintering process due to some specific reasons such as the volatilization of \(\text{Bi}_2\text{O}_3\), insufficient mixing of powders, or inadequate sintering conditions, it will be difficult to keep the stoichiometry of \(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\) and hence to form single-phase ceramics.5,7 The reaction mechanisms are as follows:

\[
\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \Rightarrow (1-x)\text{BiFeO}_3 + (x/2)\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \quad \text{[no reaction]}. \quad (1)
\]

\[
(1-x)\text{Bi}_2\text{O}_3 + x\text{Nd}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \Rightarrow 2(1-x)\text{BiFeO}_3 + x(\text{Nd}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \quad \text{[no reaction]}. \quad (2)
\]

\[
\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \Rightarrow (4/25)\text{Bi}_{12/25}\text{Fe}_{12/25}\text{O}_{19} + (24/25)\text{Fe}_2\text{O}_3 \quad \text{[no reaction]}. \quad (3)
\]

\[
\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \Rightarrow (1/18)\text{Bi}_{16/18}\text{Fe}_{2/18}\text{O}_{57} + (17/18)\text{Fe}_2\text{O}_3 \quad \text{[no reaction]}. \quad (4)
\]

\[
\text{Bi}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \Rightarrow (1/2)\text{Bi}_2\text{Fe}_2\text{O}_9 + (1/2)\text{Bi}_2\text{O}_3 \quad \text{[volatilization or no reaction]}. \quad (5)
\]

In addition, Eqs. (6) and (7) suggest that if \(\text{Fe}^{3+}\) ions partially transfer to \(\text{Fe}^{2+}\) ions, or if \(\text{Bi}^{3+}\) ions volatilize in single-phase \(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\), it will be hard to reduce oxygen vacancies \((V_{\text{O}}^{\text{V}})\) or bismuth vacancies \((V_{\text{Bi}}^{\text{V}})\), leading to highly conductive samples.5,6,8

\[
\text{2Fe}^{3+} + \text{O}^{2-} \Rightarrow 2\text{Fe}^{2+} + (1/2)\text{O}_2 \quad \text{[volatilization]} + V_{\text{O}}^{\text{V}}. \quad (6)
\]

\[
\text{2Bi}^{3+} + 3\text{O}^{2-} \Rightarrow \text{Bi}_2\text{O}_3 + 2V_{\text{Bi}}^{\text{V}} + 3V_{\text{O}}^{\text{V}}. \quad (7)
\]

Therefore, it is our aim in the present work to study the preparation and polarization of low-conductive single-phase multiferroic \(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3 \) \((x=0\text{–}0.15)\) 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.

\(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\) 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 \(\text{Bi}_2\text{O}_3\) \((99.9\%)\), \(\text{Fe}_2\text{O}_3\) \((99.9\%)\), and \(\text{Nd}_2\text{O}_3\) \((99.9\%)\) were weighed, and each type of powder was milled into an average size of 1 \(\mu\text{m}\). 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 \(200\,\text{°C}\) for 10 h in a vacuum chamber before being sintered at a relatively high temperature of \(855\,\text{°C}\) for a short time of 20 min with a high heating rate of \(100\,\text{°C/s}\).
The crystalline structure of the sintered samples was examined using an x-ray diffractometer at a scan rate of 0.02° per 4 s (Bruker 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 P6621P). 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 (d33) of the polarized samples was measured at 60 Hz using a piezo-d33 meter (IAAS ZJ-30). The dielectric constant (εr/ε0) was obtained at 1 kHz using an impedance analyzer (HP 4294A). The planar (kν) and thickness (kθ) electromechanical coupling coefficients and their associated mechanical quality factors (Qm,κκ and Qm,κθ) were determined using the impedance analyzer according to the resonance method.9 The pyroelectric coefficient (p) and pyroelectric figure of merit (Rν) were measured at 0.01 Hz with an in-house pyroelectric coefficient measurement system.

Figure 1 shows the x-ray diffraction (XRD) patterns of Bi1-xNdFeO3 ceramics with x=0, 0.05, 0.1, and 0.15. Besides the peaks associated with single-phase ABO3-type perovskite structure, no other peaks are detected within the uncertainty of XRD. It has been reported that single-phase BiFeO3 sample has a rhombohedral structure with R3C space group at room temperature.3,4 From the inset of Fig. 1, the (001) 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 Bi3+ ions (radius = 1.03 Å) by the smaller Nd3+ 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 Bi2O3, Fe2O3, Nd2O3, 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 Fe2+ ions, V2O+ vacancies, and V2O+ vacancies is believed to be the main cause of high leakage current in BiFeO3 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-E2, ln J-E1/2, and ln(J/E)-E1/2, 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)-E1/2 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 JPF expressed as follows:

\[ J_{PF} \propto E \exp \left( - \frac{q}{kT} (\phi_{PF} + \beta_{PF}E) \right) \]  

where q is the electron charge, k is the Boltzmann constant, T is the temperature, \( \phi_{PF} \) is the barrier height, and \( \beta_{PF} \) is the temperature-dependent slope of the ln(J/E)-E1/2 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 Fe2+ ions, V2O+ 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 ($\varepsilon'_T/\varepsilon_0$) and piezoelectric ($d_{33}$, $k_p$, $k_t$, $Q_{m,p}$, and $Q_{m,t}$) properties of Bi$_{1-x}$Nd$_x$FeO$_3$ ($x=0–0.15$) ceramics as functions of $x$.

(855 °C) in the sintering process so that the relatively low melting Bi$_2$O$_3$ (817 °C) is immediately transformed into liquid phase and reacted with other constituent powders (Fe$_2$O$_3$ and Nd$_2$O$_3$). 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$_{2+}$O$_2^-$, V$_0^-$, and V$_{O'}^3-$ in the samples [Eqs. (6) and (7)]. Comparing to V$_{Bi}^3-$, V$_{O'}^3-$ has a smaller radius and a larger density so that V$_{O'}$ vacancies are comparatively easy to migrate. 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. Therefore, V$_{O'}^3-$ 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 ($\varepsilon'_T/\varepsilon_0$) and piezoelectric ($d_{33}$, $k_p$, $k_t$, $Q_{m,p}$, and $Q_{m,t}$) properties of the ceramics as functions of $x$. A small increase in $\varepsilon'_T/\varepsilon_0$ 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 monocrinally 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 $Q_{m,p}$ and $Q_{m,t}$ 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 $T_c$=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-

![Pyroelectric coefficient (p) and figure of merit ($R_V$) of Bi$_{1-x}$Nd$_x$FeO$_3$ ($x=0–0.15$) ceramics as a function of $x$.](image)

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$_3$Bi$_{2}$Ti$_{5}$O$_{15}$ ($x=1, 2$) 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 $\mu$C/Km$^2$, respectively.

In conclusion, favorable piezoelectric and pyroelectric properties have been reported in polarized single-phase multiferroic Bi$_{1-x}$Nd$_x$FeO$_3$ ($x=0–0.15$) 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 $E$=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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