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Short communication

Temperature dependent, large electromechanical strain in Nd-doped BiFeO₃-BaTiO₃ lead-free ceramics

Dawei Wang, Amir Khesro, Shunsuke Murakami, Antonio Feteira, Quanliang Zhao, Ian M. Reaney

ABSTRACT

Lead-free piezoceramics with the composition 0.7(Bi₀.₃Ndₓ)FeO₃-0.3BaTiO₃+0.1 wt% MnO₂ (BNxF-BT) were prepared using a conventional solid state route. X-ray diffraction and temperature dependent permittivity measurements indicated a transition from a composition lying at a morphotropic phase boundary (MPB) to a pseudocubic phase as a function of Nd concentration. The highest maximum strain (∆amax ∼0.2% at 60 kV/cm) and effective piezoelectric coefficient (d33*) ∼333 pm/V were obtained at room temperature for the composition BN0.02F-BT. The decrease in remanent polarization (Pₑ) and Berlincourt d₃₃ with increase in Nd concentration can be attributed to the coexistence of ferroelectric and relaxor phases. In-situ polarisation and strain measurements revealed an increase in Pₑ and d₃₃* with temperature and a reduction in the coercive field Eₑ. Presumably this behavior is due to a combination of thermally activated domain wall motion and lowering of the activation energy for a field induced relaxor-ferroelectric transition, as the Curie maximum is approached.

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1. Introduction

Bismuth ferrite (BiFeO₃, BF) is a multiferroic material with a rhombohedrally distorted perovskite structure (space group R3c) at room temperature (RT). BF is popular for the rare coexistence of the antiferromagnetic and ferroelectric order with a Neel temperature (Tₙ) of ∼643 K and a Curie temperature (Tᶜ) of ∼1103 K [1,2]. The latter property is of interest for high temperature piezoelectric applications. Furthermore, BF is environmentally-friendly in comparison to lead containing piezoelectric materials and can therefore meet the regulations on protection of environment and human health [2]. However, BF exists only in a narrow temperature range, making the synthesis of single phase BF without secondary phases such as Bi₂Fe₂O₆ and Bi₂FeO₄ a difficult task by conventional methods [2–4]. Furthermore, BF ceramics usually exhibit high electrical leakage because of the reduction of Fe ions from Fe³⁺ to Fe²⁺ during sintering and the formation of oxygen vacancies for charge compensation [5,6], leading to the difficulties in obtaining saturated polarization hysteresis loop and piezoelectric response. Therefore, to reduce the leakage current, inhibit the formation of secondary phases and improve properties, extensive studies have been carried out, including the substitution of various ions for Bi³⁺/Fe³⁺ in BF [7–13] and the formation of BF-based solid solutions with other ABO₃ type perovskites (e.g. BaTiO₃, Ba(Fe₀.₅Zr₀.₅)O₃ and Bi₁₋ₓKₓTiO₃) [14–19]. It should be noted that multiferroic BiFeO₃-BaTiO₃ (BF-BT) solid solution has been frequently studied and proved to be a high-Tᶜ lead-free piezoelectric ceramic [14–17]. However, most of these investigations on BF-BT focus on the properties at RT and rarely provide the temperature dependence of properties, which is critical for practical applications. In addition, it is reported that the substitution of rare earth ions for Bi³⁺ in BF can enhance their piezoelectricity and ferroelectricity [7–13]. Consequently, in this work, Nd-doped BF-BT lead-free ceramics were prepared by a conventional sintering technique and the composition and temperature dependence of the ferroelectricity and electric-field induced strain were investigated.

2. Experimental procedure

The BF-based ceramics with compositions of 0.7(Bi₀.₃Ndₓ)FeO₃-0.3BaTiO₃+0.1 wt% MnO₂ (BNxF-BT, x = 0, 0.005, 0.01, 0.02, 0.05) were prepared using a conventional solid state reaction. A small
amount of MnO₂ was added to increase the resistivity of BF-BT ceramics, which is commonly used in previous reports [15–19]. Raw materials, including Bi₂O₃ (99.9%, Sigma-Aldrich), Fe₂O₃ (99.5%, Sigma-Aldrich), Nd₂O₃ (99.5%, Sigma-Aldrich), TiO₂ (99.9%, Sigma-Aldrich), and BaCO₃ (99%, Sigma-Aldrich) were batched stoichiometrically according to the nominal compositions and ball-milled in isopropanol for 24 h. The dried mixed powders were calcined at 700 to 800 °C for 2 h to synthesize the compound and then ball milled in isopropanol with MnO₂ (99%, Sigma-Aldrich) for 12 h. The calcined powders were mixed with a polyvinyl alcohol (PVA) binder solution, granulated and pressed into pellets with a diameter of 10 mm. Following binder burnout at 550 °C, the pellets were sintered in a sealed crucible at 1010–1040 °C for 2 h.

The density of the sintered samples was measured using Archimedes method. The relative density of all studied samples was higher than 95%. The phase structure of the sintered samples was studied using a Bruker D2 Phaser X-ray powder diffraction (XRD). For electrical tests, sintered samples were electrodeed using fired-on silver paste, followed by the samples being poled in silicone oil at 100–120 °C with an applied electric field of 40–60 kV/cm. Piezoelectric coefficient (d₃₃) was measured using a Piezotest PM300 d₃₃ meter. Polarization hysteresis and strain-electric field behaviour were determined using a modified Sawyer-Tower circuit driven by a lock-in amplifier (Model SR830, Stanford Research System, Sunnyvale, CA) at a frequency of 1 Hz from RT to 150 °C. The temperature dependent of dielectric property from RT to 550 °C was carried out using an Agilent 4184A multi-frequency precision LCR meter.

3. Results and discussion

The RT XRD patterns of BNxF-BT in the 2θ range of 20°–70° are shown in Fig. 1(a). All peaks could be attributed to a single perovskite phase, indicating that a stable solid solution was formed in the studied range. Diffraction peaks shifted to a higher diffraction angle with increasing Nd concentration, consistent with the smaller relative ionic radius of Nd³⁺ ions compared to that of Bi³⁺ ions in the matrix composition [11,12]. Splitting of (012)/(110) diffraction peak at ~20° = 32° was used to determine the likely symmetry of compositions. From the expanded XRD patterns (Fig. 1a), phase coexistence in the BF-BT matrix is apparent at RT as shown by the broad multiple peaks, which have been reported to indicate a morphotropic phase boundary (MPB) [14,15,20]. As Nd concentration increased, a pseudocubic phase followed by the appearance of one merged peak as observed in refs [14,15,20].

The temperature dependence of dielectric permittivity (εᵣ) and loss (tan δ) for BNxF-BT at 100 kHz is given in Fig. 1(b). With increasing Nd concentration, the Tₑ/Curie maximum (Tₑmax) decreased monotonously (inset of Fig. 1b), presumably due to disruption of polar coupling by the substitution of the less polarizable Nd for Bi [20,21]. The decrease in polar coupling also manifested itself by relaxor-like characteristics, with the appearance of broad frequency-dependent dielectric peaks. Despite these changes, tan δ remained low below 400 °C, but then increased sharply (Fig. 1b), indicating an increase in dc conductivity at high temperature.

The high electric field bipolar polarization hysteresis (P-E) and unipolar strain (S-E) loops for BNxF-BT are shown in Fig. 2(a) and b), from which the remanent polarization (Pᵣ), coercive field (Eₙ) and average electric field induced maximum strain (Sₘₐₓ) as a function of Nd content can be obtained, Fig. 2(c) and d). The normalized strain coefficient d₃₃, representing the average strain per unit electric field, is calculated by d₃₃ = Sₘₐₓ/Eₘₐₓ, where Eₘₐₓ is the maximum electric field value. The BF-BT sample possessed a typical saturated hysteresis loops (Fig. 2a), indicating high resistivity and good sintering behaviour of the fabricated samples. With increasing

![Image](https://example.com/image.png)

**Fig. 1.** (a) RT XRD patterns of BNxF-BT and (b) Temperature dependence of εᵣ and tanδ at 100 kHz for BNxF-BT, inset shows Tₑmax as a function of Nd concentration.

| Material | Temperature range | Increase in d₃₃ (°C) | Reference |
|----------|-------------------|---------------------|-----------|
| PZT-4    | RT-160 °C         | 15%                 | 23        |
| PZT-5H   | RT-80 °C          | >40%                | 24        |
| BNT-BT   | RT-100 °C         | 273%                | 25        |
| BF       | RT-262 °C         | 258%                | 22        |
| BF-0.3BT | RT-150 °C         | 42%                 | This work |
| BNO-02F-0.3BT | RT-150 °C   | 117%                | This work |

Table 1 Comparison of temperature dependence of d₃₃ for various piezoelectric ceramics (PZT, Pb(Zr,Ti)O₃; BNT-BT-BKT, Bi₁₀.₃Na₂O₃TiO₃-BaTiO₃-Bi₂₀.₃K₂O₃TiO₃).

Nd concentration, P-E loops became slim and unsaturated (Fig. 2a), with Pᵣ, Eₙ and d₃₃ continuously decreasing (Fig. 2c), consistent with the broad permittivity maximum (Fig. 1b) and indicative of relaxor-like behaviour. The highest value of Pᵣ ~ 36.6 μC/cm², Eₙ ~ 33.6 kV/cm and d₃₃ ~ 190 pC/N was achieved for the BF-BT matrix without Nd doping due to the presence of an MPB (Fig. 1a) [14,15]. At the same time, the Sₘₐₓ and d₃₃ values increased significantly with increasing Nd concentration, reaching a maximum of 0.2% and 333 pm/V at x = 0.02, above which it reduced, Fig. 2(d). The enhancement of the Sₘₐₓ and d₃₃ in BNO-02F-0.3BT is attributed to the crossover from normal to relaxor ferroelectric behaviour.

The in-situ temperature dependence of bipolar P-E and unipolar S-E loops for two compositions are shown in Fig. 3(a) and b), from which the Pₑ, Eₑ and d₃₃ as a function of temperature were obtained, Fig. 3(c). As temperature increased, the P-E loops for each composition became saturated and slim (Fig. 3a), which implies that higher temperature effectively promotes the movement of domain walls and/or facilitates an easier field induced transition from a relaxor to a ferroelectric state, resulting in higher Pₑ, d₃₃ and lower Eₑ as shown in Fig. 3(c). Similar behaviour has also been found in other lead-based/lead-free ceramics as given in Table 1 [22–25]. For example, the increase in d₃₃ for pure BF-BT is ~42%.
Fig. 2. High electric field (a) bipolar polarization hysteresis and (b) unipolar strain loops for BNxF-BT; (c) $P_r$ and $E_C$ as a function of Nd concentration, inset shows $d_{33}$ as a function of Nd concentration; (d) $S_{max}$ and $d_{33}^*$ as a function of Nd concentration.

Fig. 3. The in-situ temperature dependence of high electric field (a) bipolar polarization hysteresis and (b) unipolar strain loops for BF-BT and BN0.02F-BT; (c) $P_r$, $E_C$ and $d_{33}^*$ as a function of temperature.

lower than that of BN0.02F-BT (~117%). However, detailed knowledge of the domain morphology and its field dependence is required to fully appreciate the relative contributions of domain wall motion versus field induced transitions to $d_{33}^*$ in BN0.02F-BT ceramics.

4. Conclusion

In this work, BNxF-BT lead-free piezoelectric ceramics were successfully prepared using a conventional solid state route. With increasing Nd concentration, the phase assemblage of BNxF-BT gradually transformed from an MPB to a pseudocubic phase. The
highest $P_t \sim 36.6 \mu C/cm^2$, $E_C \sim 33.6 \text{kV/cm}$ and $d_{33} = 190 \text{pC/N}$ were obtained for the pure BF-BT due the presence of the MPB. However, the optimum $S_{\text{max}} \sim 0.2\%$ and $d_{33}^\ast = 333 \text{pm/V}$ were achieved at RT for the composition doped with 0.02 mol% Nd, attributed to the coexistence of ferroelectric and relaxor phases. In addition, the in-situ temperature dependence of ferroelectric and strain behavior indicated that the P-E loops became more and more saturated and slim with increasing temperature, resulting in higher $P_t$, $d_{33}^\ast$ and lower $E_C$.

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