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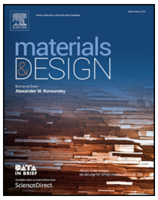


Enhanced piezoelectric properties and strain response in ⟨001⟩ textured BNT-BKT-BT ceramics

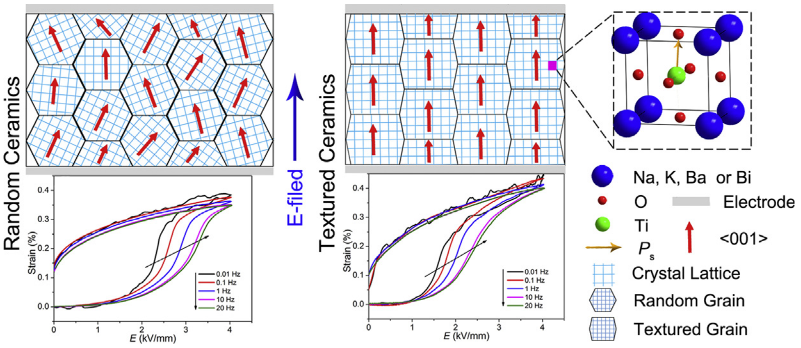
Zhi-Hao Zhao [a], Meng-Yang Ye [a], Hui-Ming Ji [a], Xiao-Lei Li [a,*], Xiaowen Zhang [b], Yejing Dai [a,*]

[a] Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
[b] The State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- High piezoelectric constant and electro-strain response could be obtained in textured $Na_{0.5}Bi_{0.5}TiO_3$ ceramics.
- Defect dipole would stabilize ferroelectric domains and polar nanoregions under applied electric field.
- The electric-field-induced transition could appear at lower electric field for textured $Na_{0.5}Bi_{0.5}TiO_3$ ceramics.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly ⟨001⟩ textured (~81%) ternary BNT-BKT-BT ceramics are prepared by reactive templated grain growth (RTGG) method with plate-like $Bi_4Ti_3O_{12}$ particles as templates. Outstanding electric properties, which are both higher than state of art BNT-based ceramics, emerge in the aforementioned sample due to the grain orientation. For the textured ceramics, a high piezoelectric constant d_{33} of 314 pC/N could be obtained, which is ~1.4-fold larger than that of a random one (221 pC/N). A high electro-strain response (~0.41%) is obtained at a low applied electric field (4 kV/mm) in textured ceramics, with the normalized strain d_{33}^* $(S_{max}/E_{max}) = 1030$ pm/V near the $T_{F\text{-}R}$ (the temperature of ferroelectric to ergodic relaxor state transition). Moreover, the evolution process of relaxor phases is studied. The texture technique also could improve the $T_{F\text{-}R}$ from 70 °C to 100 °C, enhancing the temperature stability. In addition, the polarization switching process in ferroelectric phase and ergodic relaxor state are analyzed in this work, respectively.

1. Introduction

As the core component of actuators, sensors, and transducers, piezoelectric materials have been widely researched for decades [1,2]. In recent years, lead-free piezoelectric ceramics have got people's attention due to the environment problem of traditional Pb-contained piezoelectric ceramics [3–5]. However, the lower performance of lead-free ceramics limits the development of becoming alternatives of lead-based ceramics. There are generally two solutions to improve the performance: a) designing an appropriate composition near the polymorphic transition or morphotropic phase boundary with solid solution; [6–10] b) optimizing the microstructures of piezoelectric ceramics, *i.e.* making grains orient to a specified direction [11,12], or synthesizing core-shell structure in ceramics [13].

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* Corresponding authors.
E-mail addresses: lxlei@tju.edu.cn (X.-L. Li), daiyj04@tju.edu.cn (Y. Dai).

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$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT)-based lead-free piezoelectric ceramics, as one of the potential candidates to replace Pb-based ceramics, had attracted much attention [14,15]. Many researchers have improved the properties of BNT-based ceramics by doping one or more compositions (*i.e.* $BaTiO_3$ [14], $(Bi_{0.5}K_{0.5})TiO_3$ [16], $(K_{0.5}Na_{0.5})NbO_3$ [17] *etc.*). Among these compositions, $(1-x)$BNT − xBaTiO$_3$ and $(1-y)$BNT − $y(Bi_{0.5}K_{0.5})TiO_3$ compounds show predominant properties near the rhombohedral-tetragonal morphotropic phase boundary, where $x = 0.05–0.07$ and $y = 0.16–0.20$ [18,19]. Based on these two compounds, a ternary BNT-$(Bi_{0.5}K_{0.5})TiO_3$-$BaTiO_3$ (BNT-BKT-BT) system was developed and drew much attention due to its outstanding electric properties [7,15]. However, the piezoelectric response d_{33} in most of the random binary or ternary BNT-based systems is always lower than 250 pC/N [15–19]. Compared with traditional randomly oriented ceramics, textured BNT-based ceramics could obtain larger piezoelectric properties. In $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$ system, the piezoelectric response in textured sample was found to be twice as much as the un-textured ceramics [20,21]. Hu et al. fabricated oriented BNT ceramics by reactive templated grain growth (RTGG) method, and the strain response is 1.2-fold of the random ceramics' [22].

In addition, increasingly attention has been paid recently on BNT-based ceramics' reversible phase transition between ergodic relaxor phase and normal ferroelectric state under applied electric field (AEF) [23]. This process could achieve a giant strain, compared with that of soft $Pb(Zr,Ti)O_3$ ceramics [24]. In the BNT-based single crystals, an ultra-giant strain ~0.87% could be obtained in a tetragonal BNT-BKT-BT single crystal slice with ⟨001⟩ direction under a low AEF (4 kV/mm) [25], showing largely enhanced properties in this direction. Despite the performance of piezoelectric single crystal is higher than that of polycrystalline ceramics, the synthetic process of the single crystal is quite complex, time-consuming and with high cost. Therefore, the texturing process for piezoelectric ceramics, making the grains align to a specific direction, is a feasible way to utilize the anisotropic nature of piezoelectric constants [11,12].

Herein, ⟨001⟩ textured ternary BNT-BKT-BT ceramics, near rhombohedral-tetragonal MPB region, were prepared with RTGG method and demonstrated outstanding electric properties. For the textured ceramic, a high piezoelectric constant d_{33} of 314 pC/N could be obtained, which is ~1.4-fold larger than that of a random one (221 pC/N). The evolution process of relaxor phases, which was rarely investigated in textured BNT-BKT-BT piezoelectric system, was studied and a high electro-strain response (~0.41%) was obtained at low AEF (4 kV/mm) near the ferroelectric to ergodic relaxor transition temperature. The good piezoelectric performance of the textured ceramics may enable to replace lead-based ceramics in some functional devices, such as printed pressure sensors and actuators, piezo-hydraulic pumps, ultrasonic imaging and energy harvesting devices.

2. Experimental procedure

⟨001⟩ textured $0.85Na_{0.5}Bi_{0.5}TiO_3$-$0.11K_{0.5}Bi_{0.5}TiO_3$-$0.04BaTiO_3$ (BNT-BKT-BT) ceramics were prepared through RTGG method. Pure phase $Bi_4Ti_3O_{12}$ particles with plate-like shape (particle size ~5–12 μm; thickness <1 μm), synthesized by the molten salt method [26], were used as templates shown in Figs. S1 and S2 in Supporting information. Chemically pure Na_2CO_3 (99.0%), K_2CO_3 (99.0%), Bi_2O_3 (99.0%), TiO_2 (98.0%), $BaTiO_3$ (99.0%) powder was used as raw materials. The textured ceramics were prepared by the following reaction with excess 3% Bi_2O_3:

$$0.12Bi_4Ti_3O_{12} + 0.2125Na_2CO_3 + 0.0275K_2CO_3 + 0.6TiO_2 + 0.04BaTiO_3 \rightarrow 0.85BNT - 0.11BKT - 0.04BT + 0.24CO_2 \tag{1}$$

The green compacts were prepared as reported in our previous work [12]. The compacts were heated at 600 °C for 1.5 h to burn out binder and plasticizer, and then consolidated by isostatic pressing at 200 MPa. Textured and random BNT-BKT-BT specimens were sintered at 1175 °C for 10 h and 2 h, respectively.

Densities of BNT-BKT-BT ceramics were measured by the Archimedes method. The phase structure and degree of orientation were analyzed by X-ray diffractometer (XRD, Rigaku D/Max 2500, Tokyo, Japan). The degree of orientation (f) was calculated according to XRD pattern using Lotgering's method, shown as follows: [27]

$$F_{h00} = (P - P_0)/(1 - P_0) \tag{2}$$

$$P = \Sigma I_{(h00)}/\Sigma I_{(hkl)} \tag{3}$$

$$P_0 = \Sigma I_{0(h00)}/\Sigma I_{0(hkl)} \tag{4}$$

where I and I_0 were intensity of the diffraction lines (hkl) of textured and randomly samples, respectively. The diffraction lines between $2\theta = 20°$ and $2\theta = 60°$ were used to obtain degree of orientation (f). Scanning electron microscopy (S4800, Hitachi, Japan) was utilized to obtain the micrographs of the ceramics. Silver electrodes were painted on the upper and bottom surfaces of the polished samples. Specimens were poled in the silicone oil under 4.0 kV/mm at room temperature for 15 min. The polarization hysteresis (P-E) loops and bipolar strain *vs.* E field (S-E) curves were measured using a ferroelectric tester (aixACCTF Analyzer 1000) at a fixed frequency of 1 Hz. Relative dielectric permittivity and loss tangent *versus* electric field curves (ε_r-E and tanδ-E) were measured with a same device at a triangular signal of 4 kV/mm (test frequency: 1 Hz) superimposed an alternating current (AC) voltage of 20 V (frequency of AC: 1 kHz). Dielectric properties were obtained by an LCR meter (Hewlett-Packard, Palo Alto, CA). Planar electromechanical coupling factor k_p and mechanical quality factor Q_m were calculated following IEEE standards. The piezoelectric constant d_{33} was measured by the quasistatic d_{33} meter (ZJ-3AN, Institute of Acoustics Academic Sinica, Beijing, China) based on Berlincourt method.

3. Results and discussion

As shown in Fig. 1, the XRD patterns of the textured and random samples with perovskite structure. It can be seen that the highest reflection peak is (110) in random BNT-BKT-BT ceramics. However, the intensity of (h00) peaks in textured ceramics greatly increased, while that of other peaks decreased. The degree of (h00) orientation $f_{(h00)}$ is about 81%, suggesting that the samples have a preferred crystallographic orientation along ⟨00l⟩ direction. The grain sizes of random BNT-BKT-BT ceramics are about 2.7 μm, shown in Fig. S3(a). The textured ceramics present a wide distribution of grain size and show unusually

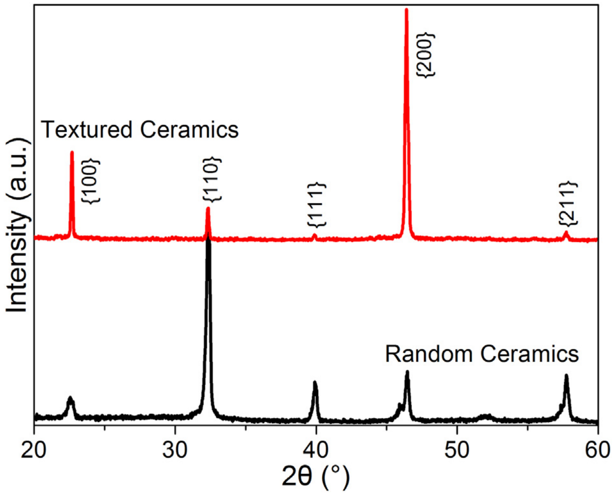

Fig. 1. XRD patterns of textured and random BNT-BKT-BT ceramics.