Texture development and enhanced electromechanical properties in <00l>-textured BNT-based materials

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Abstract: Grain-oriented lead-free piezoceramics $0.83(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $0.17(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ was synthesized with different grain orientation along the <00l> crystallographic orientation using plate-like NaNbO_3 templates. The effects of degree of texturing on the microstructure, phase transition temperature and resulting changes in piezoelectric and strain response of ceramics were explored. The electromechanical properties increased monotonously with increasing the degree of texturing. A high <00l> texture degree of 91% was obtained, giving rise to larger electromechanical properties of $d_{33}=217\text{pC/N}$, $k_p=35\%$, $S=0.246\%$, and $S_{\max}/E_{\max}=410\text{pm/V}$ in textured samples relative to the conventional polycrystalline counterparts. Furthermore, the grain oriented ceramics exhibited improved temperature stability as compared to its randomly oriented form. This work opens the possibility of achieving BNT-based high performance ceramics.

Key Words: Electrical properties; Electroceramics; Piezoelectric materials; Texture.

1. Introduction

In view of environmental concerns, lead-free materials have been developed to replace dominated lead-based materials. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - BaTiO_3 (BNT-BT) and $\text{BNT-Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BNT-BKT) solid solutions have been deemed to be potential candidates of lead-free piezoelectric ceramics due to large piezoelectric and strain responses [1]. Nevertheless, BNT-based ceramics still exhibited inferior piezoelectric properties in comparison to lead-containing ceramics.

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Texturing provides an opportunity in that the piezoelectric response is maximized owing to cooperating domains with uniformly aligned polarizations when poling along the specific direction[2]. Recent works have demonstrated that inducing a $\langle 001 \rangle$ crystallographic texture can significantly enhance the piezoelectric properties [3,4]. In particular, $\langle 001 \rangle$ textured BNT-BT piezoelectric ceramics with Lotgering factor $\sim 92\%$ fabricated by templated grain growth (TGG) showed enhanced piezoelectric properties ($d_{33}=322\text{pC/N}$)[4]. *In situ* electric-field studies have indicated that a $\langle 001 \rangle$ texture strongly affects the poling-induced phase transformation[5]. However, the effect texturing has on the piezoelectric and strain response is not well explored.

Herein, $\langle 001 \rangle$ -textured 0.83BNT-0.17BKT (BNT-BKT) ceramics with different grain orientation have been fabricated via TGG technique using NaNbO_3 (NN) templates. The textured ceramics is compared to the randomly oriented counterparts and the correlation between texture development and piezoelectric properties was clarified.

2. Experimental

Synthesis of $\langle 001 \rangle$ textured 0.83BNT-0.17BKT ceramics was performed by the TGG process using 2mol% NaNbO_3 (NN) templates (BNT-BKT-NN) described in detail elsewhere [4,6-8]. The NN templates were synthesized from $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$ using double molten salt synthesis method and possess broad faces on the order of 5-10 μm and a thickness of $\sim 1\mu\text{m}$. BNT-BKT-NN textured ceramics were fabricated by tape casting using NN templates. The NN templates and BNT-BKT matrix were mixed with the solvent (toluene and ethanol in the weight ratio of 2:1) for 10-12h using tumbling mill. Then the LS modelbond was added in the slurry and milled for 2h. The attained stable slurry was applied to tape casting and the tapes were dried, cut and laminated into a multilayer sheet. The samples were sintered at 1175°C for 4-50h. To reduce the volatility of Bi,

Na, and K, the disks were embedded in the powders with the same composition. For comparison, random ceramics were synthesized via conventional solid state reaction method.

The structures were examined by X-ray diffraction (XRD, Bruker D8 Advanced, Germany) and scanning electron microscopy (SEM, JSM, EMP-800; JEOL, Tokyo, Japan). The degree of $\langle 00l \rangle$ texturing was determined by Lotgering factor method[2,4]. The ceramics were coated with silver electrodes fired at 600°C for 10 min. The dielectric properties were measured by a high-precision LCR meter (HP 4284A; Agilent, Palo Alto, CA). The FE hysteresis loops and strain curves measurements were conducted by using a FE test system (Precision Premier II; Radiant Technologies Inc, Albuquerque, NM) connected with a Miniature Plane-mirror Interferometer and the accessory Laser Interferometric Vibrometer (SP-S 120/500; SIOS Me b technik GmbH, Ilmenau, Germany). The d_{33} and k_p were measured with resonance and anti-resonance technique using an impedance analyzer (HP 4294A, Hewlett-Packard Development Company) and d_{33} meter (Institute of acoustic, Chinese Academic Society, ZJ-6A, Beijing, China).

3. Results and discussion

Figure 1(a) illustrates the XRD patterns with different degrees of texturing. All sintered samples display a pure perovskite structure, suggesting that the NN templates had completely diffused into the lattice of BNT-BKT matrix and formed a stable homogeneous solid solution between NN templates and BNT-BKT matrix. For randomly oriented ceramics, the intensity of the (110) peak was the highest. In contrast, the intensity of (110) peak in textured samples decreased along with the increase in the intensity of (100) and (200) peaks. This clearly indicates the formation of a strong preferred crystallographic orientation along $\langle 00l \rangle$ direction. Simultaneously, the degree of $\langle 00l \rangle$ texturing exhibited the maximum 91% in the optimized processing. The

cross-sectional SEM micrographs of randomly oriented and 91% textured BNT-BKT-NN ceramics are shown in Fig.1(b) and (c), respectively. The nearly equiaxed grains with average grain size of 1.4 μ m was detected for the random ceramics, however, samples having 91% grain orientation exhibited a brick wall-like microstructure with strip-like grains representing the development of texture. The microstructure is in line with the high texture degree ($F_{001}=91\%$).

Figure 2(a) depicts temperature-dependent dielectric constant and loss under different frequencies for textured poled BNT-BKT-NN samples. The samples displayed two notable diffuse dielectric anomalies, namely, a ferroelectric-relaxor phase transition temperature (T_{F-R}) and a dielectric constant maximum temperature (T_m). Broad and strong frequency dispersion at low temperature can be observed, implying the relaxor nature of BNT-BKT-NN samples[1]. Temperature-dependent dielectric constant and loss measured at 1kHz for poled randomly oriented and textured specimens are provided in Fig.2(b). The overall dielectric constant of the textured ceramics appeared to be lower than that of the randomly oriented one due to the higher residual pore concentration in textured samples. On the other hand, the decrease of dielectric constant for the textured ceramics after poling may be ascribed to a decrease of ferroelectric domain walls density (an extrinsic contribution to the dielectric constant) and the anisotropic dielectric properties of lead-free ceramics[9]. Compared to the randomly oriented specimens, the textured ones possess higher values of T_{F-R} , revealing enhanced temperature range of operation and a higher temperature stability for samples after texturing.

Polarization hysteresis loops were recorded at RT, as shown in Fig.3(a). Both types of ceramics behaved as ferroelectrics, as confirmed by the presence of current peaks linked with coercive field E_c and domain switching (see the *inset* of Fig.3(a)) [10,11]. The remnant

polarization P_r and coercive field E_c of oriented ceramics were higher than those of random ones. This could be a result of larger electric field-induced lattice distortion, dipole polarization[12], and the reduction of the coherence length of in-phase tilted region [13]. Consistent with the polarization hysteresis loops, the bipolar strain curves, as shown in Fig.3(b), showed a typical butterfly shape as evidenced by large negative strain. The random and textured samples exhibited maximum values of strain $\sim 0.18\%$ and 0.24% , respectively. Based on TEM results on textured BNT-7BT[3,4,12], the texture method with NN template facilitates the long-range-ordered polarization of ferroelectric phase with significant coherent lamellar domains, thereby resulting in larger ferroelectricity and strain response in textured samples as compared to non-textured ones.

Unipolar strain curves of random and textured ceramics are shown in Fig.4(a). Compared to the randomly oriented specimens, the textured ones exhibited a higher strain response. For textured ferroelectric ceramics, $\langle 00l \rangle$ crystallographic orientation promotes non-180° domain switching[3]. Therefore, after texturing, the enhanced strain response can be achieved. Figure 4(b) describes the evolution of d_{33} for random and textured ceramics as a function of poling electric field. After poling at 60kV/cm, the textured ceramics displayed a higher d_{33} up to 217pC/N as compared to random counterparts ($d_{33}=148\text{pC/N}$), which is mainly attributed to the larger electric field-induced lattice distortion and dipole displacement in textured samples[12]. Interestingly, the random and textured ceramics presented an abrupt increase in d_{33} after the threshold field magnitude. Note that, compared to random ceramics (25kV/cm), the threshold field was lower (20 kV/cm). This may be due to pre-oriented grains along the electric field direction and thus can promote a long-range-ordered polarization under a lower electric field. On the other hand, from the d_{33} as a function of temperature (not shown here), d_{33} values remained stable up to 65°C for

textured sample and almost unchanged only up to 45°C for non-textured one, reflecting the enhanced temperature stability for textured specimen.

Figure 4(c) shows the variation of electromechanical properties d_{33} , k_p , S , $S_{\max}/E_{\max}$ with different degree of texturing for BNT-BKT-NN ceramics. Apparently, $\langle 00l \rangle$ crystallographic texture makes an significant impact on the electromechanical properties, that is , the values of d_{33} , k_p , S , $S_{\max}/E_{\max}$ increase rapidly with the increase in the degree of texturing. This demonstrates the advantage of texturing in achieving promising electromechanical response in BNT-based ceramics. Samples having a 91% texturing had $d_{33} \sim 217 \text{pC/N}$, $k_p \sim 35\%$, $S \sim 0.246\%$, and $S_{\max}/E_{\max} \sim 410 \text{pm/V}$, respectively, which is due to the more favorable domain configuration benefiting from the remarkable enhancement of $\langle 00l \rangle$ orientation. In general, rhombohedral distorted perovskite exhibits highest piezoelectric properties in the $\langle 00l \rangle$ -textured specimen[4]. On the other hand, strong texturing leads to extra structural distortions (a decreasing lattice parameter and an increasing rhombohedral angle), which are proportional to the spontaneous strain and the obtained piezoelectricity arising from breaking of inversion symmetry[5].

4. Conclusions

Highly textured $0.83(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}0.17(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ lead-free ceramics with $F_{00l}=91\%$ has been fabricated with the introduction of 2mol.% NaNbO_3 templates. The microstructures and electromechanical properties were explored as a function of grain orientation. The electromechanical properties were strongly depended on the degree of texturing and increasing the degree of texturing resulted in the substantially enhancement in piezoelectric and strain response. The optimized microstructure provided excellent electromechanical performance ($d_{33}=217 \text{pC/N}$, $k_p=35\%$, $S=0.246\%$, and $S_{\max}/E_{\max}=410 \text{pm/V}$) along with enhanced temperature stability as

compared to randomly oriented counterparts.

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Figures and captions

Fig.1. (a) XRD patterns with different degrees of texturing. SEM micrographs of (b) textured and (c) randomly oriented BNT-BKT-NN ceramics.

Fig.2. Temperature-dependent dielectric constant and loss for (a) textured poled sample under different frequencies and (b) random and textured sample measured at 1kHz.

Fig.3. (a) Polarization hysteresis loops (the *inset* shows the current-electric field loops) and (b) bipolar strain curves for randomly oriented and textured BNT-BKT-NN ceramics.

Fig.4. (a) Unipolar strain curves, (b) d_{33} versus applied poling electric field, (c) electromechanical properties $d_{33}, k_p, S, S_{\max}/E_{\max}$ versus Lotgering factor in BNT-BKT-NN ceramics.

Fig.1

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Fig.4