

# Properties of piezoelectric ceramic with textured structure for energy harvesting

S.-J. Jeong<sup>a,\*</sup>, D.-S. Lee<sup>a,b</sup>, M.-S. Kim<sup>a</sup>, D.-H. Im<sup>a</sup>, I.-S. Kim<sup>a</sup>, K.-H. Cho<sup>c</sup>

<sup>a</sup>Advanced Materials and Application Research Laboratory, Korea Electrotechnology Research Institute,  
28-1 Seongju-dong, Changwon 641-120, Republic of Korea

<sup>b</sup>National Core Research Center for Hybrid Materials Solution, Busan National University Geumjeong-Gu, Busan 609-735, Republic of Korea

<sup>c</sup>Agency for Defense Development, Jochiwongil 462, Yuseong, Daejeon, Republic of Korea

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## Abstract

Piezoelectric ceramics with microstructure texturing were fabricated and evaluated to investigate its feasibility to use in piezoelectric energy harvesting in response to external mechanical impact. Textured  $0.945(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $0.55\text{BaTiO}_3$  (BNTBT) ceramics were prepared by tape casting of slurries containing a template  $\text{SrTiO}_3$  (STO). The orientation factor of more than 60% was obtained successfully when a plate-like  $\text{SrTiO}_3$  was used as the templates using a tape casting process. The sections perpendicular to the sheet plane of BNTBT ceramics exhibited preferentially  $[0\ 0\ 1]$  oriented orientation. Under low stress-loading, the voltage and power value of STO-added BNTBT were slightly higher than those of the specimen without STO. Meanwhile, the STO-added specimens showed excellent power over the STO-free specimen when a high stress was applied. When low stress was applied to the specimens, the reduction of piezoelectric characteristics by the addition of STO in BNTBT may be prominent in that the mixture of ferroelectric BNTBT and the non-ferroelectric STO has less ferroelectric features compared with the pure ferroelectric BNTBT. In contrast, under high field and stress signal the textured microstructure along to  $\langle 1\ 0\ 0 \rangle$  is a feature of the improved piezoelectric behavior.

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## 1. Introduction

Self-powered system draws an attention for micro- and milli-scale devices in accordance to the need of renewable energy generation [1]. To achieve the goal of “self-powered system”, harvesting from environmental waste energy to electrical energy, several approaches have been proposed; electromagnetic type, electrostatic type, piezoelectric type, bimetal type and thermo-air pressure type [2,3]. The piezoelectric type energy harvesting possesses several advantages including high energy conversion efficiency and large energy density from the environment [4]. In order to supply large energy to the small electronic system, many ideas to draw high conversion efficiency from piezoelectrics, have been proposed, including the modification of device geometric shape,

frequency matching between environmental vibration source and piezo-device [5,6]. In material aspect, single crystal possesses outstanding performance over polycrystalline ceramics and thus is expected to exhibit much larger output energy than ever other materials. It is difficult for single crystal to use in harvesting device owing to its complicated and expensive fabrication. To maximize the output electrical energy, instead, the ceramics with microstructure texturing were introduced in this study. Many investigations have shown that the ceramic with textured microstructure exhibited high piezoelectric response, which is between 50% of single crystal and 150% of normal ceramics in performance [7,8]. Most cases regarding textured ceramics have focused on how their dielectric properties can be enhanced in a use of sensors and actuators. In the present study, the relationship between the degree of grain orientation and electrical energy was investigated in the textured ceramics. A material,  $0.945(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $0.55\text{BaTiO}_3$  (BNTBT), was chosen as a ceramic matrix because it has excellent piezoelectric properties.  $\text{SrTiO}_3$

\* Corresponding author. Tel.: +82 55 280 1644; fax: +82 55 280 1590.

E-mail address: [sjjeong@keri.re.kr](mailto:sjjeong@keri.re.kr) (S.J. Jeong).

(STO) was chosen as a template of the BNTBT in that the STO has same crystal structure and similar lattice parameter with the ceramic matrix.

## 2. Experimental

Plate-like  $\text{SrTiO}_3$  (STO) particles were synthesized by a two-step process. In the first reaction,  $\text{Bi}_2\text{O}_3$  (Cerac Co., 99.99%),  $\text{TiO}_2$  (Cerac Co., 99.9%) and  $\text{SrCO}_3$  (Cerac Co., 99.999% pure) powders were reacted in a KCl (Cerac Co., 99.9%) flux at  $1100^\circ\text{C}$  for 4 h to obtain plate-like  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  precursor particles. In the second reaction, using plate-like SBIT precursor particles, the topochemical microcrystal conversion from  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  to  $\text{SrTiO}_3$  was carried out at  $950^\circ\text{C}$  for 8 h in a KCl flux. Residual KCl was removed from the plate-like particles by repeated washing in deionized hot-water. The by-product  $\text{Bi}_2\text{O}_3$  was removed by dissolution process in aqueous 2.5 mol/l  $\text{HNO}_3$  acid solution.

To control the degree of grain orientation in specimens, the amounts of STO template in range of 1–15% were added in the BNTBT matrix. The STO platelets, corresponding to 5 vol% of the 0.945BNT–0.055BT powder, were added to the slurry and then ball milled for 12 h. The ball milled powder was mixed with Methyl Ethyl Ketone (MEK, molecular weight 72.11) and ethanol (molar mass, 46.07 g/mol). Polyvinyl butyral (Dupont Chemical Co.) and a plasticizer were added to the slurry after 24 h mixing, and ball-milling was continued. The slurry was tape-cast by a doctor blade technique, and then a dried monolayer sheet with a thickness of approximately  $100\ \mu\text{m}$  was cut and laminated into multilayer sheet with a size of  $5 \times 5 \times 6\ \text{mm}$ . The binder was burned out by heating at  $300\text{--}400^\circ\text{C}$  for 12 h with heating and cooling rates of  $0.2^\circ\text{C}/\text{min}$ . The STO-added specimens were sintered at  $1200^\circ\text{C}$  for 24 h and the pure BNTBT specimen was sintered at  $1200^\circ\text{C}$  for 3 h.

The crystal structure of specimen was determined by an X-ray diffractometer (XRD, 200 Philips Co.). The morphology of the textured ceramics was determined by a field emission scanning electron microscopy (FESEM, Hitachi 2300). For electrical properties evaluation, Ag electrodes with a thickness of  $1\text{--}2\ \mu\text{m}$  were made on both side of the specimen by screen printing. The dielectric properties were measured with an HP4294A precision impedance analyzer.

To evaluate the energy conversion from external compressive stress to electrical voltage on the specimens, an air pressure-based compressive loading system was used. The pushing stress (force) was in a range of 4 MPa (100 N)–40 MPa (1000 N). The power output acquired from the specimen was determined by detecting voltage drop obtained from the resistor connecting to the device and bridge circuit. The resistive load was in a range of  $100\ \text{k}\Omega\text{--}1\ \text{M}\Omega$ .

## 3. Results and discussion

Fig. 1 is the scanning electron images showing microstructural evolution for BNTBT without and with the STO template. When the template was added in the specimen, the enlarged grains were observed. The similar change could be

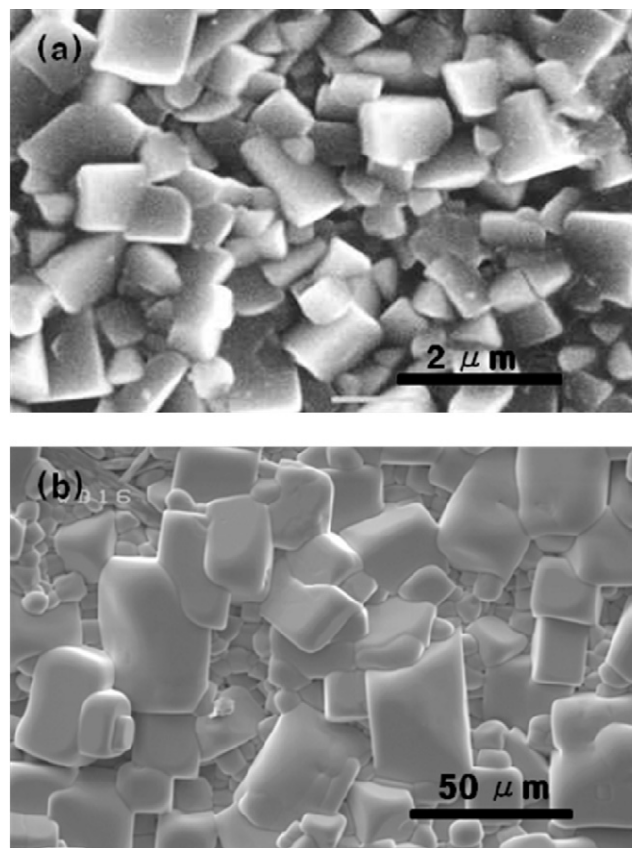


Fig. 1. Scanning electron images showing morphologies of BNTBT specimens (a) non-textured BNTBT and (b) textured BNTBT with 10% STO.

obtained in X-ray diffraction pattern (XRD) analysis. Fig. 2 shows the XRD patterns of the STO-added BNTBT ceramics. In pure specimens, the (1 1 0) peak has the highest intensity, which is almost same as the XRD pattern of powder. For the specimen containing 5% STO, the (0 0 2) and (2 0 0) peaks increases relative to other peaks, although (1 1 0) peak is still major one. In cases of 10% and 15% STO-added specimens, the highest peak of (0 0 2) was observed, indicating the formation of a preferential grain orientation to  $\langle 1\ 0\ 0 \rangle$ . To evaluate the degree of grain orientation, the Lotgering factor of the STO-enriched specimens was calculated on a basis of the data of the X-ray diffractions. The degree of the grain orientation was evaluated in Fig. 2(b) [9]. The degree of orientation increases with increasing the STO content, and the value along [0 0 1] is about 62% for specimens containing 10% and 15% STO.

In order to evaluate the performance of piezoelectric ceramics, the dielectric and piezoelectric characteristics of STO-added specimen were measured. Table 1 shows the piezoelectric  $d_{33}$  coefficient, the electromechanical coupling coefficient  $k_p$  and the relative dielectric constant  $\epsilon_r$  of all specimens. The  $d_{33}$  coefficient, the  $k_p$  and the  $\epsilon_r$  increase with increasing the STO content. However, the 15% STO-added specimen showed the lower properties than 5% and 10%-added specimens. This decrease in electrical properties may be due to the fact that the STO has non-ferroelectric properties, although the texturing of microstructure was expected to contribute the enhancement of electrical properties. Many investigations have

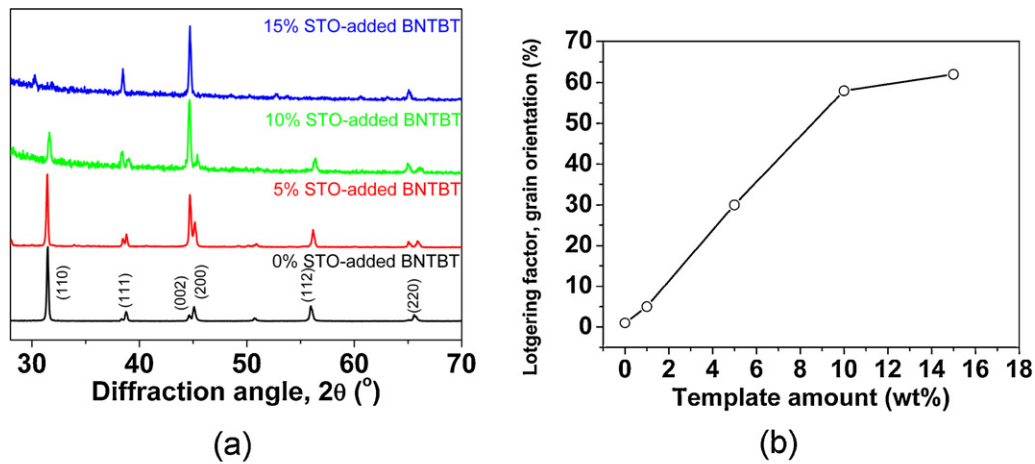


Fig. 2. XRD patterns and grain orientation degree of STO-added specimens (a) X-ray diffraction patterns of pure BNTBT, 5%, 10%, and 15% STO-added BNTBT specimens and (b) Lotgering factor of the films with respect to template content.

shown that the piezoelectric ceramics with textured microstructure exhibited the improvement of properties under electric fields [7]. In such studies, however, the low piezoelectric responses were observed when the excessive amount of template was added. With bearing a mind that the ceramics containing excessive template content would be different from those of ceramics with effective amount of template, the

generated voltage as a function of compressive mechanical stress for the specimens were measured as shown in Fig. 3.

Fig. 3 shows output voltage produced from the specimens as a function of input compressive stress ranging 4 MPa (100 N)–40 MPa (1000 N) with an interval of 2 s and duration time 1 s. A resistive load of 10 M $\Omega$  was connected to the ceramic specimens in a parallel circuit mode in order to determine the

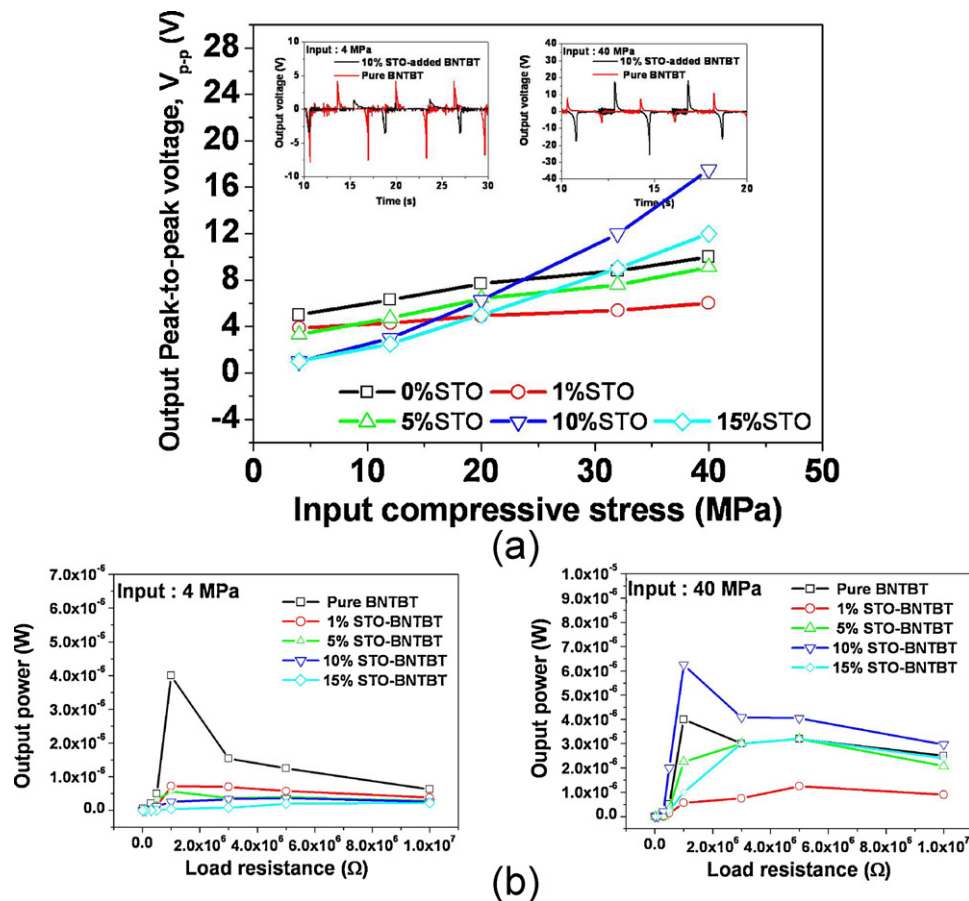


Fig. 3. Output voltage and power for specimens (a) output peak-to-peak voltage with respect to input stress and (b) output powder as a function of load resistance for specimens subjected to compressive stress (forces) of 4 MPa (100 N) and 40 MPa (1000 N).

Table 1

Dielectric constant, electromechanical coupling coefficient  $k_p$  and piezoelectric coefficient,  $d_{33}$  for specimens with respect to template content.

STO template (at.%)	Dielectric constant, $\epsilon_r$	Electromechanical coupling coefficient, $k_{31}$	Piezoelectric coefficient, $d_{33}$ (pC/N)
0	664.5	0.28	156
1	650	0.28	150
5	71605	0.3	165
10	772.5	0.35	201
15	740	0.35	210

voltage and power generated from the specimen. The inlet of Fig. 3(a) showed the change in voltage as a function of time for pure and 10% STO-added specimens. Under the input stress of 4 MPa, the pure BNTBT specimen showed the largest change in voltage during the application and removal of the mechanical stress. When the input stress was 40 MPa, the specimen containing 10% STO had the highest voltage change. The maximum power was determined for all specimens by changing load resistance. The results for all specimens under the lowest input stress 4 MPa and highest stress 40 MPa were shown in Fig. 3(b), and are similar to the trend of voltage change.

Taken into a consideration that different piezoelectric properties, and the changes in voltage and power were observed with the content of template under low and high compressive stresses, two contributions might be possibly at least involved in exertion of power generation from the non-textured and textured ceramics. One possible contribution is related to the presence of the non-ferroelectric template STO, which makes the performance of piezoelectric ceramic matrix deteriorate. Texturing of microstructure is another contribute of the enhancement of the power generation in ceramic. Consequently, the reduced voltage and power of 15% STO-added specimen under input stress is due to the fact that the presence of STO allows the ceramics to have lower piezoelectric property and its resultant power generation. When subjected to high stress-loading, the microstructural texturing effect on performance is dominant, resulting in the large power generation from the ceramic. If ferroelectric substance is used as template like BaTiO<sub>3</sub>, the enhancement of power generation would be more efficient.

## 4. Conclusions

Piezoelectric ceramics with textured microstructure were fabricated and evaluated in response to external mechanical impact. The STO-added specimens showed excellent power generation in comparison with the STO-free specimen. When the excessive amount of template (15% in this study) was added to the specimens, the piezoelectric characteristics in BNTBT were reduced. This may be caused by the fact that the mixture of ferroelectric BNTBT and the non-ferroelectric STO has less ferroelectric features. In contrast, for the specimens with the effective content of template the textured microstructure along to  $\langle 1\ 0\ 0 \rangle$  is a feature of the enhanced piezoelectric behavior.

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