Ferroelectric and piezoelectric properties of BaTiO$_3$-templated 0.36BiScO$_3$-0.64PbTiO$_3$ thick films for piezoelectric device applications

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ABSTRACT
A novel 0.36BiScO$_3$-0.64PbTiO$_3$ (0.36BS-0.64PT) textured ceramic was developed using plate-like BaTiO$_3$ (BT) templates for high temperature piezoelectric device applications. Sintering temperature and amount of BT template played important roles in improving the density, crystal orientation, and ferroelectric and piezoelectric properties of the BT-templated 0.36BS-0.64PT thick films. When sintered at 1000°C, highly dense BS-PT textured films were obtained without formation of a secondary phase. The increased amount of BT template facilitated the degree of texture but deteriorated the relative density of BS-PT thick film. In particular, enhanced ferroelectric and piezoelectric properties were obtained for 1 vol% BT-templated 0.36BS-0.64PT thick film sintered at 1000°C; this film exhibited the very large $P_r$ (44.2 μC/cm$^2$ at 4 kV/mm), $d_{33}$ (444 pC/N), $K_p$ (57.4%), and $g_{31}$ (36 × 10$^{-3}$V/m/N) values. In addition, considering the inverse relation between $T_c$ and strain, the electrostrain of d$_{33}$* (622 pm/V at 4 kV/mm) was excellent, showing potential for piezoelectric actuator applications.

1. Introduction
The BiScO$_3$-PbTiO$_3$ (BS-PT) ceramic has attracted considerable attention because of its good piezoelectric properties and a high Curie temperature ($T_c$) of approximately 450°C [1]. In particular, the (1-x)BiScO$_3$-xPbTiO$_3$ ($x$ = 0.64 or 0.63) composition, near the morphotropic-phase boundary (MPB), has for decades been reported by many researchers to have excellent piezoelectric performance [2-4]. Recently, various 0.36BS-0.64PT ceramics with dopant-modified A or B sites and perovskite symmetry have been demonstrated to have enhanced piezoelectric properties [5-7]. In particular, extremely high piezoelectricity (>800 pC/N) over 400°C has been introduced in BiScO$_3$-PbTiO$_3$-CaTiO$_3$ ceramics [8].

Template grain growth (TGG) is a widely known process technique used to achieve textured ceramics with a preferred orientation, typically a c-axis orientation normal to the lateral direction [9,10]. The textured grain morphology tailored by the TGG process can be successfully used to enhance certain piezoelectric properties, including the electrostrain ($d_{33}^*$) constants and electromechanical coupling factor ($k_p$), along the c-axis direction [11-13]. Accordingly, it is thought that the piezoelectric performance of high-temperature 0.36BS-0.64PT piezoelectric ceramics can be further improved, if the TGG process can be used to develop c-axis oriented 0.36BS-0.64PT textured ceramics. Several Ti-based oxides of BaTiO$_3$ [14,15], SrTiO$_3$ [16,17], and PbTiO$_3$ [18] have been traditionally used as template materials for the implementation of piezoelectric TGG process. Meanwhile, reactive Bi-based template materials such as Bi$_{0.5}$Na$_{0.5}$TiO$_3$ [19,20] and Bi$_4$Ti$_3$O$_{12}$ [21,22] have been introduced for TGG ceramics including Bi element. The use of BaTiO$_3$ (BT) platelets, which is the most widely used template in the TGG process, is also beneficial to the texture of the 0.36BS-0.64PT ceramic because the lattice parameters ($a = b = 3.9958$ Å, $c = 4.0363$ Å) [23] of BT with tetragonal symmetry are highly similar to those of the 0.36BS-0.64PT. In addition, there is a strong economic benefit of using plate-like BT, which is already commercialized by mass-production with high yield. In contrast to the other candidates for template material, BT features cost-effectiveness, implying that development of BT-templated piezoelectric films can strongly save time and cost for practical applications. Nevertheless, it is not easy to find studies about the BS-PT ceramics fabricated by TGG process. Although recent study on TGG in Bi(Zn$_{0.5}$Zr$_{0.5}$)O$_3$ modified BS-PT ceramics [24] was reported by Akca et al., the incorporation of Bi(Zn$_{0.5}$Zr$_{0.5}$)O$_3$ resulted in significantly decreased $T_c$ of BS-PT. Thus, more studies on textured BS-PT ceramics are necessary to develop superior piezoelectric ceramics suitable for high temperature range applications. It is also of importance to determine what kind and how much template material
should be incorporated into the matrix ceramic, because overdosed and heterogeneous template materials can play negative role in achievement of textured ceramics [11,12]. Table 1 shows the summary of piezoelectric charge/strain properties of textured ceramics with various seed materials.

Therefore, in this work, the microstructural evolution of BT-templated 0.36BS-0.64PT thick films was investigated based on the sintering temperature. The ferroelectric and piezoelectric properties of the textured 0.36BS-0.64PT thick films were then further investigated to clarify the effects of the BT templates. The unipolar electrostrain characteristics were also evaluated for piezoelectric actuator applications.

2. Experimental procedure

2.1. Preparation of the BaTiO₃ (BT) templates

BT templates were synthesized using a two-step topochemical microcrystal conversion method. First, raw powders of Bi₂O₃ (99.5%, Kojundo Chemical Laboratory, Japan), TiO₂ (≥99.9%, Sigma-Aldrich, USA), and NaCl (≥99.0%, Sigma-Aldrich, USA) were mixed with an equal weight of NaCl as a salt. The mixture was ball-milled for 24 h and dried at 120°C. Then, the dried powders were annealed at 1100°C for 2 h in molten salt to synthesize Bi₄Ti₃O₁₂ (BiT) precursors. The product was washed several times with hot de-ionized water to dissolve salt until Cl⁻ ions were not detected using an AgNO₃ solution. Second, the BT templates were synthesized from the BT precursors with BaCO₃ and NaCl at 1050°C for 3 h. Then, the BT templates were washed again with nitric acid and de-ionized and dried.

| Composition | Template material (Amount) | \(d_{31}\) (pC/N) | \(d_{33}\) (pm/V) | Strain (%) |
|-------------|-----------------------------|-------------------|-------------------|------------|
| \(0.69\text{Pb} (\text{Zr}_{0.57} \text{Ti}_{0.53}) \) - \(0.31\text{Pb} (\text{Zn}_{0.05} \text{Nb}_{0.25} \text{Ta}_{0.05}) \) | \( \text{BaTiO}_3 \) (5 vol\%) | 545 | 1040 | 0.33 | [11] |
| \(0.55\text{Pb} (\text{Ni}_{0.45} \text{Nb}_{0.55}) \) - \(0.15\text{Pb} (\text{Zr}_{0.83} \text{Bi}_{0.17}) \) | \( \text{BaTiO}_3 \) (2 vol\%) | 1210 | 1773 | 0.052 | [12] |
| \(0.69\text{Pb} (\text{Zr}_{0.57} \text{Ti}_{0.53}) \) - \(0.31\text{Pb} (\text{Zn}_{0.05} \text{Nb}_{0.25} \text{Ta}_{0.05}) \) | \( \text{BaTiO}_3 \) (10 vol\%) | 430 | 920 | 0.276 | [13] |
| \(0.67\text{Pb} (\text{Mg}_{0.15} \text{Bi}_{0.85}) \) - \(0.32\text{Pb} (\text{TiO}_3) \) | \( \text{BaTiO}_3 \) (5 vol\%) | 630 | - | 0.27 | [14] |
| \(0.28\text{Pb} (\text{Mg}_{0.15} \text{Bi}_{0.85}) \) - \(0.40\text{Pb} (\text{Mg}_{0.15} \text{Bi}_{0.85}) \) - \(0.32\text{Pb} (\text{TiO}_3) \) | \( \text{BaTiO}_3 \) (5 vol\%) | 1620 | - | 0.4 | [15] |
| \(0.83\text{Bi}_{0.38} \text{Na}_{0.62} \text{TiO}_3 \) - \(0.17\text{Bi}_{0.38} \text{Na}_{0.62} \text{TiO}_3 \) | \( \text{SrTiO}_3 \) (15 mol%) | - | 626 | 0.38 | [16] |
| \(\text{Ba} (\text{Zr}_{0.67} \text{Ti}_{0.33}) \text{O}_3 \) | \( \text{SrTiO}_3 \) (5 vol\%) | 975 | - | 0.19 | [17] |
| \(0.91\text{Bi}_{0.38} \text{Na}_{0.62} \text{TiO}_3 \) - \(0.06\text{BaTiO}_3 \) - \(0.03\text{AgNbO}_3 \) | \( \text{Ba} (\text{Zr}_{0.67} \text{Ti}_{0.33}) \text{O}_3 \) (5 vol%) | - | - | 0.3 | [20] |
| \(0.36\text{BiScO}_3 \) - \(0.36\text{PbTiO}_3 \) | \( \text{Bi}_{0.38} \text{Na}_{0.62} \text{TiO}_3 \) (4 wt%) | 440 | - | - | [22] |
| \(2.5\text{Bi} (\text{Zr}_{0.5} \text{Zr}_{0.5}) \text{O}_3 \) - \(37.5\text{BiScO}_3 \) - \(60\text{PbTiO}_3 \) | \( \text{BaTiO}_3 \) (3 vol%) | 353 | 910 | 0.3 | [24] |

2.2. Preparation of 0.36BiScO₃ - 0.64PbTiO₃ (0.36BS-0.64PT) powders

0.36BS-0.64PT powders were synthesized using a conventional solid-state reaction. Bi₂O₃ (99.99%, Kojundo Chemical Laboratory, Japan), Sc₂O₃ (99.9%, Kojundo Chemical Laboratory, Japan), PbO (99.9%, Sigma-Aldrich, USA), and TiO₂ (≥99.9%, Sigma-Aldrich, USA) powders were prepared as raw materials. They were mixed in the stoichiometric amount using various zirconia ball medias (\( \phi = 1 \text{ mm, 3 mm, 5 mm, 10 mm} \) in ethanol for 24 h and dried at 120°C in a drying oven. Then, the dried mixture was calcined at 775°C for 4 h. The calcined powder was re-milled for 47 h and dried.

2.3. Fabrication of BT-templated 0.36BS-0.64PT thick films

The calcined 0.36BS-0.64PT powders were mixed with ethyl alcohol (99.9%, Daegung Chemical, Korea), toluene (99.5%, Daegung Chemical, Korea), dibutyl phthalate (99%, Daegung Chemical, Korea), polyvinyl butyral (BM-SZ, Sekisui, Japan), and dispersant (BYK-111, BYK-Chemie GmbH, Germany) at an optimized ratio to prepare a slurry for tape casting. They were milled with zirconia balls (\( \phi = 3 \text{ mm, 5 mm, 10 mm} \) for 24 h. After milling, the slurry was sieved, and air bubbles were eliminated in a vacuum of \(-760 \text{ mmHg for 20 min in a vacuum deaerator. Then, the BT templates were prepared with ethanol and dispersant in vials for 5 min using a sonicator and then dispersed BT template was added to the prepared slurry. Subsequently, aging was carried out at 10 rpm for 2 h to stabilize the slurry. Highly uniform BT-templated 0.36BS-0.64PT green sheets were fabricated using a tape casting machine.

Table 1. Summary of piezoelectric charge/strain properties of textured ceramics with various seed materials.
(TCA-2000, Techgen, Korea). All green sheets were slightly different in thickness, with values ranging from 45 μm to 51 μm depending on the slurry viscosity.

After the sheets were cut out with a regular shape, they were laminated at 60°C using a laminator (Keko, Slovenia). The laminated sheets were treated using a warm isostatic press (MO-20-036, Ilsin Autoclave, Korea) at 65°C under 25 MPa for 20 min. The laminated green bodies were cut to sizes of 10 mm × 10 mm again using a blade cutter. Then, sintering was carried out at various temperatures from 950°C to 1100°C for 24 h, at a heating rate of 0.5°C/min. Subsequently, an Ag paste (WT-APPI7-1, Winner Technology, Korea) was printed onto both surfaces of the laminated green body to form an outer electrode, and the samples were annealed again at 700°C for 10 min to stabilize the electrode layer.

2.4. Characterization

The crystal structure of the sintered 0.36BS-0.64PT thick films was analyzed by X-ray diffractometry (XRD) (D8 Advance A25, Bruker, USA) with CuKα radiation. The densities of the specimens were measured by Archimedes method. The microstructures of the specimens were examined by field-emission scanning electron microscope (MIRA3 LM, TESCAN, Czech) and high-resolution transmission electron microscope (Themis Z, FEI, Japan). An energy-dispersive X-ray spectroscopy (Aztec, Oxford Instruments, UK) was also used to quantitatively analyze the thick films. The piezoelectric and dielectric properties were measured using a d33 meter (ZJ-6B, IACAS, Taiwan) and an impedance analyzer (E4990A, Keysight, USA). After that, a polarization versus electric field (P-E) hysteresis loop was obtained using a ferroelectric tester (Radiant Technologies, USA). For the measurement of deformation characteristics, electric fields ranged from 1 to 4 kV/mm were applied to the specimens under test. Subsequently, the strain-electric field curve was obtained using a linear variable differential transformer sensor.

3. Results and discussion

Figure 1(a) shows XRD patterns of the 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at various temperatures from 950°C to 1100°C for 24 h. When the

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**Figure 1.** (a) XRD patterns (right figure: logarithmic coordination) of 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at various temperatures from 950°C to 1100°C for 24 h and (b) backscattered electron SEM image of 1 vol% BT-templated 0.36BS-0.64PT thick film sintered at 1100°C (right table: quantitative elemental analyses taken from the areas of A and B).
sintering temperature was 950°C, the specimen showed a pure perovskite crystal structure despite its relatively poor sinterability. As the sintering temperature was increased to 1000°C, all peaks indicating perovskite symmetry were intensified and the (100) plane near 2θ of 22.7° was especially noticeable. Furthermore, the (100)-oriented peak intensity was further enhanced by increasing the sintering temperature to 1050°C, while the other peaks belonging to (110), (111), (210) and (211) were concurrently weakened. This tendency was heavily enhanced when the sintering temperature reached 1100°C. The preferred orientation along the [100] direction implies that the BT-templated 0.36BS-0.64PT thick films were successfully textured when the sintering temperature exceeded 950°C.

It should be also noted that a secondary phase, marked by red squares, was observed for the specimens sintered at 1050°C and higher. The peak intensity of the secondary phase was further enhanced when the sintering temperature was increased higher to 1100°C. The formation of the secondary phase is probably due to the volatile elements of Bi and Pb, based on evidences obtained from the quantitative elemental analysis of the specimen sintered at 1100°C.

In the backscattered electron scanning electron microscope (SEM) image of the specimen sintered at 1100°C shown in Figure 1(b), several darker particles with a rectangular shape indicated by red arrows can be clearly distinguished from the neighboring BS-PT grains. According to the quantitative elemental analyses of the dark rectangular grain and bright round grain, obtained from the areas marked A and B, it was found that the secondary phase of the rectangular grain was rich for the Sc element but relatively deficient for Bi, Pb, and Ti elements, as confirmed from the right table in Figure 1(b). Similar results were also obtained from other particles with the dark phase. A long dark platelet, which is identical to BT template, and an epitaxial BS-PT grain surrounding the BT are also shown at the center of the FE-SEM image in Figure 1(b). Several residues formed during sample preparation for thermal etching process were examined along with some pores. XRD patterns, also shown in the right side of Figure 1(a), which were enlarged from 35° to 55° by logarithmic coordination, exhibited more clear reflections corresponding to the secondary phase for both specimens sintered at temperatures higher than 1000°C.

It was also interesting that the matrix 0.36BS-0.64PT ceramic with a morphotropic phase boundary of rhombohedral and tetragonal phase became textured on the rhombohedral side, over the tetragonal side, with increasing sintering temperature. The enhanced degree of epitaxially grown grain orientation on a template material in textured ceramics can be represented by the Lotgering factor (fL). Figure 2 exhibits the variation in fL, relative density, d33, kL, and g33 for the 1

**Figure 2.** Variation in fL, relative density, d33, kL, and g33 values for 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at 950°C, 1000°C, 1050°C, and 1100°C for 24 h.
vol% BT-templated 0.36BS-0.64PT thick films as a function of sintering temperatures from 950°C to 1100°C. To estimate the fraction of ⟨00 1⟩-textured specimens, $f_L$ was determined using Equations (1) and (2),

$$f_L = \frac{P - P_0}{1 - P_0}$$

$$P = \frac{\sum I(hkl)}{\sum T(hkl)}$$

where $I(hkl)$ is the intensity of the (hkl) reflection and $P$ and $P_0$ are for the textured and randomly oriented materials. As the sintering temperature increased from 1000°C to 1100°C, the $f_L$ of the textured specimens showed a linearly increasing tendency with drastically intensified values from 17.1% to 78.5%. However, as seen in Figure 2, showing the temperature-dependent piezoelectric properties of $d_{33}$, $k_p$, and $g_{33}$, the best piezoelectric values were obtained for the specimen sintered at 1000°C, being 444 pC/N, 57.4%, and $36 \times 10^{-3}$ Vm/N, respectively. Given that the specimen sintered at 950°C was not fully sintered, its poor piezoelectric properties were reasonable. However, despite the steadily increasing $f_L$ values and relatively stable densities, the decrease in the piezoelectric properties of the specimens sintered above 1000°C is hard to explain. Probably, the Sc-rich secondary phase, which is commonly observed in the specimens sintered above 1000°C, might be related to the poorer piezoelectric characteristics.

Figure 3(a–d) show cross-sectional FE-SEM images of 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at various temperatures from 950°C to 1100°C for 24 h. It was observed that μm-scale BT platelets distinctively impinged on the matrix BS-PT ceramic, as indicated by the white arrows. In addition, FE-SEM images of the 0.36BS-0.64PT ceramic exhibited further textured grain morphology with increasing sintering temperature, in good agreement with the XRD results shown in Figure 1(a). Grain growth of the 0.36BS-0.64PT ceramic tended to be steadily enhanced, showing a strong dependency on sintering temperature, along with the evolution of epitaxial grains on the BT templates. The specimen sintered at 950°C exhibits a relatively porous microstructure, but a denser microstructure developed for the specimen sintered at 1000°C. In contrast to the extremely fine-grained specimen sintered at 950°C, a relatively coarse-grained morphology was observed for the specimens sintered at temperatures higher than 950°C. However, further increases in sintering temperature to 1050°C and 1100°C facilitated formation of more pores in those specimens. Therefore, it seems that the grain sizes of both the polycrystalline grains and the epitaxial grains in the textured BS-PT ceramic are significantly dependent on the sintering temperature.

Grain size analysis using Image J software in Figure 4 shows that the dominant grain size increased with increasing sintering temperature from 950°C to 1100°C. Table 2 shows the average grain size of the polycrystalline grains and epitaxial grains for each specimen sintered at the corresponding temperatures. There is a steadily increasing
average grain size with increasing sintering temperature. The thickness of BT template is excluded in size evaluation of the epitaxial 0.36BS-0.64PT grains. The average grain size varied from 0.72 μm to 2.45 μm and from 180 nm to 5.56 μm with increasing sintering temperature from 950°C and to 1100°C, for polycrystalline and epitaxial grains, respectively. The polycrystalline grain growth was less dependent on the increase of sintering temperature than the epitaxial grain growth along the thickness direction.

In general, pore-controlled grain growth results in a fine-grained morphology that consequently deteriorates the ferroelectric and piezoelectric properties of piezoelectric materials [25–27]. However, considering the morphology in the FE-SEM images, with coarser
Table 2. Comparison of grain sizes of polycrystalline and epitaxial grains in the 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at 950°C, 1000°C, 1050°C, and 1100°C.

| Sintering Temperature (°C) | Average Grain Size (µm) | Standard Error of Mean (µm) | Average Grain Size (µm) | Standard Error of Mean (µm) | Porosity (%) |
|----------------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|--------------|
| 950                        | 0.18                     | 0.02                        | 0.72                     | 0.03                        | 2.27         |
| 1000                       | 3.17                     | 0.06                        | 1.76                     | 0.05                        | 1.92         |
| 1050                       | 5.05                     | 0.21                        | 1.92                     | 0.07                        | 2.11         |
| 1100                       | 5.56                     | 0.13                        | 2.45                     | 0.07                        | 2.37         |

Table 3. Variation of slurry viscosity and film thicknesses for fabrication of BT-templated 0.36BS-0.64PT thick films, depending on amount of BT template.

| Amount of BT | Viscosity (cps) | Thickness (µm) |
|--------------|-----------------|----------------|
| 0            | 2167            | 51             |
| 1            | 2054            | 50             |
| 2            | 1958            | 49             |
| 4            | 1823            | 47             |
| 8            | 1721            | 45             |

grains in specimens sintered above 1000°C, porosity seemed to not be a significant factor in the deterioration of sintering temperature dependent piezoelectric properties. This strongly suggests that the Sc-rich secondary phase resulted in the degradation of piezoelectricity in the specimens sintered at 1050°C and 1100°C.

Trends in ferroelectric characteristics similar to the piezoelectric behavior were also experimentally observed, by evaluating the voltage-dependent polarization of the BS-PT thick films as a function of sintering temperature. Table 3 shows a summary of the remnant polarization (P_r) and coercive electric field (E_r) values for the 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at 950°C, 1000°C, 1050°C, and 1100°C. All the data summarized in Table 2 were obtained from ferroelectric polarization (P) vs. bipolar electric field (E) hysteresis loops measured at 1 Hz. Like the tendencies of the piezoelectric d_{33}, k_p, and g_{33} values, excellent ferroelectric properties, with a P_r of 44.2 µC/cm² and E_r of 2.4 kV/mm, were obtained for the specimen sintered at 1000°C. As expected, the ferroelectric characteristics of both specimens sintered above 1000°C were dramatically weakened, probably due to the secondary phase. Therefore, to develop BT-templated 0.36BS-0.64PT thick films for high performance piezoelectric device applications, the optimum sintering temperature was determined to be 1000°C.

Figure 5 depicts the P-E hysteresis loops of the x vol% BT-templated 0.36BS-0.64PT (x = 0, 1, 2, 4, and 8) thick films sintered at 1000°C for 24 h. All of the films exhibited typical ferroelectric characteristics. For the untextured specimen, the template-free 0.36BS-0.64PT thick film, a relatively large P_r of 35.3 µC/cm² and E_r of 2.5 kV/mm were observed at 4 kV/mm. However, the textured specimen with a small amount of BT templates (x = 1) resulted in a highly enhanced P_r of 44.2 µC/cm² and E_r of 2.4 kV/mm, implying that a small amount of BT template is responsible for softening the 0.36BS-0.64PT piezoelectric film. Meanwhile, for x higher than 1, additional BT templates caused more severe degradation of the P-E hysteresis. All of the P_r and E_r values of the x vol% BT-templated 0.36BS-0.64PT thick films sintered at 1000°C are summarized in the inset in Figure 5. Although P_r values gradually intensified from 17.1% for x = 1 to 56.5% for x = 8 with the aid of anisotropic BT templates, deterioration in ferroelectric behavior was observed for the specimens when the amount of BT exceeded 1 vol%. To elucidate the degradation of ferroelectric characteristics in the specimens with heavily incorporated BT templates, transmission electron microscope (TEM) analyses were carried out on both the 0.36BS-0.64PT thick films with an x of 1 and 8.

Figure 6(a,b) show low magnification TEM images of the 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at 1000°C for 24 h. The BT template was easily found because its color was brighter than that of the 0.36BS-0.64PT ceramic. No structural defects, such as pore or delamination, were found on the interfacial area between the template BT and surrounding BS-BT grains. This indicates the templated BT platelet was well harmonized with the matrix BS-PT ceramic, in good agreement with the lattice match between both materials. In Figure 6(b), showing an enlarged image of the dashed blue box in Figure 6(a), the epitaxial grain of textured 0.36BS-0.64PT was easily distinguished from the polycrystalline grains. In particular, it was highly notable that many stripes and herringbone-shaped domains formed in the textured 0.36BS-0.64PT ceramic, implying that the dominant morphology of the epitaxial grain is a 90° domain wall. Meanwhile, in Figure 6(c,d), showing magnified TEM images of the 8 vol% BT-templated specimen, a porous microstructure can be observed, indicating a comparatively low relative density. As seen in Figure 6(c), many micrometer-scale pores are distributed along the grain boundaries. Figure 6(d), showing an enlarged image of the dashed red box in Figure 6(c), clearly shows the presence of micro-pores, marked by red arrows, at the grain boundary. Unlike a conventional solid-state reaction, a relatively large volume of organic components such as binders and dispersants are necessarily contained in the slurry for fabrication processes such as tape casting. During sintering, these materials transform to the vapor phase by decomposition, and subsequently, pores are left in the ceramic body, which can hinder grain growth. Depending on the kinetics of the templated grain growth in the piezoelectric material, porosity evolution can significantly influence the grain growth of matrix polycrystalline grains and epitaxial
grains on the surface of the template material [28]. Since the presence of pores retards grain-boundary migration, the overall rate of grain growth decreases as the amount of porosity increases [29,30].

Figure 7(a,b) exhibit cross-sectional FE-SEM images of the thermally etched 0.36BS-0.64PT thick films with BT templates of 1 and 8 vol%, sintered at 1000°C for 24 h. In this work, the pore volume in the 0.36BS-0.64PT thick film seemed to be steadily increased as the amount of BT templates increased. This phenomenon can be also confirmed in the cross-sectional FE-SEM image of the thermally etched specimens with x of 1 and 8. It was found that the fabricated film for x=1 was approximately 265 μm thick, but thickness slightly decreased to 240 μm for the film with x=8, as shown in Figure 7(a,b). This is because the films as laminated before sintering were different. The original green sheet for both cases was differentiated in thickness after tape casting process because of different viscosity of slurry. The higher viscosity of the slurry for film x=1 resulted in thicker green sheet, whereas the dilute slurry for film x=8 led to a thinner green sheet.

Table 4 summarizes all variation of the slurry viscosity and film thickness for fabrication of BT-templated 0.36BS-0.64PT thick films, depending on the amount of BT template. In Figure 7(a,b), the Ag-electrode layer was also found at the top and bottom surfaces of each specimen. Figure 7(c,d) are enlarged backscattered electron images of Figure 7(a,b), and also indicate that the average size of polycrystalline grains for the textured BS-PT ceramics slightly decreased, from 1.76 μm to 1.64 μm, with the increase of x from 1 to 8. In contrast, that of the epitaxially-grown BS-PT grains increased from approximately 2.16 μm to 2.84 μm along the thickness direction. Additionally, it was found that several epitaxial grains were linked with neighboring epitaxial grains in the textured specimen with an x of 8. Considering the correlation between grain size and piezoelectricity, these results suggest that the influence of grain morphology on piezoelectric properties should be considered for both the matrix crystalline grains and epitaxial grains on the anisotropic template crystal in the TGG process. The enhancement of the epitaxially grown grain morphology with increasing amounts of BT templates also resulted in an enforced tetragonal phase in the MPB BS-PT ceramics, as shown in the XRD patterns of both specimens in Figure 7(e). Therefore, it can be concluded that the additional BT templates positively affect epitaxial grain growth with tetragonal symmetry, but negatively or negligibly affect polycrystalline grain growth in the textured BS-PT thick films. This behavior is also responsible for pore growth in the matrix ceramic, and the consequently degraded piezoelectric properties in the BT-templated BS-PT ceramics.

Table 4. Summary of remnant polarization (P_r) and coercive electric field (E_c) values of the 1 vol% BT-templated 0.36BS-0.64PT thick films sintered at various temperatures.

| Sintering Temperature | 950°C | 1000°C | 1050°C | 1100°C |
|-----------------------|-------|--------|--------|--------|
| P_r (μC/cm²)          | 25.5  | 44.2   | 26.8   | 13.3   |
| E_c (kV/mm)           | 2.7   | 2.4    | 2.9    | 2.0    |

Figure 5. Ferroelectric polarization (P) vs. bipolar electric field (E) hysteresis loops of the x vol% (x = 0, 1, 2, 4, 8) BT-templated 0.36BS-0.64PT thick films sintered at 1000°C for 24 h, measured at 1 Hz.
According to a previous report, various microstructural features, such as differently oriented grains, grain boundaries, residual pores, and heterogeneous growth templates, can together control the performance of textured piezoelectric ceramics [31]. Theoretically, an ideally textured ceramic having an $f_t$ value near 100% should possess an extremely large $d_{33}$ value, almost identical to that of single crystal. However, in practice, experiments to add extreme heterogeneous templates to matrix piezoelectric ceramics in the TGG process deteriorated piezoelectric charge, and the strain characteristics of $d_{33}$ and $d_{33}^*$ can be found in many previous reports [11,12,32,33]. In this work, the effects of secondary phase, grain size, and residual pores were investigated to clarify the deterioration of piezoelectric properties in highly BT-templated and high-temperature-sintered 0.36BS-0.64PT thick films. However, additional criterion such as hetero-epitaxial grain orientation on template material should be considered.

In order to evaluate the electric field-induced strain characteristics of the BT-templated 0.36BS-0.64PT thick film for piezoelectric actuators, their strain behavior was also analyzed. Figure 8 shows the relative density and unipolar strain vs electric field ($S$-$E$) curves at 1 Hz for the $x$ vol% ($x = 0, 1, 2, 4,$ and $8$) BT-templated 0.36BS-0.64PT thick films sintered at 1000°C for 24 h. Notably, it is found that the steady increased BT template resulted in the decrease of relative density for the specimens. The large signal piezoelectric coefficient $d_{33}^*$, which was the same as the ratio of maximum $S$ ($S_{max}$) to maximum $E$ ($E_{max}$), was obtained from the unipolar $S$-$E$ plots at maximum 4.0 kV/mm. The untextured 0.36BS-0.64PT thick film showed a relatively large strain of 0.205% at 4.0 kV/mm, corresponding to $d_{33}^*$ of 515 pm/V. In addition, it is notable that $d_{33}^*$ was further enhanced only when as little as 1 vol% BT templates was incorporated into the 0.36BS-0.64PT thick films. The highest values of the enhanced strain and $d_{33}^*$ reached 0.246% and 622 pm/V. The 90° domains, typically found in the textured BS-PT films with enhanced tetragonal phase, can contribute to larger electrostrain because they have easier domain rotation. Thus, the other textured specimens with $x$ of 2% and higher still displayed satisfying $d_{33}^*$ values higher than 450 pm/V, which might be due to the enhanced $f_t$ despite relatively increased porosity.
However, it should be noted that the 1 vol% BT-templated 0.36BS-0.64PT thick film showed the best electrostrain characteristic because of its highly dense microstructure. Although the specimens with BT of more than 1 vol% had larger $f_L$ values, even the 8 vol% BT-templated specimen reached an unsatisfactory $f_L$ of 56.5%. This value implies that the untextured part of the specimen still plays a significant role in piezoelectric performance enhancement. More importantly, as

![Figure 7](image.png)

**Figure 7.** Cross-sectional FE-SEM images of x vol% BT-templated 0.36BS-0.64PT thick films with (a and c) $x = 1$ and (b and d) $x = 8$ and (e) XRD patterns of the corresponding specimens.

| Phase   | $x = 1$ | $x = 8$ |
|---------|---------|---------|
| Rhombohedral | 26% | 22% |
| Tetragonal | 74% | 78% |
| Total   | 100% | 100% |

**Table 5.** Variation in electrostrain $d_{33}$* for the x vol% ($x = 0, 1, 2, 4, 8$) BT-templated 0.36BS-0.64PT thick films sintered at 1000°C for 24 h as a function of electric field.

| x    | @ 1 kV/mm | @ 2 kV/mm | @ 3 kV/mm | @ 4 kV/mm |
|------|-----------|-----------|-----------|-----------|
| 0    | 847       | 709       | 636       | 515       |
| 1    | 897       | 773       | 696       | 622       |
| 2    | 794       | 676       | 612       | 490       |
| 4    | 710       | 628       | 577       | 480       |
| 8    | 650       | 600       | 563       | 455       |
shown in Table 4, which shows the variation in $d_{33^*}$ for the x vol% (x = 0, 1, 2, 4, and 8) BT-templated 0.36BS-0.64PT thick films as a function of electric field, the 1 vol% BT-templated 0.36BS-0.64PT thick film exhibited an extremely strong electrostrain characteristic, nearly 900 pm/V, in the low electric field of 1 kV/mm (see Table 5). These results suggest that the BT-templated 0.36BS-0.64PT thick films are sufficiently promising for use in high performance piezoelectric device applications such as actuators and transducers.

4. Conclusions

In summary, the microstructural evolution of BT-templated 0.36BS-0.64PT thick films was investigated in relation to sintering temperatures from 950°C to 1000°C. For the 1 vol% BT-templated 0.36BS-0.64PT thick film, the optimum sintering temperature was considered to be 1000°C because it satisfied the improved crystal orientation to (100), implying a structural transition to texture, and it also showed a homogeneous perovskite phase without secondary phase. A Sr-rich secondary phase which formed in the specimens sintered at 1050°C and 1100°C was presumed to degrade the piezoelectric properties of the BT-templated 0.36BS-0.64PT thick film despite the enforced $f_t$. Therefore, 1000°C was determined as the optimum sintering temperature to develop high performance BT-templated 0.36BS-0.64PT piezoelectric thick film. The ferroelectric and piezoelectric properties of the textured 0.36BS-0.64PT thick films were further investigated to clarify the effect on BT templates when the films were sintered at 1000°C for 24 h. As the amount of BT template was increased from 1 vol% to 8 vol%, the $f_t$ values of the textured 0.36BS-0.64PT thick films were steadily enhanced, from 17.1% to 56.5%. Meanwhile, the ferroelectric and piezoelectric characteristics were optimized in the 1 vol% BT-templated specimen, reaching maximum values of $P_c$ (44.2 μC/cm²) and $E_c$ (2.4 kV/mm) as well as a $d_{33}$ of 444 pC/N, $k_p$ of 57.4%, and $g_{33}$ of 36 × 10⁻³ Vm/N, respectively. Ferroelectric and piezoelectric deterioration, which was observed in textured specimens with amounts of anisotropic BT template higher than 1%, was probably due to the increase in pores distributed along the grain boundaries and untextured small grains in the 0.36BS-0.64PT thick film. Consequently, the electric field-induced strain of the 1 vol% BT-templated specimen with extremely high $T_C$ (higher than 400°C) was excellent, with a $d_{33^*}$ of 622 pm/V at 4.0 kV/mm, considering the typically inverse relationship between $T_C$ and strain characteristics ($d_{33}$ and $d_{33^*}$). This also implies that this film is particularly promising for use in high performance piezoelectric devices such as actuators and transducers.

Disclosure statement

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