Optimization of preparation conditions of highly textured piezoelectric (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ ceramics

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Layered titanate H$_{1.08}$Ti$_{1.73}$O$_4$·nH$_2$O (HTO) particles with plate-like morphology were used as a template for the fabrication of grain-oriented bismuth potassium titanate [(Bi$_{0.5}$K$_{0.5}$)TiO$_3$, or BKT] ceramics by a reactive-templated grain growth method. Single perovskite-phase textured BKT ceramics were successfully fabricated with optimizing the preparation conditions such as mixing procedure of matrix and template particles with a binder solution, temperature programs for binder removal and sintering, and sintering conditions. Microstructure evaluation suggested that the sintering with or without weight-pressing and a temperature program used could significantly affect the degree of texture development. The debinding and sintering with weight-pressing helped on the proper alignment of oriented particles and/or grains along with promoting the growth of the oriented plate-like BKT particles, formed by an in situ topotactic transformation reaction of plate-like HTO templates, resulting in a high degree of orientation. Using optimum preparation conditions, single perovskite-phase BKT ceramics with grain-orientation over 85% were successfully fabricated for the first time via a conventional sintering method.

Key-words : HTO templates, Oriented, (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ ceramics, Single perovskite-phase, Conventional sintering, RTGG, Weighted and embedded sintering

1. Introduction

(Bi$_{0.5}$K$_{0.5}$)TiO$_3$ (BKT) ceramics have been viewed as promising lead-free candidate piezoelectric ceramics in actuator application for a wide range of working temperature.$^{1,3}$ However, the reported value of the piezoelectric coefficient ($\sim$100 pC/N$^4$)-$^6$ is not sufficient for practical actuator application.

The preparation of polycrystalline ceramics with grain alignment along a specific crystallographic axis has long been well known for appreciable property enhancement. Various grain-orientation techniques have been reported for enhancing piezoelectric properties in various ferroelectric materials,$^{7,12}$ among which a reactive templated grain growth (RTGG) method is the widely used process in perovskite-structured ferroelectric materials.$^{13,25}$ The RTGG method has been reported to be well-suited for fabricating grain-oriented BKT and BKT-based ceramics.$^{13,26,27}$ Nagata et al. reported a high degree of texturing (over 80%) in hot-pressed BKT ceramics. However, dense and single-perovskite phase BKT ceramics is very difficult to prepare by conventional sintering, because of its narrow sintering temperature$^{4,6}$

For the fabrication of grain-oriented ceramics by the RTGG method, the selection of template particles with appropriate morphology holds a great importance. Plate-like Bi$_4$Ti$_3$O$_{12}$ (BIT) particles prepared by molten salt synthesis have been reported to be used as the templates for the preparation of textured BKT and BKT-based ceramics. However, the plate-like BIT particles prepared using molten salt method have been reported to exhibit large size and non-uniform morphology,$^{7,28,31}$ with the use of which densification could be hard to achieve.$^{32}$ The small and uniform plate-like particles of layered titanate; H$_{1.08}$Ti$_{1.73}$O$_4$·nH$_2$O (HTO) particles with a lepidocrocite-like structure, synthesized by hydrothermal reaction,$^{33,35}$ have been reported to be suitable for the preparation of textured and fine-grained piezoelectric ceramics.$^{32}$ With using the HTO template particles, (110)-oriented plate-like BaTiO$_3$ particles, (110)-oriented 0.15BaTiO$_3$–0.85(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramics, and (100)-oriented (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramics have been successfully fabricated recently.$^{32,34,36}$ In this study, we optimized various preparation conditions and successfully fabricated single-perovskite phase and highly textured BKT ceramics using
HTO template particles by the RTGG method via a conventional sintering method.

2. Experimental procedure

2.1 Ceramics processing

Bi$_2$O$_3$ (Mitsuwa’s Pure Chemicals) and KHCO$_3$ (Kanto Chemicals, coarse particles) were used as matrix particles, while plate-like HTO particles (Kontoshima Chemical) were used as a template. Firstly, all raw materials weighed according to the chemical formula of (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ were mixed with an organic binder solution (Hayashi Chemical Industry) by ball-milling for 48 h at a speed of 60 rpm. The resultant slurry was cast on a polyethylene terephthalate (PET) film using a doctor blade technique. The green sheet cast on a PET film contained some traces of uncrushed KHCO$_3$ particles, which were due to the low ball-milling speed and the used viscous medium. To ensure the well crushing, raw materials; Bi$_2$O$_3$ and KHCO$_3$ were ball-milled in ethanol medium with zirconia balls for 48 h at a speed of 250 rpm prior to the addition of HTO templates. Ethanol from the ball-milled slurry was dried at 80°C for 24 h and mixed with HTO templates and the binder solution by ball-milling for 48 h at a speed of 60 rpm. A smooth green sheet with well dispersed raw materials was obtained after the tape casting. Square sheets with a size of 20 × 20 mm$^2$ were cut from the green sheet that had a thickness of 20 μm. The cut sheets were stacked and pressed at 61 MPa for 10 min at 80°C to form a green compact with a thickness of 1.2 mm. The green compacts were then cut into a size of 6 × 6 mm$^2$ and binder removal was done at 600°C for 5 h using an optimized temperature program (detailed discussion in the result and discussion section) in order to prevent the delamination of the stacked sheets. The effect of weight-pressing during the binder removal treatment (weighted debinding) was also investigated. The samples after the binder removal (debound and weighted-debinded samples) were sintered at 1050°C for 5 h under different conditions using one- or three-step sintering. During the one-step sintering, the temperature was raised to 1050°C at a rate of 2°C/min and kept for 5 h. On the other hand, in three-step sintering, the debinded BKT ceramics were soaked at 600, 950, and 1050°C for 5 h. The rate of temperature increase was 0.5°C/min until attaining the temperature of 600°C and after that temperature was increased at a rate of 2°C/min. Additionally, one- and three-step sintering procedures were conducted with weight-pressing without and with an atmosphere powder, which were hereafter referred to weighted-sintering (WS) and weighted-and-embedded-sintering (WES), respectively. Furthermore, the effect of cold isostatic pressing (CIP) on the crystal structure, relative density, orientation, and microstructures was also studied. The values of relative densities (R. D.) are mentioned on the top-right corner of each scanning electron microscopy (SEM) images.

2.2 Characterization

Crystal structure and the degree of texture development were studied by X-ray diffraction (XRD; Rigaku Ultima IV) analysis for the as-sintered ceramics with Cu Kα radiation. The degree of (100) or (001)-orientation ($F_{100}$) was evaluated from diffraction peaks located between 2θ = 10 and 60° using the following relations (a Lotgering method):

$$ F_{100} = \frac{P - P_0}{1 - P_0} ,$$  

(1)

$$ P = \frac{\sum I_{(100)}}{\sum I_{hkl}} , \quad P_0 = \frac{\sum I_{010}}{\sum I_{hkl}} ,$$

(2)

where I and $I_0$ were the intensities of the diffraction peaks from the oriented and randomly oriented BKT ceramics, respectively. The randomly oriented ceramics were prepared using Bi$_2$O$_3$ (Mitsuwa’s Pure Chemicals), KHCO$_3$ (Kanto Chemicals, coarse particles), and TiO$_2$ (Ishihara Sangyo). The relative density of the sintered ceramics was measured by the Archimedes method. The microstructures of the plane parallel and perpendicular to the sheet-stacking direction of the sintered ceramics were observed by SEM (JEOL JSM-6510).

3. Results and discussion

3.1 Green and sintered ceramics without the uses of a weight-pressing and an atmosphere powder

The SEM image of the HTO template particles is shown in Fig. 1(a). The particles had a plate-like morphology with a size of 3–5 μm in width and ~0.2 μm in thickness, and the aspect ratio was higher than previously reported value. Liquid-like HTO particles in the tape-cast sheet indicated that the templates were distributed uniformly in the green compact. The degree of texture development using one-step sintering (1050°C for 5 h) is shown in Fig. 1(b) and 1(c), respectively. Both the fractured planes, perpendicular and parallel to the sheet-stacking direction, exhibited well aligned and homogeneously distributed templates in the matrix particles. The well preserved plate-like morphology of the HTO template particles in the tape-cast sheet indicated that the templates’ morphology was not damaged during the ball-milling treatment. The organic component used during the preparation of slurry was removed by subjecting the samples to a heat treatment at 600°C for 5 h. The rapid heating of the sample caused the delamination of stacked sheets, which could be attributed to the rapid release of CO$_2$ and H$_2$O during the decomposition of KHCO$_3$ that occurs around 120–140°C. To facilitate the slow degassing, the binder-burnout temperature of 600°C was attained in 4 steps with specific temperatures of 100, 200, 480, and 600°C. That is, the compact was slowly heated at a rate of 0.25°C/min until achieving the temperature of 480°C that was proceeded through the first- and second-step temperature of 100 and 200°C, with soaking for 10 and 5 h, respectively. Then, the temperature was raised from 480 to 600°C at a rate of 0.5°C/min and kept for 5 h followed by furnace cooling.

The XRD patterns of the debinded samples sintered at 1050°C using either one- or three-step temperature sequence (first- and second-step temperature of 600°C and 1050°C, respectively). The relative density of the sintered ceramics was measured by the Archimedes method. The microstructures of the plane parallel and perpendicular to the sheet-stacking direction of the sintered ceramics were observed by SEM (JEOL JSM-6510).
program and that of the randomly oriented ceramics are shown in Fig. 2(a). The randomly oriented ceramics exhibited tetragonal symmetry with high XRD peak intensities for the (110) diffraction peaks, while the intensities of the (001), (100), (002), and (200) peaks increased in the textured ceramics, suggesting an increase in the volume of grains with the (001) or (100) orientation. The BKT ceramics subjected to the one-step sintering at 1050°C for 5 h showed a grain-orientation ($F_{100}$) of 43%. On the contrary, the BKT ceramics after the three-step sintering [600°C (5 h)- 950°C (5 h)- 1050°C (5 h)] exhibited an enhanced degree of texture development ($F_{100} = 50\%$).

The enhancement in the degree of orientation [43% for the one-step sintered ceramics to 50% for the three-step sintered ceramics] could be attributed to the improved alignment patterns and the increased thickness of the oriented particles after the three-step sintering. The development of (100)-orientation in (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ ceramics prepared using HTO-Bi$_2$O$_3$-Na$_2$CO$_3$ reaction system has been explained by an in situ topotactic transformation reaction and an epitaxial growth mechanism. Likewise, the formation of oriented BKT ceramics is expected to proceed by a topotactic transformation reaction of plate-like HTO particles with Bi and K matrix components into BKT nanoparticles and then to plate-like BKT particles by the epitaxial growth mechanism followed by the growth of the oriented plate-like BKT particles. Temperature programs during calcination/sintering have been reported to affect the epitaxial crystal growth reaction in the textured Bi-based ceramics fabricated using HTO template particles. Meanwhile, the XRD patterns of the ceramics sintered under both conditions revealed a presence of impurity peaks. Hiruma et al. reported the appearance of impurity phases in ordinarily-fired BKT ceramics in a sintering temperature range from 1040 to 1060°C. The observed impurity phases could be related to the volatilization of bismuth as the vapor pressure of bismuth over BKT has
been reported to be two orders of magnitude higher than that of the potassium.\textsuperscript{39)}

The microstructures of the fractured surfaces parallel to the sheet-stacking direction for the one- and three-step sintered ceramics are shown in Figs. 2(b) and 2(c). BKT particles formed by the topotactic transformation reaction with HTO template particles showed their plate-like assembly. The BKT particles in one-step sintered ceramics were aggregated comparatively to a larger extent than that of the three-step sintered ceramics. Moreover, after the three-step sintering, the size of pores appeared to be reduced. Furthermore, plate-like structures with increased thickness were observed in larger extent in comparison to that of one-step sintered ceramics. Therefore, the increase of relative density from 51 to 56\%\textsuperscript{36)} for the three-step sintered ceramics could be ascribed to the reduced pore size and slightly increased thickness of plate-like particles.

However, both the values of orientation factors and relative densities need appreciable enhancement. Meanwhile, both ceramics revealed some degrees of the warping of the oriented particles. Suppression of which could be effective on enhancing the degree of texturing. Sintering with weight-pressing could control the warpage associated with the oriented grains.\textsuperscript{36)}

The warpage observed in the ceramics was controlled by pressing the debinded samples which was wrapped in platinum foil during sintering (WS). A crucible containing zirconia balls was used to impose a pressure of 17 kPa. Additionally, the WS was carried out with embedding the BKT ceramics in calcined BKT powder synthesized by solid state reaction method (WES).

3.2 Ceramics sintered with weight-pressing and/or an atmosphere powder (No weight-pressing on the green ceramics during debinding)

Figure 3(a) shows the XRD patterns of the WS- and WES-BKT ceramics sintered by one- and three-step temperature programs. Here, the effects of the weight-pressing and the atmosphere powder were studied. The degree of the grain-orientation of the one-step sintered ceramics was increased from 43 to 52\% with weight-pressing. Furthermore, the $F_{100}$ of 50\% increased to 66\% with the use of the weight-pressed three-step sintering. The weight-pressed sintering of the debinded samples was effective on suppressing the sample’s warping with controlling the alignment of oriented particle, and this was considered to assist on the increase in the grain-orientation in both the one- and three-step sintered ceramics. However, the impurity phase persisted in both cases. With embedding the samples in the calcined BKT powder during the WS, the XRD patterns without any impurity phases were obtained with maintaining the value of $F_{100}$.

The microstructures of the samples are shown in Figs. 3(b)–3(e). The alignment of the platelet was improved and the thickness was increased in both cases: in particular, more significantly in the three-step WS ceramics [Fig. 3(d)]. Relative densities were also increased to 61 and 58\% by weight-pressing in the one- and three-step sintered samples, respectively. With optimizing the sintering conditions, single perovskite-phase BKT ceramics with appreciably high $F_{100}$ were obtained. In order to further increase the orientation and relative density, weight-pressing was performed during the debinding process and ceramics were fabricated by the WS and WES.

3.3 Weight-pressing on the green ceramics during debinding and its effect on microstructures and grain-orientation

For the green ceramics subjected to debinding at 600°C for 5 h without weight-pressing, the SEM images of the surfaces perpendicular and parallel to the sheet-stacking direction revealed a significant amount of standing plate-like oriented particles as shown in Figs. 4(a) and 4(b), respectively. In addition, the alignment of the plate-like particles appeared bent to a certain extent. During the binder-removal treatment at 600°C for 5 h, green samples were pressed with an alumina ceramic plate with a pressure of ~2 kPa (weighted debinding). The microstructure of the weighted-debinded green ceramics along the plane perpendicular to the sheet-stacking direction [Fig. 4(c)] showed plate-like particles aligned better than that of the debinded green ceramics without weight-pressing [Fig. 4(a)]. Likewise, a fractured surface parallel to the
controlling and promoting the alignment and growth of the oriented particles. On the other hand, interestingly, the values of grain-orientations were almost similar for the weighted-debinded samples after the conventional sintering, the weighted sintering, and the weighted and embedded sintering. The values of $F_{100}$ were 87, 92, and 86% for the conventionally sintered, WS, and WES BKT ceramics, respectively. The plate-like oriented particles were well aligned in the weighted-debinded sample [Figs. 4(c) and 4(d)]. Thus, the differences observed in the texturing behavior of the debinded- and weighted-debinded ceramics, after the weighted sintering, pointed out the large impact of the alignment patterns of plate-like particles in the binder-burnout ceramics. Grain-orientation over 85% was achieved via the conventional sintering of the weighted-debinded green BKT ceramics that possessed well-aligned oriented particles. Despite the appreciable increase of grain-orientation factor, the relative density was hardly improved. The relative densities of both the debinded- and weighted-debinded samples, after the three-step conventional sintering, weighted sintering, and weighted and embedded sintering were less than 65%. The high relative density of green ceramics is necessary to achieve good texturing in grain-oriented Bi-based piezoelectric ceramics.25) To this end, the weighted-debinded BKT green ceramics were further treated by CIP at 392 MPa for 10 min prior to the three-step weighted and embedded sintering. The relative density of 35% in the weighted-debinded green ceramics was increased to 59% after the CIP treatment of the weighted-debinded BKT green ceramics.

3.4 Effect of cold isostatic pressing on weighted-debinded green ceramics

Figure 6 shows the XRD patterns and microstructures of the weighted-debinded BKT ceramics, with and without the CIP treatment, after the three-step weighted and embedded sintering. With the weighted-debinding treatment followed by the CIP treatment, the BKT ceramics after the three-step WES exhibited a significantly enhanced relative density (increased from 54 to 84%). Meanwhile, the grain-orientation factor decreased from 86 to 77% by the CIP treatment for the sample. The decrement was originated from the rotation and/or misalignment of the BKT oriented particles, as shown in Fig. 6(c). These could occur by the pressure imposed on the sides of the compact during the CIP treatment.40) The microstructure evaluation suggested the formation of small grains with the disappearance of the large plate-like particles (about 4μm in width) in the WES CIP-treated ceramics, which was barely observed in the ceramics without the CIP treatment where mostly the plate-like particles with a width of about 2μm remained. The grain size of the ceramics with the CIP treatment was about 300 to 500 nm. The formation of such small particles by the collapse of large plate-like particles with increasing the calcination/sintering temperature was reported for a HTO-Bi$_2$O$_3$-Na$_2$CO$_3$ reaction system.37) The SEM image of the

![Figure 4](image1.png)

Figure 4. Microstructure of the sample debinded (600°C-5 h) without weight-pressing (a, b) and with weight-pressing (c, d) along a plane perpendicular (a, c) and parallel (b, d) to the sheet-stacking direction.

![Figure 5](image2.png)

Figure 5. Comparison of grain-orientation factor ($F_{100}$) in three-step conventional sintered (CS), WS, and WES-BKT ceramics as a function debinding and weighted debinding treatment prior to sintering.
surface parallel to the sheet-stacking direction in the CIP-treated ceramics after the WES treatment [Fig. 6(e)] exhibited the oriented grains with increased thickness. The thickness of the oriented grains varied from 500 nm to 1 μm in the WES-CIP-treated ceramics [Fig. 6(e)], while that in the WES-BKT ceramics was in the range of 200 to 300 nm [Fig. 6(c)]. Thus, the observed appreciable increase in thickness of the oriented particles and an initiation of small grains formation with the disappearance of the large plate-like particles were associated with the increased relative density.

With optimizing the preparation conditions such as the mixing procedure of the matrix and template particles with a binder solution, the temperature programs for binder removal and sintering, and the sintering conditions, the single perovskite-phase and highly textured BKT ceramics were successfully fabricated. That is, the suppression of the sintering-associated-samples’ bending via weighted sintering resulted in a higher degree of texturing (F\textsubscript{100} = 92\%). On the other hand, the BKT ceramics without having any secondary phases with F\textsubscript{100} over 85% were fabricated by embedding the sample in a calcined BKT powder during the weighted sintering. The cold isostatic pressing of the weighted-debinded green compact prior to the weighted and embedded sintering resulted in a grain-orientation as high as 77% and a relative density over 80%. The (100)-oriented (Bi\textsubscript{0.5}Na\textsubscript{0.5})TiO\textsubscript{3} and (110)-oriented Ba\textsubscript{0.9}Ca\textsubscript{0.1}TiO\textsubscript{3} plate-like particles formed by the topotactic transformation reaction of HTO templates particles have been used for the successful fabrication of fine-grained and highly-textured (100)-oriented (Bi\textsubscript{0.5}Na\textsubscript{0.5})TiO\textsubscript{3} and (110)-oriented Ba\textsubscript{0.9}Ca\textsubscript{0.1}TiO\textsubscript{3} ceramics, respectively.\textsuperscript{37,41} Thus, the preparation conditions optimized in this study for the synthesis of (100)-oriented BKT ceramics could be successfully implemented on imparting (100)-orientation in other BKT-based ceramics by utilizing the (100)-oriented BKT plate-like particles formed by an in situ topotactic transformation reaction to achieve ultrahigh piezoelectric properties.

4. Conclusions

Plate-like H\textsubscript{1.08}Ti\textsubscript{1.73}O\textsubscript{4}·nH\textsubscript{2}O template particles and Bi\textsubscript{2}O\textsubscript{3} and KHCO\textsubscript{3} matrix particles were used for the preparation of (100)-textured (Bi\textsubscript{0.5}K\textsubscript{0.5})TiO\textsubscript{3} ceramics by the RTGG method. For homogeneous distribution and well-mixing of the raw materials, starting materials except the template particles were crushed by ball-milling for 48 h in ethanol medium prior to mixing with binder solution and templates. The temperature program for the removal of the organic component from the green compacts was optimized to prevent delamination of the stacked sheets. Microstructure evaluation suggested the significant impact of alignment patterns of the orientated particles on the degree of texture development as a function of sintering conditions and the temperature programs used. On the other hand, the impact of sintering conditions and temperature programs used during the sintering had a feeble impact on the degree of grain-orientation in the BKT ceramics that possessed well-arranged oriented particles (weighted-debinded ceramics) prior to the sintering. The BKT ceramics debinded with weight-pressing exhibited well-aligned and orderly distributed oriented particles, which furthermore, on sintering resulted highly (100)-textured BKT ceramics. With optimum preparation conditions single perovskite-phase BKT ceramics with F\textsubscript{100} over 85% were prepared via a conventional sintering method.

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