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[100]-Texturing of Barium Titanate Ceramics Using Sodium Bismuth Titanate Templates: Challenges and Insights

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Abstract: This research explores the development of [100]-textured barium titanate ($BaTiO_3$, BT) ceramics using sodium bismuth titanate ($Na_{0.5}Bi_{4.5}Ti_4O_{15}$, NBiT) templates, aimed at leveraging the inherent high dielectric property of BT. However, the attempted texturing was unsuccessful, primarily due to bismuth diffusion from the NBiT templates into the BT matrix below the sintering temperature, at 1,000℃. Systematical exploration about the cause of the failure is involved and alternative approaches are proposed in detail to overcome the challenge. These findings contribute to the understanding of techniques and conditions for textured ceramic fabrication and highlight the need for further research in this area.

Keywords: [100]-textured barium titanate, Sodium bismuth titanate template, Dielectric property, Chemical stability

Textured ceramic has drawn scientific and commercial attention due to the high cost of crystal growth and challenges in managing crystal stoichiometry [1,2]. Templated grain growth (TGG), reactive templated grain growth (RTGG) or heterogeneous-templated grain growth (HTGG) are used to fabricate textured ceramics where grain orientation is ordered in one direction [3,4]. The texturing direction is determined by the desired application and can be controlled by the crystallographic orientation of a template, a platelike microcrystal seeding the arranged matrix grain growth along its orientation. Templates should satisfy following conditions [5]. First, the morphology should be anisotropic with an aspect ratio greater than 10. Second, chemical inertness is necessary to resist the template from dissolving into or reacting with the matrix during heat treatment, preventing the occurrence of composition changes (especially for HTGG) or the formation of secondary phases. Lastly, the lattice parameter between a template and a matrix should have a similarity of less than 15% mismatch.

Barium titanate ($BaTiO_3$, BT) has been widely used in capacitors thanks to its high dielectric properties and good electromechanical properties [6]. The dielectric constant of the BT crystal along the [100] is known to be over 20 times larger than that along the [001] at room temperature [7]. Ahn et al. reported the significant enhancement of (200) X-ray diffraction (XRD) peak of the $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ based textured ceramic using $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NBiT) templates [8]. NBiT template has been reported to have the Curie temperature of 655℃ [9,10], which is much higher than that of BT (120~130℃) [11,12]. While the exact melting point of NBiT is not reported in the literature, NBiT is known to be relatively stable even up to ~1,200℃ [13]. The objective of this study is to fabricate [100]-textured BT by NBiT templates, abbreviated as BT-NBiT, with a focus on demonstrating the gigantic dielectric constant. Textured BT-NBiT is also expected to exhibit self-poling effect when it is cooled down below 120℃ after being heated to temperatures below 655℃. BT-NBiT specimens were synthesized following procedure.

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$BaTiO_3$ powder was provided by Samsung Electro-Mechanics. The powder has a stoichiometric composition prepared by a hydrothermal synthesis method. The average particle size of the powder is 80 nm. The NBiT templates were synthesized following the procedure outlined in the given reference [8]. The raw powders, Na_2CO_3 (99.0%, Sigma Aldrich, USA), Bi_2O_3 (99.9%, High Purity Chemicals, Japan), TiO_2 (99.9%, High Purity Chemicals, Japan), NaCl (99.5%, Sigma Aldrich, USA) were used to synthesize NBiT templates. The oxide reactants (Bi_2O_3, Na_2CO_3, and TiO_2) were ball milled with NaCl in ethanol for 24 hours. The weight of the oxide reactants and salt were equal. The mixture was dried at 80℃ for 24 hours. The dried powder was heated at 1,100℃ for 4 hours in a covered alumina crucible. The product was washed with hot deionized water to separate NBiT templates.

The solvent comprised 60 vol% methyl ethyl ketone (low particulate grade, SK chemical, Republic of Korea) with 40 vol% ethyl alcohol (99.5%, Daejung Chemical & Metals Co., Ltd, Republic of Korea). Polyvinyl butyral (Butvar® B-98, Solutia Inc., USA), dibutyl phthalate (94%, Daejung Chemical & Metals Co., Ltd, Republic of Korea), and BYK-111 (BYK Chemical, Germany) were employed in the slurry as a binder, plasticizer and dispersant, respectively. The slurry was mixed for 24 hours. In case of BT-NBiT, 5 wt% NBiT templates were added, and the slurry mixed for additional 24 hours. The prepared slurry was tape-cast with uniform thickness of 31 μm. The green sheets were stacked and pressed at 70℃ under a uniaxial pressure of 10 MPa for 3 minutes. Laminated sheets were cut in a circle with 10 mm diameter. The processed chips were heated at 450℃ for 10 hours to remove organic elements and then heated on a MgO plate in an alumina crucible at 900~1,300℃ for 0~10 hours.

The surface of specimen, grinded using a sandpaper and annealed at 400℃ for 30 minutes to remove residual strain, was determined by powder X-ray diffraction (D/MAX2500V/PC, Rigaku, Tokyo, Japan) with Cu Kα radiation (λ=1.5406 Å) by 60 rpm spin to observe the crystalline phase. The cross-section of the sample sintered at 1,300℃ for 10 hours was polished to a finish of 0.04 μm and chemically etched in a mixed solution $HCl:HF:H_2O$=20:100:1 (in a volume ratio) for 10 seconds. HCl (35~37%, Samchun Chemicals, Republic of Korea) and HF (48~51%, Alfa Aesar, USA) were used for etchant. The other samples were simply cut without polishing and etching. Specimens were coated with platinum using a sputter (E-1045, Hitachi High-Technologies Corporation, Tokyo, Japan) before being observed with scanning electron microscopy (SEM, Nova Nano230SEM, FEI Company, Hillsboro, USA). Elemental composition and distribution were analyzed using energy dispersive spectroscopy (EDS, AMETEK-EDAX, Mahwah, USA).

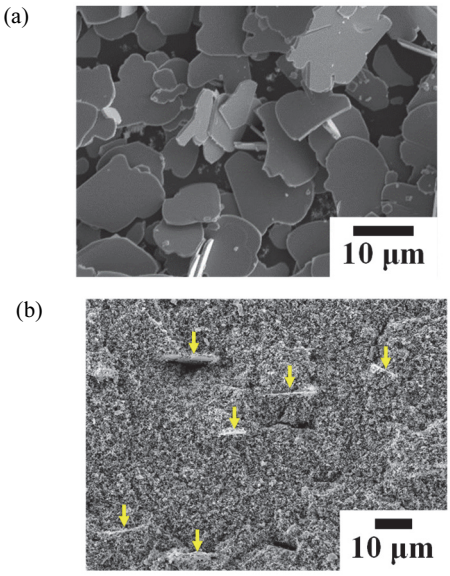

Fig. 1. SEM micrographs of (a) NBiT templates, and (b) the fracture surface of BT-NBiT chip after the binder burn-out process (yellow arrows point to the buried NBiT templates).

Platelike NBiT templates were successfully synthesized as confirmed in Fig. 1(a). The templates were distributed and arranged parallel to the casting direction within the BT matrix as observed in the fracture surface of a BT-NBiT burn-out chip [Fig. 1(b)].

The crystal structures of sintered BT and BT-NBiT were observed by XRD in Fig. 2. All specimens show a single perovskite phase. However, no remarkable high {h00} peaks, strong evidence of a texturing effect, were observed in BT-NBiT. Additionally, significant suppression of the (200) peak was not detected in either case of BT-NBiT sintered for 5 hours or 10 hours, contrary to the result reported by Ahn et al [8]. A clear peak shift towards higher angles indicates a substitution of bismuth for barium possibly due the increase in the entropy of mixing, though the crystal structure remains the same. This finding is consistent with structural studies about

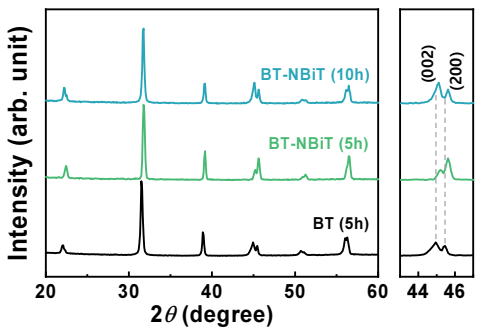

Fig. 2. XRD patterns of BT and BT-NBiT surface sintered at 1,300℃ for different holding time.

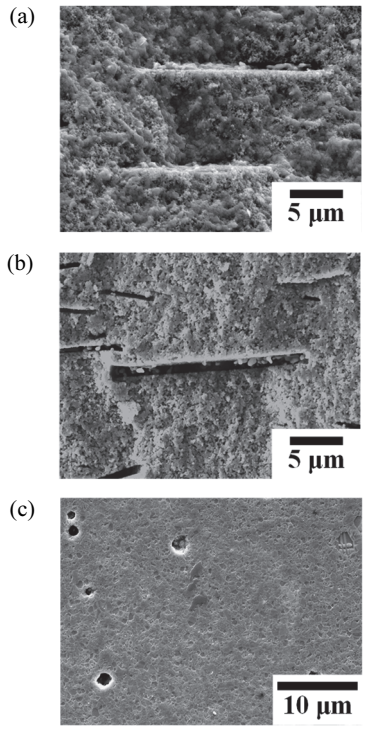

Fig. 3. SEM micrographs of BT-NBiT cross-section sintered at (a) 900℃ for 10 hours and (b) 1,000℃ for an hour.

bismuth modified barium titanate reported by Zhou et al. and Mahapatra et al [14,15].

Microstructural analysis with SEM in Fig. 3 and EDS elemental mapping in Fig. 4 also support the diffusion of NBiT template into BT. NBiT templates remained in the BT matrix after the heat treatment at 900℃ for 10 hours [Fig. 3(a)], however, the dissolution of the templates occurred when the sintering proceeded at 1,000℃ for an hour [Fig. 3(b)]. It is a

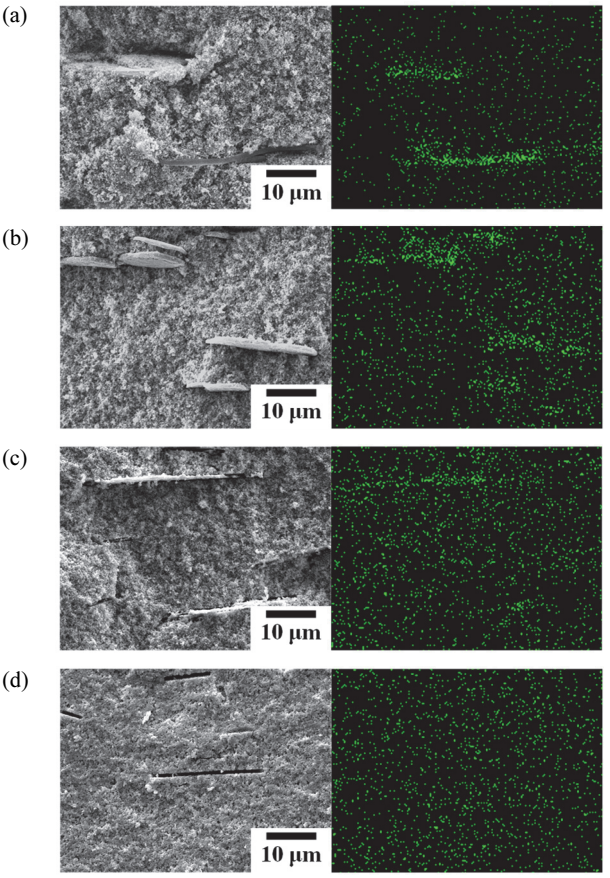

Fig. 4. SEM images (left) and EDS mapping analyses of the bismuth element (right) in the cross-section of BT-NBiT: (a) after the binder burn-out process, sintered at (b) 900℃ for an hour, (c) 1,000℃ without holding time, and (d) 1,000℃ for an hour.

temperature lower than NBiT template synthesis temperature of 1,100℃. This indicates that NBiT was not thermally decomposed. Instead, as depicted in Fig. 4, with increasing sintering temperature and duration, bismuth, initially concentrated within the template, gradually diffused into the surrounding BT, consistent with the XRD results in Fig. 2. The fully sintered sample shown in Fig. 3(c) exhibited densified grains without abnormal grain growth, another feature of textured ceramic. This serves as evidence that templated grain growth did not occur.

The dissolution of NBiT templates in the BT matrix was identified through XRD, SEM, and EDS analyses. The chemical stability of the NBiT template appears to be insufficient to prevent a reaction with BT, possibly due to the looser structure of the Aurivillius phase compared to perovskite. Subsequent investigations are ongoing to achieve

textured ceramics with colossal dielectric properties: i) other [100]-oriented templates compatible with BT, ii) matrix compositions that can be textured with NBiT templates and exhibit a larger dielectric constant along [100] than [001].

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REFERENCES

[1] G. L. Messing, S. Trolier-McKinstry, E. M. Sabolsky, C. Duran, S. Kwon, B. Brahmaroutu, P. Park, H. Yilmaz, P. W. Rehrig, K. B. Eitel, E. Suvaci, M. Seabaugh, and K. S. Oh, *Crit. Rev. Solid State Mater. Sci.*, **29**, 45 (2004). doi: https://doi.org/10.1080/10408430490490905

[2] T. T. Zate, J. W. Sun, N. R. Ko, B. K. Koo, H. L. Yu, M. S. Kim, W. J. Choi, S. J. Jeong, J. H. Jeon, and W. Jo, *J. Korean Inst. Electr. Electron. Mater. Eng.*, **36**, 362 (2023). doi: https://doi.org/10.4313/JKEM.2023.36.4.6

[3] T. Kimura, *J. Ceram. Soc. Jpn.*, **114**, 15 (2006). doi: https://doi.org/10.2109/jcersj.114.15

[4] T. T. Zate, N. R. Ko, H. L. Yu, J. W. Sun, W. Jo, and J. H. Jeon, *Sens. Actuators, A*, **366**, 114929 (2024). doi: https://doi.org/10.1016/j.sna.2023.114929

[5] M. Kim, A. Upadhyay, K. W. Lim, T. T. Zate, and J. H. Jeon, *J. Eur. Ceram. Soc.*, **41**, 7639 (2021). doi: https://doi.org/10.1016/j.jeurceramsoc.2021.08.044

[6] K. Uchino, *Ferroelectric Devices* (CRC Press, Boca Raton, USA, 2018) p. 115.

[7] W. J. Merz, *Phys. Rev.*, **75**, 687 (1949). doi: https://doi.org/10.1103/PhysRev.75.687

[8] C. W. Ahn, G. Choi, I. W. Kim, J. S. Lee, K. Wang, Y. Hwang, and W. Jo, *NPG Asia Mater.*, **9**, e346 (2017). doi: https://doi.org/10.1038/am.2016.210

[9] E. C. Subbarao, *J. Phys. Chem. Solids*, **23**, 665 (1962). doi: https://doi.org/10.1016/0022-3697(62)90526-7

[10] D. B. Jannet, M. El Maaoui, and J. P. Mercurio, *J. Electroceram.*, **11**, 101 (2003). doi: https://doi.org/10.1023/B:JECR.0000015666.44917.a8

[11] K. Uchino, E. Sadanaga, and T. Hirose, *J. Am. Ceram. Soc.*, **72**, 1555 (1989). doi: https://doi.org/10.1111/j.1151-2916.1989.tb07706.x

[12] C. A. Randall, R. E. Newnham, and L. E. Cross, *History of the First Ferroelectric Oxide, $BaTiO_3$*, Materials Research Institute, The Pennsylvania State University, University Park, USA (2004).

[13] M. Dunce, E. Birks, M. Antonova, L. Bikse, K. Kundzins, O. Freimanis, M. Livins, S. Dutkevica, and A. Sternberg, *J. Am. Ceram. Soc.*, **105**, 3874 (2022). doi: https://doi.org/10.1111/jace.18395

[14] L. Zhou, P. M. Vilarinho, and J. L. Baptista, *J. Am. Ceram. Soc.*, **82**, 1064 (1999). doi: https://doi.org/10.1111/j.1151-2916.1999.tb01875.x

[15] A. K. Mahapatra, T. Badapanda, and S. Sarangi, *Appl. Phys. A*, **127**, 593 (2021). doi: https://doi.org/10.1007/s00339-021-04747-8