

Particle Size Control, Sinterability and Piezoelectric Properties of BaTiO₃ Prepared by a Novel Composite-Hydroxide-Mediated Approach

Yahong Xie^{1,3}, Takesi Kimura¹, Shu Yin¹, Takatoshi Hashimoto², Yuichi Tokano², Atsushi Sasaki², Tsugio Sato²

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan; ²NEC Tokin Corporation, Koriyama, Taihaku-ku, Japan; ³Xin Jiang University, Urumqi, China.
Email: xyh0707@sina.com

Received February 18th, 2011; revised March 9th, 2011; accepted March 21th, 2011.

ABSTRACT

The size of BaTiO₃ particles was controlled by adjusting the molar ratio of the starting materials (BaCl₂ + TiO₂) to mineralizer (NaOH + KOH) during a composite-hydroxide-mediated approach using a novel hydrothermal reaction apparatus with a rolling system. The mean particle diameter decreased from 500 to 50 nm with a decrease in the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio from 0.44 to 0.04. The powders were sintered by normal one-step sintering at 1200 °C for 5 h and two-step sintering in which temperature was raised to 1200 °C at first and then decreased to 1100 °C and kept at 1100 °C for 5 h. The BaTiO₃ particles prepared with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.32 and 0.22 showed excellent sinterability and could be sintered to almost full theoretical density by both method. The sintered bodies obtained by both methods showed similarly excellent dielectric and piezoelectric properties.

Keywords: BaTiO₃, Synthesis, Low Temperature Sintering, Piezoelectric Properties

1. Introduction

The excellent dielectric and ferroelectric properties of barium titanate make it attractive material in the field of electrceramic and microelectronics. However, the conventional synthetic methods for BaTiO₃ involves calcination of a BaCO₃ and TiO₂ powder mixture above 1200 °C, and thus often results in polydispersity and the introduction of impurities and the powders prepared by this method consist of non-uniform and coarse particles [1-3]. To overcome these deficiencies, a number of innovative synthesis methods and chemical pcedures have been developed [4-7]. Among them, the composite-hydroxide-mediated (CHM) approach has been considered as an effective method to synthesize high purity BaTiO₃ [8-10].

In the present research a novel ball-milling assisted hydrothermal reaction was used to promote the diffusion of chemical species for a higher reaction rate as well as the uniformity of the product [11-12]. By combining with the addition of a Li₂CO₃ and V₂O₅ mixed sintering additive [13-16], BaTiO₃ could be sintered to almost full theoretical density at a low sintering temperature of

1200 °C for 5 h.

The tendency of the electronic industry towards miniaturization leads to high interest in fabricating some materials with nanometer-scale structure. The conventional sintering pcesses are generally accompanied by rapid grain growth, which has greatly hampered efforts to produce dense materials with nanometer-scale structure. Two-step sintering is a promising approach to obtain dense nanograin ceramics because it suppresses grain growth in the final stage of sintering. The two-step sintering pcedure consists of the following two steps: (1) at first step, sintering at a constant rapid heating rate until a normal sintering temperature; (2) lowering the temperature by ca.100 °C afterwards followed by sintering at a lowered temperature until it is fully dense. In this paper, two-step sintering approach is used to densify the prepared BaTiO₃ ceramics at low temperature [17-19].

2. Experimental

2.1. Synthesis Techniques

A mixture of 460 mmol of anhydrous hydroxides (NaOH/KOH molar ratio = 51.5:48.5) was put into a Teflon[®]-

lined stainless steel autoclave with 100 cm³ of internal volume and a 5.5 cm outer diameter, followed by the addition of 100, 75, 50, 30, 10 mmol of BaCl₂ and TiO₂ (anatase) with ten Teflon[®] balls, 1.1 cm in diameter. Then, the autoclave was sealed and placed in an electric oven and heated at 200°C for 24 h with a rotation speed of 100 rpm during the reaction. After the reaction, the autoclave was taken out to allow to cool down to room temperature. The product was dispersed in deionized water to remove the hydroxide on the surface of the particles, then centrifuged and rinsed with ethanol, deionized water and acetone, three times, respectively. Finally, the obtained powders were dried overnight at 60°C in a vacuum oven.

The prepared BaTiO₃ powders and commercial BaTiO₃ powders (Sakai Chemical Industry Co., BT-05, which is considered the best commercial pure BaTiO₃ having excellent properties) were precalcined at 800°C for 1 h followed by mixing well with 0.3 wt% Li₂CO₃ and 0.04 wt% V₂O₅ powder by a wet-ball milling with acetone and ZrO₂ balls of 10 mm in diameter in a Teflon[®] container at a rolling rate of 90 rpm for 12 h, respectively. Then, the powders were collected, dried and uniaxially pressed at 20 MPa in a steel die to form pellets, 20 mm in diameter and 3 mm thick, and then isostatically pressed at 200 MPa. The pellets were then sintered by normal one-step sintering at 1200°C for 5 h which was designated as (1200/5) with a heating rate of 10°C/min. The two-step sintering designated as (1200/1100/5) was also conducted, in which the sample was heated at first from room temperature to the first sintering temperature T_1 (1200°C) with a heating rate of 10°C/min, then the temperature was held at 1200°C for 1 min, after that rapidly decreased to T_2 (1100°C), and held at T_2 for 5 h, as illustrated in **Figure 5** (insert). The densities of the sintered pellets were measured by the Archimedes' methods. The rectangular bars of 2 mm × 4 mm × 12 mm were prepared for piezoelectric measurements. Gold paste was fired on both sides of the disks at 800°C as electrode. The specimens were poled in a stirred silicon oil at 80°C by applying DC electrical fields of 2 - 3 kV/mm for 30 min. About 24 h later of the poling, the dielectric and piezoelectric properties were measured using an Agilent 4294 A precision impedance analyzer at a frequency of 100 kHz.

2.2. Characterizations

The X-ray diffraction (XRD) analysis of the obtained powder samples was carried out using CuK radiation with a pyrolytic graphite monochromator mounted on a powder diffractometer (Shimadzu XD-D1). Thermogravimetric analysis (TG-DTA, Rigaku, TG8101D) was

performed for the powders from room temperature to 1200°C with a heating rate of 10°C/min in air. The particle morphology and the microstructures of the sintered bodies were observed by a scanning electron microscope (SEM; Hitachi S-4100).

3. Results and Discussion

3.1. Crystalline Phase

Figure 1 shows the XRD patterns of the BaTiO₃ powders synthesized by the composite-hydroxide-mediated approach at 200°C for 24 h with the molar ratio of starting materials (BaCl₂ + TiO₂) to mineralizer (NaOH + KOH) of (A) 0.44, (B) 0.32, (C) 0.22, (D) 0.12, (E) 0.04. The peaks of (002) and (200) around $2\theta = 45.5^\circ$ were enlarged in the insert to compare the powder tetragonality. All peaks of the synthesized powders were consistent with the single perovskite phase. The slight peak splitting around $2\theta = 45.5^\circ$ to (002) and (200) suggested the formation of the tetragonal BaTiO₃. The tetragonality (c/a) decreased from 1.0055 to 1.0038, 1.0032, 1.0025 and 1.0013 with a decrease of the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio from 0.44 to 0.32, 0.22, 0.12 and 0.04, respectively, which probably due to the difference in the particle size, since the tetragonality (c/a) of barium titanate is strongly dependent on particle size.

3.2. Thermal Analysis

The TG-DTA curves of the samples are shown in **Figure 2**. All samples showed three steps of weight losses. The weight loss up to 200°C, 200°C - 800°C and above 800°C may be due to the elimination of water adsorbed on the surface, dehydration from the OH incorporated in the lattice and elimination of CO₂ from the contaminated BaCO₃, respectively. The weight losses of the present samples were much smaller than those prepared by conventional hydrothermal reactions [24], especially the samples with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.32 and 0.22 showed quite little weight losses of ca. 1.05 and 1.30%, respectively, indicating formation of high purity stoichiometric BaTiO₃ powder. According to the TG-DTA curves, the powders were calcined at 800°C for 1 h prior to the sintering.

3.3. Morphology of the Powders

Figure 3 shows the morphologies of the prepared BaTiO₃ powders together with those of commercial BaTiO₃ powders. All samples showed high quality crystal characteristics of cubes or tetrahedrons. The average particle size of BaTiO₃ prepared in the present study decreased as 400, 200, 100, 60 and 50 nm with a decrease in the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio as 0.44, 0.32,

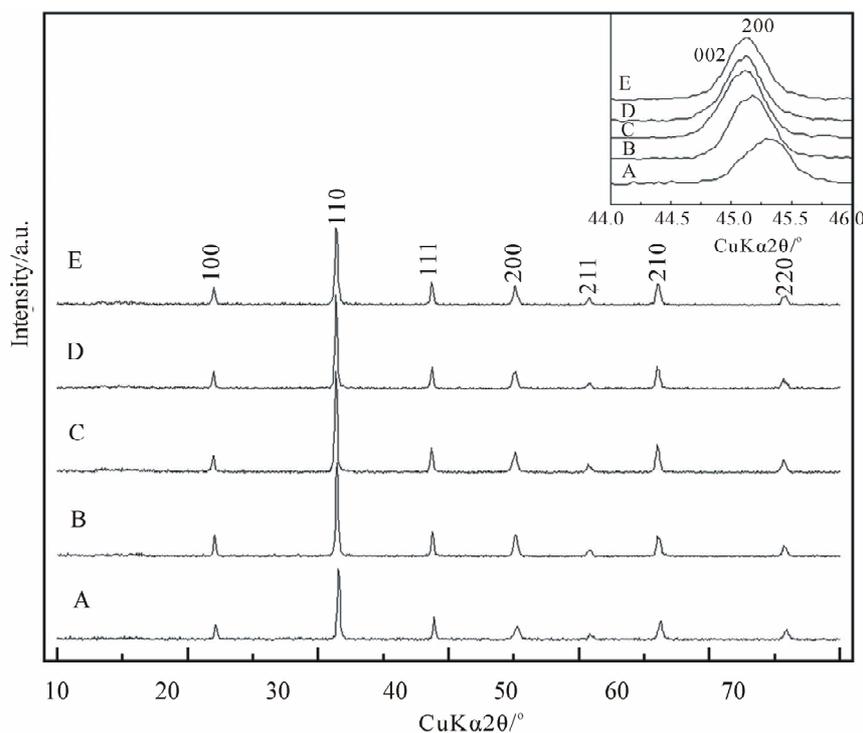


Figure 1. XRD patterns of the samples prepared with the $(\text{BaCl}_2 + \text{TiO}_2)/(\text{NaOH} + \text{KOH})$ molar ratio of (A) 0.44, (B) 0.32, (C) 0.22, (D) 0.12 and (E) 0.04.

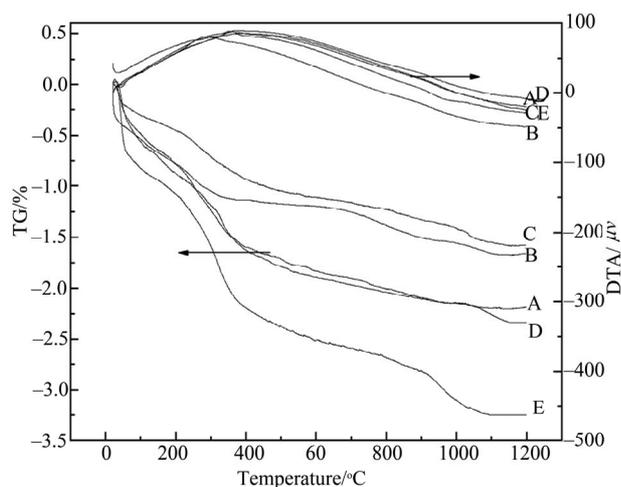


Figure 2. TG-DTA curves of the samples prepared with the $(\text{BaCl}_2 + \text{TiO}_2)/(\text{NaOH} + \text{KOH})$ molar ratio of (A) 0.44, (B) 0.32, (C) 0.22, (D) 0.12 and (E) 0.04.

0.22, 0.12 and 0.04 (Figure 3 A, B, C, D and E), respectively. The samples A and B showed broad size distribution from 50 to 500 nm. In contrast, the samples C, D and E showed relatively narrower size distribution of 30 to 100 nm. Generally, in the solution process the formation of nuclei and growth of crystals cur. When the $(\text{BaCl}_2 + \text{TiO}_2)/(\text{NaOH} + \text{KOH})$ molar ratio is low, the

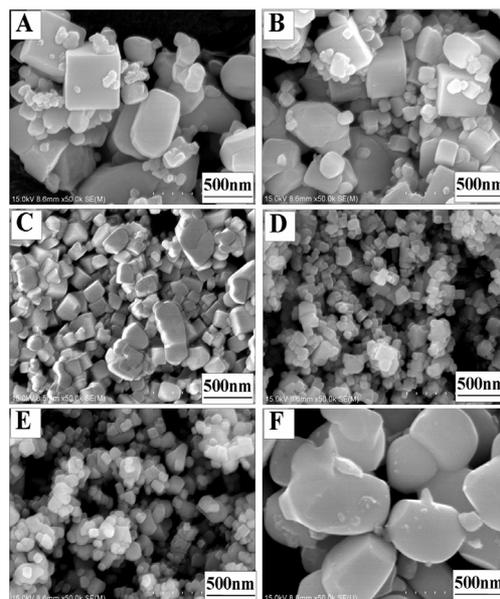


Figure 3. SEM images of the samples prepared with the $(\text{BaCl}_2 + \text{TiO}_2)/(\text{NaOH} + \text{KOH})$ molar ratio of (A) 0.44, (B) 0.32, (C) 0.22, (D) 0.12, (E) 0.04 and (F) commercial BaTiO₃.

formation rate of BaTiO₃ is slow, therefore, the BaTiO₃ crystals grow from the initially produced nuclei without

agglomeration because of the high viscosity of the NaOH/KOH melt, resulting in final nanostructure with narrow size distribution (sample C, D and E). On the other hand, at higher molar ratio (sample A and B) since the formation rate of BaTiO₃ is fast, the nuclei are formed not only in the initial stage but also in the middle stage of the reaction, and the agglomeration of particles and grain growth tends to proceed due to the decrease of the viscosity because of the formation of water as shown by Eq. (1).



Therefore, the product consisted of larger crystals with a large particle distribution. These results indicate that the lower (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio seems to be beneficial to obtain a narrower size distribution as well as a smaller particle size. Comparing with the commercial BaTiO₃ particles showing irregular phase with average particle size of ca. 400 - 500 nm (Figure 3. F), BaTiO₃ powders prepared in the present study exhibited a smaller average particle size (Sample C, D and E) and a regular cubical shape.

3.4. Sinterability

The sample powder was sintered at 1200°C for 5 h with a heating rate of 10°C min⁻¹ with a 0.3 wt% Li₂CO₃ and 0.04 wt% V₂O₅ complex sintering additive. The relative densities and grain sizes of the sintered bodies are shown in Figure 4 as a function of the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio. The average grain size changed as 10 μm, 25 μm, 20 μm, 8 μm and 5 μm for the samples with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.44, 0.32, 0.22, 0.12 and 0.04. The samples with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.32 and 0.22 could be sintered to almost full theoretical density (> 98%), but the density of other samples were less than 94%. From Figure 4, it is seen that the powder prepared with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.22 possessed the highest sinterability in the present samples. These results agreed with the results that the sample showed the high purity, small particle size and uniform particle size distribution (Figures 2 and 3).

Morphology of Ceramics Bodies

Figure 5 showed the scanning electron micrographs of the fracture surfaces of the sintered bodies by normal one-step sintering (1200/5) and two-step sintering (1200/1100/5) using the powders with the (BaCl₂+ TiO₂)/(NaOH + KOH) molar ratio of 0.22 without and with a 0.3 wt% Li₂CO₃ and 0.04 wt% V₂O₅ complex sintering additive. For comparison the morphology of sintered bodies using the commercial BaTiO₃ powder are also shown.

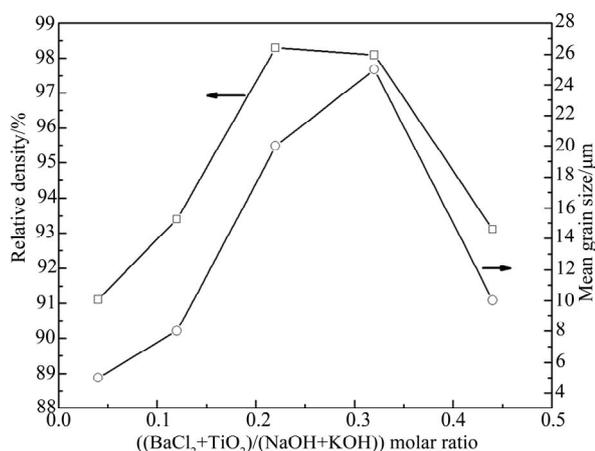


Figure 4. Relative densities and grain sizes of the BaTiO₃ ceramics sintered at 1200°C for 5 h using a 0.3 wt% Li₂CO₃-0.04 wt% V₂O₅ mixed sintering additive as a function of the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio.

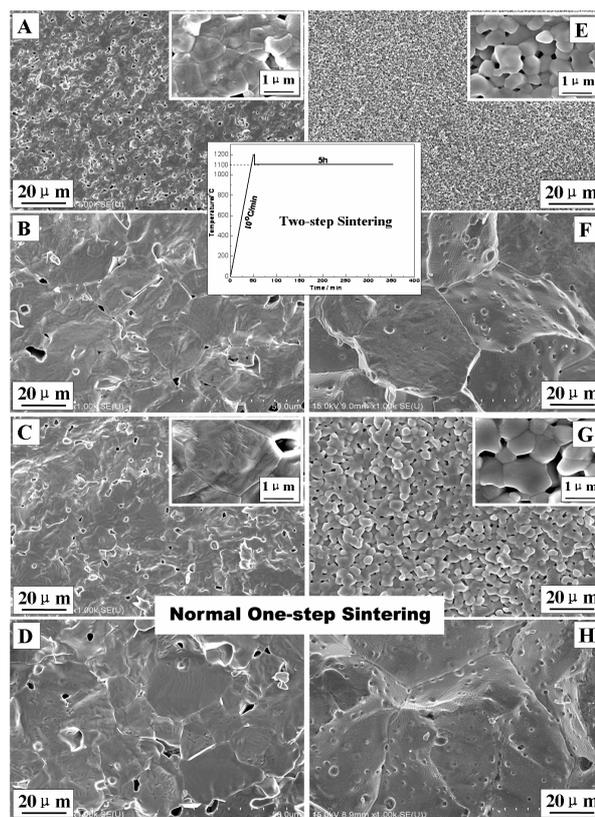


Figure 5. SEM images of the polished surfaces of the sintered bodies. A, B, C, D: BaTiO₃ with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.22., E, F, G, H: commercial BaTiO₃, A, E: two-step sintering (1200/1100/5) without additive, B, F: two-step sintering (1200/1100/5) with a 0.3 wt% Li₂CO₃-0.04 wt% V₂O₅ mixed sintering additive, F, G: one-step sintering (1200/5) without additive, D, H: one-step sintering (1200/5) with a 0.3 wt% Li₂CO₃-0.04 wt% V₂O₅ mixed sintering additive.

Table 1. Density, grain size and dielectric and piezoelectric properties of the BaTiO₃ samples prepared with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.22 and commercial BaTiO₃ sintered by the normal one-step sintering (1200/5) and two-step sintering (1200/1100/5).

	Prepared BaTiO ₃				Commercial BaTiO ₃			
	Two-step sintering (1200/1100/5)		One-step sintering (1200/5)		Two-step sintering (1200/1100/5)		One-step sintering (1200/5)	
	Without additive	With additive	Without additive	With additive	Without additive	With additive	Without additive	With additive
Density/%	98.1	96.3	99.1	98.3	89.6	97.4	90.2	96.8
Grain size / μm	1	15	5	20	0.5	30	1	80
$\epsilon_{33}^T/\epsilon_0$ (100KHz)	1785	1256	1668	1274	2478	1452	3081	1074
Q_m (-)	476	245	584	749	106	811	123	221
k_p (-)	0.27	0.29	0.29	0.38	0.16	0.32	0.18	0.34
S_{11}^E (pm^2/N)	8.03	4.8	8.0	7.9	15.0	6.3	17.2	7.3
k_{31} (-)	0.16	0.26	0.19	0.21	0.05	0.15	0.13	0.20
d_{31} (pC/N)	56.8	63.5	68.9	67.2	31.4	48.7	46.9	59.0
d_{33} (pC/N)	173	152	226	181	154	183	168	180
$\tan \delta$ (%)	0.31	0.96	0.38	0.68	1.13	2.21	0.24	0.40

Although it was difficult to densify the commercial powder without sintering aid by both sintering process (**Figure 5 E and G**), where the mean grain sizes of the sintered bodies by two-step sintering and one-step sintering were 0.5 and 1 μm , respectively, the prepared BaTiO₃ could be densified without sintering aid (**Figure 5 A and C**), where the mean grain sizes of the sintered bodies by two-step sintering and one-step sintering were 1 and 8 μm , respectively. It can be observed that the average grain sizes of the samples prepared by the two-step sintering were smaller than those by normal one-step sintering. Additionally, the addition of a 0.3 wt% Li₂CO₃ and 0.04 wt% V₂O₅ complex sintering additive greatly increased the average grain size and decreased the porosity, especially in the case of the commercial powder.

3.5. Dielectric Properties of Ceramics Bodies

The relative density, grain size, dielectric constant (ϵ), dielectric loss ($\tan \delta$), piezoelectric constant (d_{31} , d_{33} , k_{31} , S_{11}), mechanical quality factor (Q_m) and electrochemical coupling factor (k_p) of the BaTiO₃ samples prepared with the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio of 0.22 and commercial BaTiO₃ sintered by the normal sintering (1200/5) and two-step sintering (1200/1100/5), respectively, are listed in **Table 1**. All samples could be sintered to almost full theoretical density using a 0.3 wt% Li₂CO₃ and 0.04 wt% V₂O₅ complex sintering additive, and the dielectric properties of the sample prepared by the one-step sintering and two-step sintering did not change so much, indicating that the two-step sintering is useful to decrease the sintering temperature without loss of the dielectric properties. It is notable that the samples using prepared BaTiO₃ powders showed lower dielectric constant and larger piezoelectric constant than those

prepared using the commercial powder, this result can be illustrated by the grain size effect and the dielectric constant at room temperature decreased with increasing mean grain size from grain size of 1 μm ($GS > 1 \mu\text{m}$), but below 1 μm , dielectric constant at room temperature decreased with decreasing the mean grain size for the same sample. Comparing with the samples sintered without sintering additive, it can be seen that the addition of sintering additive decreased the dielectric constant at the room temperature, increased dielectric loss and changed the piezoelectric properties for the specimens sintered by both one-step sintering and two-step sintering.

4. Conclusions

The size of BaTiO₃ particles was controlled by adjusting the (BaCl₂ + TiO₂)/(NaOH + KOH) molar ratio during a composite-hydroxide-mediated approach using a novel hydrothermal reaction apparatus with a rolling system. The mean particle diameter decreased from 500 nm to 50 nm with the decrease of the (BaCl₂ + TiO₂)/(NaOH+KOH) molar ratio from 0.44 to 0.04, where the sample with the molar ratio of 0.22 exhibited the excellent sinterability and dielectric properties due to the small particle size, uniform morphology and narrow size distribution. The two-step sintering was useful to decrease the sintering temperature and to obtain the mean grain size without loss of the dielectric properties.

5. Acknowledgements

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, "Special Education and Research Expenses, Post-Silicon Materials and Devices Research Alliance" and G-COE program "International Center of Research & Education

for Molecular Complex Chemistry (IREMC)”.

REFERENCES

- [1] D. L. Polla and F. F. Lorraine, “Processing and Characterization of Piezoelectric Materials and Intergation into Microelectromechanical Systems,” *Annual Review Mater Science*, Vol. 28, 1998, pp. 563-597. [doi:10.1146/annurev.matsci.28.1.563](https://doi.org/10.1146/annurev.matsci.28.1.563)
- [2] T. Takenaka and H. Nagata, “Current Status and Prospects of Lead-Free Piezoelectric Ceramics,” *Journal Europe Ceram Science*, Vol. 25, No.12, 2005, pp. 2693-2700. [doi:10.1016/j.jeurceramsc.2005.03.125](https://doi.org/10.1016/j.jeurceramsc.2005.03.125)
- [3] H. I. Won, H. H. Nersisyan and C. W. Won, “Low Temperature Solid-Phase Synthesis of Tetragonal BaTiO₃ Powders and Its Characterization,” *Materials Letters*, Vol. 61, No.7, 2007, pp. 1492-1496. [doi:10.1016/j.matlet.2006.07.059](https://doi.org/10.1016/j.matlet.2006.07.059)
- [4] Z. X. Hua, Z. J. Min, Z. S. Hua, L. Z. Guo, M. N. Ben and H. Dietrich, “BaTiO₃ Nanocrystals: Hydrothermal Synthesis and Structural Characterization,” *Journal of Crystal Growth*, Vol. 283, No. 3-4, 2005, pp. 553-562. [doi:10.1016/j.jcrysgro.2005.05.080](https://doi.org/10.1016/j.jcrysgro.2005.05.080)
- [5] K. Matsui, T. Noguchi, N. M. Islam and Y. Hakuta, “Hayashi, Rapid Synthesis of BaTiO₃ Nanoparticles in Supercritical Water by Continuous Hydrothermal Flow Reaction System,” *Journal of Crystal Growth*, Vol. 310, No. 3, 2008, pp. 2584-2589. [doi:10.1016/j.matlet.2006.06.006](https://doi.org/10.1016/j.matlet.2006.06.006)
- [6] T. K. Mandal, “Characterization of Tetragonal BaTiO₃ Nanopowders Prepared with a New Soft Chemistry Route,” *Material Letters*, Vol. 61, No. 3, 2007, pp. 850-854. [doi:10.1016/j.matlet.2006.06.006](https://doi.org/10.1016/j.matlet.2006.06.006)
- [7] Y. Ma, E. Vilenko, S. L. Suib and P. K. Dutta, “Synthesis of Tetragonal BaTiO₃ by Microwave Heating and Conventional Heating,” *Chemical Material*, Vol. 9, No. 12, 1997, pp. 23-31. [doi:10.1021/cm970371n](https://doi.org/10.1021/cm970371n)
- [8] H. Liu, C. Hu and Z. L. Wang, “Composite-Hydroxide-Mediated Approach for the Synthesis of Nanostructures of Complex Functional-Oxides,” *Nano Letters*, Vol. 6, No. 7, 2006, pp. 1535-1540. [doi:10.1021/nl061253e](https://doi.org/10.1021/nl061253e)
- [9] M. Jing, H. C. Guo, L. Hong and X. Y. Feng, “BaTiO₃ Nanocubes: Size-Selective Formation and Structure Analysis,” *Material Letters*, Vol. 62, No. 2, 2008, pp. 235-238. [doi:10.1016/j.matlet.2007.05.009](https://doi.org/10.1016/j.matlet.2007.05.009)
- [10] S. Qin, D. Liu, H. Liu and Z. Zuo, “Size-Dependent Selective Etching Mechanism: Cavity Formation on Barium Titanate Nanocubes,” *Journal Physical Chemical C*, Vol. 112, No. 44, 2008, pp. 17171-17174. [doi:10.1021/jp8057993](https://doi.org/10.1021/jp8057993)
- [11] Y. Hotta, K. Tsunekawa, C. Duran, K. Sato, T. Nagaoka and K. Watari, “Low-Temperature Sintering of BaTiO₃ Powders Prepared by a Hydrothermal Process with Ball Milling System,” *Materials Science Engineering A*, Vol. 475, No. 1-2, 2008, pp. 57-61. [doi:10.1016/j.msea.2006.12.138](https://doi.org/10.1016/j.msea.2006.12.138)
- [12] Y. Hotta, C. Duran, K. Sato, T. Nagaoka and K. Watari, “Densification and Grain Growth in BaTiO₃ Ceramics Fabricated from Nanopowders Synthesized by Ball-Milling Assisted Hydrothermal Reaction,” *Journal Europe Ceram Science*, Vol. 28, No. 3, 2008, pp. 599-604. [doi:10.1016/j.jeurceramsc.2007.07.007](https://doi.org/10.1016/j.jeurceramsc.2007.07.007)
- [13] H. Takatoshi, S. Toru, S. Tsugio, Y. Shu and X. Yahong, “Dielectric Ceramic and Its Synthesis Method,” Japan Patent, Tokugan, 2009, pp. 2010-215435A.
- [14] Y. Zhang, J. Han and L. Hu, “The Effect of Sintering Additive on Fracture Behavior of Carbon-Whisker-Reinforced Silicon Carbide Composites,” *Maerial Science Engineering A*, Vol. 480, No. 1-2, 2008, pp. 62-67. [doi:10.1016/j.msea.2007.08.034](https://doi.org/10.1016/j.msea.2007.08.034)
- [15] K. Chunga, J. Yoo, C. Lee, D. Lee, Y. Jeong and H. Lee, “Microstructural Dielectric and Piezoelectric Properties of Low-Temperature Sintering Pb(Co_{1/2}W_{1/2})O₃-Pb(Mn_{1/2}Nb_{2/3})O₃-Pb(Zr,Ti)O₃ Ceramics with the Addition of Li₂CO₃ and Bi₂O₃,” *Sensor Actuat A*, Vol. 125, No. 2, 2006, pp. 340-345. [doi:10.1016/j.sna.2005.06.018](https://doi.org/10.1016/j.sna.2005.06.018)
- [16] H. You, S. Koo, J. Ha, J. Koh and J. Park, “Microstructure and Dielectric Properties of Li₂CO₃ Doped 0.7 (Ba,Sr)TiO₃-0.3MgO Ceramics,” *Current Applied Physics*, Vol. 9, No. 5, 2009, pp. 875-879. [doi:10.1016/j.cap.2008.08.008](https://doi.org/10.1016/j.cap.2008.08.008)
- [17] T. Karaki, K. Yan and M. Adachi, “Barium Titanate Piezoelectric Ceramics Manufactured by Two-Step Sintering,” *Japenese Journal Applied Physical*, Vol. 46, 2007, pp. 7035-7038. [doi:10.1143/JJAP.46.7035](https://doi.org/10.1143/JJAP.46.7035)
- [18] I. Wei Chen and X. H. Wang, “Sintering Dense Nanocrystalline Ceramics Without Final-Stage Grain Growth,” *Nature*, Vol. 404, 2000, pp. 168-171. [doi:10.1038/35004548](https://doi.org/10.1038/35004548)
- [19] A. Polotai, K. Breece, E. Dickey and C. Randallw, “A Novel Approach to Sintering Nanocrystalline Barium Titanate Ceramics,” *Journal of the American Ceramic Society*, Vol. 88, No. 11, 2005, pp. 3008-3012. [doi:10.1111/j.1551-2916.2005.00552.x](https://doi.org/10.1111/j.1551-2916.2005.00552.x)
- [20] G. Arit, D. Hennings and G. de With, “Dielectric Properties of Fine-Grained Barium Titanate Ceramics,” *Applied Physical*, Vol. 58, 1985, pp. 1619-1625.
- [21] V. Buscaglia, M. T. Buscaglia, M. Viviani, L. Mitoseriu, P. Nanni, V. Trefiletti, P. Piaggio, I. Gregora, T. Ostapchuk, J. Pokorny and J. Petzelt, “Grain Size And Grain Boundary-Related Effects on the Properties of Nanocrystalline Barium Titanate Ceramics,” *Journal Europe Ceram Science*, Vol. 26, No. 14, 2006, pp. 2889-2898. [doi:10.1016/j.jeurcerams.2006.02.005](https://doi.org/10.1016/j.jeurcerams.2006.02.005)
- [22] S. Zhao, H. Wu and Q. Sun, “Study on PSN-PZN-PZT Quaternary Piezoelectric Ceramics near the Morphotropic Phase Boundary,” *Material Science Engineering B*, Vol. 123, No. 11, 2005, pp. 203-210. [doi:10.1016/j.matlet.2004.12.041](https://doi.org/10.1016/j.matlet.2004.12.041)
- [23] Y. Li, W. Chen, Q. Xu, J. Zhou and X. Gu, “Piezoelectric and Ferroelectric Properties of Na_{0.5}Bi_{0.5}TiO₃-K_{0.5}Bi_{0.5}TiO₃-BaTiO₃ Piezoelectric Ceramics,” *Material Letters*,

Vol. 59, No. 11, 2005, pp. 1361-1364.

[doi:10.1016/j.matlet.2004.12.041](https://doi.org/10.1016/j.matlet.2004.12.041)

- [24] Y. H. Xie, S. Yin, T. Hashimoto, H. Kimura and T. Sato, "Microwave-Hydrothermal Synthesis of Nano-Sized Sn²⁺-

Doped BaTiO₃ Powders and Dielectric Properties of Corresponding Ceramics Obtained by Spark Plasma Sintering Method," *Journal Material Science*, Vol. 44, No. 18, 2009, pp. 4834-4839. [doi:10.1007/s10853-009-3737-8](https://doi.org/10.1007/s10853-009-3737-8)