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Effect of washing of barium titanate powders synthesized by hydrothermal method on their sinterability and piezoelectric properties

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Abstract

$BaTiO_3$ (BT) powders were synthesized by the hydrothermal method for fabricating lead-free barium titanate piezoelectric ceramics. The obtained powders were washed by distilled water and 0.01N acetic acid solutions separately, and utilized to obtain piezoelectric ceramics by traditional sintering. BT ceramics with the highest piezoelectric properties (d_{33} value is over 190 pC/N) was obtained from the BT powder synthesized at 250 °C and washed by acetic acid solution. The influence of washing method and sintering temperature on the piezoelectric properties of BT ceramics were studied. The reasons were investigated by comparing the properties of BT powders and their compacts sintered at different temperature.

Keywords: A. Powders: chemical preparation; C. Piezoelectric properties; D. $BaTiO_3$; Lead-free

1. Introduction

Lead zirconium titanate (PZT) ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices [1]. PZT ceramics contain more than 60 wt% lead. From the viewpoint of environmental protection, it is desirable that piezoelectric ceramics should be lead-free. In addition, a trend is to develop biocompatible piezoelectric materials for use as sensors and actuators that are implanted directly into living tissue, including human body. Thus, there is an increasing tendency to look for alternative materials.

Saito et al. [2] reported that piezoelectric properties of lead-free ceramics can be comparable to those of the PZT, a fact which encourages many researchers to develop candidate materials for environmentally friendly piezoelectric devices. Recently, many lead-free piezoelectric materials have been developed, which include $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ [3], $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ [4], $(K_{0.5}Na_{0.5}NbO_3)$ [5,6], $Na_xK_{1-x}NbO_3$ [7] and $(K_{0.5}Na_{0.5})(Nb_{0.7}Ta_{0.3})O_3$ [5] and so on. BT is a lead-free material. However, the low piezoelectric properties of BT ceramics have been the main obstacle to their application in actuators and sensors.

In order to improve the piezoelectric properties of lead-free ceramics, many novel sintering methods including microwave sintering [8], hybrid sintering process [9], spark plasma sintering [6,7] have been developed. However, the synthesis method of starting powders is also very important for fabrication of piezoelectric ceramics. It is well known that hydrothermal method is a wet-chemical technique for directly forming complex oxide powders. A product niche for the process has been identified in advanced electronic ceramic powders [10]. Many works [11–17] have been done to synthesize BT powders using hydrothermal method.

In this work, hydrothermal method was used to synthesize BT powders under different conditions defined according to a previous work [18], and then the BT powders were utilized to fabricate the piezoelectric ceramics using traditional sintering method. The influence of synthesis conditions of BT powders and sintering temperature on the piezoelectric properties of BT ceramics were investigated.

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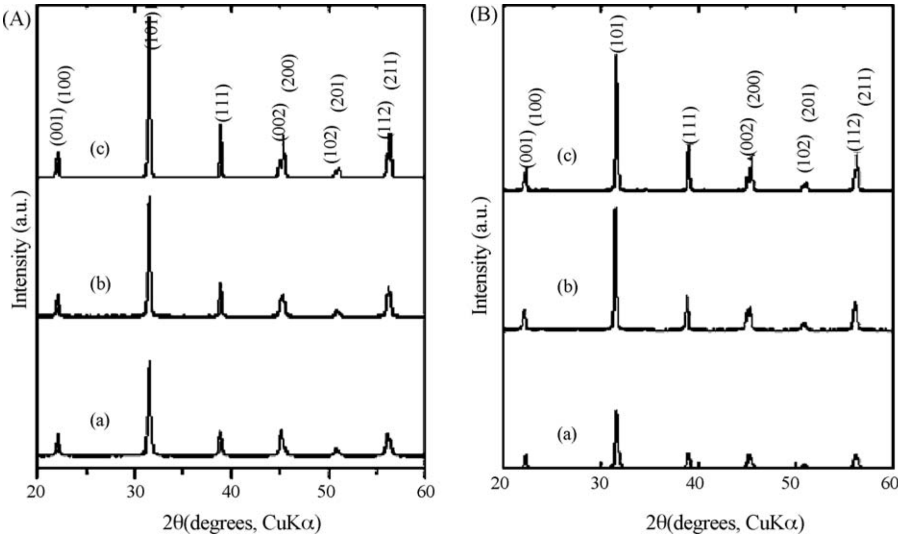

Fig. 1. X-ray diffraction patterns of BT powders synthesized by hydrothermal method at (a) 150 °C, (b) 200 °C, (c) 250 °C and washed by (A) acetic acid solution and (B) distilled water separately.

2. Experimental

The raw materials are barium hydrate ($Ba(OH)_2 \cdot 8H_2O$, 99.0%, Wako Pure Chemical, Japan) and tetrabutyl titanate ($Ti(OC_4H_9)_4$, 95.0%, Wako Pure Chemical, Japan). BT powders were prepared at different temperatures by hydrothermal method. After hydrothermal reaction for 16 h, the obtained powders were washed by distilled water and 0.01N acetic acid solutions separately, and then dried at room temperature in vacuum. The BT powders (0.75 g) mixed with polyvinyl alcohol (1 wt%) were formed into a cylinder of 15 mm in diameter by die pressing at a pressure of 200 MPa. The binder was burned out at 700 °C. Each specimen was submitted to a different sintering temperature from 1200 to 1300 °C, which was maintained for 2 h. The heating rate was 100 °C/h.

The BT powders and specimens were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co., Japan) with Cu Kα radiation (36 kV and 20 mA). The compositions of the BT powders were determined for Ba/Ti molar ratio by inductively coupled plasma (ICP) spectrometry (SPS7000A, Seiko, Japan) after dissolving in a hydrochloric acid. The specific surface areas of the powders were calculated by applying the BET equation (NOVA 1200, Quanta Chorome, USA) to the N_2 adsorption isotherm. The density of obtained specimens was measured by Archimedes technique using water. The microstructure was observed with a scanning electron microscope (SEM; JSM551, JEOL, Japan). Electrodes were deposited on the specimens by sputtering gold on both surfaces. The specimens were then polarized in a silicon oil bath under a DC field of 2 kV/mm at 110 °C for 10 min. The value of d_{33} was measured using a d_{33} meter (Model ZJ-3D, Institute of Acoustic Academia Sinica, China).

3. Results and discussion

The X-ray diffraction patterns of obtained BT powders are shown in (Fig. 1). The results indicate that BT powders A-a and B-a have a simple cubic perovskite structure according to the JCPDS No. 31-174, while the BT powders A-b, A-c, B-b and B-c have a tetragonal perovskite structure fitting well with the JCPDS No. 5-626. The cubic BT phase can be unmistakably distinguished from tetragonal BT phase, since there are two overlapping peaks at 44.85° and 45.38° for tetragonal BT.

The respective specific surface areas and Ba/Ti atomic ratios of BT powders are shown in (Table 1). The particle size was calculated according to the following formula: $R = 6/Sd$, where R is the particle diameter, S is specific surface area, and d is theoretical density of BT (6.012 g/cm^3). Obviously, with the increase in the reaction temperature, the specific surface area decreased and the particle size increased whenever the BT powders were washed by acetic acid solution or distilled water. The BT powders washed by acetic acid solution are Ti-rich BT phases while the BT powders washed by distilled water are

Table 1
The specific surface area and Ba/Ti atomic ratios of BT powders before sintering.

	Washed by acetic acid			Washed by distilled water		
	150 °C	200 °C	250 °C	150 °C	200 °C	250 °C
Specific surface area (m^2/g)	21.78	5.90	1.88	22.34	5.90	1.88
Particle size (nm)	45.8	169.2	530.9	44.7	169.2	530.9
Ba/Ti atomic ratios	0.958	0.983	0.983	1.077	1.040	1.025

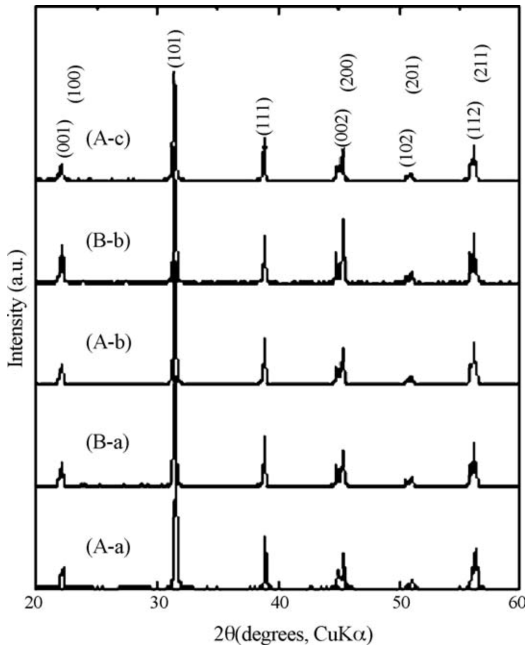

Fig. 2. The X-ray diffraction patterns of BT specimens sintered at 1250 °C from different BT powders synthesized at different temperatures: (a) 150 °C, (b) 200 °C, (c) 250 °C and then washed by (A) acetic acid solution and (B) distilled water.

Ba-rich with respect to the nonchemical composition of BT. Furthermore the compositions of the BT powders tend to the stoichiometric composition when the synthesis temperature increases.

Fig. 2 shows the X-ray diffraction patterns of BT specimens sintered at 1250 °C from the obtained BT powders synthesized at different temperature and washed by acetic acid solution and distilled water separately. In this work, because the BT powder B-c did not give specimens with good mechanical and insulating properties, the samples are broke down electrically during polarization. Thus the data measuring the B-c specimen are not included. The XRD indicate that the structure changed from cubic to tetragonal in the specimens issued from the BT powders A-a and B-a, while it did not change in the specimens prepared from the BT powders A-b, B-b and A-c. The peaks observed for the specimens from the BT powders washed with distilled water are sharper than that those obtained after washing with acetic acid solution.

SEM micrographs of specimens sintered at 1250 °C from the different BT powders are shown in (Fig. 3). A dense microstructure was observed in the specimens sintered at 1250 °C from the BT powders washed by distilled water. It indicates that the BT powders washed by distilled water are sintered easily. In the case of the BT powders washed by acetic acid solution, different synthesis temperature confers the BT powders different sintering properties. Homogeneous large grains were observed in the specimen fabricated from the BT powders A-a and B-a, while smaller and homogeneous grains were observed in the specimen fabricated from the BT powders B-b and A-c. Larger particles prepared at higher synthesis temperature are difficult to sinter. Some unusual large grains were observed in the specimens fabricated from the BT powder A-b, the phenomenon was also observed in the specimens fabricated at different sintering temperature from the BT powders A-a and A-c. It may be considered that the Ti-rich BT particles are subjected to grain growth.

The relative density of the specimens sintered at different temperature from different BT powders are reported in (Fig. 4). Almost no change of the relative density was observed for the specimens sintered from the BT powders B-a and B-b. It indicates that the BT powders washed by distilled water can be sintered completely before 1200 °C. However, the relative density of the BT specimens fabricated from the BT powders A-a, A-b and A-c increased with the increase in the sintering temperature. For the BT specimens sintered over 1250 °C from the BT powder A-b, the grains grew large in these specimens, which resulted in the increase of the relative density.

The results concerning the piezoelectric constant d_{33} of the specimens sintered at different temperature from the BT

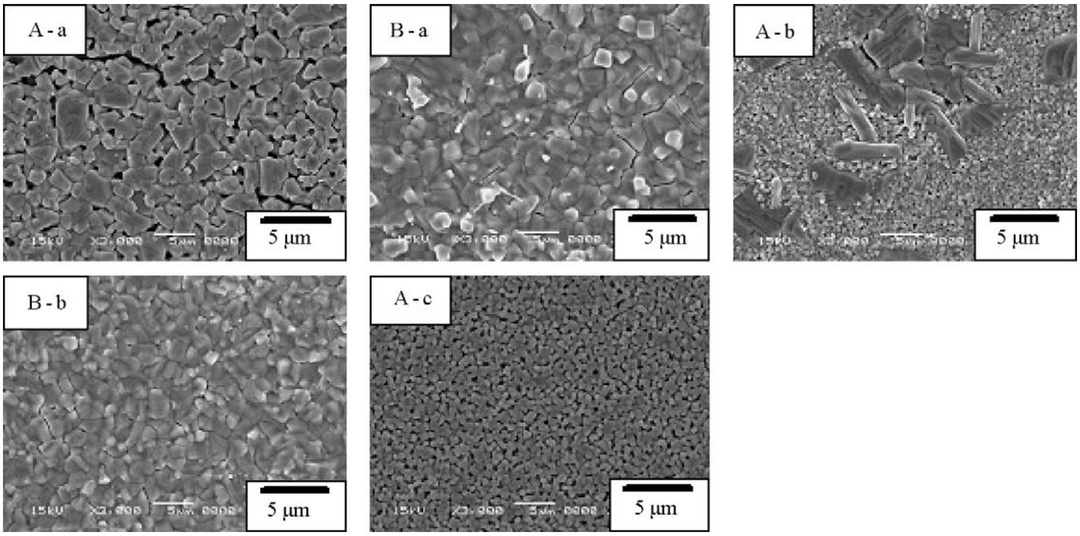

Fig. 3. SEM micrographs of the specimens sintered at 1250 °C from different BT powders synthesized at different temperatures: (a) 150 °C, (b) 200 °C, (c) 250 °C and then washed by (A) acetic acid solution and (B) distilled water.

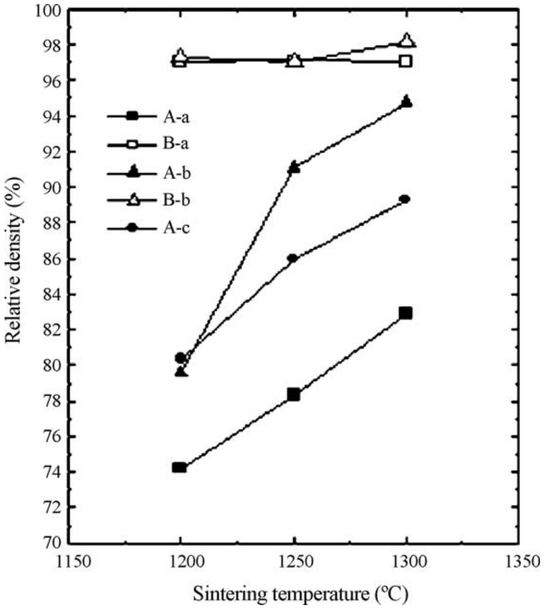

Fig. 4. The relative density of the BT specimens sintered at different temperature from different BT powders synthesized at different temperatures: (a) 150 °C, (b) 200 °C, (c) 250 °C and then washed by (A) acetic acid solution and (B) distilled water.

powders are shown in (Fig. 5). The maximum value was observed for the specimen sintered at 1250 °C from the BT powder A-c, and it amounts to more than 190 pC/N. It is higher than the value (about 150 pC/N) obtained for the material fabricated at 1360 °C from the BT powder prepared by solid-state reaction [10]. It indicates that the hydrothermal method is very useful to prepare BT powder for piezoelectric materials. The variations of d_{33} of the specimens with the sintering temperature are similar except that of the specimens fabricated from the BT powder B-a, which has small particles and many OH^- defects and $CO_3{}^{2-}$ groups [18]. The BT powder A-c leads to specimens with higher piezoelectric properties. It indicates that the well-crystallized BT powder with less OH^- defects can improve the sintering behavior to confer higher piezoelectric constants. The d_{33} value of the specimen fabricated at 1250 °C from the BT powder A-b is smaller than that from the BT powders A-a and B-b. It can be considered that the grain growth observed (Fig. 3A-b) for this specimen, results in the decrease of the d_{33} value.

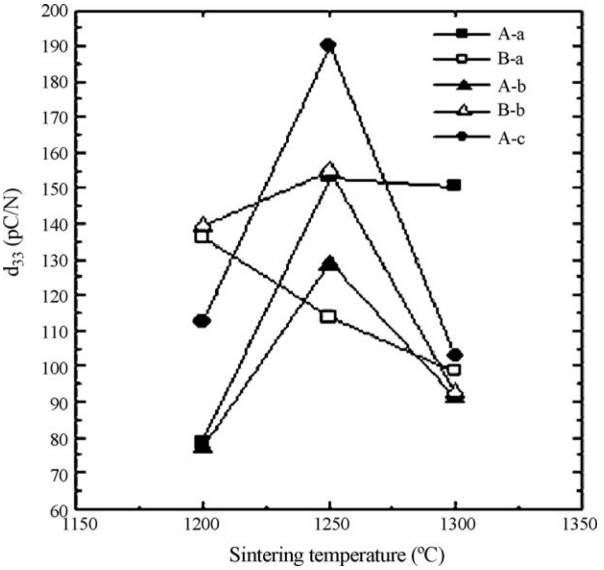

Fig. 5. Piezoelectric constant d_{33} of the specimens sintered at different temperature from different BT powders synthesized at different temperatures: (a) 150 °C, (b) 200 °C, (c) 250 °C and then washed by (A) acetic acid solution and (B) distilled water.

4. Conclusions

The cubic $BaTiO_3$ powders with smaller grain size, more OH^- defects and lower crystallinity were obtained at low temperature and the tetragonal $BaTiO_3$ powders with larger grain size, less OH^- defects and higher crystallinity were obtained at high temperature by hydrothermal method. The BT powders washed by acetic acid solution are Ti-rich BT phases while the BT powders washed by distilled water are Ba-rich BT. Piezoelectric ceramics with high d_{33} value (over 190 pC/N) were fabricated from hydrothermally synthesized BT powders. Results indicate that hydrothermal method is very useful to prepare BT powder for piezoelectric materials. The BT powder synthesized at 250 °C and washed by acetic acid solution gave the specimens the highest piezoelectric properties. It indicates that the well-crystallized BT powder with less OH^- defects can improve the sintering property to give the specimen the higher piezoelectric constants. In contrast, the existence of large grains in the specimens and over-sintering resulted in the decrease of the piezoelectric properties.

Acknowledgements

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References

[1] T. Yamamoto, Ferroelectric properties of the $PbZrO_3$–$PbTiO_3$ system, Jpn. J. Appl. Phys. 35 (1996) 5104–5108.

[2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–87.

[3] X. Jing, Y. Li, Q. Yang, J. Zeng, Q. Yin, Influence of different templates on the textured $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ piezoelectric ceramics by the reactive templated grain growth process, Ceram. Int. 30 (2004) 1889–1893.

[4] H. Li, C. Feng, W. Yao, Some effects of different additives on dielectric and piezoelectric properties of $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ morphotropic-phase-boundary composition, Mater. Lett. 58 (2004) 1194–1198.

[5] M. Matsubara, T. Yamaguchi, K. Kikuta, S. Hirano, Sintering and piezoelectric properties of potassium sodium niobate ceramics with newly developed sintering aid, Jpn. J. Appl. Phys. 44 (2005) 258–263.

[6] J. Li, K. Wang, B. Zhang, L. Zhang, Ferroelectric and piezoelectric properties of fine-grained $Na_{0.5}K_{0.5}NbO_3$ lead-free piezoelectric ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 89 (2) (2006) 706–709.

[7] B. Zhang, J. Li, K. Wang, L. Zhang, Compositional dependence of piezoelectric properties in $Na_xK_{1-x}NbO_3$ lead-free ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 89 (5) (2006) 1605–1609.

[8] H. Takahashi, Y. Numamoto, J. Tani, K. Matsuta, J. Qiu, S. Tsurekawa, Lead-free barium titanate ceramics with large piezoelectric constant fabricated by microwave sintering, Jpn. J. Appl. Phys. 45 (2006) L30–L32.

[9] J. Qiu, J. Tani, K. Orikasa, H. Takahashi, Fabrication of a lead-free BNT piezoelectric material using a hybrid sintering process, Int. J. Appl. Electromagn. 21 (2005) 171–181.

[10] W.J. Dawson, Hydrothermal synthesis of advanced ceramic powder, Ceram. Bull. 67 (10) (1988) 1673–1678.

[11] K.-Y. Chen, Y.-W. Chen, Preparation of barium titanate ultrafine particles from rutile titania by a hydrothermal conversion, Powder Technol. 141 (2004) 69–74.

[12] J.G. Lisoni, C.H. Lei, T. Hoffmann, V.M. Fuenzalida, Hydrothermal growth of $BaTiO_3$ on TiO_2 single crystals, Surf. Sci. 515 (2002) 431–440.

[13] G.J. Choi, H.S. Kim, Y.S. Cho, $BaTiO_3$ particles prepared by microwave-assisted hydrothermal reaction using titanium acylate precursors, Mater. Lett. 41 (1999) 122–127.

[14] P. Pinceloup, C. Courtois, J. Vicens, A. Leriche, B. Thierry, Evidence of a dissolution-precipitation mechanism in hydrothermal synthesis of barium titanate powders, J. Eur. Ceram. Soc. 19 (1999) 973–977.

[15] H. Xu, L. Gao, Hydrothermal synthesis of high-purity $BaTiO_3$ powders: control of powder phase and size, sintering density, and dielectric properties, Mater. Lett. 58 (2004) 1582–1586.

[16] J. Moon, E. Suvaci, A. Morrone, S.A. Costantino, J.H. Adair, Formation mechanisms and morphological changes during the hydrothermal synthesis of $BaTiO_3$ particles from a chemically modified, amorphous titanium (hydrous) oxide precursor, J. Eur. Ceram. Soc. 23 (2003) 2153–2161.

[17] B.I. Lee, X. Wang, S.J. Kwon, H. Maie, R. Kota, J.H. Hwang, J.G. Park, M. Hu, Synthesis of high tetragonality nanoparticle $BaTiO_3$, Microelectron. Eng. 83 (2006) 463–470.

[18] K. Kajiyoshi, M. Takai, A. Onda, K. Yanagisawa, Presented at the 42nd Symposium on Basic Science of Ceramics, Nagaoka-shi, Japan, 2004.