Solvothermal Synthesis and Characterization of Nano-sized Barium Titanate Powder

Kyoon Choi[1,a], Soon-Gyu Kwon[1], and Byung-Ik Kim[1]

[1]Korea Inst. of Ceram. Eng. & Tech., Seoul 153-801, Republic of Korea
[a]knchoi@kicet.re.kr

Abstract

Multilayer ceramic capacitor (MLCC) miniaturization has increased the demand for superfine $BaTiO_3$ powder due to its thin dielectric layer. Hydrothermally synthesized $BaTiO_3$ powdera pseudo-cubic phase resulting in poor dielectric properties due to size effect and hydroxyl ion inclusion in the $BaTiO_3$ lattice. We attempted a superfine (lower than 100 nm) highly tetragonal $BaTiO_3$ powder via a solvothermal method without precipitating agent. The lattice parameters and the relative amounts of tetragonal and cubic phases were determined using Rietveld refinement.

Keywords : nanomaterials; solvothermal synthesis; batio$_3$; capacitors; tetragonality

1. Introduction

Hydrothermally synthesized barium titanate (BT) powder has superfine particle size and narrow particle size distribution (PSD) with good crystallinity. However it has a critical shortcoming of low tetragonality, resulting in poor MLCC dielectric properties. Low tetragonality comes from two origins: 1) size effect [1-3] reflecting a thermodynamic phase transition due to an isotropic pressure and 2) hydroxyl ion incorporation on oxygen site of BT [4]. Size effect is unavoidable for a small particle, irrespective of powder synthesis route. Hydroxyl ion substitution for oxygen site is often detrimental not only to dielectric properties but chip failure caused by bloating phenomenon [4].

Several attempts in order to make superfine BT powder have been made by solvothermal synthesis. Alcohol based solvents such as ethanol, methanol and n-propanol, yielded nano-sized cubic-phase powders [5]. In this study, we have synthesized BT powders of various sizes using deionized (DI) water, ethanol and their mixture as reaction media. Tetragonalities, particle size distributions (PSDs) and particle morphologies of synthesized powders were compared each other and the way to distinguish the size and solvent effect was discussed.

2. Experimental and Results

2-1 Experimental Procedures

BT powders were prepared by a solvothermal method using barium hydroxide octahydrate and anatase as raw materials. Barium and titanium (2:1 molar ratio) were mixed with DI water and ethanol (reagent grade, 95%, Daejung Chemical Co., Ltd, Korea) as a solvent. The 80 vol % of the mixture (Ba:Ti=2:1 in molar ratio) placed inside a Teflon-lined vessel and solvent ratio was changed from 100 % EtOH to 80 %, 60 %, 50 %, 40 %, 20 % and 0 % with DI water. The mixture was sealed in the vessel and then annealed 24 hours at 190 - 210 ^oC.

BT powder X-ray diffraction (XRD) patterns were obtained with a diffractometer (MXP3, MAC Science Co. Ltd., Japan) using a Ni-filtered CuKα line (1.5406Å). Two 2θ ranges were taken at different scan rates; 4^o/min for a wide range from 20^o to 70^o and 0.5^o/min for a specific range from 44° to 46^o. Lattice constants a and c were calculated from the (200) and (002) reflections, respectively. Equivalent spherical diameters (ESDs) of BT powders were calculated from specific surface areas measured with a surface area and porosimetry analyzer (ASAP-2010, Micromeritics Co., Ltd., USA).

2-2 Particle size and its distribution with solvent composition (EtOH/H_2O ratio)

The specific surface areas measured were converted to equivalent spherical diameters (ESDs) using an equation, $d_{BET} = 6/(\rho \cdot S_{BET})$, where ρ is density and S_{BET} is specific surface area. Particle size strongly depended on solvent composition as shown in Fig. 1. Particles synthesized in DI water were the largest whilst those in 100% EtOH the smallest. However, particle size did not change proportionally and showed a local maximum near 50-60% EtOH. Further, PSD measured with a zeta potentiometer also showed high solvent composition dependence. Particle morphologies appear to be very uniform without agglomeration. Angular particles of a rounded cube shape were frequently seen in high EtOH samples. Particles synthesized in DI water had an irregular shape and a broad PSD.

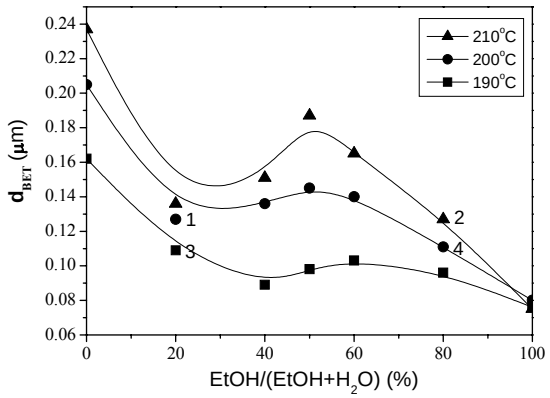

Fig. 1. Equivalent spherical diameter variation with solvent composition.

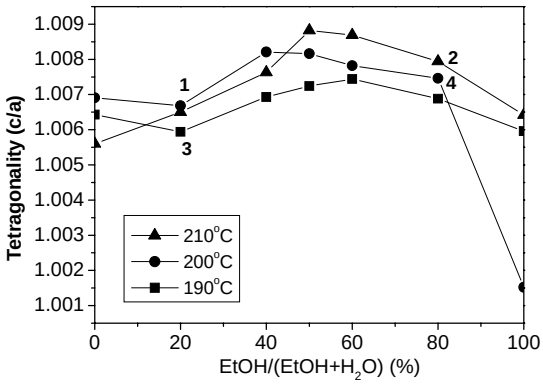

Fig. 2. Variation of tetragonality as a function content in mixed solvent.

2-3 Determination of tetragonality using XRD

XRD peaks near 45 degree were fitted to two Gaussian curves which correspond to BT (200) and (002) peaks using Microcal 'Origin' program (Microcal (TM) Origin, Ver. 6.0, Microcal Software, Inc., Northampton, USA.). Measured powder tetragonalities (c/a) were plotted as a function of ethanol content in Fig. 2. The powder tetragonality depended strongly on solvent composition.

Uchino et al. [1] argued that the tetragonality (c/a) of barium titanate particle is strongly dependent on particle size. We chose two powders with equal particle size to elucidate solvent effects on the powder tetragonality. Samples 1, 2 and 3, 4 in Fig. 1 were the same size (110 and 127 nm, respectively) but synthesized with different solvent composition. Sample 1 and 2 tetragonality changed from 1.0067 to 1.0079 and 1.0059 to 1.0075 for samples 3 and 4 just by changing solvent composition from 20 % to 80 % EtOH, respectively. This supports ethanol addition to DI water was useful for increasing BT powder tetragonality.

The sudden tetragonality decrease near the ethanol side in Fig. 2 is thought to be related to particle size. The pure ethanol ESD reached only about 80 nm. This value is very close to the 50nm critical size where particles lose their tetragonal character by size effect. Chen et al. [5] synthesized cubic BT powders of below 60 nm using ethanol and attributed loss of tetragonality to low permittivity of the solvent. However, this study shows that the ethanol itself is not detrimental rather it is effective for tetragonal BT synthesis as recently shown by authors [6, 7].

3. Summary

Superfine BT particles having narrow size distribution and uniform morphology were obtained using ethanol as a solvent. Adding ethanol to deionized water was an effective way to enhance BT powder tetragonality. Highly tetragonal BT powders up to 1.0088 (c/a) were synthesized at 210°C using 50% ethanol solvent.

4. References

1. Uchino, K., Sadanaga, E. and Hirose, T., *J. Am. Ceram. Soc*., **72,** 1555 (1989).
2.Chattopadhyay, S., Ayyub, P., Palkar, V. R. and Multani, M., *Phys. Rev.,* **B52,** 13177 (1995).
3. Zhang, M. S., Yin, Z., Chen, Q., Zhang, W. and Chen, W., *Solid State Comm*., **119,** 659 (2001).
4. Hennings, D. F. K., Metzmacher, C. and Schreinemacher, B. S., *J. Am. Ceram. Soc.,* **84,** 179 (2001).
5. Chen, D. and Jiao, X., *J. Am. Ceram. Soc*., **83,** 2637 (2000).
6. S.-G. Kwon, B.-H. Park, K. Choi, E.-S. Choi, S. Nam, J.-W. Kim, J.-H. Kim, *J. Europ. Ceram. Soc*., **26,** 1401 (2006).
7. S.-G. Kwon, K. Choi, B.-I. Kim, *Mater. Lett.*, **60,** 979 (2006).