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Solvothermally synthesized tetragonal barium titanate powders using H_2O/EtOH solvent

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Abstract

Multilayer ceramic capacitor (MLCC) miniaturization has increased the demand for superfine $BaTiO_3$ powder due to its thin dielectric layer. Hydrothermally synthesized $BaTiO_3$ powder has submicron size, high purity and good crystalline nature at low synthetic temperature. However, the powder has a 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. Solvent composition effects on the $BaTiO_3$ powder tetragonality were discussed.

Keywords: Powders-chemical preparation; Dielectric properties; $BaTiO_3$; 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]

Few successful cases of tetragonal $BaTiO_3$ powder synthesis below 100 nm size have been reported.[3,5] A 70 nm barium titanate powder hydrothemally synthesized with chloride source materials at 240 °C was noted to be highly tetragonal.[5] Seventy nanometers is the smallest barium titanate powder having high tetragonality synthesized in a hydrothermal condition. There have been controversies[1–3,5] about the barium titanate critical size where it loses its tetragonality due to size effect. Hsiang and Yen[6] determined the critical size to be 49 nm using a transmission electron microscope, which was consistent with the result of Zhang et al.[3] using X-ray diffraction techniques.

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.[7] Kim et al.[8] made partially tetragonal BT powder using 1,4-butanediol as a solvent. In this study, we have synthesized BT powders of various sizes using deionized (DI) water, ethanol and their mixture as reaction media. Tetragonalities, PSDs and particle morphologies of synthesized powders were compared each other and the way to distinguish the size and solvent effect was discussed.

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2. Experimental procedures

BT powders were prepared by a solvothermal method using barium hydroxide octahydrate ($Ba(OH)_2 \cdot 8H_2O$, reagent grade, Junsei Chemical Co., Ltd., Japan) and anatase (98% reagent grade, Yakuri Pure Chemicals Co., Ltd., Japan) as raw materials. Barium and titanium (2:1 molar ratio) were placed inside a Teflon-lined vessel and mixed with DI water and ethanol (reagent grade, 95%, Daejung Chemical Co., Ltd, Korea) as a solvent. The total volume of the mixture was 80% of the vessel capacity. Solvent ratio in volume percent 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 h at 190–210 °C. The synthesized powders were neutralized with 10 N formic acid (reagent grade, Daejung Chemical Co., Ltd., Korea) then filtered and dried 12 h at 90 °C in a box-type oven.

BT powder X-ray diffraction (XRD) patterns were obtained with a diffractometer (MXP3, MAC Science Co. Ltd., Japan) using a Ni-filtered Cu Kα line (1.5406 Å). Two 2θ ranges were taken at different scan rates; 4 °/min for a wide range from 20° to 70° and 0.5 °/min for a specific range from 44° to 46°. Lattice constants a and c were calculated from the (2 0 0) and (0 0 2) 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). PSD was measured with an electrophoretic light scattering spectrophotometer (ELS-800, Ostuka Co., Ltd., Japan) using a 10 mW He–Ne laser. Particle morphology was observed with a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL).

3. Results and discussion

3.1. 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, $d_{BET} = 6/(\rho S_{BET})$, 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, particle size distribution (PSD) measured with a zeta potentiometer also showed high solvent composition dependence. Two BT samples synthesized at 210 °C in 0% and 80% EtOH are depicted in Fig. 2(a) and (b), respectively. The 80% EtOH synthesized powder showed a very narrow PSD with a 60 nm median particle size.

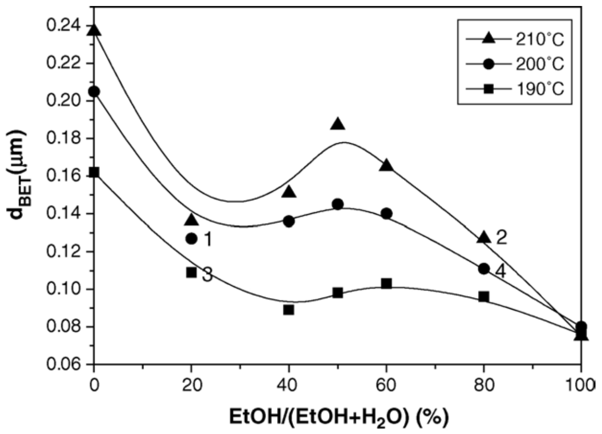


Fig. 1. Equivalent spherical diameter variation with solvent composition.

Fig. 3 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 irregular shape and broad PSD. Fig. 3 particle morphologies were consistent with Fig. 1 ESDs and Fig. 2 PSDs. By choosing the adequate EtOH and H_2O solvent composition, we could control particle size and PSD.

3.2. Determination of tetragonality using X-ray diffraction

Fig. 4(a) shows XRD patterns for BT powders synthesized at 210 °C. Peaks (0 0 2) and (2 0 0) are enlarged in Fig. 4(b) to compare the powder tetragonality. Curves of Fig. 4(b) were

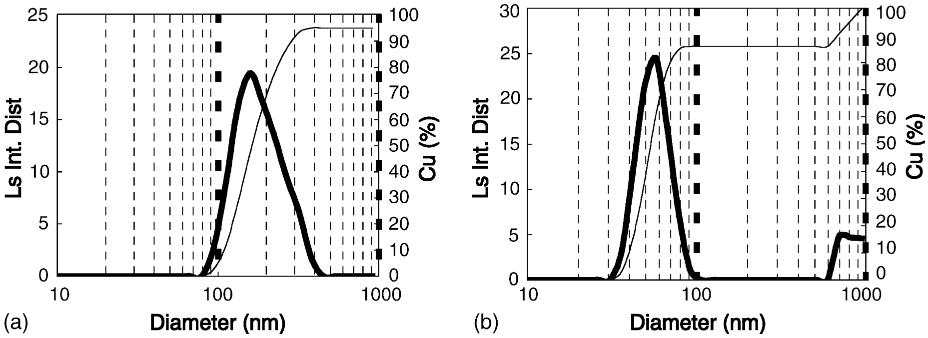
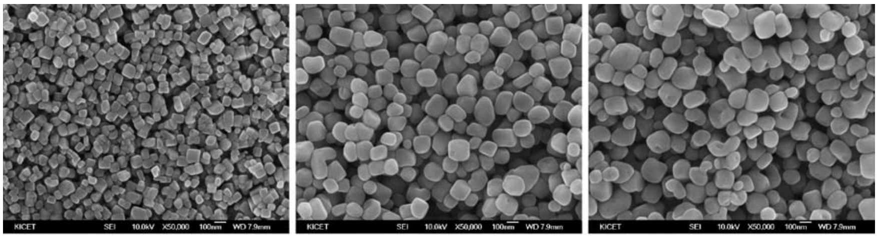
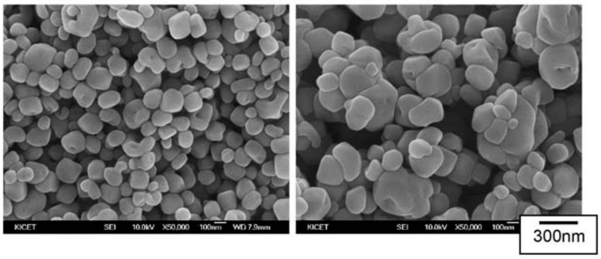


Fig. 2. Barium titanate particle size distribution synthesized in: (a) DI water and (b) 80% EtOH solvent measured with a zeta potentiometer.



(a) EtOH 100% (b) EtOH 80% (c) EtOH 50%



(d) EtOH 20% (e) EtOH 0%

Fig. 3. SEM images of barium titanate powders synthesized in ethanol and DI water solutions at 210 °C.

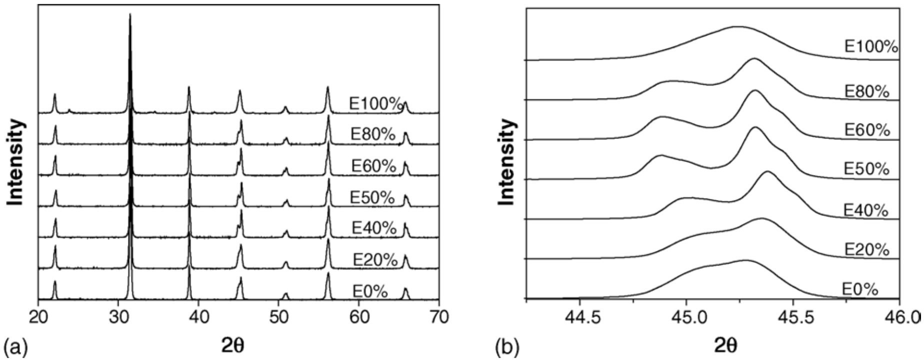


Fig. 4. Barium titanate powder: (a) XRD patterns and (b) their partial enlargement solvothermally synthesized at 210 °C.

fitted to two Gaussian curves which correspond to BT (2 0 0) and (0 0 2) peaks using Microcal 'Origin' program.[1] Measured powder tetragonalities (*c*/*a*) were plotted as a function of ethanol content in Fig. 5. 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. 5 is thought to be related to particle size. The pure ethanol ESD reached only about 80 nm. This value is very close to the 50 nm critical size where particles lose their tetragonal character by size effect. Chen et al.[7] 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

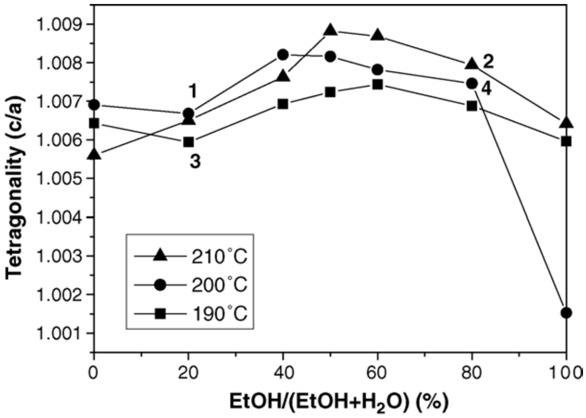


Fig. 5. Variation of tetragonality as a function content in mixed solvent.

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[1] Microcal (TM) Origin, Ver. 6.0, Microcal Software, Inc., Northampton, USA.

that the ethanol itself is not detrimental rather it is effective for tetragonal BT synthesis.

4. Conclusion

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.

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