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Tetragonality of nano-sized barium titanate powder prepared with growth inhibitors upon heat treatment

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Abstract

Nano-sized barium titanate powders with high dielectric constant are preferred for many reasons in industry, while it is generally known that the dielectric constant is decreasing with the decrease in particle size. In order to enhance the dielectric constant of fine hydrothermal $BaTiO_3$ powders by eliminating the internal defects, heat treatment at various temperatures is performed. The behavior of tetragonality, an indirect measure of dielectric constant, is investigated as a function of particle size and heat treatment temperature. Growth inhibitors such as carbon black and corn starch are added to minimize the drawbacks of heat treatment such as hard agglomeration and particle growth. Controlling the particle size is possible by using inhibitors, but the efficiency of tetragonality enhancement by heat treatment is relatively low. Explanations for these results are included.

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Keywords: Dielectric properties; $BaTiO_3$; Capacitors; X-ray methods; Tetragonality

1. Introduction

Barium titanate ($BaTiO_3$) undergoes a tetragonal to cubic phase transition at Curie temperature which is generally located at 120–130 °C.[1] Cubic phase shows paraelectric properties, while tetragonal one shows ferroelectric properties which are more interesting properties for dielectric application due to its high dielectric constant. Fine $BaTiO_3$ powders with high dielectric constant are preferred for many reasons in industry, especially for the low sintering temperature and for the high volumetric efficiency of electronic components. In order to get high dielectric constant, the crystal structure should have high tetragonality that is defined as the relative ratio of lattice parameter of c- to a-axis ($=c/a$).[2,3] Besides the temperature effect, it is known that particle size is also an important factor on phase transition.[4–12] The crystal structure becomes less and less tetragonal as the particle size decreases and finally shows complete cubic phase below a critical particle size. However, all the research reports show difference in critical particle size of $BaTiO_3$ produced by different synthetic methods.[4–12] Researchers explain that this difference might come from the different elastic strain energy associated with chemical impurity and crystalline defects levels incorporated during the process. According to a suggested model,[13] strains imposed by the presence of defects such as hydroxyl ions increase the critical particle size by leading the existence of the metastable cubic phase. Researchers actually observed the annihilation of incorporated defects by heat treatment at temperatures higher than 800 °C using hydrothermally synthesized $BaTiO_3$ powders.[14]

However, there are problems associated with high temperature heat treatment such as hard agglomeration and particle growth, which decrease the quality and the volumetric efficiency of a product in final application. A possible way to expose powders at high temperature in order to increase the tetragonality and dielectric constant while minimizing these problems is utilizing a growth inhibitor.[15,16] Inhibitors retard particle growth and agglomeration during heat treatment. They should be burned out completely without leaving any residues not to affect to the final properties of powders.

The purposes of this research are to check the effects of inhibitors on the tetragonality of hydrothermal $BaTiO_3$ powders during heat treatment and to investigate the evolution of particle size at different temperatures with and without the growth inhibitor. Two kinds of inhibitors with different

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burnout temperatures were used by varying the amount of their addition.

2. Experimental procedure

A hydrothermally produced BT-01 (Sakai Chemicals, Japan) with a mean particle size of 140 nm, a specific surface area of 12.36 m^2/g, and a Ba/Ti ratio of 0.994 was used for this experiment. Thermo-gravimetric analysis (TGA) was performed for BT-01 and five kinds of potential inhibitors: two kinds of carbon blacks with different particle sizes, one kind of potato starch and two kinds of corn starches. The thermo-gravimetric behavior of two carbon blacks was different from that of three kinds of starches. Based on the TGA results, each of a carbon black (HIBLACK 20L, $D_{\mathrm{mean}} = 28$ nm, Shin Woo Materials, Korea) and a corn starch ($D_{\mathrm{mean}} = 8.44$ μm, Duksan Pure chemicals, Korea) were chosen for growth inhibitors. The SEM micrographs of BT-01, carbon black and corn starch are shown in Fig. 1. Different amounts of each inhibitor (0, 1, 3, 5 and 10 wt.% with respect to BT-01) were added to 200 g of BT-01, which was already dispersed in 300 cc of deionized water. 0.5 wt.% of ammonium salt of polycarboxylic acid (Cerasperse 5468-CF, San Nopco, Korea) with respect to the powder was added as a dispersant. Depending on the type of growth inhibitor and the amount of addition, samples were named as CB00, CB01, CB03, CB05 and CB10 for carbon black added; CS00, CS01, CS03, CS05 and CS10 for corn starch added samples. Ten kinds of slurries were milled separately using a high-energy mill (MiniCer, Netzsch, Germany) for 5 min at 600 rpm of rotor speed with 0.45Ø ZrO_2 beads. In order to minimize the milling effect of powders during this mixing process, short time and low milling speed were selected. After drying these slurries, each powder was heat treated at 800, 900, 950, 1000, 1050 and 1100 °C for 2 h in air with a heating rate of 3 °C/min. Characterization such as SEM, XRD and particle size analysis was followed after crushing the powders. In order to measure the average primary particle size with SEM images, maximum and minimum diameters of particles were measured for 100 particles at least using an image analyzer software (SigmaScan, Systat Software, USA). X-ray diffraction (RINT 2200, Rigaku using Cu Kα line) patterns were utilized to determine tetragonality.

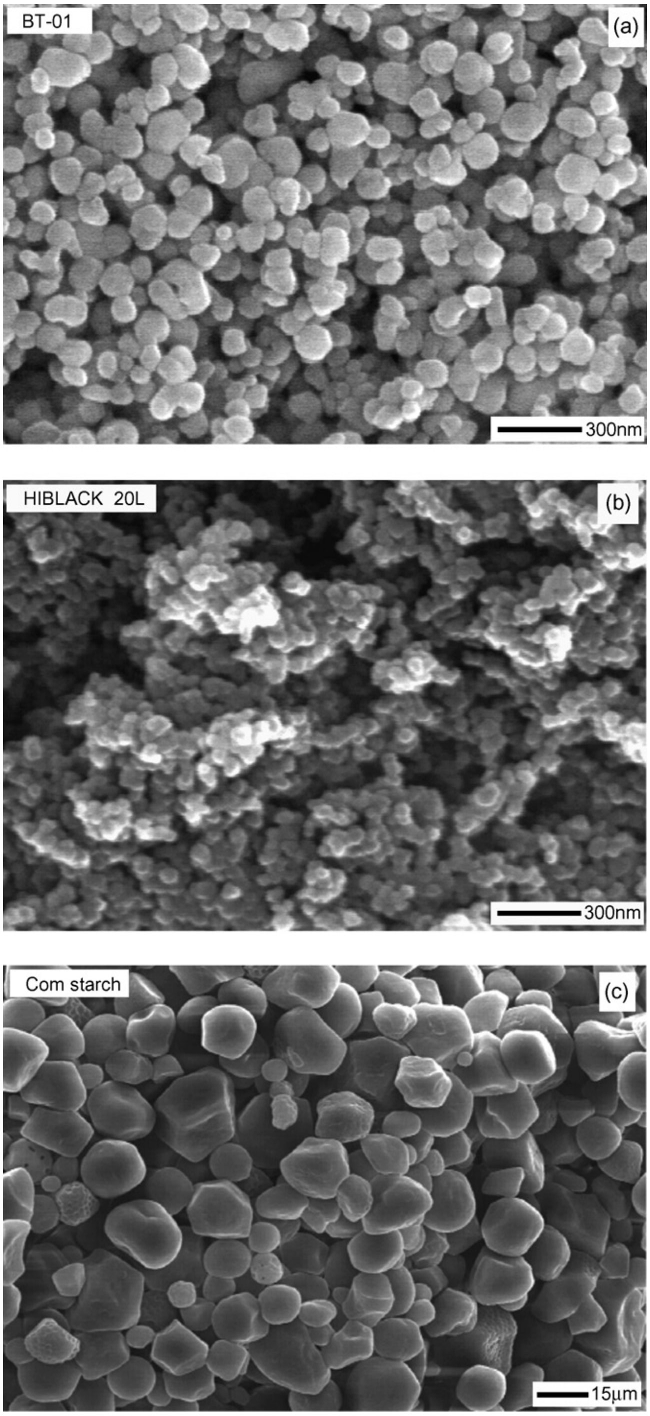

Fig. 1. SEM micrographs of (a) BT-01, (b) carbon black (HIBLACK 20L) and (c) corn starch.

3. Results and discussion

Most industries prefer to use spherical, chemically homogeneous and unagglomerated fine ceramic powders, which are the general characteristics of hydrothermally synthesized BT-01 as

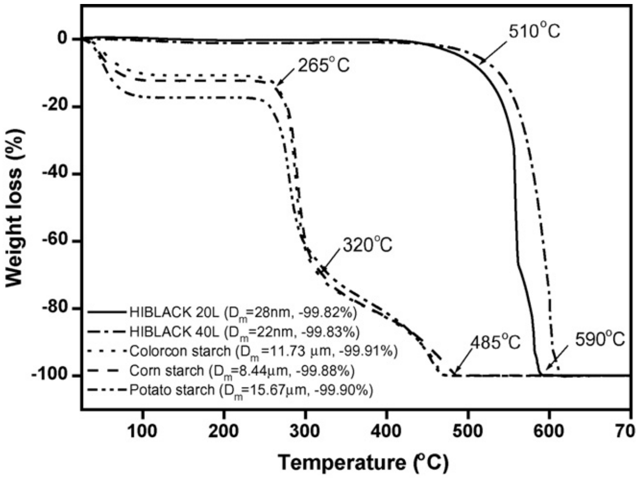

Fig. 2. Thermo-gravimetric behavior of carbon blacks and starches in air with a heating rate of 3 °C/min.

shown in Fig. 1(a). However, TGA of this powder in air shows 1.2% of weight loss up to 1000 °C, which is much greater than that of a solid-state reacted powder with less than 0.3 wt.%. This additional weight loss of hydrothermal powder attributes to the release of defects such as hydroxyl ions (OH^-), protons (H^+) and the carbonates ($CO_3{}^{2-}$), which are incorporated into the lattice during the synthesis at high water pressure.[14,17] These defects stabilize the cubic phase, and hence decrease the tetragonality of the powder.[5,14]

As shown in Fig. 2, most of corn starch is burnt up to 300 °C, while carbon black exists almost up to 600 °C. Both inhibitors leave a negligible amount of residues which is less than 0.2 wt.% at 600 °C. Inhibitors should be burnt out completely while generating gas phase at high temperature in order

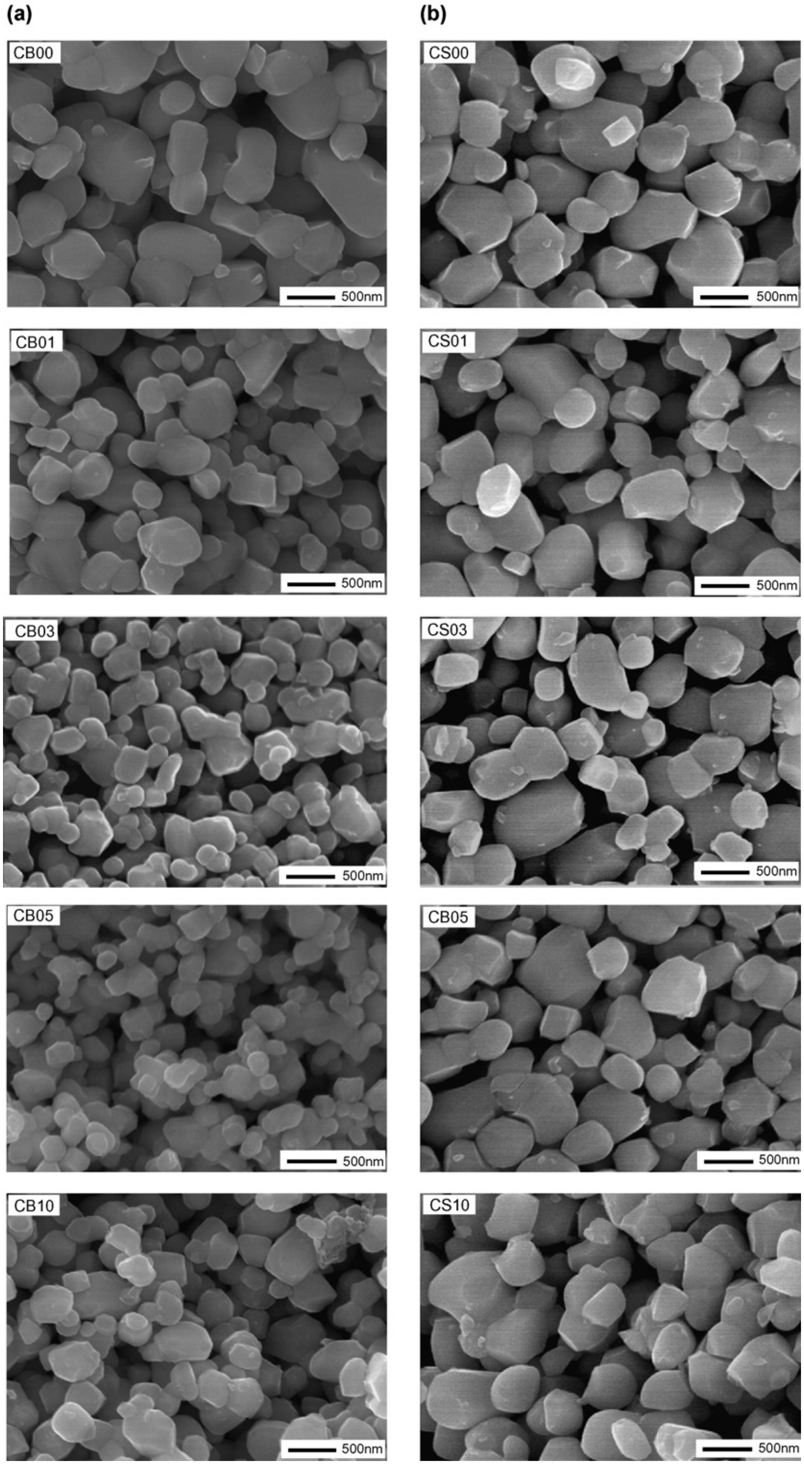

Fig. 3. Evolution of particle morphology heat treated at 1000 °C with different amounts of (a) carbon black and (b) corn starch.

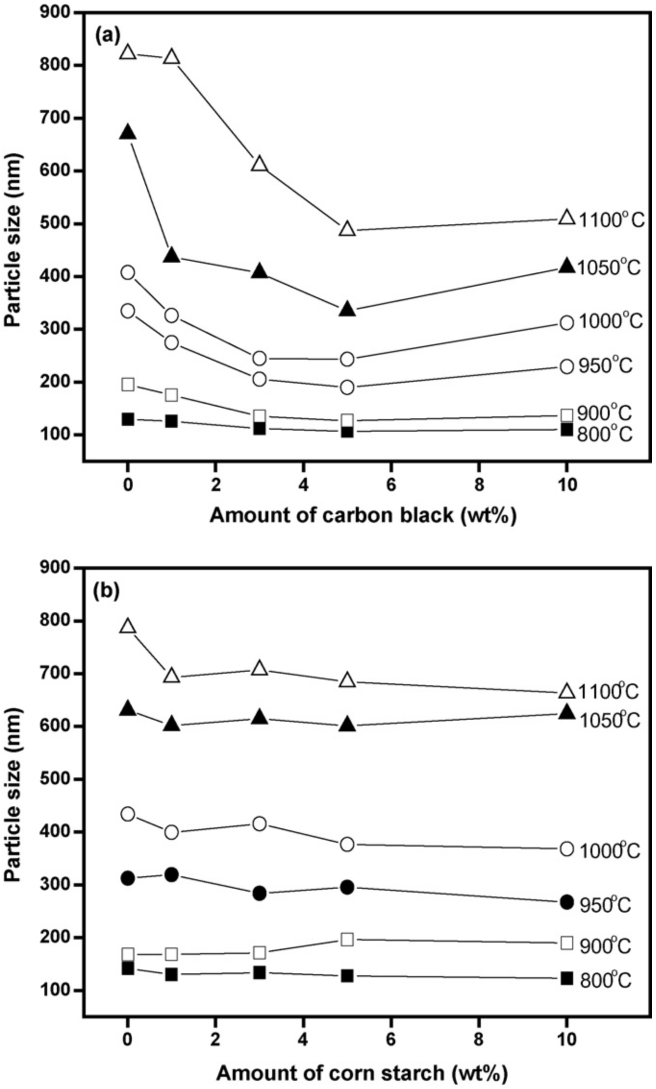

Fig. 4. Comparison of particle size of BT-01 heat treated at various temperatures with different amounts of (a) carbon black and (b) corn starch.

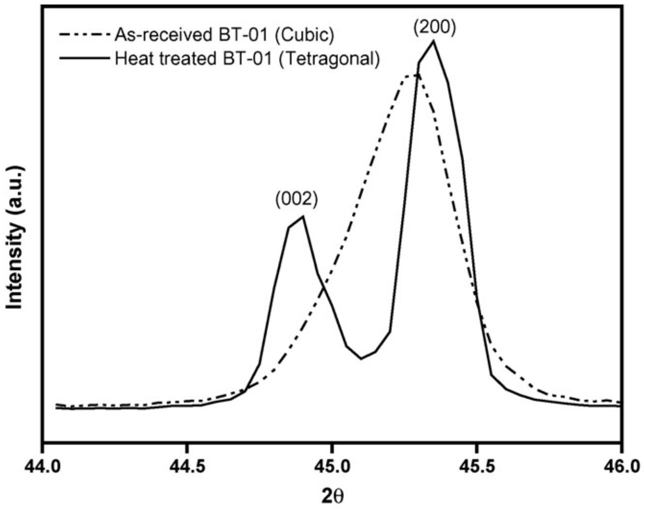

Fig. 5. XRD patterns of cubic phase showing one peak and tetragonal $BaTiO_3$ with peak splitting at $2\theta = 44–46\,^{\circ}C$.

to hinder the particle growth by increasing the distance among particles. Particle morphologies heat treated at 1000 °C with different amounts of carbon black and corn starch are shown in Fig. 3(a) and (b), respectively. The average particle size with carbon black decreases significantly with the increase in the amount of inhibitor, while the decrease in particle size with corn starch is trivial. For example, the average particle size heat treated at 1000 °C is approximately 420 nm without inhibitor (both of CB00 and CS00), while 240 nm for CB05 and 380 nm for CS05 samples. This trend is found for various heat treatment temperatures as shown in Fig. 4. However, one can find from Fig. 4(a) that the average particle size with 10 wt.% of carbon black (CB10) is generally larger than that with 5 wt.% of same inhibitor (CB05). The reason is not sure, but it may attribute to the poor dispersion of carbon black with CB10 samples. Compared to the high tendency for agglomeration of nano-sized carbon black, it seems that 5 min milling at 600 rpm is not sufficient even though carbon black with larger particle size is used. The difference in efficiency of inhibitors between carbon black and corn starch comes from the difference in their burn-out temperature. The burn-out temperature of inhibitor should be high enough to prevent particles from growth during the heat treatment at high temperature.

Fig. 5 shows the XRD patterns of as-received cubic BT-01 without $\{2\,0\,0\}$ peak splitting, and tetragonal CS00 sample heat treated at 1000 °C with peak splitting of (2 0 0) and (0 0 2) planes for $2\theta = 44–46\,^{\circ}C$. The tetragonality, the relative ratio of lattice parameter of *c*- to *a*-axis, can be calculated from the XRD data and be used for the estimation of the dielectric constant of powders. The tetragonality of powders heat treated at 1000 °C decreases with the increase in the amount of carbon black, while no change is found for corn starch added samples as shown in Fig. 6. It is found that the tetragonality is a function of the particle size: gradual increase between the particle size of 170 and 330 nm, saturation with its value of approximately 1.0105 for

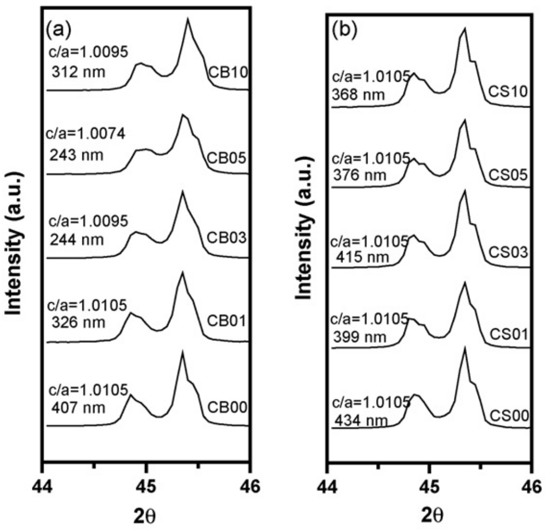

Fig. 6. Comparison of XRD patterns for 1000 °C heat treated BT-01 with various amounts of (a) carbon black and (b) corn starch for $2\theta = 44–46\,^{\circ}C$. Average particle size and tetragonality are shown.

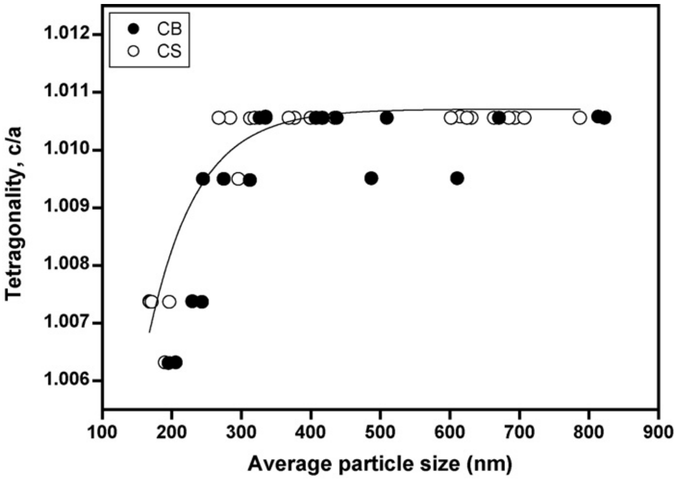

Fig. 7. The relationship between tetragonality and the average particle size of BT-01 heat treated with various amounts of carbon black and corn starch.

particles larger than 330 nm as shown in Fig. 7. Tetragonality value cannot be calculated for particles less than 170 nm, since distinct peak splitting is not observed. In order to examine the relationship between tetragonality and heat treatment temperature, five samples having similar particle size of approximately 330 nm among 60 samples are chosen. Their particle sizes and corresponding tetragonality values are shown in Fig. 8. From this figure, two things should be noted: one is that the primary particles with similar size can be obtained at various heat treatment temperatures (950, 1000, and 1050 °C) by using growth inhibitors and by changing their amount. The second is that all five samples with similar particle size show the same tetragonality regardless their heat treatment temperature. It means that the tetragonality enhancement by heat treatment, while maintaining the particle size as small as possible by adding inhibitors, is not efficient, although it is conceptually possible by offering enough thermal energy required for the defect removal. It can be translated into two aspects that the contribution of internal defects is not too high compared to the effect of free surface in stabilizing the metastable cubic phase, or the thermal energy corresponding to the heat treatment at 950 °C is large enough to remove the internal defects for the tetragonality enhancement of hydrothermal $BaTiO_3$. It seems that, therefore, investigation of factors associated with various synthetic routes necessitates instead of the modification of synthesized particles to increase the tetragonality while maintaining the small particle size of $BaTiO_3$.

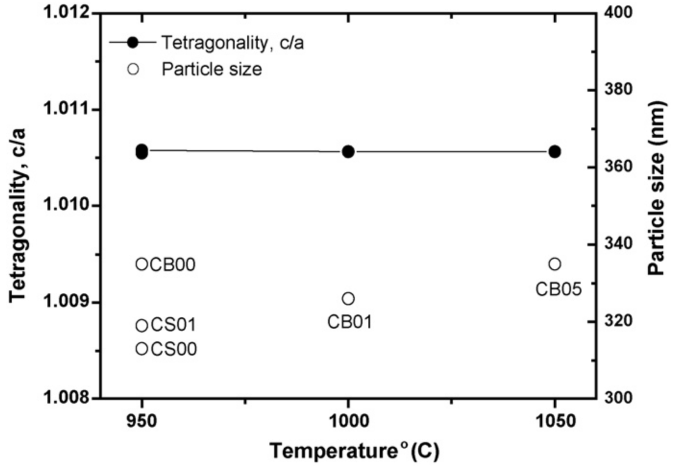

Fig. 8. The relationship between tetragonality and temperature of BT-01 having similar particle size.

4. Conclusions

In order to investigate a concept which is the tetragonality enhancement of fine $BaTiO_3$ powder by removing the internal defects while minimizing the particle growth during a heat treatment simultaneously, this experiment was performed. The results presented in this paper enable the following conclusions to be drawn:

(1) Controlling of particle size under the same heat treatment condition was possible by using growth inhibitors. Carbon black was a more efficient inhibitor than corn starch due to its high burn-out temperature compared to that of corn starch.
(2) Tetragonality (=*c*/*a*) increases gradually between the particle size of 170–330 nm and shows saturation for the particle size larger than 330 nm. However, it is found that the tetragonality enhancement by heat treatment while minimizing the particle growth is not efficient.
(3) The above results may indicate the relatively smaller contribution of internal defects than free surface in stabilizing the metastable cubic phase and/or high enough thermal energy corresponding to the heat treatment at 950 °C or higher temperature for the removal of internal defects.

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