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Effects of heat treatment and particle size on the tetragonality of nano-sized barium titanate powder

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Abstract

Although fine $BaTiO_3$ powders with high tetragonality (=*c*/*a*) are required to increase the volumetric efficiency of a multilayer ceramic capacitor in industry, the tetragonality decreases and disappears below a certain particle size. In order to check the effects of particle size and processing temperature on tetragonality, heat treatment and X-ray diffraction were performed using commercial hydrothermal $BaTiO_3$ powders after adding different amounts of carbon black. Carbon black was burned out completely up to 600 °C during the heat treatment while acting as an effective particle growth inhibitor even at high temperature like 1100 °C. By changing the amount of carbon black, the synthesis of $BaTiO_3$ particles having similar size at different processing temperatures was possible. Tetragonality depended linearly on the average particle size up to 330 nm, while showing a saturated value of 1.0105 for larger particles. Tetragonality was not a function of processing temperature for particles heat treated above 950 °C, which implied that the heat treatment above 950 °C was not helpful for the enhancement of tetragonality.

Keywords: A. Firing; B. X-ray methods; D. $BaTiO_3$ and titanates; E. Capacitors

1. Introduction

One of the most popular passive ceramic components is a multilayer ceramic capacitor (MLCC) which has alternating layers of dielectric materials and internal metal electrodes. In order to increase the volumetric efficiency of an MLCC, significant advances have been achieved in the reduction of dielectric thickness. An MLCC having the highest volumetric efficiency is currently as thin as 1 μm and is comprised of several hundred of dielectric layers. It is believed that each sintered layer of MLCC needs at least five grains to get long-term stability and reliability [1]. When the thickness of dielectric layer becomes 1 μm, the grain size of sintered ceramic layer should be controlled to 200 nm or less to meet the reliability requirement of the final products. Since the grain size of sintered body is affected significantly by the particle size of starting material [2,3], obtaining the ultra-fine $BaTiO_3$ with stringent characteristics is the prerequisite to get a reliable MLCC. For this reason, current MLCC industries prefer to use $BaTiO_3$ powders with high tetragonality which results in favorable dielectric properties [4]. Tetragonality (=*c*/*a*), the degree of ferroelectricity, is defined as the relative ratio of lattice parameter of *c*-axis to *a*-axis.

However, it is known that the degree of ferroelectricity of $BaTiO_3$ decreases with decrease in particle size and disappears below a certain critical size because of the crystallographic phase transition from tetragonal to cubic [5]. Even though this size effect of fine $BaTiO_3$ particles is of great importance to the industry, all the reports on the critical particle size show difference [5–12]. The hydrothermal $BaTiO_3$ powder which is synthesized under an aqueous and high pressure environment tends to incorporate hydroxyl ions due to the processing condition [13], although the powder produced with this method is widely used due to its extremely fine particle size with narrow size distribution among many kinds of synthetic methods [4]. According to the pure phase model [5,14], the presence of cubic phase with a fine $BaTiO_3$ at room temperature is stabilized by the large surface area [5] and the strains imposed by the presence of lattice hydroxyl ions [14]. In order to increase the tetragonality of a fine powder by eliminating defects including incorporated hydroxyl ions, heat treatment at high temperature can be considered. However, heat treatment at high temperature

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generally produces hard agglomeration and particle growth which are not desirable for MLCC application.

One possible concept to expose a powder at high temperature to decrease the defect level without particle growth is using a particle growth inhibitor. An inhibitor should be burned out completely at high temperature as long as it does not affect the properties of the final product. During the burning process, it generates gas phase which hinders the particle growth by separating the distance among particles. Using a carbon black as a growth inhibitor, the morphological evolution of hydrothermal $BaTiO_3$ powder after heat treatment at various temperatures was investigated in this study. The dependence of the particle size and processing temperature on the tetragonality was also examined.

2. Experimental procedure

The ceramic powder used in this study was BT-01 (Sakai Chemical, 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. As-received BT-01 was hydrothermally produced without any further heat treatment, and the SEM micrograph of this powder is shown in Fig. 1. Carbon black used as a particle growth inhibitor was HIBLACK 20L (Shin Woo Materials, Korea) with a mean particle size of 28 nm and a specific surface area of 86.00 m^2/g and the SEM image is shown in Fig. 2. Thermogravimetric analysis (TGA) of carbon black was performed to check the burnout temperature and the amount of residue up to 700 °C with a heating rate of 3 °C/min in air.

Five types of slurries with different amounts of carbon black (0, 1, 3, 5 and 10 wt.% with respect to 200 g of BT-01) were prepared. The water to powder ratio was 1.5/1. An ammonium salt of polycarboxylic acid (Cerasperse 5468-CF, San Nopco, Korea) was used as a dispersant by adding 0.5 wt.% with respect to the powder. Depending on the amount of carbon black, samples were named as CB00, CB01, CB03, CB05 and CB10, respectively. Slurries were milled using a high-energy mill (MiniCer, Netzsch, Germany) with 0.45 Ø ZrO_2 beads for 5 min at 600 rpm for homogeneous mixing. Although the milling speed up to 4500 rpm was allowed with this equipment, this mild milling condition was set for homogeneous mixing

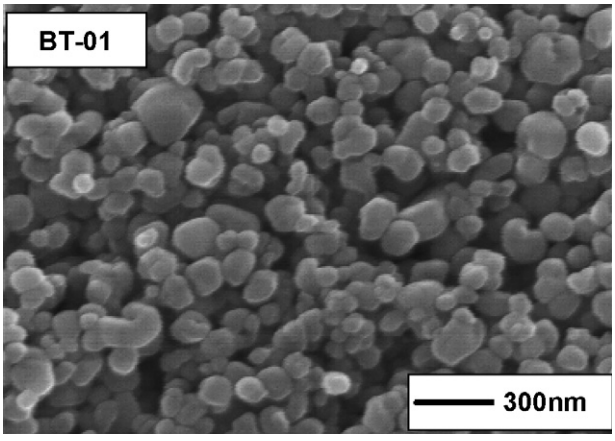


Fig. 1. SEM micrograph of as-received BT-01.

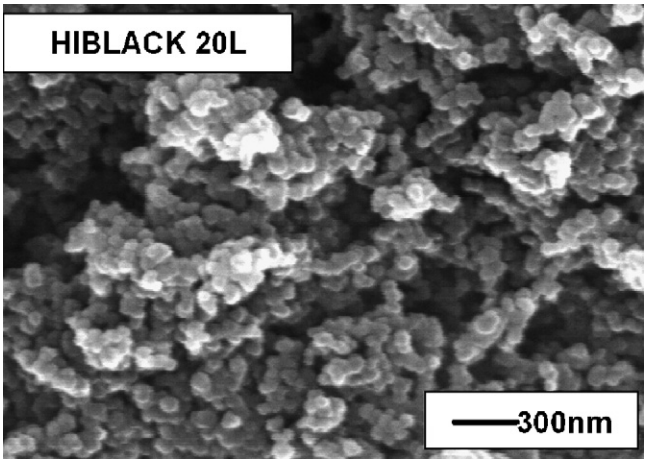


Fig. 2. SEM micrograph of carbon black which is used as a particle growth inhibitor.

while minimizing the milling effect. After drying these slurries overnight at 110 °C, powder was heat treated at 800, 900, 950, 1000, 1050 and 1100 °C for 2 h with a heating and cooling rate of 3 °C/min in air. After crushing these powders using a mortar and pestle, characterization was performed. Average particle size was determined by measuring the lengths of maximum and minimum diameter for 100 particles using an image analyzing software (SigmaScan, Systat Software, USA) based on the micrographs of scanning electron microscope (SEM, S-4100, Hitachi). Room temperature X-ray diffraction (XRD, RINT 2200, Rigaku using Cu Kα with λ = 0.15406 nm) data was used to determine the tetragonality of powder.

3. Results and discussion

TGA results in Fig. 3 shows that carbon black starts to burn near 500 °C and completely burns out up to 600 °C remaining 0.2 wt.% of residue. Fig. 4 shows the SEM images of 950 °C heat treated BT-01 with different amounts of carbon black. The average particle size decreases with an increase in the amount

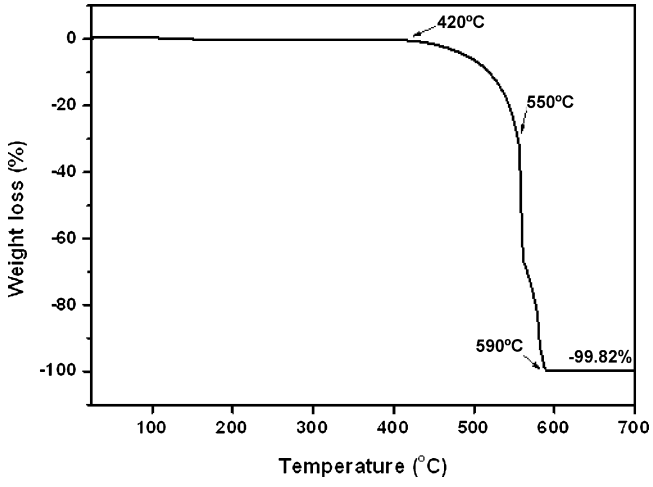


Fig. 3. Thermogravimetric analysis of carbon black in air with the heating rate of 3 °C/min.

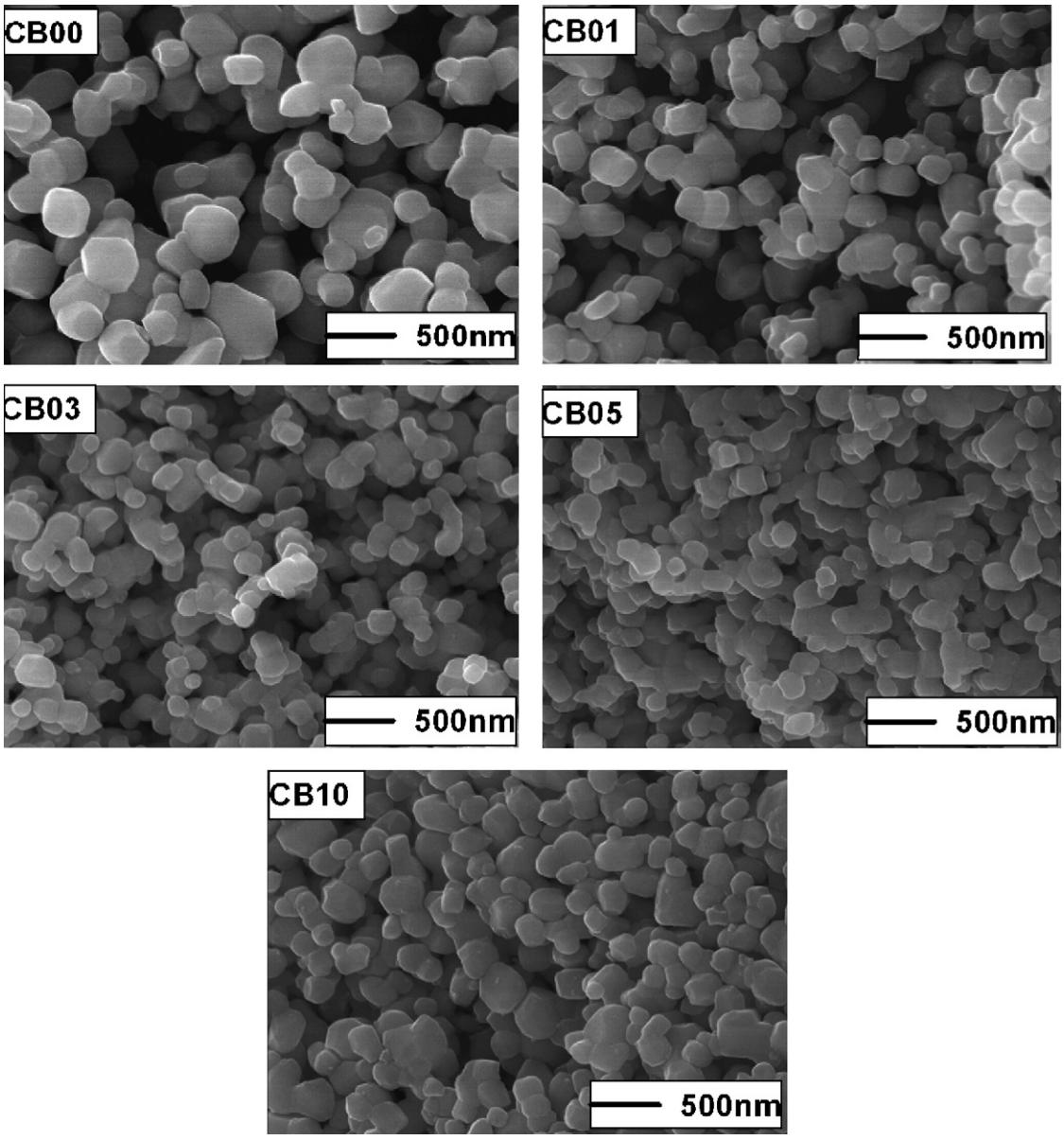


Fig. 4. SEM images of 950 °C heat treated BT-01 with different amounts of carbon black.

of carbon black in general, which means the carbon black acts as an effective particle growth inhibitor. The average particle size without carbon black at this temperature is 335 nm, while that with 5 wt.% carbon black is 190 nm for example. However, the sample with 10 wt.% carbon black shows a slightly larger particle size than that of 3 or 5 wt.% added one. The reason is not clear, but it may be attributed to the poor dispersion of the nano-sized carbon black which has a high tendency for agglomeration with 10 wt.% added sample. The decrease in the particle size with increasing the amount of carbon black is shown for all sample groups as shown in Fig. 5. Carbon black still acts as a growth inhibitor for such a high temperature like 1100 °C even though it burns out completely near 600 °C. It means that we can control the particle size by combining the amount of growth inhibitor and processing temperature. In addition, this type of material may be used as a sintering inhibitor for the preparation of porous sintered bodies which are necessary for the application of gas sensor [15] or electrode materials of solid oxide fuel cells [16]. In order to use heat treated $BaTiO_3$ particles for MLCC application in industry, in addition, neck-breaking process in mild milling condition is usually followed to remove the aggregated particles. Since one of the roles of carbon black is to minimize the solid-state reaction among particles during the heat treatment, it is not difficult to estimate that utilizing carbon black is effective in decrease the hard agglomerates of particles.

XRD patterns of as-received BT-01 and 1050 °C heat treated one without carbon black in the 44–46° of 2θ region are shown in Fig. 6. As-received BT-01 has a cubic structure, while the 1050 °C heat treated one has a tetragonal structure with the peak splitting of {2 0 0} plane in this 2θ region. Besides the tetragonality, the other useful parameter that can be obtained from the XRD data is a *K*-factor which is defined as the relative ratio of the peak intensity of (2 0 0) plane to the peak intensity

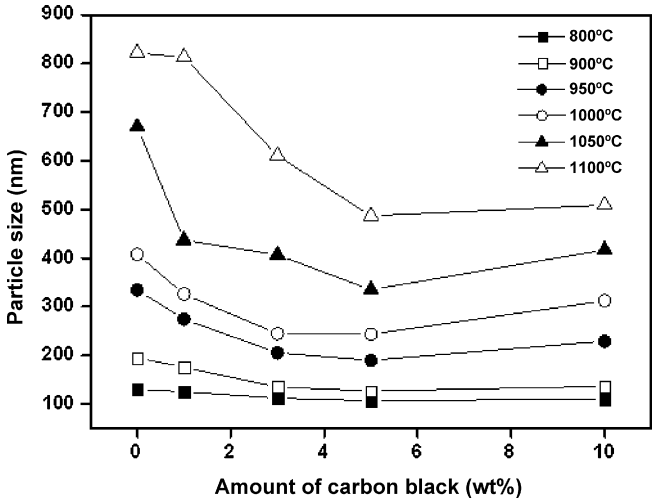


Fig. 5. Particle size of BT-01 heat treated at various temperatures with different amounts of carbon black.

of hollow between two shoulders (=$h1/h2$) in Fig. 6. *K*-factor indicates the relative ratio of tetragonal to non-tetragonal phase such as cubic and amorphous phase of the powder and it is generally used recently in industry for the purpose of $BaTiO_3$ powder characterization [17]. The MLCC industry prefers $BaTiO_3$ powders with tetragonality higher than 1.008 and a *K*-factor higher than 5.0 with the average particle size of a few hundred nanometers, especially for X5R or X7R application. It is believed that the high tetragonality results in the high dielectric constant of sintered body [17], while the high *K*-factor of the powder is required for less grain growth tendency during the sintering process [17]. The similar tendency of grain growth with different reactivity has been reported with TiO_2 system [18]. Regarding the samples heat treated at 800 and 900 °C, however, the calculation of tetragonality and *K*-factor is not favorable due to the incomplete peak separation of (0 0 2) and (2 0 0) planes regardless the amount of carbon black added.

Fig. 7 represents the XRD patterns of 950 °C heat treated powders showing various degrees of peak splitting of {2 0 0}

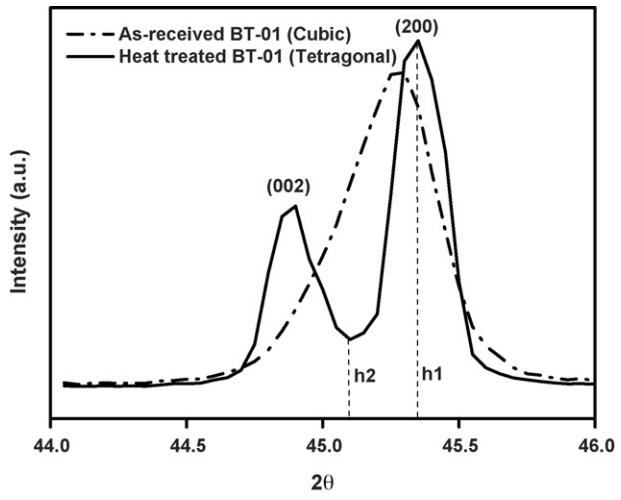


Fig. 6. XRD patterns of as-received cubic BT-01 and 1050 °C heat treated tetragonal one for $2\theta = 44–46°$.

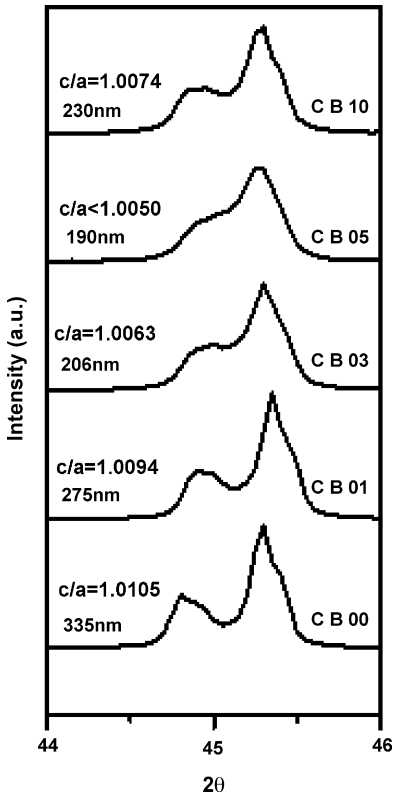
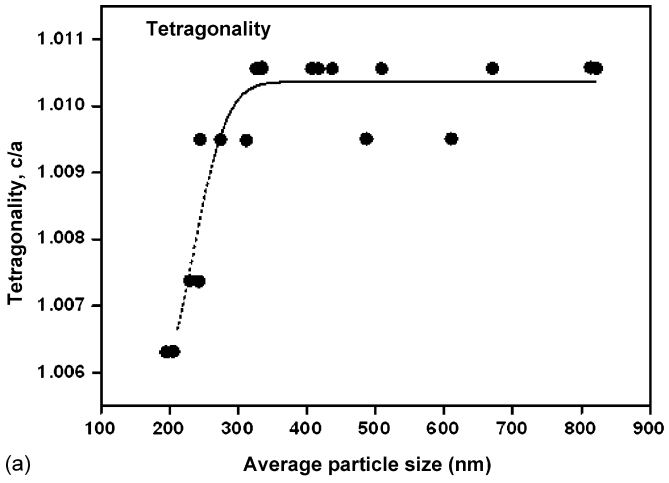


Fig. 7. XRD patterns of 950 °C heat treated BT-01 with different amounts of carbon black for $2\theta = 44–46°$. Average particle size and tetragonality are shown.

peaks with the different amounts of carbon black. By considering the degree of peak splitting in Fig. 7, one can find that the tetragonality of each sample correlates with the average particle size of the sample. The dependency of tetragonality and *K*-factor on the average particle size is demonstrated further in Fig. 8a and b. The maximum tetragonality obtainable by heat treatment is 1.0105 with the particles larger than 330 nm, and the tetragonality higher than 1.008 is obtained with BT-01 larger than 230 nm. The tetragonality of BT-01 having particle size smaller than 300 nm decreases drastically to 200 nm and cannot be measured for particles less than 200 nm because (0 0 2) peak does not show a local peak. According to Uchino et al. [5], the maximum tetragonality is 1.0095 for a single crystal which is smaller than our observation, and the tetragonality decreases with decrease in particle size. The same maximum tetragonality of 1.0105 with calcined hydrothermal powders at 1150 °C is also reported by Chen and Chen [19]. The higher tetragonality with powder than with single crystal is possible if we consider the size effect on the cell polarizability. According to Kinoshita and Yamaji [20], when $BaTiO_3$ particle size decreases from 53 to 1.1 μm, the cell polarizability increases due to the reduced tetragonal deformation which is generated by cubic to tetragonal transition. It means that a large single crystal may contain more strains and resultantly shows low tetragonality than small particle with less internal strains [21]. By decreasing the particle size further, however, the polarizability decreases because of the increased tetragonal deformation due to the high



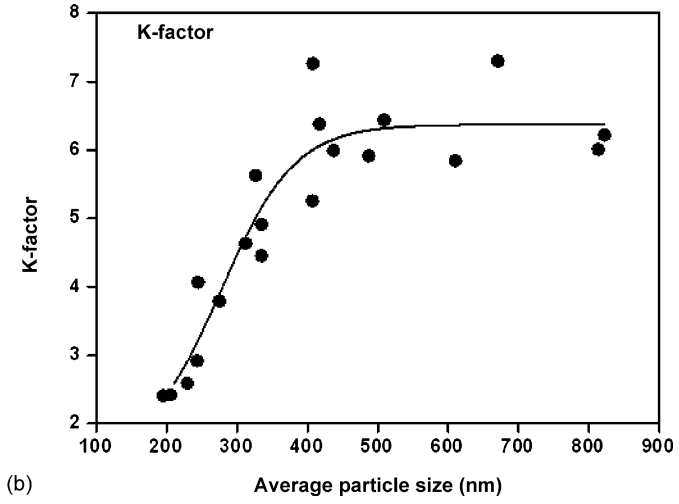


Fig. 8. (a) Tetragonality and (b) *K*-factor as a function of the average particle size of BT-01 heat treated at various temperatures.

surface area to bulk ratio [22]. The *K*-factor shows similar behavior showing a plateau with the particle size larger than 400 nm as shown in Fig. 8b. The maximum *K*-factor of these samples is 7.30, and the *K*-factor higher than 5.00 is obtained with BT-01 larger than 330 nm.

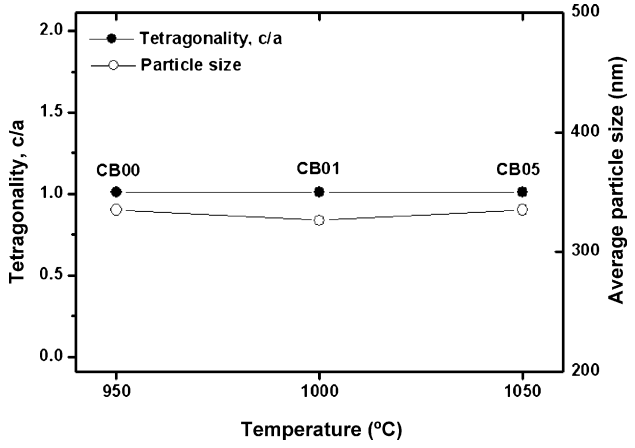


Fig. 9. Relationship between tetragonality and temperature of BT-01 having similar particle size.

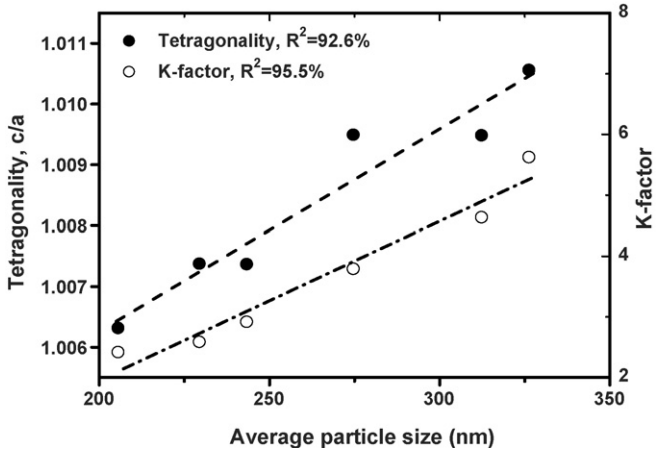


Fig. 10. Linear dependence of tetragonality and *K*-factor on the average particle size of BT-01.

In order to examine the effect of heat treatment on tetragonality at room temperature, three samples which have similar average particle sizes with different amounts of carbon black were chosen. One is the sample heat treated at 950 °C without carbon black, another is the sample treated at 1000 °C with 1 wt.% carbon black, and the third is sample treated at 1050 °C with 5 wt.% carbon black. The average particle size of these samples is between 326 and 335 nm. As shown in Fig. 9, the tetragonality of BT-01 is not a function of processing temperature for these samples with the tetragonality of 1.0105. On the other hand, both of the tetragonality and *K*-factor show almost linear relationships with the average particle size for the particles up to 330 nm as shown in Fig. 10. From these results, we may conclude that the tetragonality of heat treated hydrothermal $BaTiO_3$ larger than 330 nm does not depend on processing temperature, while it is a function of the average particle size up to 330 nm. In addition, the particles heat treated above 950 °C or with the particle size larger than 330 nm show the saturated tetragonality value of 1.0105. Even though the increase of tetragonality of hydrothermal powder is conceptually possible by offering enough thermal energy required for the defect removal, 950 °C is shown as the maximum processing temperature for this purpose.

4. Conclusions

After checking the effects of heat treatment and particle size on the tetragonality of hydrothermal $BaTiO_3$ by adding a particle growth inhibitor, the following trends were observed:

(1) Carbon black was an efficient particle growth inhibitor during heat treatment; 335 nm of particle size of $BaTiO_3$ heat treated at 950 °C decreased to 190 nm by adding 5 wt.% of carbon black. Therefore, the controlling of particle size was possible by varying the amount of carbon black and the processing temperature.
(2) Tetragonality increased linearly with the average particle size up to 330 nm, and did not depend on the processing temperature above 950 °C. This suggested that 950 °C was

the maximum temperature for the enhancement of the tetragonality of hydrothermal $BaTiO_3$, although the increase of tetragonality was conceptually possible by offering thermal energy required for the defect removal.

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