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Properties of $BaTiO_3$ synthesized from barium titanyl oxalate

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Abstract

In order to enhance the tetragonality of $BaTiO_3$ derived from barium titanyl oxalate (BTO), various treatments were carried out by considering the thermal decomposition mechanism of BTO in air. A multi-step heat treatment process and the addition of carbon black, as a particle growth inhibitor, were effective in increasing the tetragonality, whilst maintaining a particle size smaller than 200 nm. The synthesized $BaTiO_3$ powder with a mean particle size of 177 nm showed a tetragonality and *K*-factor of 1.0064 and approximately 3, respectively.

Keywords: A. Firing; C. Dielectric properties; D. $BaTiO_3$ and titanates; E. Capacitors

1. Introduction

Barium titanate ($BaTiO_3$) with a tetragonal phase shows a high dielectric constant of several thousand, while the cubic phase exhibits paraelectric properties with a much smaller value [1]. $BaTiO_3$ particles generally undergo a tetragonal-to-cubic phase transition at the Curie point, which is most often located at 120–130 °C. However, this temperature decreases with decreasing particle size, and only the cubic phase is eventually stabilized under a critical particle size due to the 'size effect' [2,3]. On the other hand, the multi-layer ceramic chip capacitor (MLCC) industry prefers to use very fine $BaTiO_3$ particles with a high dielectric constant to enhance the volumetric efficiency. Therefore, many studies have attempted to increase the dielectric constant of this powder whilst maintaining a particle size as small as possible [4–8].

The dielectric constant is generally measured using a sintered body, where the dielectric properties of the powder can vary during the sintering process. Therefore, an indirect method using the XRD pattern has been used to estimate the dielectric constant of particles [9]. Fig. 1 shows a typical XRD pattern of cubic and tetragonal $BaTiO_3$ in the 2θ range of 44–46° region. Cubic $BaTiO_3$ shows a single peak due to the symmetry of the lattice, while the tetragonal one shows peak splitting of the {2 0 0} plane in this region. In order to achieve a high dielectric constant, the crystal structure should have high tetragonality, which is defined as the relative *c*- to *a*-axis ratio (=*c*/*a*). Besides the tetragonality, another useful parameter that can be obtained from the XRD pattern is the *K*-factor, which is defined as the relative ratio of the peak intensity of the (2 0 0) plane to the peak intensity of the hollow between the two shoulders (=h1/h2), as shown in Fig. 1. The *K*-factor indicates the degree of crystallinity which is the relative ratio of the tetragonal to disordered phase of the powder. The MLCC industry prefers $BaTiO_3$ powders with a particle size <200 nm with high tetragonality and *K*-factor due to the resulting high dielectric constant and lower tendency for grain growth during the sintering process for a high capacitance X5R or X7R application [9,10].

However, all the reports showed a difference in the critical particle size for the tetragonal-to-cubic transition of $BaTiO_3$. This was explained by the different elastic strain energy, which is associated with the free surface, chemical impurities and crystalline defects levels [11]. According to the phenomenological surface layer model proposed to explain the phase transition [12], $BaTiO_3$ particles consist of a surface cubic layer, a tetragonal core and a gradient lattice strain layer (GLSL) between the two layers. Based on theoretical calculations, the thickness of the surface cubic layer can be reduced to approximately 10 nm [13,14]. Therefore, tetragonal $BaTiO_3$ particles with several tens of nanometers in size may be synthesized by minimizing the content of internal defects and impurities as well as by maximizing the degree of crystallinity. Heat treatment at high temperatures can be considered as one of

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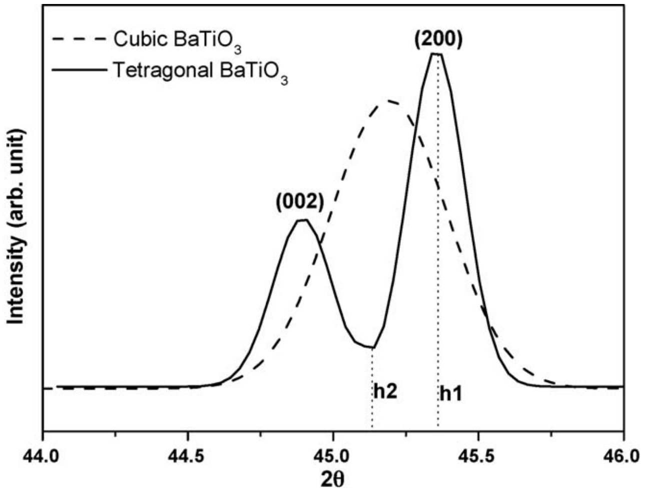

Fig. 1. Typical XRD patterns for cubic and tetragonal $BaTiO_3$ for $2\theta = 44–46^\circ$.

the best methods for increasing the crystallinity by reducing the number of lattice defects. However, this process also causes hard agglomeration and particle growth. In order to minimize these side effects, a particle growth inhibitor, such as carbon black and corn starch, can be considered. It retards particle growth during heat treatment due to the generated gas phase which increases the distance among particles.

This study examined the effects of temperature and heating profiles on the $BaTiO_3$ particle size and tetragonality using barium titanyl oxalate (BTO) as a starting material. The effect of carbon black addition as a particle growth inhibitor on the above output responses was also investigated.

2. Experimental procedure

Barium titanyl oxalate (BTO: $BaTiO(C_2O_4)_2{\cdot}4H_2O$) was obtained from a commercial $BaTiO_3$ powder manufacturing company. The Ba/Ti atomic ratio of the material was 1.001. Three hundred grams of BTO mixed with 450 g of ethanol were milled using a high-energy mill (MiniCer, Netzsch, Germany) for 7 h at a rotor speed of 3000 rpm with 0.45 mm ZrO_2 beads after adding 1 wt.% of a dispersant (BYK-103, BYK Chemie, USA). A small amount of sample was taken at a planned time for the characterization. Thermo-gravimetric with differential thermal analysis (TG/DTA: SDT Q600, TA Instruments, USA) was performed using 20 mg of the un-milled and 7 h-milled BTO in a flowing air atmosphere at a heating rate of 5 °C/min.

Heat treatment was carried out using the 7 h-milled BTO from 800 to 1200 °C for 1 h at a heating rate of 5 °C/min. In order to check the effect of the holding temperature on powder properties, a 2- and 3-step heat treatment process was performed at the selected temperatures, simultaneously. The 2-step heat treatment was performed by holding the temperature at 500 °C for 1 h, while the temperature was held at 500 and 800 °C for 1 h each for the 3-step treatment process before heating to the target temperature. The holding temperature was selected according to the BTO decomposition mechanism based on the TG/DTA results. In addition, 5 wt.% carbon black (HIBLACK 20L, $D_{mean} = 28$ nm, Shin Woo Materials, Korea) was added as a particle growth inhibitor, and the same heat treatments were performed.

The particle shape, and crystal structure and tetragonality were determined by scanning electron microscopy (SEM: S-4100, Hitachi using 10 kV and a working distance of 5–8 mm) and X-ray diffraction (XRD: RINT 2200, Rigaku using Cu Kα line, 40 kV and 100 mA), respectively. The average particle size was estimated from the SEM images by measuring the maximum and minimum diameter of 100 particles using image analyzing software (SigmaScan, Systat Software, USA).

3. Results and discussion

Fig. 2 shows the SEM images of the (a) as-received and (b) 7 h of high-energy milled BTO. According to the evolution of BTO size as a function of milling time shown in Fig. 2(c), there was a continuous decrease in the mean particle size to 85 nm from the coarse as-received one. The size of the BTO particles decreased rapidly up to 3 h of milling with no further significant decreases observed between 3 and 7 h of milling time. Since $BaTiO_3$ is formed by the decomposition of BTO, it can be anticipated that fine BTO is more desirable for producing small $BaTiO_3$ particles. Moreover, a higher BTO decomposition rate with high-energy milled BTO can be expected at lower temperatures than that without milling due to mechanochemical activation [15].

Fig. 3 shows the TG/DTA results for the un-milled and 7 h of high-energy milled BTO in air. Obvious weight losses were observed at temperatures ranging from room temperature (RT) to 225 °C, 225 to 600 °C, and 600 to 750 °C, which are characterized by strong endothermic, exothermic and endothermic reactions, respectively, under both milling conditions. The overall DTA peak for BTO after 7 h milling for temperature higher than 450 °C showed a temperature decrease by 10–30 °C than that without milling due to mechanochemical activation. Although there is some controversy regarding the formation of $BaCO_3$ as an intermediate phase during BTO decomposition [16], many researchers adopt the decomposition mechanism proposed by Murthy et al. [17], which can be divided into three steps as follows:

$$(1)\ BaTiO(C_2O_4)_2 \cdot 4H_2O \xrightarrow{RT-225\,^\circ C} BaTiO(C_2O_4)_2 + 4H_2O$$

$$(2)\ 2BaTiO(C_2O_4)_2 \xrightarrow{225-600\,^\circ C} Ba_2Ti_2O_5(CO_3) + 3CO_2 + 4CO$$

$$(3)\ Ba_2Ti_2O_5(CO_3) \xrightarrow{600-750\,^\circ C} 2BaTiO_3 + CO_2$$

Based on the comparison between the experimentally observed and theoretically calculated weight losses, both were quite consistent for the above three steps.

Fig. 4(a) shows the mean particle size of synthesized $BaTiO_3$ as a function of the heat treatment temperature between 800 and 1200 °C for 1 h. The mean particle size increased gradually with increasing temperature from 119 at 800 °C to 438 nm at 1200 °C. The mean $BaTiO_3$ size synthesized from un-milled BTO was 555 nm after heat treatment at 1000 °C, which is much bigger than 178 nm with 7 h of high-energy milled BTO

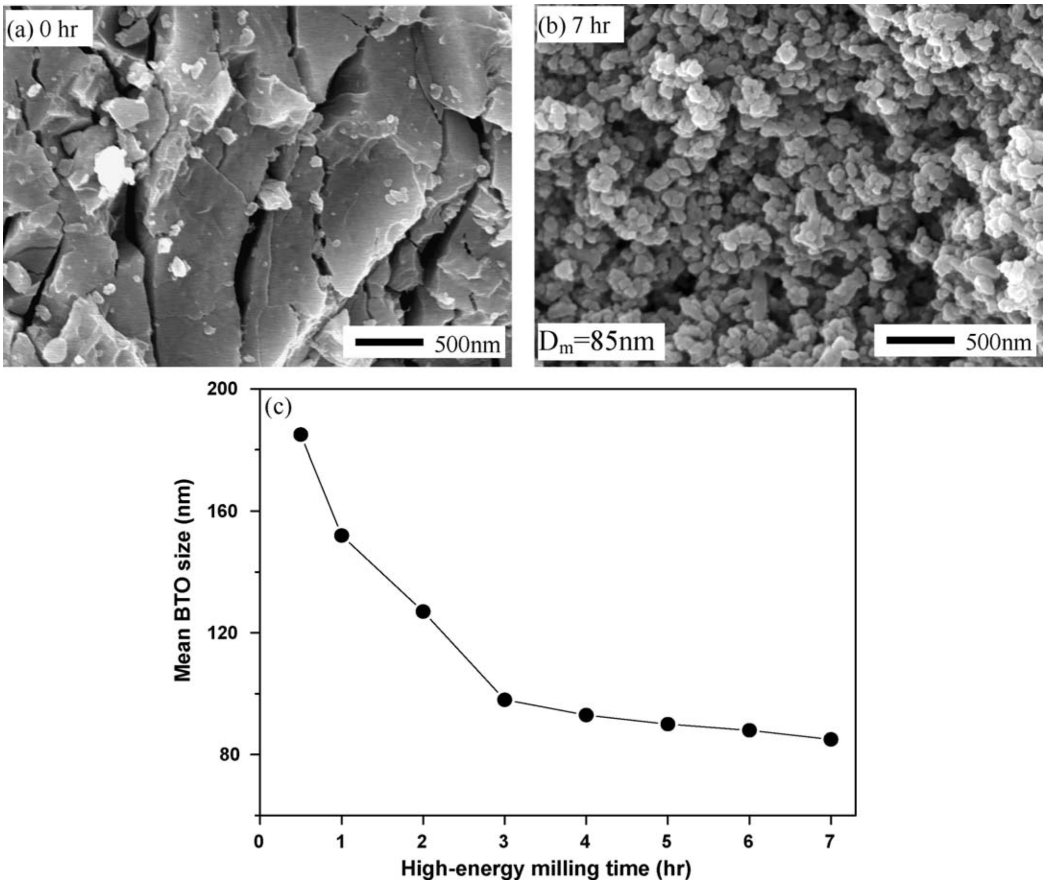

Fig. 2. SEM micrographs of (a) as-received and (b) 7-h milled BTO. The mean BTO size as a function of the milling time is shown in (c).

at the same heat treatment temperature, indicating the importance of milling in acquiring fine particles. According to the XRD patterns for the synthesized powder (not shown here), BTO had completely transformed to $BaTiO_3$ at 800 °C, which is consistent with the TG/DTA results shown in Fig. 3. However, the $BaTiO_3$ synthesized at temperature up to 900 °C was mainly a cubic phase with only one Gaussian {2 0 0} peak at $2\theta = 45^\circ$ as shown in Fig. 4(b). The tetragonal phase with peak splitting in this region began to form at temperature >1000 °C. The *c*/*a* ratio was 1.0064 and 1.0084 after heat treatment at 1100 and 1200 °C, respectively, where the particle size exceeds 200 nm.

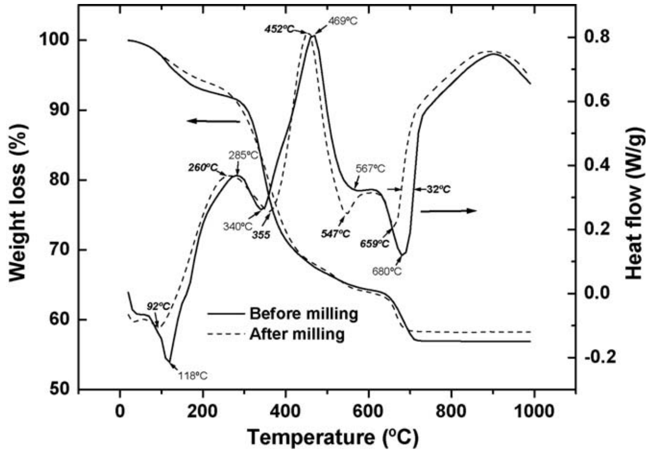

Fig. 3. TG/DTA results of the un-milled and 7-h high-energy milled BTO in air.

According to the TG results shown in Fig. 3, there was a rapid decrease in the BTO weight at approximately 400 and 700 °C under flowing dry air conditions. Since the reaction temperature for a large batch would be higher than that observed under TG conditions, 500 and 800 °C were chosen as the holding temperatures for the step treatment. By holding at these temperatures, there was sufficient time to enhance the decomposition of BTO and formation of $BaTiO_3$ crystallites. Fig. 5 shows the synthesized $BaTiO_3$ morphology at 1000 °C using the different heating profiles. The results show a slight increase in particle size with increasing number of holding steps. At the same time, the tetragonality was also increased with a *c*/*a* ratio of 1.0063 and 1.0065 for the 2- and 3-step heat treatments, respectively, while the tetragonality for $BaTiO_3$ with the 1-step heat treatment could not be calculated, as shown in Fig. 6. In particular, a tetragonality higher than 1.006 was obtained for the particle size less than 200 nm using a multi-step heat treatment process. This is comparable to that of the 1-step heat treatment process at 1100 °C with a particle size of 259 nm, as shown in Fig. 4. The increase in tetragonality with decreasing particle size indicates that the multi-step heat treatment enhances the crystallization of $BaTiO_3$ and decreases the internal strain within the framework of the phenomenological surface layer model [12].

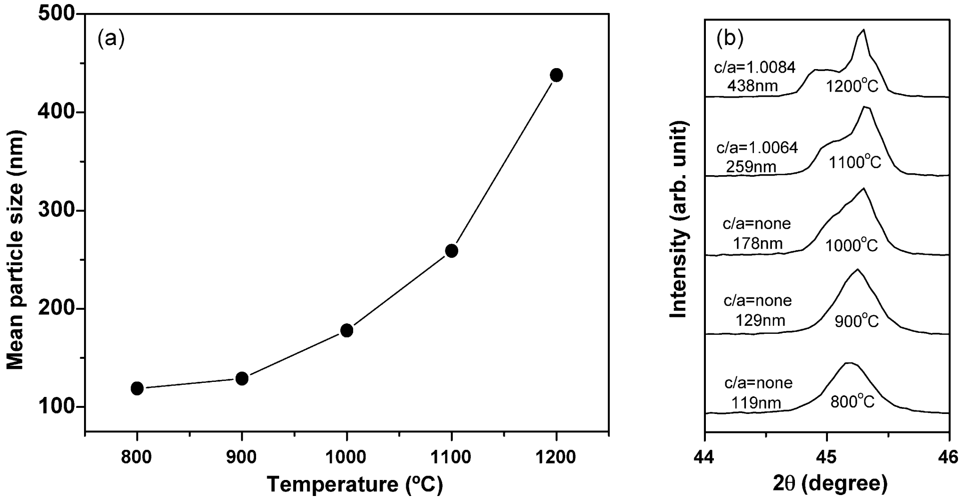

Fig. 4. (a) Mean particle size of $BaTiO_3$ as a function of the temperature and (b) XRD patterns at 44–46° of 2θ showing the peak splitting of {2 0 0}.

Heat treatment at high temperature would be effective in increasing the crystallinity of a fine powder by eliminating defects. However, hard agglomeration and particle growth would occur, which are not desirable for practical applications. In order to minimize these side effects, 5 wt.% carbon black was added to the BTO. When carbon black burns out, it generates a gas phase that hinders particle growth by separating the particles. Therefore, it acts as a particle growth inhibitor. Fig. 7(a) shows the SEM morphology of the nm-sized carbon black and (b) the TGA results, showing a negligible amount of residue at 600 °C.

Fig. 8(a) and (b) shows the XRD peaks at 44–46° of 2θ for the carbon black-added $BaTiO_3$ and the $BaTiO_3$ without carbon black addition after heat treatment at 1000 and 1100 °C, respectively. The CB in the figure denotes the addition of 5 wt.% carbon black, while the mean particle size and tetragonality are shown for the different heating profiles. At both temperatures, the size of the particles after addition of the particle growth inhibitor was significantly decreased compared to that of the particles without the carbon black: from 178 to 133 nm at 1000 °C, and 259 nm to 173 nm at 1100 °C, highlighting the effectiveness of carbon black as a particle growth inhibitor. The mean particle size with carbon black was increased slightly by increasing the number of holding steps at a fixed temperature, which can explain the prolonged heating time. The tetragonality of the powders heat-treated at 1000 °C

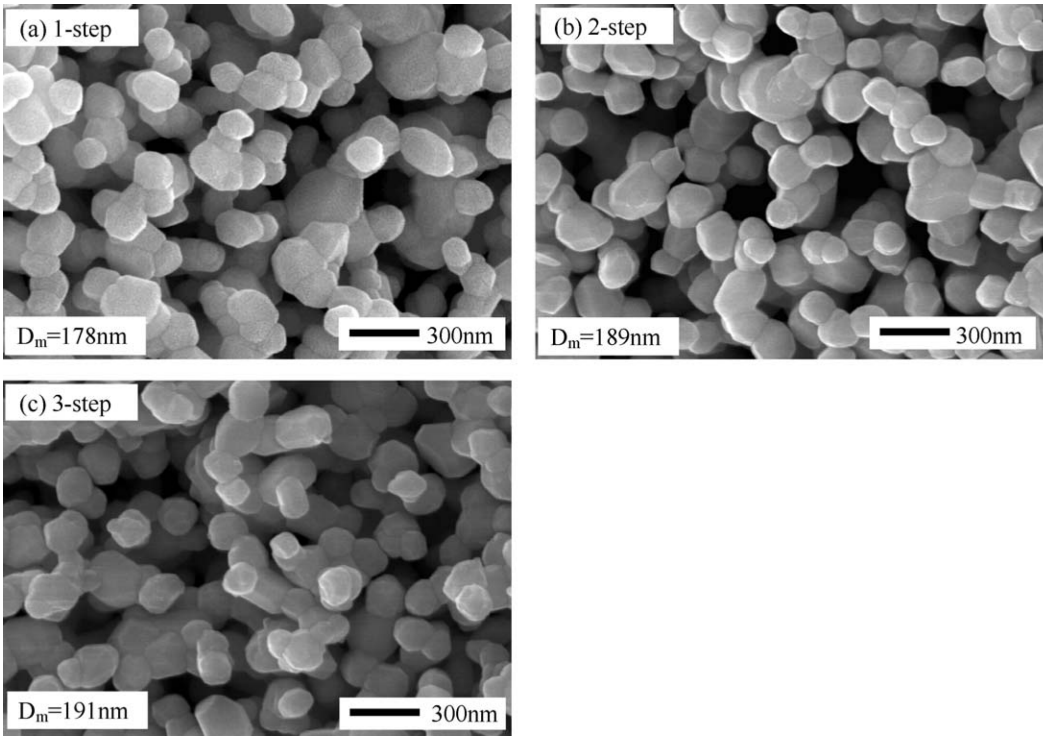

Fig. 5. SEM morphology of $BaTiO_3$ heat-treated at 1000 °C using different heating steps. The mean particle size is shown.

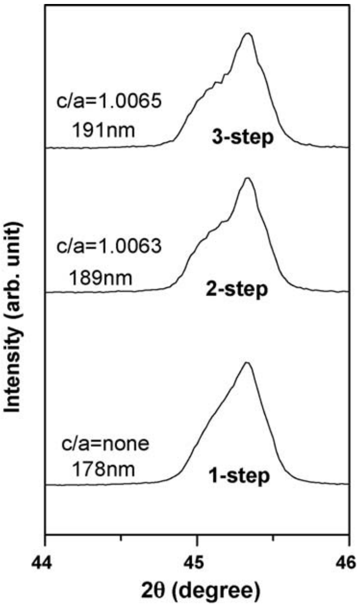

Fig. 6. XRD patterns of $BaTiO_3$ showing peak splitting at 44–46° of 2θ with different steps heat-treated at 1000 °C.

could not be measured from the XRD patterns regardless the addition of carbon black, as shown in Fig. 8(a). On the other hand, all samples heat-treated at 1100 °C showed peak splitting, as shown in Fig. 8(b). In particular, the $BaTiO_3$ powder produced from the 3-step heat treatment process after adding carbon black showed similar tetragonality of 1.0064 to that without carbon black, even though the particle size had decreased from 259 to 177 nm. The *K*-factors for these samples were less than 3.

Two observations can be made from the above results. One is that the heating steps after considering the BTO decomposition mechanism can enhance the degree of tetragonality due to the sufficient time for BTO decomposition and $BaTiO_3$ crystallite formation. The second is that the utilization of a particle growth inhibitor enhances the tetragonality whilst maintaining the small particle size of $BaTiO_3$. Therefore, heat treatment at higher temperatures, which is effective in increasing the tetragonality, is possible using a particle growth inhibitor.

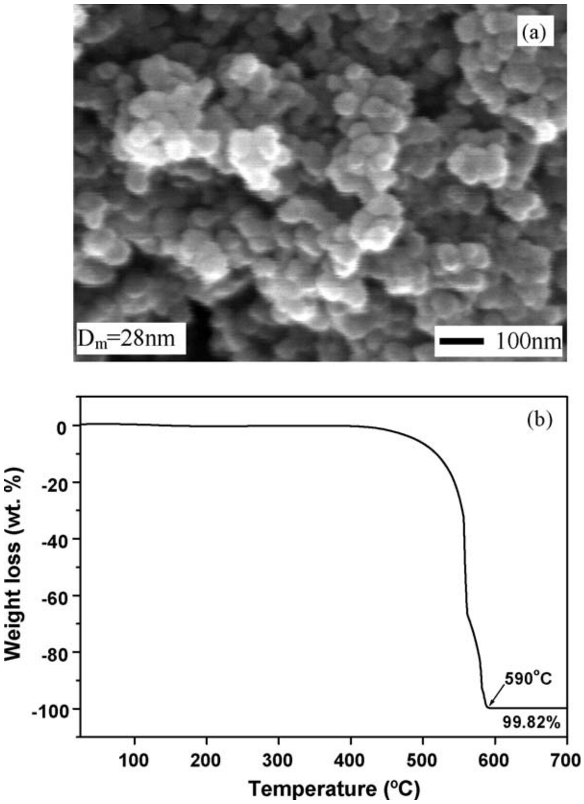

Fig. 7. (a) SEM micrograph and (b) TG results of carbon black used as a particle growth inhibitor.

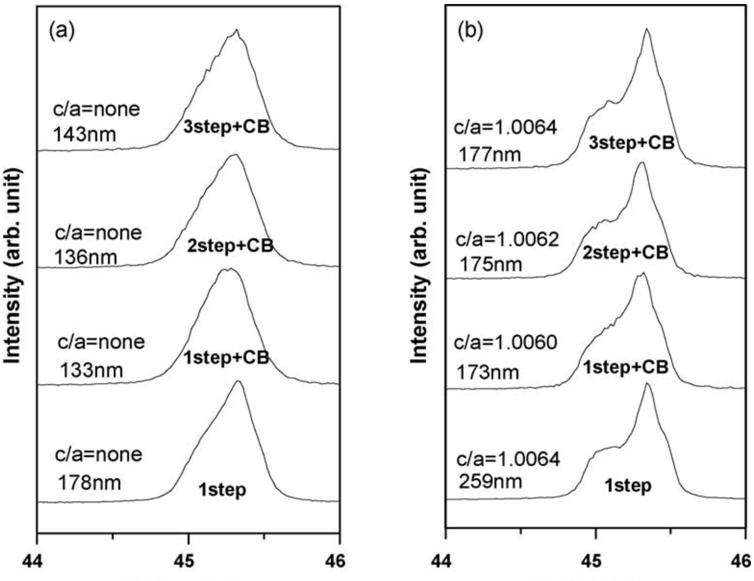

Fig. 8. XRD peak splitting of $BaTiO_3$ heat-treated using the particle growth inhibitor and different heating steps for a maximum temperature of (a) 1000 °C and (b) 1100 °C.

4. Conclusions

In this study, a multi-step heat treatment and the addition of 5 wt.% carbon black as a particle growth inhibitor were used to increase the tetragonality of $BaTiO_3$ synthesized from barium titanyl oxalate but maintain a particle size under 200 nm. The conventional 1-step heat treatment without the particle growth inhibitor did not show peak splitting of the {2 0 0} peak due to the main cubic phase at the particle size smaller than 200 nm. On the other hand, multi-heating steps considering the BTO decomposition mechanism and the addition of carbon black were effective in increasing the teragonality. The *c*/*a* ratio of 1.0064 along with a *K*-factor of approximately 3 was obtained for a particle size of 177 nm using the above methods.

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