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Synthesis and characteristics of near-stoichiometric barium titanate powder by low temperature hydrothermal reaction using titanium tetra(methoxyethoxide)

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Near-stoichiometric $BaTiO_3$ powders with ultrafine particle size and high crystallinity were prepared by low temperature hydrothermal reaction of $Ba(OAc)_2$ and $Ti(OCH_2CH_2OCH_3)_4$. $BaTiO_3$ particles were synthesized in the spherical, metastable cubic crystalline grains with size distribution between 60–90 nm in diameter. Ultrafine particle size was resulted from the control of the hydration rate and the decrease of Ti-O-Ti cross-linking extent of titanium precursor, $Ti(OCH_2CH_2OCH_3)_4$, which gives electronic, steric, and weakly chelating effect to titanium ion. Increasing the Ba/Ti mole ratio in reactant could not overcome the notorious Ba-deficiency but, improved stoichiometry and produced finer and less agglomerated particles. Interestingly, adding a slight pressure to autogeneous hydrothermal condition (total 4–10 atm) has yielded near-stoichiometric, highly crystalline, and less agglomerated $BaTiO_3$ particles. These particles, which were in metastable cubic form as synthesized, initiated phasetransition to tetragonal form by calcination at below 400 °C. © *2000 Kluwer Academic Publishers*

1. Introduction

Preparation of ultrafine and monodispersed $BaTiO_3$ powder with precisely controlled stoichiometry ($Ba/Ti = 1$) has been of great concern due to its high electronic applications. Commercial $BaTiO_3$ is usually synthesized by solid state reaction [1–3] of $BaCO_3$ and TiO_2 at high temperature (∼1200 °C) or by chemical precipitation processes [4–6] that need a calcination step at relatively high temperature (700–800 °C). $BaTiO_3$ powders prepared from these methods result in limited size scale, microstructural variations, non-stoichiometric compositions, and poor electrical reproducibility. Thus the current trend of device miniaturization in the electronics industry is quite limited by these methods. A chemical method, hydrothermal synthesis [7–9] of $BaTiO_3$ powder has been developed because of the advantage of getting crystalline powders directly from solution at temperatures far below the required for conventional powder preparation. It is well known that hydrothermal reaction using TiO_2 as a Ti-precursor needs still relatively high reaction temperature (380–500 °C) and high pressure (300–500 atm) as well as long reaction time. These conditions make it difficult to control the particle size and its distribution precisely. For this method to be useful for chemical industry, temperature should be less than 200 °C, so that the conventional reactor technology can be utilized. Also is desirable short period of reaction time and moderate pressure for commercial production.

Low temperature hydrothermal reaction [10–13] that uses short period of time, autogeneous pressure, and reactive Ti-precursor has been developed and can be a plausible candidate for chemical industry. The major difficulties in this process are to slow down hydrolysis rate and to avoid very fast and spontaneous self-condensation between Ti-OH groups. Without control of these difficulties, this process leads to large and polydispersed particles in size. Besides that, very rapidly forming Ti-O-Ti cross-linking may result in the phase segregation of TiO_2 and $BaTiO_3$. Chelating organic ligands such as glycols, organic acid, or β-diketones [14] have been tried to control the Ti-O-Ti cross-linking formations but, they need more vigorous reaction conditions than simple titanium alkoxides as well as high heat treatment above 700 °C to remove organic residues completely. So a Ti-precursor with moderate hydrolysis

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rate can be a useful alternative. Another notorious difficulty of low temperature hydrothermal process is to control Ba/Ti stoichiometry, that is, to overcome Ba-deficiency in $BaTiO_3$. Stoichiometric $BaTiO_3$ is important to get high density and high dielectric electronic materials [15, 16].

In this study is reported near-stoichiometric, highly crystalline, and ultrafine $BaTiO_3$ preparation by low temperature hydrothermal reaction using $Ba(OAc)_2$ and $Ti(OCH_2CH_2OCH_3)_4$, which has a moderate hydrolysis rate. The thermal characteristics of the synthesized particles were also investigated.

2. Experimental procedure

2.1. Materials

Degassed mili-Q plus water and nitrogen atmosphere were used throughout all the procedures. $TiCl_4$ (Aldrich, 99.9%) was used without further purification and $Ti(OCH(CH_3)_2)_4$ (Aldrich, 97%) was used after distillation under reduced pressure. 2-Methoxyethanol (Kanto Chem. Co., 99%) and 2-propanol (Kanto Chem. Co., 99.5%) were distilled according to the standard method. NH_3 (Daehan Gas Co., Seoul, Korea, 99.9%) was passed through several drying tubes filled with NaOH pellets. $Ba(OAc)_2$ (Junsei Chem. Co., 99%) and NaOH (Kanto Chem. Co., 97%) were filtered after dissolution to remove insoluble impurities.

2.2. Synthesis of $Ti(OCH_2CH_2OCH_3)_4$

$Ti(OCH(CH_3)_2)_4$ was added to excess (>4 equivalent) 2-methoxyethanol under nitrogen atmosphere. After stirring for an hour, $Ti(OCH_2CH_2OCH_3)_4$ was fractionally distilled under reduced pressure. Yield 96%. Another method [17] for the synthesis of $Ti(OCH_2CH_2OCH_3)_4$ used $TiCl_4$ NH_3, and 2-methoxyethanol as the starting materials. Yield 70%. ^1H NMR (0.70 M in C_6D_6, ppm): 4.542(t, 5.4 Hz); 3.535(t, 5.4 Hz); 3.237(s), Proton decoupled ^{13}C NMR (0.70 M in C_6D_6, ppm): 72.68, 68.80, 56.74, IR spectrum of $Ti(OCH(CH_3)_2)_4$ was taken as a thin film between NaCl windows and is shown in Fig. 1a.

2.3. Hydrolysis of Ti-precursor

Each Ti-precursor was added to large excess of water with vigorous stirring. This solution was stirred for 30 more minutes before the separation of the solid residue by centrifugation and decantation. To investigate the hydrolysis behavior of $Ti(OCH_2CH_2OCH_3)_4$ precursor in NaOH solution, the solid residue was separated from the mixed solution just before hydrothermal treatment in the synthetic process of $BaTiO_3$ (*vide infra*). The solid residues were dried at 60 °C in a vacuum oven overnight and sampled as disk specimen mixed with KBr to obtain IR spectra.

2.4. Synthesis of $BaTiO_3$

$Ti(OCH_2CH_2OCH_3)_4$ in 4eq. 2-propanol was added to 1 M $Ba(OAc)_2$ aqueous solution with vigorous stirring.

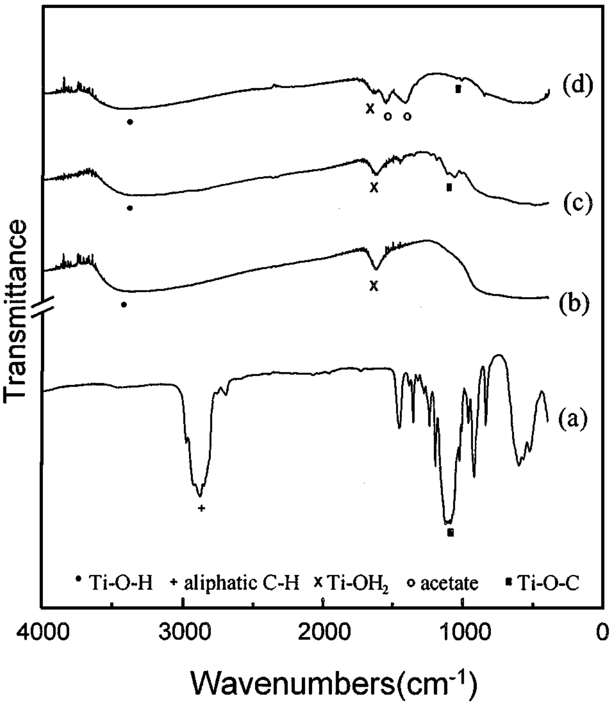


Figure 1 FT-IR spectra of Ti-precursors: (a) $Ti(OCH_2CH_2OCH_3)_4$, (b) hydrolyzed $Ti(OCH(CH_3)_2)_4$, (c) hydrolyzed $Ti(OCH_2CH_2OCH_3)_4$, (d) as precipitated powder from the mixture of $Ti(OCH_2CH_2OCH_3)_4$ and $Ba(OAc)_2$ in NaOH solution.

The combined solution was stirred for 30 more minutes for homogeneous mixing. Meanwhile, NaOH solution (1 M in the final mixture, pH > 13.5 [18]) was prepared in a PTFE lined stainless steel autoclave with stirring and heating equipment. The mixed solution was poured into the autoclave and underwent a hydrothermal reaction. The reaction variables were the time (10 min–18 hr), the temperature (60–100 °C), the pressure (autogeneous 10 atm), the concentration (0.05–0.20 M), and the Ba/Ti mole ratio (1.0–2.5) of the reactants. After the hydrothermal reaction was done, the reacted solution was cooled down in a cold water bath and washed with ammonia water of pH 10 three times using centrifugation and decantation. Then the solid product was dried at 80 °C in a vacuum oven for 12 hours. Some particles were calcined for 1 hour at various temperatures (400–1200 °C) under moisture free air using a box furnace.

2.5. Characterization

Titanium precursor and its hydrolyzed solid were characterized by FT-IR (Nicolet Magna 750) and NMR (Varian 200 MHz) spectrophotometers. Surface morphology of $BaTiO_3$ particles was measured by FE-SEM (Hitachi S-4200). Each specimen was sensitized with Au-sputtering to avoid charging during SEM analysis. The crystalline structure of $BaTiO_3$ particles was determined by XRD (Shimadzu XRD-6000 or Rigaku Miniflex) analysis using Cu K_α radiation. FT-IR spectra were obtained using a single beam spectrometer (Nicolet Magna 750). The transmission spectra were collected for disk specimen mixed with KBr. Raman spectra were obtained using Perkin-Elmer

System 2000. Thermogravitational analysis was carried out via a TGA system (TA 2960). Elemental analysis of $BaTiO_3$ powders was performed by ICP spectroscopy.

3. Result and discussion

3.1. Hydrolysis behavior of Ti-precursors

FT-IR spectra are shown in Fig. 1 to compare the hydrolysis behaviors of Ti-precursors. Peaks at 1,020–1,125 cm^{-1} correspond to Ti-*O*-*C* stretching vibrations. Intensity decrease and/or disappearance of these peaks is related to the partial and/or complete hydrolysis of titanium precursors (Fig. 1c and d vs. b). A broad band around 3,400 cm^{-1} and a strong peak at 1,648 cm^{-1} corresponding to Ti-*O*-*H* stretching and *HOH* bending vibration of $Ti\text{-}OH_2$ appeared after hydrolysis of titanium precursors (Fig. 1b–d). Aliphatic *C*-*H* stretching vibrations near 2,900 cm^{-1} should remain partially, but are hidden by the broad Ti-*O*-*H* band in Fig. 2c and d. Because of methoxy substituent, methoxyethoxide can have electronic, steric, and weakly chelating effects around titanium ion so that it makes stronger bond with titanium ion than simple alkoxide (linear alkoxide with C_1C_4 and isopropoxide). This has appeared as the partial hydrolysis of $Ti(OCH_2CH_2OCH_3)_4$ as a comparison with the case of $Ti(OCH(CH_3)_2)_4$, which underwent complete hydrolysis at the same condition (Fig. 1c vs. b). Methoxyethoxide groups were still partially retained even in as-precipitated powder (d), which was obtained after addition of the mixture of $Ti(OCH_2CH_2OCH_3)_4$ and $Ba(OAc)_2$ aqueous solution to KOH solution.

These results suggest that the partial and slow hydrolysis of $Ti(OCH_2CH_2OCH_3)_4$ precursor reduce Ti-O-Ti cross-linking extent greatly during $BaTiO_3$ synthesis. Conversely will increase the possibility of getting a homogeneous solution at atomic level by mixing of $Ti(OCH_2CH_2OCH_3)_4$ and $Ba(OAc)_2$ in aqueous solution.

The major difficulties in low temperature hydrothermal process including commercially available simple Ti-precursors are to slow down hydrolysis rate, to avoid very fast and spontaneous self-condensation between Ti-OH groups, and to reduce Ti-O-Ti cross-linking degree. Without control of these difficulties, this process leads to large and polydispersed particles in size and to the phase segregation of TiO_2 and $BaTiO_3$ [11, 19]. Using Ti-precursor containing strongly chelating organic ligands [14, 20, 21], which is not hydrolyzed in aqueous solution, would require higher reaction temperature than using simple Ti-precursors and need a post-heat treatment to remove organic residues. The stronger chelating power necessitates the higher reaction temperature and the higher post-heat treatment temperature. Therefore, a Ti-precursor with moderate hydrolysis rate would play a key role in the synthesis of ideal $BaTiO_3$ powder.

For the reasons mentioned above, we reasoned that low temperature hydrothermal reaction using $Ti(OCH_2CH_2OCH_3)_4$ as a titanium precursor may lead to homogeneous and pure $BaTiO_3$ crystalline powder with rather uniform and fine particle size. The case was found to be true as is shown in the following.

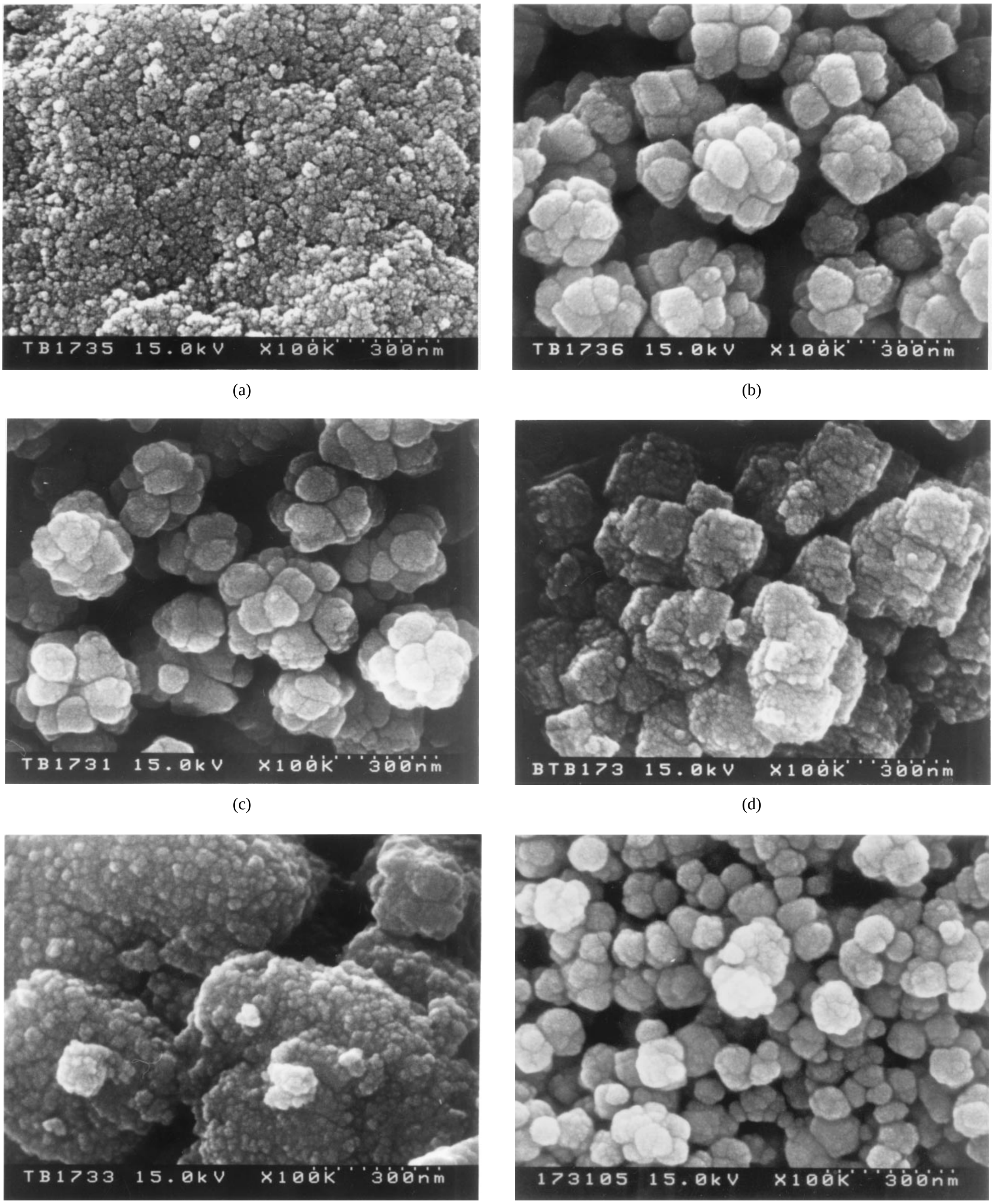
3.2. Effect of hydrothermal reaction conditions on particle characteristics

The threshold temperature for the complete conversion to $BaTiO_3$ crystalline powder was determined by treating 0.12 M ($Ba/Ti = 1$) feedstock suspensions at various temperatures for 18 hours under autogeneous pressure. XRD study showed that all the reactions produced cubic crystalline $BaTiO_3$ except the reactions treated at 60 °C, which came out as amorphous solids. SEM micrographs showed no distinguishable relationship between the reaction temperature (in a region 100 °C $\geq$ Temperature $\geq$ 70 °C) and the particle sizes. Fig. 2d shows a typical SEM micrograph of $BaTiO_3$ particles prepared at 80 °C. All $BaTiO_3$ particles prepared at 70–100 °C had a typical morphology, the fused ternary aggregates made of spherical secondary aggregates, which were around 200 nm and composed of many tiny primary grains 20–30 nm in diameter.

The effect of the reaction time on particle characteristics was investigated by treating 0.12 M ($Ba/Ti = 1$) feedstock suspensions for various times at 80 °C under autogeneous pressure. Fig. 3 shows XRD patterns. Cubic $BaTiO_3$ powders started to form from the time between 10 and 20 minutes. There was no further noticeable change in crystallinity after 1 hour. Fig. 2a–d show the selected SEM micrographs. Each particle is composed of small grains of 20–30 nm in diameter and is weakly agglomerated to make a large aggregate. Each particle is spherical shaped and begins to grow after 1 hour. The longer the reaction time, the larger the particle size grows as is known in the usual hydrothermal reaction. Combining the SEM results with XRD patterns, the optimal temperature and time for the reaction seem to be 80 °C and 1 hour.

The optimal concentration range was studied by treating various concentrations of feedstock suspensions at 80 °C for 1 hour and 18 hours under autogeneous pressure. As shown in Fig. 4 for 1 hour treatment, only 0.12 and 0.20 M suspensions produced pure cubic crystalline $BaTiO_3$ powders. Highly diluted solutions required the longer reaction time for the conversion to crystalline form. Fig. 2c and f indicate that particles were spherical and 0.20 M product was less agglomerated. On the other hand, all the suspensions treated for 18 hours gave pure cubic crystalline $BaTiO_3$ powders but, the particle morphology was not desirable as shown in Fig. 2d and e. Therefore, the optimal concentration is 0.20 M for 1 hour reaction at 80 °C. The more concentrated solutions needed the shorter reaction time and produced the finer and mono-dispersed particles in size. This reflects the kinetic aspects of crystallization and agrees well with the general hydrothermal reactions.

From above results, the effect of reaction conditions on particle size and size distribution can be summarized as follows. At a fixed temperature and concentration, the longer reaction time gave the larger and non-uniform particles. The optimum concentration range to complete the reaction within an hour at 80 °C was



(a) (b) (c) (d) (e) (f)

Figure 2 SEM micrographs of $BaTiO_3$ prepared at different reaction conditions: (a) 0.12 M, 80°C, 10 min; (b) 0.12 M, 80°C, 20 min; (c) 0.12 M, 80°C, 1 hr; (d) 0.12 M, 80°C, 18 hr; (e) 0.05 M, 80°C, 18 hr; (f) 0.20 M, 80°C, 1 hr.

0.12–0.20 M. The more concentrated solutions gave the finer and more uniform particles and needed the shorter period of reaction time for the complete conversion to crystalline $BaTiO_3$. Therefore the optimal condition for hydrothermal reaction under autogeneous pressure was chosen as 0.20 M, 80 °C, 1 hour. The resultant particles were spherical shaped, 60–90 nm in diameter, and the degree of agglomeration was greatly reduced.

3.3. Comparison of $BaTiO_3$ particles prepared from different Ti-precursors

Low temperature hydrothermal reactions were done using $Ti(OCH(CH_3)_2)_4$ as a Ti-precursor at 80 °C for 1 hour with the final feedstock concentration of 0.20 M. The SEM micrographs of $BaTiO_3$ synthesized from $Ti(OCH(CH_3)_2)_4$ and $Ti(OCH_2CH_2OCH_3)_4$ are shown in Fig. 5. $BaTiO_3$ particles prepared from

$Ti(OCH_2CH_2OCH_3)_4$ were finer, more uniform, and less agglomerated than those from $Ti(OCH(CH_3)_2)_4$. This is exactly what we expected from the hydrolysis behaviors of each Ti-precursor. Meanwhile, it was found [20] that Ti-precursor containing strongly chelating organic ligand (acetate ligand) requires more vigorous reaction condition (above 120 °C) than our precursor in a similar concentration range (0.12–0.20 M). The resultant particles were greater than those prepared from $Ti(OCH_2CH_2OCH_3)_4$ precursor. Therefore, low temperature hydrothermal reactions using $Ti(OCH_2CH_2OCH_3)_4$ as a Ti-precursor can be a useful method for the preparation of homogeneous $BaTiO_3$ with ultrafine and uniform particle sizes.

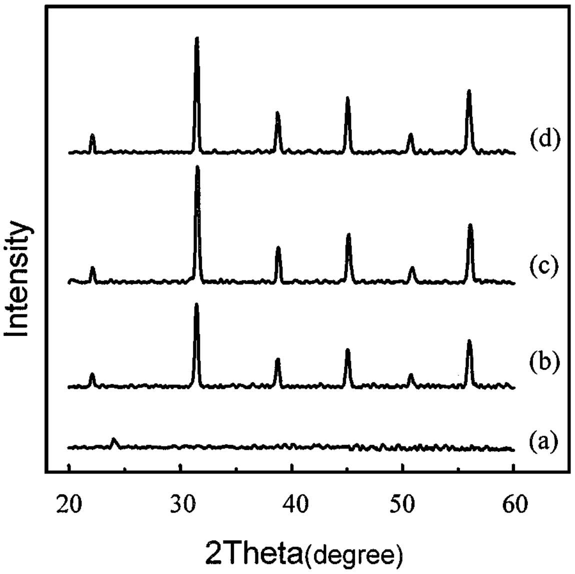


Figure 3 XRD patterns of $BaTiO_3$ prepared at 80°C from 0.12 M for various times: (a) 10 min; (b) 20 min; (c) 1 hr; (d) 18 hr.

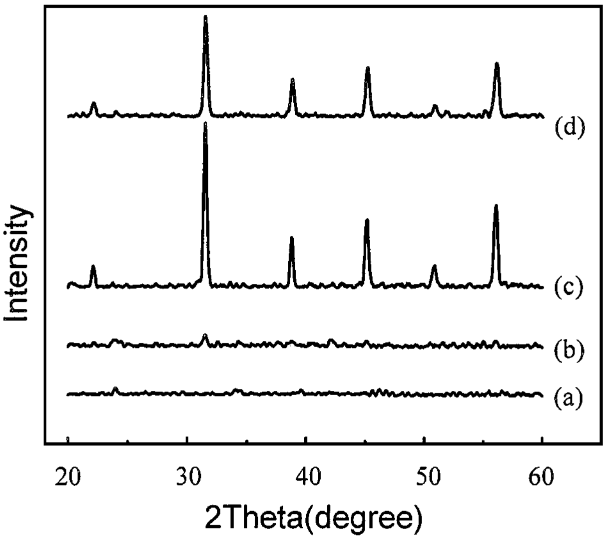
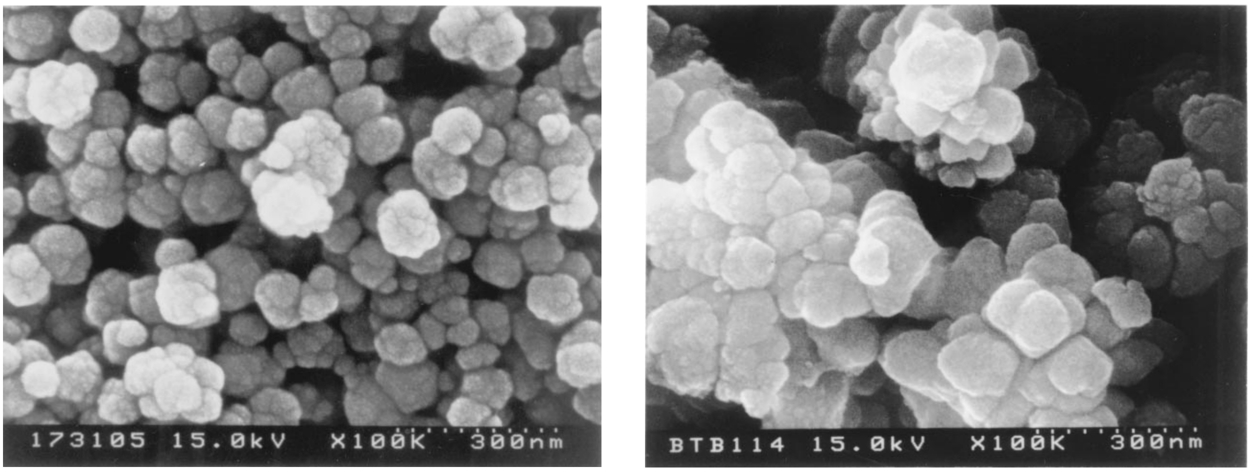


Figure 4 XRD patterns of $BaTiO_3$ prepared at 80°C for 1 hr from various concentrations: (a) 0.05 M; (b) 0.09 M; (c) 0.12 M; (d) 0.20 M.

3.4. Ba/Ti ratio effect on stoichiometry and particle characteristics

The $BaTiO_3$ particles prepared at our optimal condition showed Ba-deficiency (typically, Ba/Ti = 0.87) as usual. Generally, low temperature hydrothermal reaction for the synthesis of $BaTiO_3$ is performed using a reactive Ti-source under mild conditions such as low temperature and autogeneous pressure. In these cases, Ba-deficiency is notorious. Also existed Ba-deficiency (typically Ba/Ti = 0.83) in $BaTiO_3$ particles prepared by low temperature hydrothermal reaction using titanium acylate-based precursors [20], which were known to slow down the hydrolysis rate, to reduce the Ti-O-Ti cross-linking formations, and to lead homogeneous $BaTiO_3$. Using microwave [19] as a heating source was reported to show improved stoichiometry but, still far from the ideal value 1. Our result that used microwave heating for hydrothermal reaction agreed well with this report. It has been believed that Ba-deficiency is caused by the high solubility of barium source compared with titanium [18]. If true, excess amount of barium over titanium in the reactant solution should be able to improve Ba deficiency and theoretically, there should be the optimal Ba/Ti ratio for the production of stoichiometric $BaTiO_3$.



(a) (b)

Figure 5 SEM micrographs of $BaTiO_3$ prepared from different precursors: (a) $Ti(OCH_2CH_2OCH_3)_4$; (b) $Ti(OCH(CH_3)_2)_4$.

TABLE I Elemental analysis of $BaTiO_3$ particles synthesized at different reaction conditions

Reaction Pressure, atm	Ba/Ti mole ratio in reactant	Ba, weight %	Ti, weight %	Ba/Ti mole ratio in product
autogeneous*	1.0	54.8	20.7	0.924
autogeneous (<2)	1.0	53.4	21.5	0.866
	1.3	54.5	20.9	0.908
	1.5	54.2	20.7	0.914
	2.0	56.9	20.9	0.952
	2.2	57.0	21.1	0.943
	2.5	56.6	21.5	0.918
4	1.0	56.4	20.1	0.978
7	1.0	56.2	20.3	0.965
10	1.0	56.5	20.1	0.978
Commercial (oxalate process)		55.9	20.5	0.974
Theoretically calculated for $BaTiO_3$		58.9	20.5	1.000

* used microwave heating for hydrothermal reaction.

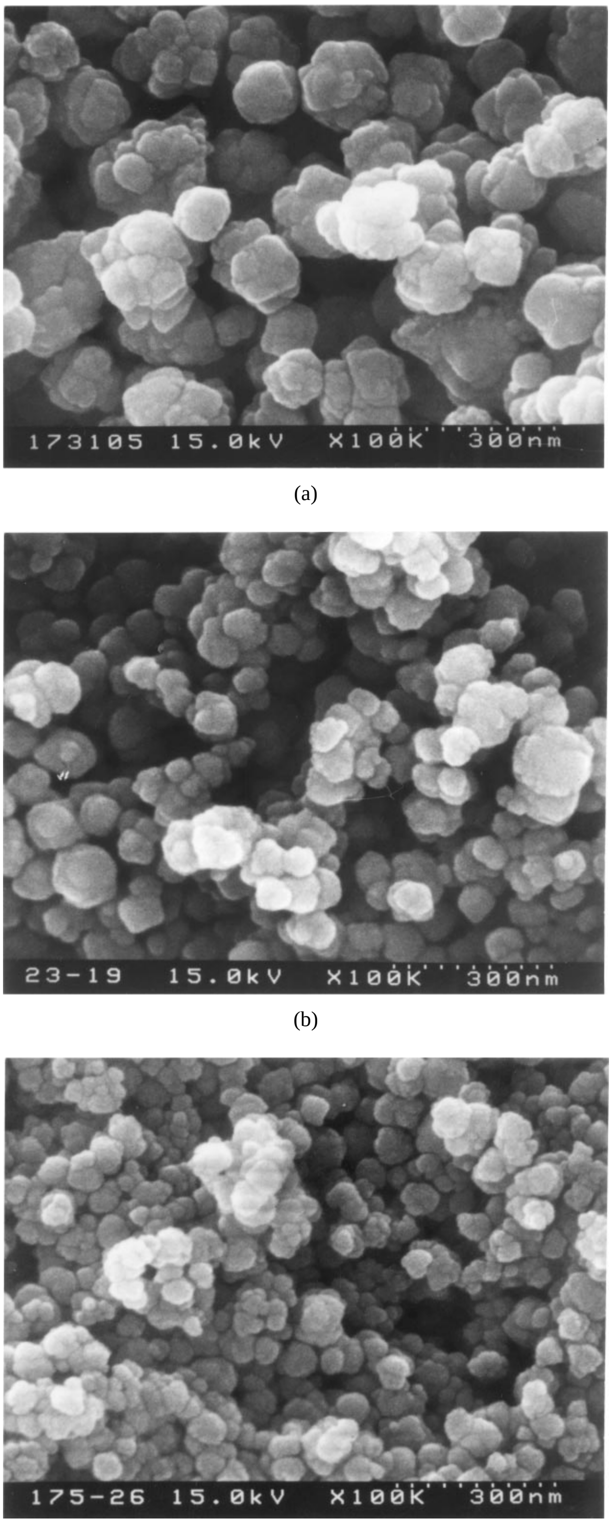
Table I shows the elemental analysis results. As the Ba/Ti mole ratio of the reactant increases, that of the product increases but, decreases after it reaches a maximum value, which is still far less than 1. Washing the solid product with the saturated $Ba(OH)_2$ aqueous solution have not improved the stoichiometry of the final powder meaningfully. These observations suggest that the solubility difference of barium and titanium be not the major cause of Ba-deficiency.

Nonetheless, a consistency is illustrated for the morphology change in Fig. 6. As the Ba/Ti mole ratio of the reactant increases, the resultant particle size and the degree of agglomeration decrease. It seems like that excess $Ba(OAc)_2$ acts as a kind of impurity so that inhibits the growth and the agglomeration of $BaTiO_3$ particles.

3.5. Pressure effect on stoichiometry and particle characteristics

The good control of stoichiometry has been accomplished by adding a slight pressure to the autogeneous one during low temperature hydrothermal treatment using 1 : 1 mole ratio of Ba and Ti reactants. The elemental analysis results are illustrated in Table I. The typical Ba-deficiency was dramatically improved just by adding some external pressure to make total 4–10 atm for the system. It seems like that the total pressure around 4–10 atm provides strong force enough to push Ba ions into the interstitial points of perovskite structure and stabilize it. There was no distinguishable advantage of a higher pressure over 4 atm in terms of stoichiometry. The stoichiometry of our as-synthesized particles was found to be definitely better than that of the commercial ones when it was considered that our particles were dried at 80 °C while the commercial products were presumably treated at 700 °C.

XRD patterns of $BaTiO_3$ particles prepared at various pressures are compared in Fig. 7. The crystallinity of $BaTiO_3$ particles synthesized under 4–10 atm was greater than that prepared under autogeneous pressure. No noticeable pressure effect on crystallinity was found in the range of 4–10 atm. In the pressurized reactions, the trend of increase in crystallinity coincides with that of improvement in stoichiometry.



(a)

(b)

(c)

Figure 6 SEM micrographs of $BaTiO_3$ prepared from various Ba/Ti ratios: (a) 1.0; (b) 2.0; (c) 2.2.

SEM micrographs of $BaTiO_3$ particles synthesized at various pressures are shown in Fig. 8. Interestingly, the degree of agglomeration in synthesized particles was greatly reduced as the pressure was raised up to 10 atm, under which condition produced near-stoichiometric $BaTiO_3$. This tendency of decreasing agglomeration was found in Fig. 6, too when Ba/Ti mole ratio of particles was getting close to one. It has been reported that nanoparticles tend to make an agglomerate because of their high surface energy [22]. It seems like that agglomeration is somewhat related with Ba-deficiency besides the high surface energy. TiO_2-rich (Ba-deficient) phase of $BaTiO_3$ is known to show exaggerated grain growth during sintering [15]. It could be equally possible for TiO_2-rich phase to evolve exaggerated agglomeration during hydrothermal treatment for the powder synthesis.

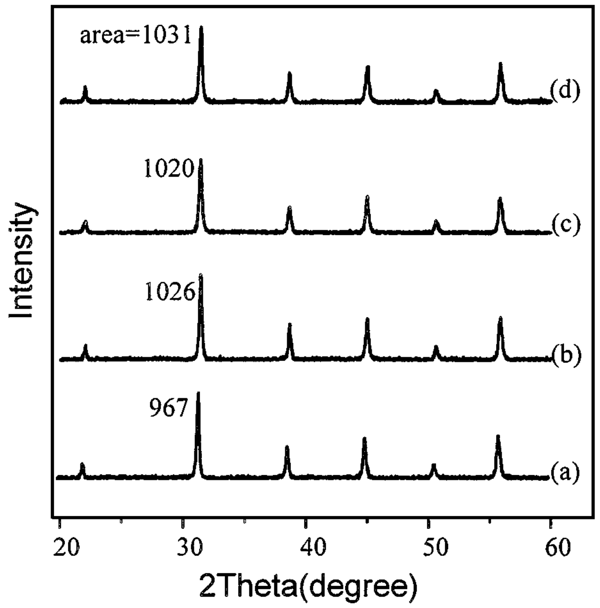
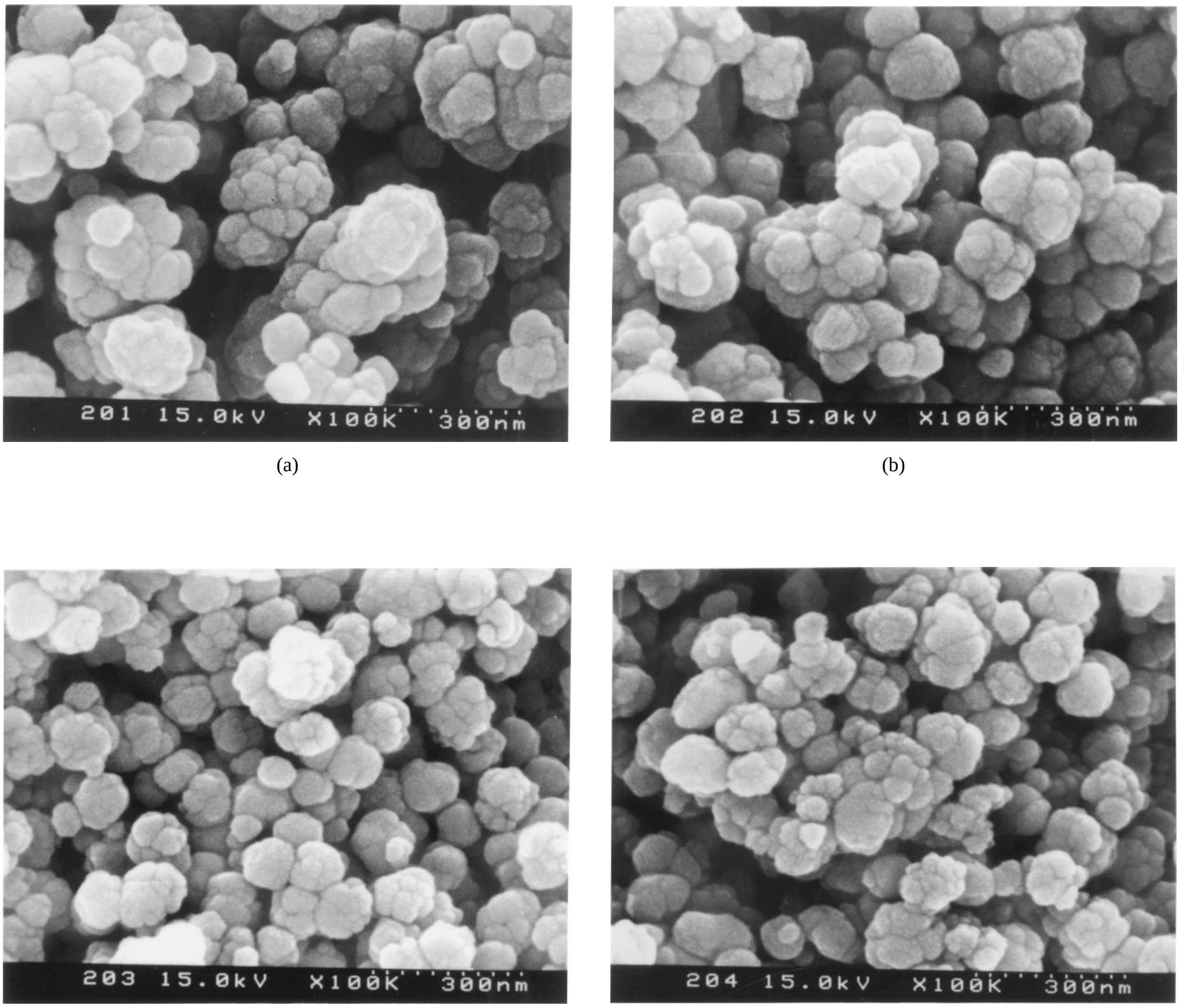


Figure 7 XRD patterns of $BaTiO_3$ prepared under various pressures: (a) autogeneous; (b) 4 atm; (c) 7 atm; (d) 10 atm.

3.6. Effect of calcination on particle characteristics

Characteristics of synthesized $BaTiO_3$ particles were remarkably changed by calcination at various temperatures. Fig. 9 illustrates the effect of calcination temperature on FT-IR spectra. All the particles showed a typical strong and broad absorption peak at 550 cm^{-1} region, which is assigned to TiO_3^{2-} groups. In addition to this major peak, as-synthesized particles showed sharp residual OH groups at 3,500 cm^{-1}, a trace amount of adsorbed water molecules around 3,400 and 1,650 cm^{-1}, and residual organic groups at 1,400 cm^{-1} region. All these impurities disappeared after calcination at 400 °C.



(a) (b) (c) (d)

Figure 8 SEM micrographs of $BaTiO_3$ prepared under various pressures: (a) autogeneous; (b) 4 atm; (c) 7 atm; (d) 10 atm.

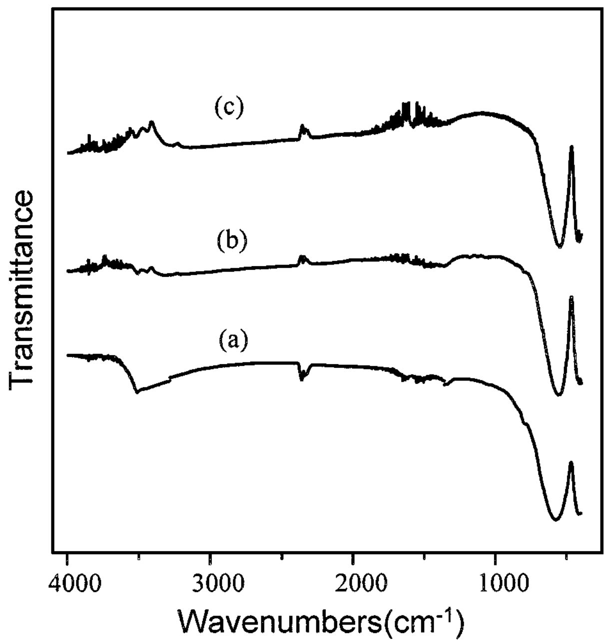


Figure 9 FT-IR spectra of $BaTiO_3$ calcined at various temperatures: (a) as-synthesized; (b) 400°C; (c) 800°C.

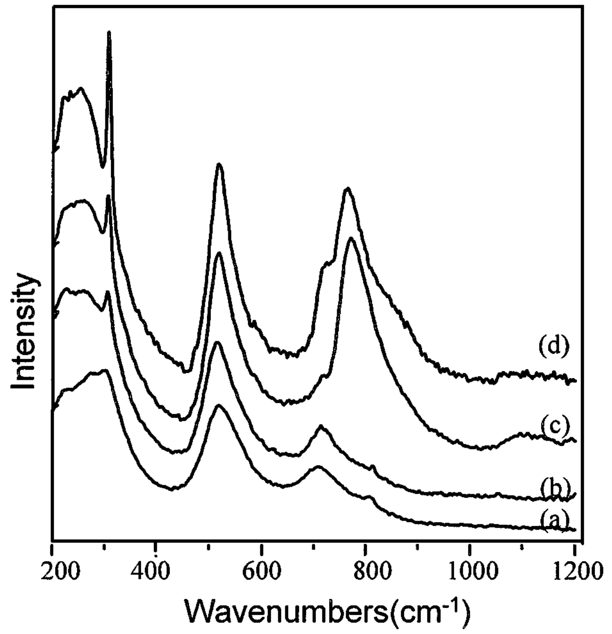


Figure 10 Raman spectra of $BaTiO_3$ calcined at various temperatures: (a) as-synthesized; (b) 400°C; (c) 800°C; (d) 1200°C.

Heat treatment at 800 °C evolved almost no further change on IR spectra.

Fig. 10 shows Raman spectra of the particles calcined at various temperatures. A sharp absorption at 304 cm^{-1} is the characteristic peak of tetragonal $BaTiO_3$ [19]. As-synthesized particles appeared as a metastable cubic form on Raman spectrum as well as on XRD. Surprisingly, tetragonality appeared clearly at 400 °C. Our recent study exhibited that the lowest temperature for the evolution of tetragonality in particles was near 200 °C on the basis of 1 hour heating at the peak temperature. The intensity of this characteristic peak increased gradually according to temperature and showed a substantial increase when particles were calcined at 1200 °C. As a reference, our particles after calcination at 400 °C have Raman and IR spectra of almost the same shapes as those of the commercial powders which are believed to be prepared by oxalate process and calcined at 700 °C. Combining IR and Raman spectra, presumably, assumes that the removal of impurities on the particles facilitated the phase transition from cubic to tetragonal form.

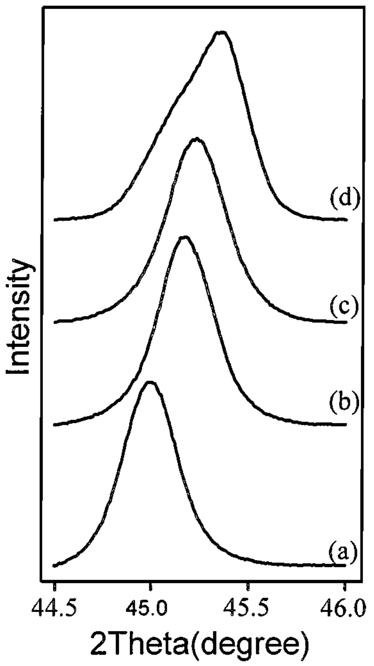


Figure 11 XRD patterns of $BaTiO_3$ calcined at various temperatures: (a) as-synthesized; (b) 400°C; (c) 800°C; (d) 1200°C.

Fig. 11 compares XRD patterns in the selected region of 2θ to investigate the evolution of tetragonality by {200} plane. As the calcination temperature increased, the maximum peak position shifted toward higher 2θ values and a shoulder appeared at 1200 °C. The appearance of this shoulder was caused by phase transition from cubic to tetragonal. That is, {002} plane in cubic phase is splitted into {002} and {200} planes in tetragonal form. These XRD patterns match well with Raman spectra, which showed the substantial increase of a characteristic peak for tetragonal form by heat treatment at 1200 °C. On the other hand, XRD patterns of the particles treated at 400 and 800 °C did not show any peak splitting, though Raman spectra evidenced a gradual increase of tetragonality as the temperature increased. It can be explained by the sensitivity difference of the measuring methods. Since XRD is not so sensitive as Raman spectroscopy, the partial tetragonality of the powders treated at 400 and 800 °C appeared only on Raman spectra but on XRD patterns.

Fig. 12 shows SEM micrographs to examine the effect of calcination temperature on particle morphology. As the calcination temperature increased, the primary grains in each aggregate became larger while the secondary aggregate size remained almost constant. After calcination at 400 °C, the grain size increased to 40–60 nm. When particles were treated at 800 °C, each aggregate appears to be composed of one fully grown single grain and to have smooth surface. Calcined at 1200 °C, the secondary aggregates were grown further by necking and fusion irregularly.

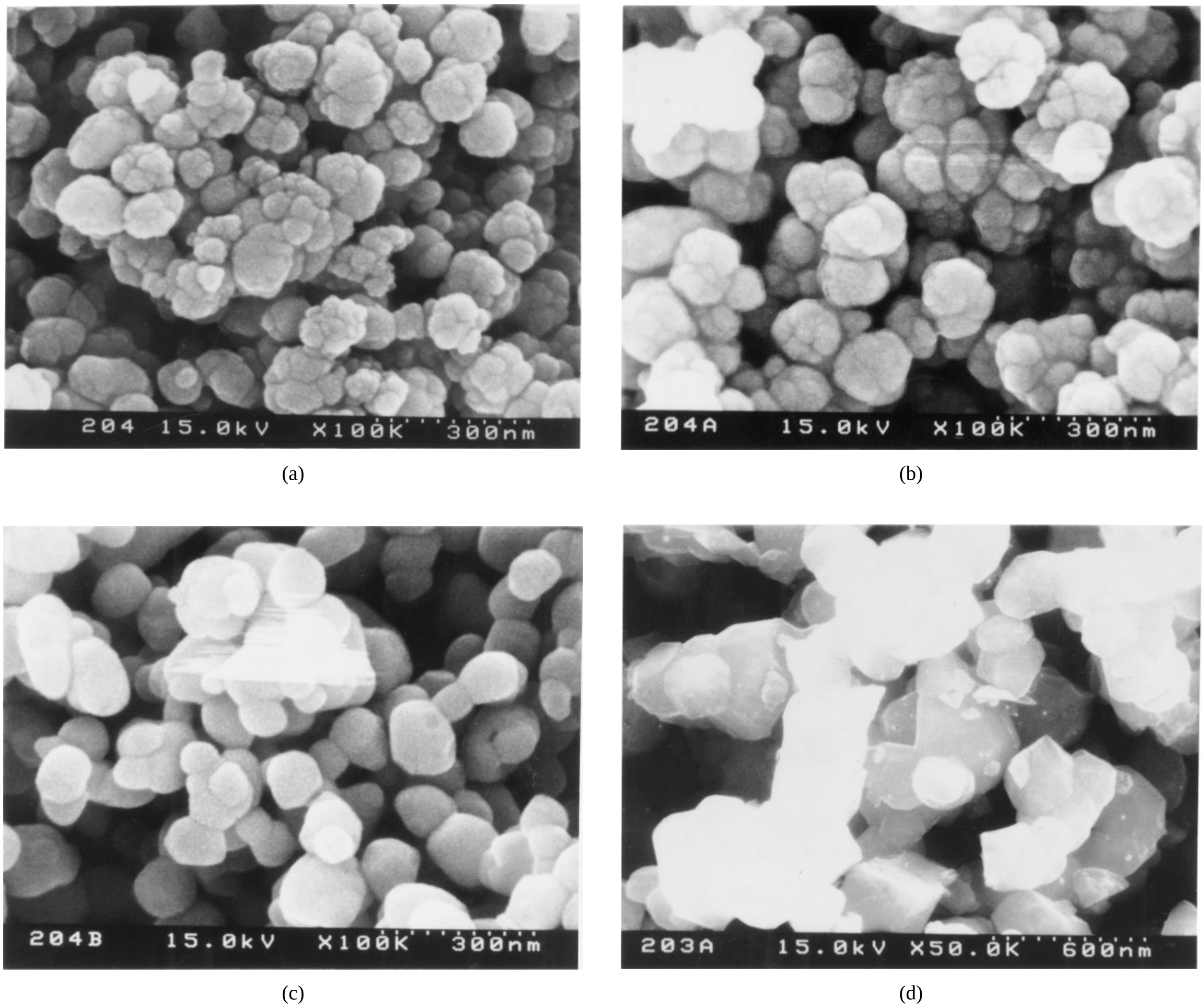


Figure 12 SEM micrographs of $BaTiO_3$ calcined at various temperatures: (a) as-synthesized; (b) 400°C; (c) 800°C; (d) 1200°C.

From above results, no tetragonality in as-synthesized particles is supposedly attributed to two major factors: (1) the existence of residual hydroxyl groups, which make the cubic phase highly stable at room temperature [23] and (2) fine crystallite size which restricts the stabilization of tetragonal phase by interfacial strain with adjacent grains [22]. The tetragonality of $BaTiO_3$ particles evolved upon calcination at below 400 °C and gradually increased by heating at higher temperature. Since such a thermal treatment caused grain growth as well as elimination of OH defects, the mechanism for tetragonality evolution would be explained with those two factors combined.

4. Conclusion

Near-stoichiometric, highly crystalline, and nano-sized $BaTiO_3$ powders were synthesized from $Ba(OAc)_2$ and $Ti(OCH_2CH_2OCH_3)$ by low temperature hydrothermal reaction at 80°C for 1 hour treatment. The electronic, steric, and weakly chelating effect of methoxyethoxide ligand attributed to the evolution of ultrafine particles. The finer particles were produced from the shorter reaction time and the more concentrated solutions. The notorious Ba-deficiency, which has been known to be caused mainly by the solubility difference between barium and titanium sources, has been overcome by adding a slight external pressure to the autogeneous one (total 4–10 atm) rather than by using a large excess amount of Ba over Ti. The slight external force seems likely to push Ba ions into the interstitial points of perovskite structure and stabilize it. Near-stoichiometric $BaTiO_3$ showed higher crystallinity than non-stoichiometric one.

As-synthesized particles were in pure cubic crystalline phase and have almost no organic residues but, have some residual OH groups. Tetragonality has evolved by 1 hour heat treatment at below 400 °C. This is the lowest temperature that has been reported for the evolution of phase transformation from cubic to tetragonal, to the authors' knowledge. At the initial stage of phase transition, the evolution of tetragonality and the disappearance of residual OH groups seem to have a close relationship. Meanwhile, at the later stage of phase transition, a substantial increase of tetragonality seems to be related with grain growth.

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