

Preparation and characterizations of tetragonal barium titanate powders by hydrothermal method

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Abstract

Tetragonal barium titanate powder with an average particle size of 80 nm has been successfully prepared by a hydrothermal process at 240 °C for only 12 h. The influence of processing parameters on the phase and the particle size of hydrothermally derived BaTiO₃ powders was investigated. Increasing NaOH excess concentration and decreasing the initial titanium tetrachloride concentration promote to increase the particle size and are benefit for preparation of tetragonal BaTiO₃ powder, while increasing the reaction temperature and time also obtain same result. There is a relationship between the particle size and the phase of BaTiO₃ powder and a critical size of transformation of cubic-BaTiO₃ to tetragonal-BaTiO₃. In the present work the critical size was 80 nm and finer than other previous works. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The characteristics of electronic and structural ceramics are markedly influenced by the technological parameters used in the processing of the ceramic powder such as the particle size, the morphology, the purity and the chemical composition. In general, using a conventional solid state reaction to synthesize ceramics requires a calcination step at high temperature for enhancing the diffusivity between raw solid materials. During calcination, solid-state diffusion results in the particle coarsening and agglomeration, thereby causing difficulty for sintering the powder. For improving the drawbacks of the solid-state reaction, various kinds of solution processes (or so called soft-chemical processes) have been investigated.^{1,2} Among the solution processing routes, recently the hydrothermal process has been proposed to be an effective method for synthesizing fine ceramic powders.^{3–6} In general the hydrothermal process progresses in a closed system at a high autogeneous pressure. By the benefit of the closed system with a high pressure, the required temperature for preparing ceramic powder can be

greatly reduced because of enhanced reactivity of reactive species, and fine particles with high sinterability can be obtained.^{7,8}

BaTiO₃, especially the tetragonal phase, has excellent dielectric properties, which make it the most important compound used in the composition of ceramic capacitors, especially for the manufacture of multilayer ceramic capacitors (MLCC).^{5,6,9} A number of investigators have examined the range of processing conditions under which hydrothermally derived BaTiO₃ may be obtained, however, in this method, the BaTiO₃ products are produced at temperatures <240 °C and usually are crystallized in a cubic form. Tetragonal BaTiO₃ powders were prepared at temperatures >450 °C under hydrothermal conditions, as reported by Kajiyoshi et al.⁵ However, conventional Teflon-lined bombs cannot be used at such high temperatures. The hydrothermal synthesis of tetragonal BaTiO₃ powders from barium halides at 240 °C was also extensively investigated by Dutta et al.^{6,9–11} However, the formation of the tetragonal form via treatment at 240°C must be for more than one week. In commercial process, a shorter reaction time is required for a high production rate of ceramic particles. For this reason, this study was aimed at the hydrothermal preparation of tetragonal BaTiO₃ particles using barium chloride as barium source and titanium tetrachloride as

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titanium source. In this way the tetragonal BaTiO₃ was successfully synthesized at 240 °C for only 12 h. The effects of the reaction temperature, time, and solution pH value, initial solute concentration on the particle size of tetragonal BaTiO₃ powder have been examined.

2. Experimental procedures

Reagent grade barium chloride, titanium tetrachloride were adopted as the source material for barium and titanium, and reagent grade sodium hydroxide as mineralizer. An aqueous solution of barium and titanium was obtained by mixing TiCl₄ in 40 ml chilled deionized water and a 0.6 molar stoichiometric excess of BaCl₂·2H₂O in 40 ml deionized water. Because Reza Asiaie et al.¹⁰ thought the formation of tetragonal BaTiO₃ was promoted by a Ba/Ti precursor ratio of 1.6, and our experiments also proved this result, in the present work the [Ba]/[Ti]_{precursor} was held constant at 1.6. A 0–2.5 molar stoichiometric excess of NaOH was added in order to neutralize HCl formed from TiCl₄ hydrolysis and to keep the solution to a certain pH value. After adding NaOH with stirring, and resulting in a white colloidal sol, the final volume was adjusted to 100 ml using deionized water. Thereafter, 40 ml sol was transferred to a 50 ml Teflon-lined stainless steel vessel. The sealed vessel was heated to required temperature and for a certain time. After cooling down to room temperature, the resultant precipitate was centrifuged and washed with water for several times, and finally dried at 80 °C for 12 h in a vacuum oven. Excess Ba²⁺, Cl⁻, Na⁺ ions were removed during washing.

BaTiO₃ powders were examined by powder X-ray diffraction (XRD) (Rigaku Geigerflex D/Max 2200) using CuK_α radiation. Powder XRD were taken in the continuous mode over two ranges of 2θ, 20–80° and 44~46°. The former was obtained at a scan speed of 2°/min with 0.02°/sampling step, and the latter was acquired at a scan speed of 0.5°/min with 0.01°/sampling interval. Powder specific surface area was measured using a BET surface area analyzer (Micromeritics Flowsorb 2300) with a gas mixture containing a 70/30 molar ratio of helium to nitrogen. All specific surface area data were collected upon desorption of nitrogen gas from the particle surface while warming from 77 K (liquid nitrogen) to room temperature. Prior to surface area measurements all powders were degassed at 200 °C for 1 h in flowing nitrogen. Particle-size and morphology were characterized by scanning electron microscopy (SEM) (Philips XL30 and DX-4I). SEM samples were prepared by sonicating BaTiO₃ particles suspended in methanol and a few drops of the suspension were deposited onto an aluminum stud, dried, and sputter coated with a gold. Differential scanning calorimetry (DSC) measurements were performed using a thermal

analysis system (DSC-2C, Peikin-Elmer, Norwalk, CT) at a heating rate of 5°/min. The impurities in the powders, such as Cl⁻, and CO₃²⁻, were confirmed by chemical analysis and X-ray fluorescence (Philips PW2400).

3. Results and discussion

3.1. Powder characteristics

XRD investigations have shown that the powder is crystallized as tetragonal-BaTiO₃. No other phase has been detected (Fig. 1). X-ray fluorescence analysis of the reaction production showed no traces of Cl⁻ ion and Na⁺ ion and X-ray diffraction showed no TiO₂ and BaCO₃. The hydrothermal reaction condition is: reaction at 240 °C for 12 h and [Ba]/[Ti]_{precursor} = 1.6, [Ti]_{initial} = 0.625 mol/l, [NaOH]_{excess} = 2.0 mol/l. The specific surface area of the powder is ~12 m²/g and SEM observation shows that the powder has an average particle size of ~80 nm. The particle size of BaTiO₃ powder from BET calculation is same as from SEM observation, so the BaTiO₃ powder is monodispersed and non-aggregation. The Ba/Ti ratio of the BaTiO₃ powder prepared by hydrothermal reaction was measured by X-ray fluorescence after fusion in Li₂B₄O₇. In the above hydrothermal condition, the Ba/Ti ratio of the prepared BaTiO₃ powder is 1.000.

3.2. Effects of [NaOH]_{excess}

The data presented in this section were obtained from powders reacted for 12 h at 240 °C in solutions with [Ti]_{initial} = 0.30 mol/l, [Ba]/[Ti]_{precursor} = 1.6, and [NaOH]_{excess} ranging from 0.25 to 1.0 mol/l. XRD patterns shown in Fig. 2 indicated that phase-pure BaTiO₃ formed when the [NaOH]_{excess} was 0.25 mol/l and higher. As [NaOH]_{excess} was 1.0 mol/l and higher, the typical Bragg reflection, which is located at ~45° 2θ and indexed as (200), split obviously, however, there is non-split when [NaOH]_{excess} was 0.25 and 0.5 mol/l. In the work of Dutta et al.⁶ the splitting of the (200) peak indicated the existence of the tetragonal form in the as-prepared BaTiO₃ powders and lower-angle shoulder was indexed as (002). And in the present work, the amount of tetragonal polymorph in the BaTiO₃ product clearly increases as [NaOH]_{excess} increases.

Calculations using X-ray peak broadening indicated that the BaTiO₃ particle size increased with increasing [NaOH]_{excess}. BET measurements of powder specific surface area decreased from 15.0 to 8.2 m²/g as the [NaOH]_{excess} increased from 0.25 to 1.0 mol/l, also indicating that the BaTiO₃ particle size increased with increasing [NaOH]_{excess}. The particle morphology slightly depended on [NaOH]_{excess}. With the increasing [NaOH]_{excess}, the particle morphology is more uniform and spherical, as showed in Fig. 2.

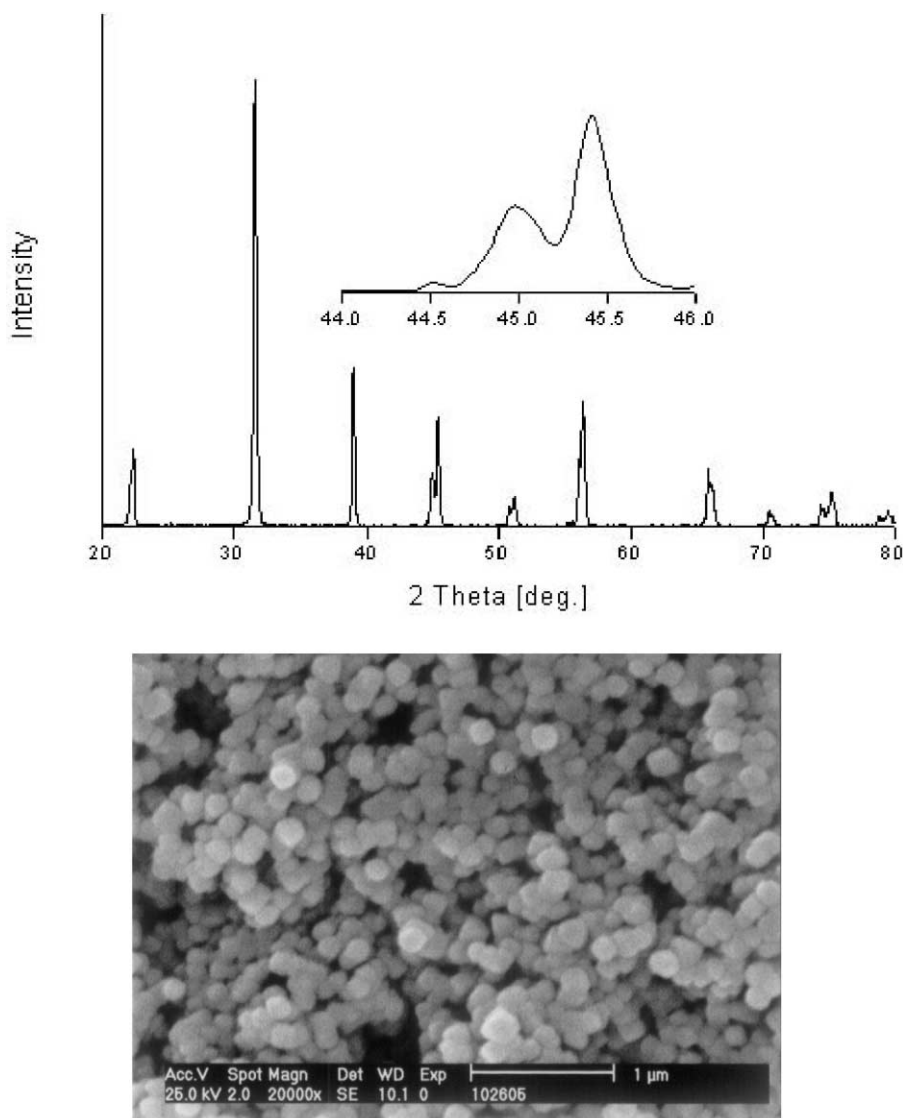


Fig. 1. Characteristics of BaTiO₃ powder prepared by hydrothermal reaction at 240 °C for 12 h and [Ba]/[Ti]_{precursor} 1.6, [Ti]_{initial} 0.625 mol/l, and [NaOH]_{excess} 2.0 mol/l. (a) XRD pattern and the inset showed the reflections around 2θ of 45°. (b) SEM photograph.

3.3. Effect of [Ti]_{initial}

A series of hydrothermal experiments were conducted in more detail to investigate the effect of [Ti]_{initial} in solution on the formation of tetragonal BaTiO₃, as shown in Figs. 3 and 2(b). With [NaOH]_{excess} 0.5 mol/l, [Ba]/[Ti]_{precursor} 1.6, reaction temperature 240 °C and time 12 h, the amount of tetragonal form clearly decreased as the [Ti]_{initial} increased.

The particle size observed by SEM clearly decreased as the [Ti]_{initial} increased (Fig. 3). The BET results also proved this correlation between particle size and [Ti]_{initial}.

3.4. Effect of reaction time

The data presented in this section were obtained from powders reacted for times ranging from 0 to 24 h at

240 °C in a 1.0 mol/l [NaOH]_{excess} solution containing [Ba]/[Ti]_{precursor} = 1.6 and [Ti]_{initial} = 0.30 mol/l.

XRD data [Fig. 4(a)] of BaTiO₃ processed just after adding NaOH to barium and titanium mixture indicated the BaTiO₃ had been formed, but there are some TiO₂. XRD data [Fig. 4(b)] of BaTiO₃ processed for 4 h indicated that the powder was nearly phase-pure BaTiO₃, and it is pure cubic-BaTiO₃, because of non-splitting of the (200) peak. There are various split in the (200) peak of the powder processed for 12 h [Fig. 2(c)] and higher, and it indicated that the powder contained tetragonal BaTiO₃.

The peaks of BaTiO₃ powder processed for 4 h displayed systematic broadening and asymmetry. The observed peak broadening and asymmetry decreased with increasing reaction time, resulting in sharp symmetrical peaks after 12 h. BET measurement

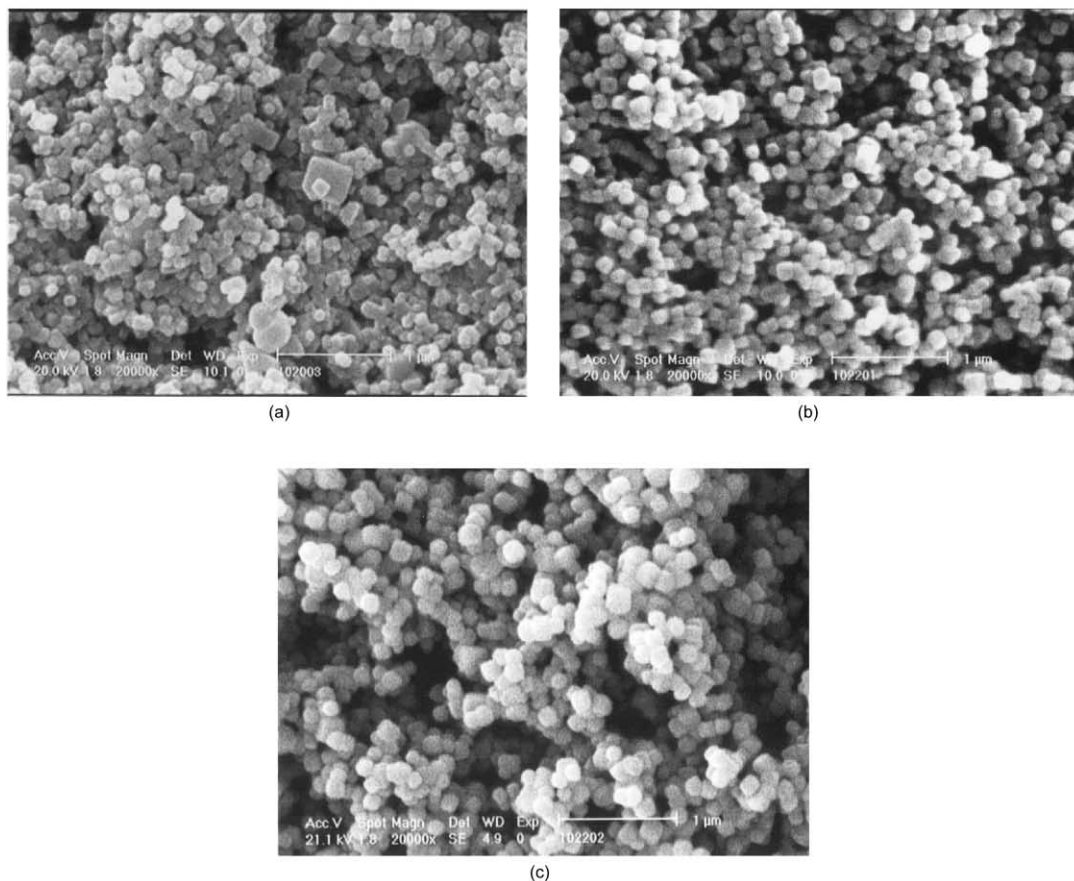
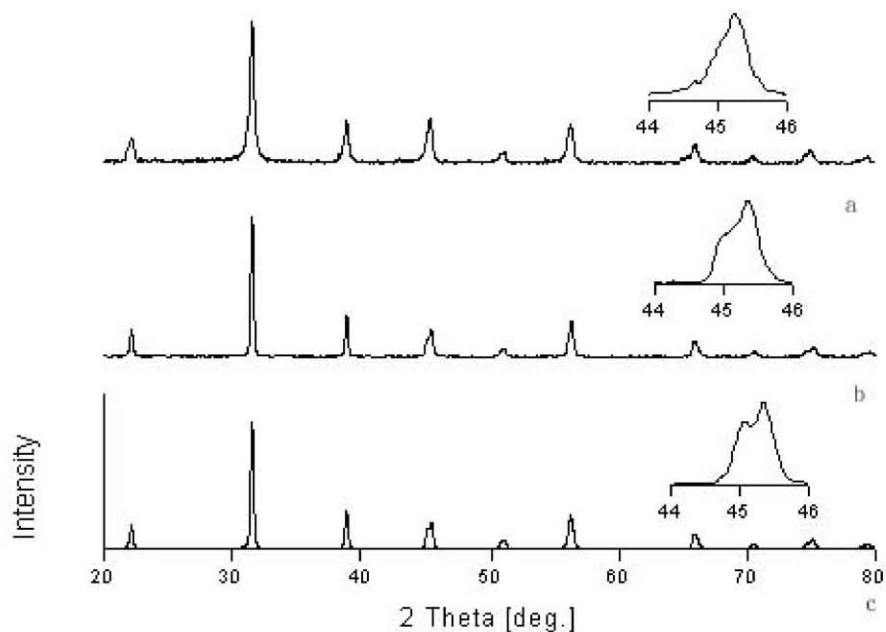


Fig. 2. Characteristics of BaTiO_3 powder prepared by hydrothermal reaction at 240°C for 12 h and $[\text{Ba}]/[\text{Ti}]_{\text{precursor}} 1.6$, $[\text{Ti}]_{\text{initial}} 0.30$ mol/l, and (a) $[\text{NaOH}]_{\text{excess}} 0.25$ mol/l, (b) 0.5 mol/l, (c) 1.0 mol/l. Top: the left XRD patterns and the inset showed the reflections around 2θ of 45° ; below: SEM photographs.

indicated that the specific surface area decreased with increasing reaction time, and is consistent with the observed increase in particle size, as shown in Fig. 4.

3.5. Effect of reaction temperature

The data presented in this section were obtained from powders reacted for 12 h in a solution containing 1.5

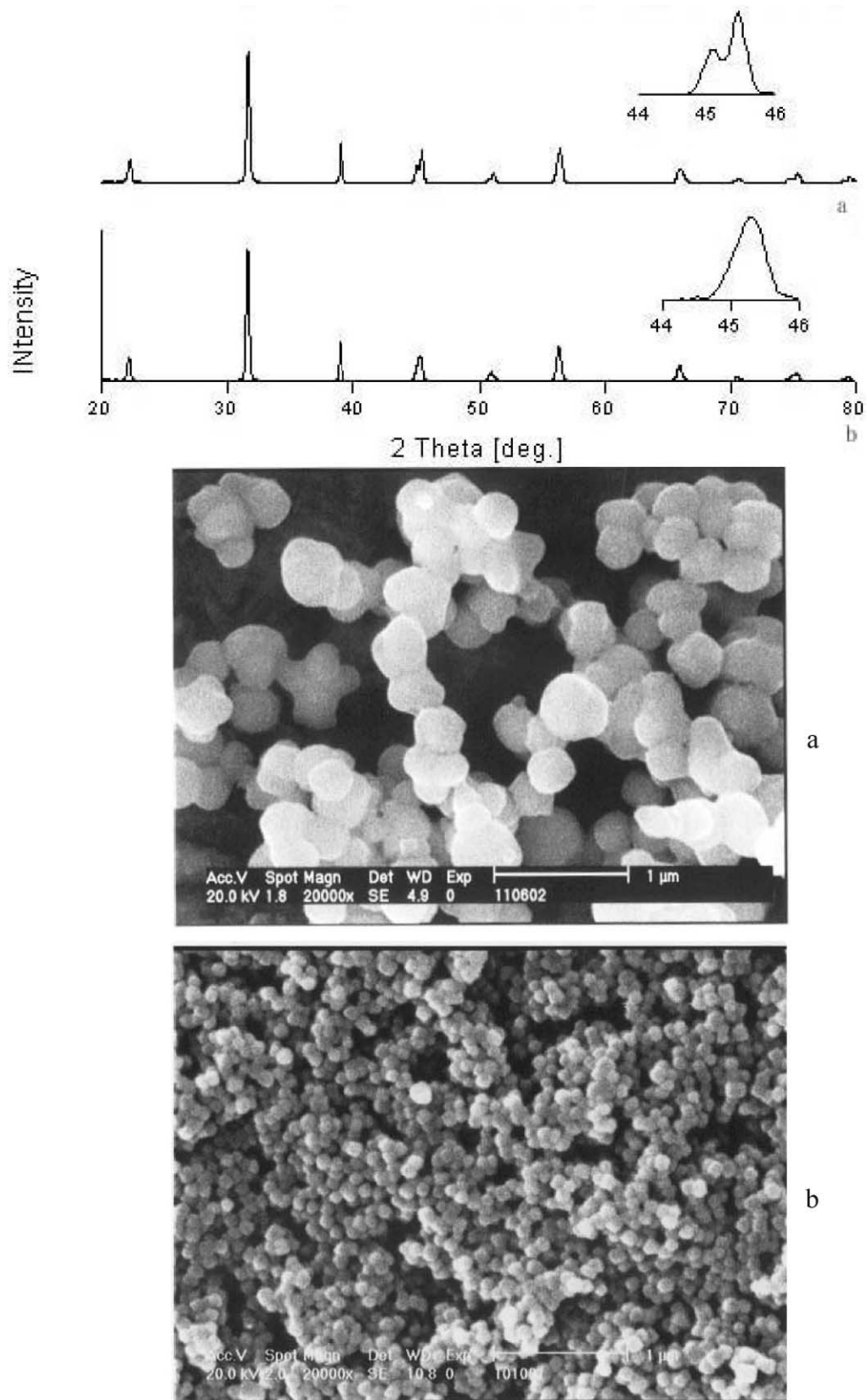


Fig. 3. Characteristics of BaTiO₃ powder prepared by hydrothermal reaction at 240 °C for 12 h and [Ba]/[Ti]_{precursor} 1.6, [NaOH]_{excess} 0.5 mol/l and (a) [Ti]_{initial} 0.15 mol/l, (b) 0.625 mol/l. Top: the left XRD patterns and the inset showed the reflections around 2θ of 45°; below: SEM photographs.

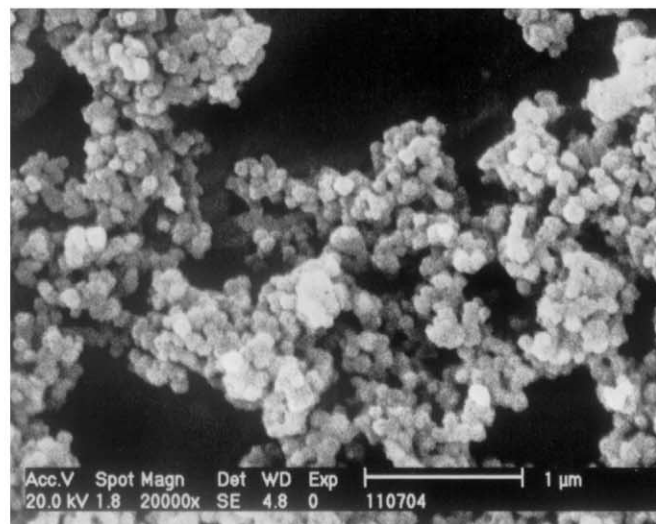
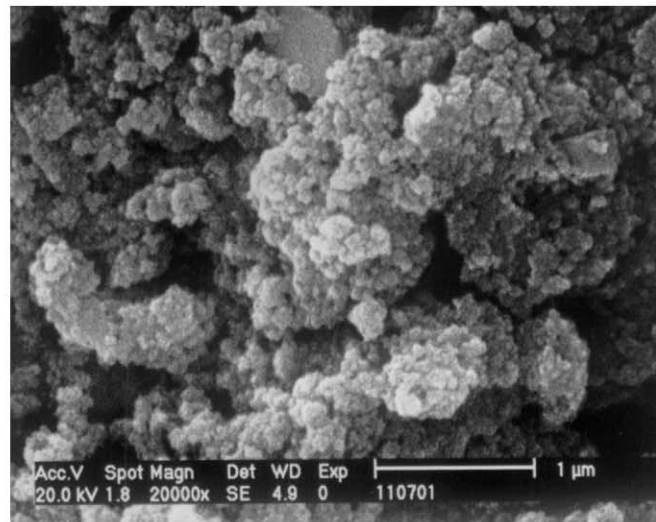
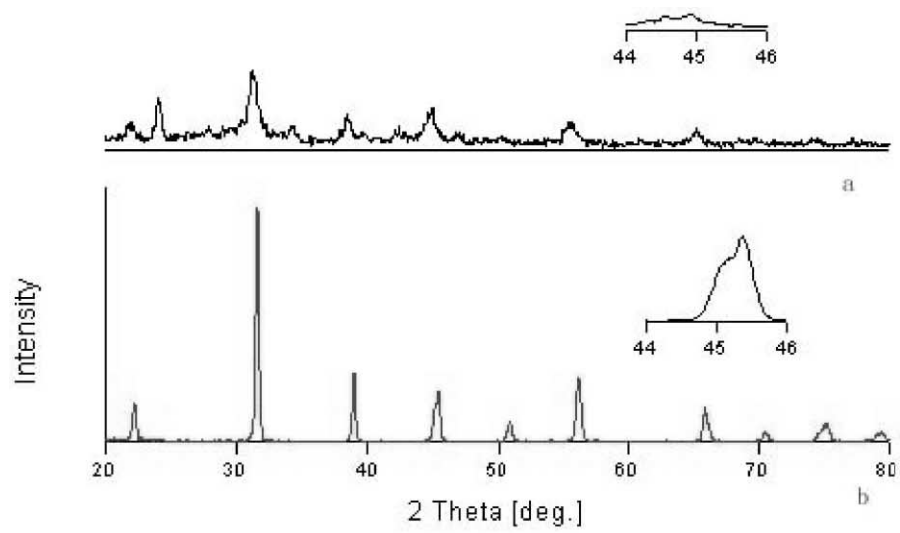


Fig. 4. Characteristics of BaTiO₃ powder prepared by hydrothermal reaction at 240 °C and [Ba]/[Ti]_{precursor} 1.6, [NaOH]_{excess} 1.0 mol/l and [Ti]_{initial} 0.30 mol/l for (a) 0 h, (b) 4 h. Top: the left XRD patterns and the inset showed the reflections around 2θ of 45°; below: SEM photographs.

mol/l $[\text{NaOH}]_{\text{excess}}$, $[\text{Ba}]/[\text{Ti}]_{\text{precursor}} = 1.6$ and $[\text{Ti}]_{\text{initial}} = 0.625$ mol/l. The reactions were performed at 200 and 240 °C.

With hydrothermal reaction conditions of the present work, the BaTiO_3 powder synthesized at 200 °C was pure cubic phase. With higher $[\text{NaOH}]_{\text{excess}}$ and smaller $[\text{Ti}]_{\text{initial}}$, the tetragonal BaTiO_3 powder can be synthesized at 240 °C by the hydrothermal method. A finer particle size BaTiO_3 powder can be synthesized at 200 °C than at 240 °C.

3.6. Tetragonal BaTiO_3 formation

The experiments described above demonstrated that tetragonal BaTiO_3 powders may be fabricated over a broad range of processing conditions. Increasing the $[\text{NaOH}]_{\text{excess}}$, reaction temperature and time or decreasing the $[\text{Ti}]_{\text{initial}}$ all promoted to obtain the tetragonal BaTiO_3 . The effects of processing parameters on tetragonal BaTiO_3 formation may be understood in the context of a dissolution-recrystallization mechanism described by Eckert et al.¹¹ Increasing titanium ions concentration was a potential rate-limiting step in the formation of hydrothermal BaTiO_3 . Compared other previous works used TiO_2 solid as titanium source, TiCl_4 could suppose more titanium ions for formation of BaTiO_3 . So even at non-hydrothermal condition and at 80 °C and air pressure, BaTiO_3 powders were prepared by Nanni et al.⁷ used titanium tetrachloride as titanium source in high pH value solution. At room temperature, when the sodium hydroxide was added in mixture solution of BaCl_2 and TiCl_4 , the TiO_2 sol was formation. Increasing $[\text{NaOH}]_{\text{excess}}$ and reaction temperature increase TiO_2 sol solubility, thereby increasing the dissolution rate of titanium into solution, and increasing the rate of BaTiO_3 formation.

From above results, it is proved the importance of the hydroxide ions (OH^-). They are not only vital in the nucleation of BaTiO_3 crystals under hydrothermal conditions, from the standpoint of thermodynamics, as Lencka et al.⁸ reported, but they also seem to act as a catalyst by promoting the growth of BaTiO_3 and accelerating the transition of cubic- BaTiO_3 to form tetragonal- BaTiO_3 . Because sodium hydroxide solubility is more than barium hydroxide, in this work there are more OH^- ions in the solution than other previous works, then present work can prepared tetragonal BaTiO_3 by hydrothermal reaction only for 12 h. As to chloride ions promoting the forming tetragonal BaTiO_3 powder, as Asiaie et al.¹⁰ reported, we could not prove it in the present work.

As previously noted, there is a relationship between the particle size and BaTiO_3 phase. Present work showed that the particle size of the cubic BaTiO_3 powder is finer than the tetragonal BaTiO_3 powder and there is a critical size between cubic BaTiO_3 powder and

tetragonal BaTiO_3 powder. This result agreed with previous conclusions, such as Dutta et al.⁶ and Kaji et al.⁵ However, they thought the critical particle size is bigger than 100 nm. In the present work, the critical particle size is smaller than 100 nm, and is ~ 80 nm. The difference between both critical particle size values is because of the different preparation mechanisms of BaTiO_3 powder, although there are under investigation.

4. Conclusions

1. Using barium chloride, titanium tetrachloride as barium and titanium source, the tetragonal BaTiO_3 powder with average particle size 80 nm can be synthesized by hydrothermal reaction at 240 °C for only 12 h. In this way, the hydroxide ions act as important reaction material and catalyst.
2. Increasing the NaOH excess concentration and decreasing the initial titanium tetrachloride concentration are benefit for preparation of tetragonal BaTiO_3 powder; and increasing the reaction temperature and time also obtain same result.
3. There may be a relationship between BaTiO_3 phase and particle size, and the particle size of the cubic BaTiO_3 powder is finer than the tetragonal BaTiO_3 powder. In the present work the critical particle size is 80 nm and smaller than other works. The reasons are under investigation.

References

1. Gherardi, P. and Matijevic, E., Homogeneous precipitation of spherical colloidal barium titanate particles. *Colloid. Surfact.*, 1988, **32**, 257–274.
2. Kerchner, J. A., Moon, J., Chodelka, R. E., Morrone, A. A. and Adair, J. H., Nucleation and formation mechanisms of hydrothermally derived barium titanate. *ACS Symp. Ser.*, 1998, **681**, 106–119.
3. Kutty, R. N., Vivekannandan, R. and Murugaraj, P., Precipitation of rutile and anatase (TiO_2) fine powders and their conversion to MTiO_3 (M = Ba, Sr, Ca) by the hydrothermal method. *Mater. Chem. Phys.*, 1998, **19**, 533–546.
4. Moon, J., Li, T., Randall, C. A. and Adair, J. H., Low temperature synthesis of lead titanate by a hydrothermal method. *J. Mater. Res.*, 1997, **12**(1), 189–197.
5. Kajiyoshi, K., Ishizawa, N. and Yoshimura, M., Preparation of tetragonal barium titanate thin film on titanium metal substrate by hydrothermal method. *J. Am. Ceram. Soc.*, 1991, **74**(2), 369–374.
6. Dutta, P. K. and Gregg, J. R., Hydrothermal synthesis of tetragonal barium titanate. *Chem. Mater.*, 1992, **4**, 843–846.
7. Nanni, P., Leoni, M., Buscaglia, V. and Aliprandi, G., Low-temperature aqueous preparation of barium metatitanate powders. *J. Eur. Ceram. Soc.*, 1994, **14**, 85–90.
8. Lencka, M. M. and Riman, E., Thermodynamic modeling of hydrothermal synthesis of ceramic powders. *Chem. Mater.*, 1993, **5**, 61–70.
9. Wu, M. M., Long, J. B., Wang, G. G., Huang, A. H., Luo, Y. J., Feng, S. H. and Xu, R. R., Hydrothermal synthesis of tetragonal barium titanate from barium hydroxide and titanium dioxide

- under moderate conditions. *J. Am. Ceram. Soc.*, 1999, **82**(11), 3254–3256.
10. Asiaie, R., Zhu, W. D., Akbar, S. A. and Dutta, P. K., Characterization of submicron particles of tetragonal BaTiO₃. *Chem. Mater.*, 1996, **8**, 226–234.
 11. Eckert, J. O. Jr., Hung-Houston, C. C., Gersten, B. L., Lencka, M. M. and Riman, R. E., Kinetics and mechanisms of hydrothermal synthesis of barium titanate. *J. Am. Ceram. Soc.*, 1996, **79**(11), 2929–2939.