JOURNAL OF MATERIALS SCIENCE **40** (2005) 991–998

Preparation of monodispersed spherical barium titanate particles

KUN-YUAN CHEN
Department of Chemical Engineering, Kuang-Wu Institute of Technology
YU-WEN CHEN
Department of Chemical and Materials Engineering, Nanocatalysis Research Center,
National Central University, Chung-Li 32054 Taiwan, R.O.C
E-mail: ywchen@cc.ncu.edu.tw

Spherical barium titanate particles with cubic phase were synthesized by a low-temperature hydrothermal reaction. Firstly, The method of hydrolysis of titanium tetrachloride was used for producing spherical TiO_2 particles (0.45–1.5 μm) with various concentrations of $TiCl_4$(0.05–0.2 M) and volume ratios of acetone to water solutions (RH = 0–4). These TiO_2 particles were converted to barium titanate by a hydrothermal conversion in a barium hydroxide solution. The size and morphology of the TiO_2 particles was controlled by the volume ratio of acetone to water (RH ratio) in the mixed solvent. At the RH ratio of 3, the morphology of TiO_2 particles was very uniform and discrete. These TiO_2 particles were in the anatase phase and were converted to the rutile phase when the calcination temperature increased to 700°C and above. Uniform and spherical barium titanate particles were successfully synthesized from the as-prepared TiO_2 particles by using a hydrothermal reaction in a barium hydroxide solution. The Ba/Ti ratios, reaction temperature, and reaction time did not influence the size and morphology of $BaTiO_3$ particles, but increased the concentration of unfavorable salts such as $Ba(OH)_2$ and $BaCO_3$. The high purity $BaTiO_3$ particles could be obtained by washing with formic acid to remove the unfavorable salts. The size and morphology of the $BaTiO_3$ particles remained the same as those of the TiO_2 particles, confirming the *in-situ* transformation mechanism for the conversion of TiO_2 to $BaTiO_3$. The as-synthesized particles were cubic phase and transformed to tetragonal phase after calcinations at 1150°C for 1 h. The mean density of the pellets sintered at 1300°C for 2 h was 5.86 g/cm^3 and accounted for 97.34% of the theoretical density. *© 2005 Springer Science + Business Media, Inc.*

1. Introduction

Barium titanate ($BaTiO_3$), a perovskite electro-ceramic material, has been widely studied because of its ferroelectric and piezoelectric properties. These characteristics promise applications of the material such as for multilayer capacitors (MLC), positive temperature coefficient (PTC), electro-optical devices and passive memory storage etc. Due to its widely applications, the study on its synthesis and material forming is still attractive [1–5].

Ultrafine, crystalline and unagglomerated particles with a narrow particle size distribution are desirable for compacting and sintering of ceramics. There are many methods for synthesizing high purity, homogeneous, reactive ultrafine $BaTiO_3$ powders at lower temperatures, such as solid reaction [6, 7], coprecipitation [8, 9], sol-gel method [10, 11], hydrothermal method [12, 13] and coprecipitation plus inverse microemulsion [14]. The monodisperse spherical particles are desirable for enhancing densification and grain growth in ceramics. However, only a few techniques have been developed to synthesize spherical TiO_2 and $BaTiO_3$ powders. Gherardi *et al.* [15] prepared spherical colloidal (submicrometer size) $BaTiO_3$ powders with a narrow size distribution by homogeneous precipitation with titanium alkoxide. Ogihara *et al.* [16] synthesized monodisperse spherical ZrO_2 powders from zirconium butoxide. The quality of the particles made by the sol-gel process is sensitive to the concentration of the alkoxide and the ratio of water to alkoxide. Several other research teams [17, 18], however, reported that the sol-gel process is difficult to reproduce. Due to the sensitivity of metal alkoxides to moisture, controlled particle size distribution and morphology is very difficult owing to the rapid hydrolysis rate of metal alkoxides.

Hydrothermal synthesis with inorganic precursors offers a promising approach to prepare monodisperse spherical particles by the changes to dielectric constant of the mixed solvent liquid. Propanol groups were chosen as the most favorable alcohol system to reduce the dielectric constant of the particle-forming medium. Park *et al.* [19] produced monodispersed spherical

TiO_2 powders by the thermal hydrolysis of $Ti(SO_4)_2$ in a solvent of *n*-propanol and water. Kato *et al.* [20] synthesized spherical TiO_2 particles from an aqueous solution of $TiO(SO_4)$ by using the urea as the precipitating agent at 70–90°C. Moon *et al.* [21] synthesized the fine spherical ZrO_2 particles by the thermal hydrolysis of $ZrOCl_2 \cdot 8H_2O$ in a mixed solvent of 2-propanol and water. Hw *et al.* [22] synthesized spherical $BaTiO_3$ particles by the hydrothermal conversion of TiO_2 microspheres in a mixed solvent of iso-propanol and water. Chen *et al.* [23] synthesized micro-spherical TiO_2 particles by the thermal hydrolysis of $TiCl_4$ in a mixed solvent of acetone and water.

In this present work, the monodisperse spherical TiO_2 particles were prepared by the thermal hydrolysis of titanium tetrachloride ($TiCl_4$) by the changes to dielectric constant of the mixed solvent liquid in a static condition. A low temperature hydrothermal conversion of micro-spherical TiO_2 particles in barium hydroxide solutions was used to synthesize micro-spherical $BaTiO_3$ particles.

2. Experimental

2.1. Preparation of starting solution

The ice-cold deionized water was added dropwisely to ice-cold titanium tetrachloride ($TiCl_4$)(99%, Hayashi Chemical Industries, Ltd., Japan) and stirred for 6 h at 5°C. The solution became yellow and gel-like during the dissolution step but gradually cleared up within 30 min. The concentration in the prepared flask solution was adjusted to 1.0 M. The above aqueous solution was then mixed with acetone (95%; Shimakyu's Pure Chemicals, Ltd., Japan) to adjust the volume ratio of acetone to water (R/H ratio) to 3. The final concentration of $TiCl_4$ was controlled to be 0.05 M, 0.1 M and 0.2 M, respectively. During the period of mixing, a long-chained molecule, hydroxypropyl cellulose (HPC) (molecular weight ~100,000; Tokyo Kasei Kogyo Co., Japan) was added as a dispersant to give steric hindrance to precipitation of particles. The above solution was stirred at 5°C for 1 h to obtain a homogeneous solution.

2.2. Synthesis of spherical titania particles

When the homogeneous solutions were kept in an oven at 70°C in a static condition for a few minutes, it became supersaturated and precipitated. The solution was then aged further to grow precipitate. After reacting for 60 min, the mother liquor was neutralized ($pH \approx 7$) by adding 6.5 ml of 3 N NH_4OH solution to avoid redissolution of the precipitates into the mother liquor during the centrifugation and washing period. The precipitates obtained from the above procedure were centrifuged (at 5000 rpm for 3-min intervals) and washed twice with deionized water and then washed with acetone. The obtained precipitates were dried in an oven at 80°C for 24 h.

The morphology and size of TiO_2 particles were influenced by many parameters such as the volume ratio of acetone to water (RH ratio), the concentration of HPC, reaction time and reaction temperature. The optimum conditions to obtain uniform and spherical TiO_2 particles were 0.1 M $TiCl_4$, R/H ratio of 3, HPC concentration of 0.001 g/cm^3, temperature of 70°C, and reaction time of 1 h.

2.3. Synthesis of spherical barium titanate particles

A predetermined quantity of barium hydroxide (98% $Ba(OH)_2 \cdot D8H_2O$) was added to a titania sol in deionized water at various Ba/Ti molar ratios in the range from 1.1 to 1.6, the solution was loaded in a 50 ml Teflon-lined stainless steel autoclave. After stirring, the pH of the sol was 10–12 (depending on the concentration of the barium hydroxide), which was sufficiently high for the formation of barium titanate. The solution was reacted at various temperatures in the range from 70–100°C for 3 to 24 h, respectively. After reaction, the precipitate settled in the bottom and was filtered, washed, and then washed with formic acid solution ($4\ mol \cdot dm^{-3}$) at 50°C for 30 min, in order to remove unfavorable barium salts such as barium carbonate and barium hydroxide. After formic acid treatment, the precipitate was filtered, washed and dried in an oven overnight at temperature of 80°C to form powder.

2.4. Characterization of spherical particles

Phase identification and crystallite size of the particle samples were analyzed by powder X-ray diffraction using a Siemens D&8 automatic powder diffractometer system, at 40 kV and 29 mA, using Cu K_α radiation. The particle size and morphology of the particle samples were analyzed by a scanning electron microscope (SEM) (Hitachi S-800) operated at 20 kV. Thick suspension of the TiO_2 and $BaTiO_3$ particles were spread on a stage especially made for SEM. Particles on the stage were then coated with Au by plasma sputtering for 3 min in preparation for SEM imaging. Particle size distribution was measured by the light scattering method (Zetasizer 3000). The spherical $BaTiO_3$ powders were pressed under 250 MPa of pressure into discs with PVA. The compacted discs were dried at 550°C in a furnace for 1 h to remove PVA. Sintered pellets were made using a 1600°C box furnace (Model DF20) at a temperature of 1300°C with a heating rate of 10°C/min for 2 h. Densities of the sintered pellets were measured using Archimedes principle.

3. Results and discussion

3.1. Synthesis of spherical TiO_2 particles

Spherical TiO_2 particles have successfully synthesized by using the acetone-water mixed solvent. According to the previous studies [24, 25], when acetone was added to an aqueous solution of the salt, the solution became supersaturated and precipitation occurred, because acetone with low dielectric constant decreases the solubility of salt in the mixed solvent. In this work, a variety of acetone/water volume ratios were employed to examine the precipitation behavior of mixed solutions

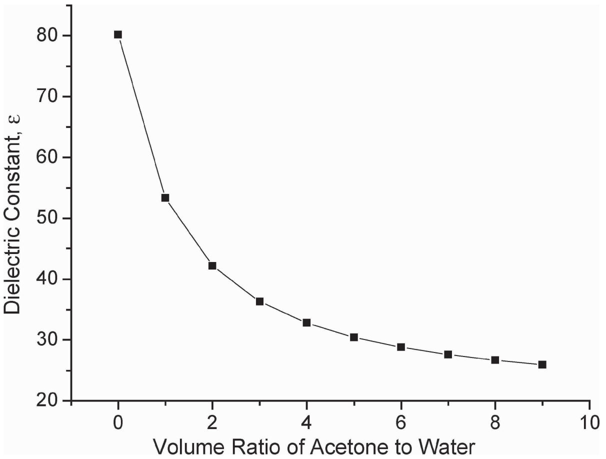

Figure 1 Dielectric constant vs. acetone/water volume ratios. The concentration of $TiCl_4$ was 0.1 M.

consisting of titanium tetrachloride, acetone, and water. Fig. 1 shows a variation of the dielectric constant of acetone-water mixtures with the volume ratios. The effect of RH ratio in the mixed solvent on the formation of the spherical TiO_2 particles is shown in Fig. 2. As the R/H ratio of 1, the dielectric constant of the solvent is high resulting the high repulsive force. Under this condition, particles were stable against the aggregation, and the particles appeared to be fine and agglomerated as shown in Fig. 2A. At the R/H ratio of 3, the dielectric constant of the solvent was low resulting the low repulsive force. Since the repulsive force increased with an increase of the particle size, the colloidal stability of the precipitates increases with increasing the particle size. Consequently, the precipitates, shown in Fig. 2C, were spherical and discrete particles. These results indicate that the composition of the solvent affects the particle size and morphology through the change of the dielectric constant of the solvent.

The effect of the initial $TiCl_4$ concentrations (0.05 M, 0.1 M, and 0.2 M, respectively) in the mixed solvent is shown in Figs 3 and 4. Particles obtained from the lowest concentration, i.e., 0.05 M, were slightly less spherical and tended to aggregate into clusters in the solution. In contrast, a less aggregation between titania particles and a better defined spherical shape (solid sphere with smooth surface) were obtained from the samples prepared with higher concentrations such as 0.1 M (Fig. 3) and 0.2 M (Fig. 4). The mean particle size as examined by DLS was 0.49 μm, 0.93 μm, and 1.43 μm respectively. It was nearly proportional

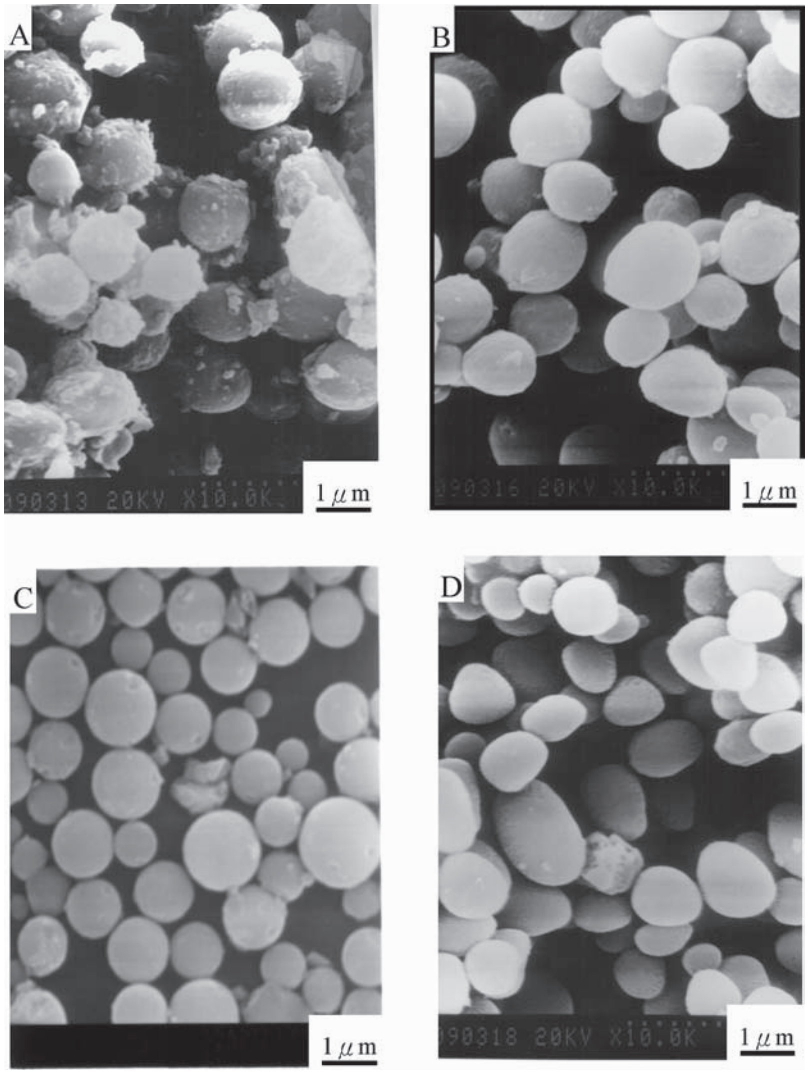

Figure 2 SEM micrographs of TiO_2 particles prepared at 70°C for 1 h with various RH ratios (acetone/water volume ratios). (A) 1 (B) 2 (C) 3 (D) 4. The concentration of $TiCl_4$ was 0.1 M.

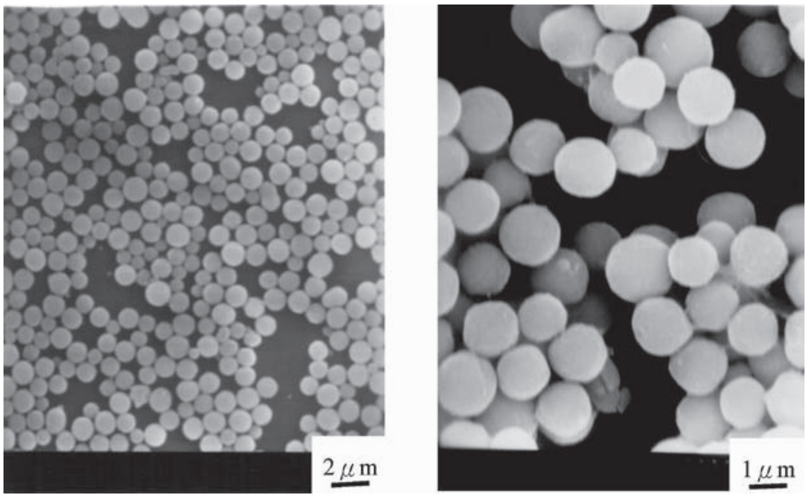

Figure 3 SEM micrographs of TiO_2 prepared at the conditions of 0.1 M $TiCl_4$, RH = 3, 0.001 g/cm^3 HPC, 70°C, 1 h reaction time.

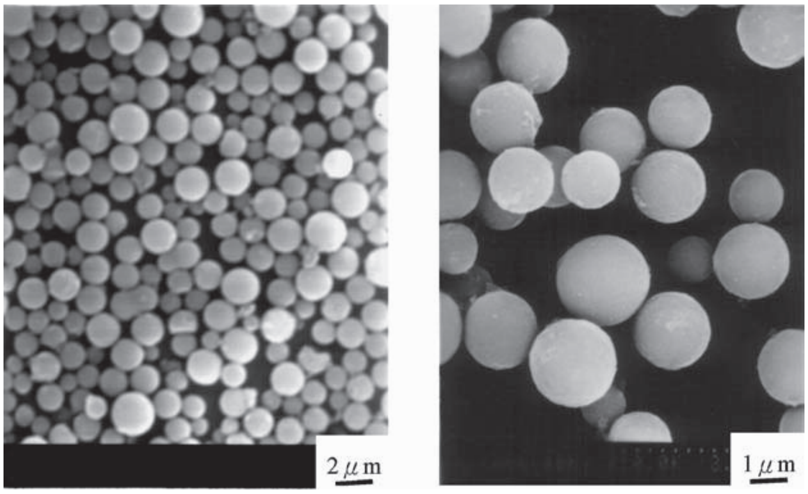

Figure 4 SEM micrographs of TiO_2 prepared at the conditions of 0.2 M $TiCl_4$, RH = 3, 0.001 g/cm^3 HPC, 70°C, 1 h reaction time.

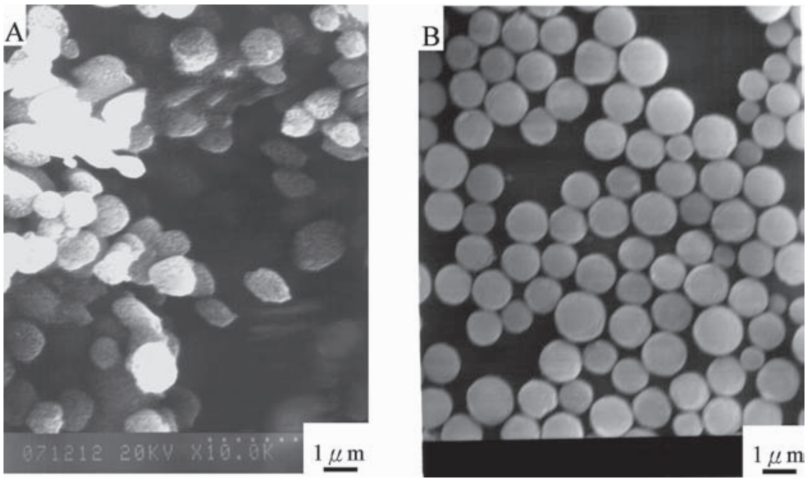

Figure 5 SEM micrographs of TiO_2 particles prepared at acetone/water volume ratio of 3 at 70°C. The reaction time was (A) 15 min, and (B) 60 min. The concentration of $TiCl_4$ was 0.1 M.

to the initial concentration of $TiCl_4$. These results indicate that the higher concentrations (0.1 M and 0.2 M) yielded unagglomerated and perfect spherical particles.

The effects of the reaction time was examined by using three different times, 15 min, 30 min, and 1 h, while other process parameters remained the same (0.1 M TiCl4, R/H ratio of 3, 0.001 g/cm^3 HPC, 70°C). The sample prepared in a shorter reaction time (15 min) resulted in the particles with less spherical shape, more particle aggregation, lower TiO_2 concentration, and some residual precursor chemicals (probably from unreacted chemicals) (Fig. 5A). As the reaction time

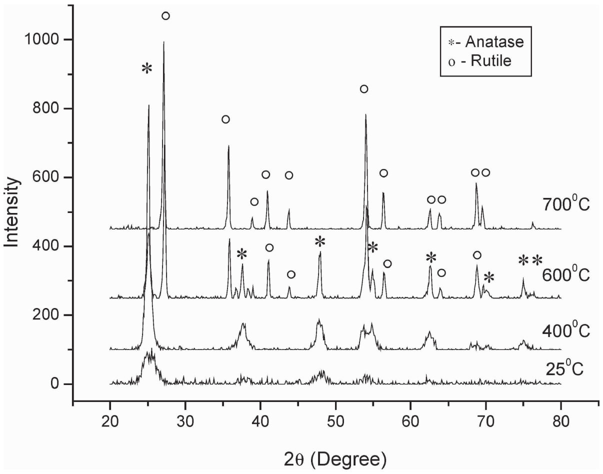

Figure 6 XRD patterns of TiO_2 particles after being calcined at different temperatures for 1 h.

increased to 30 min, particles became more spherical shape. When the reaction time increased to 60 min, particles became more uniform and spherical (Fig. 5B). Although precipitation occurred in a short time at this mixed solvent system, a longer reaction time ensured that the spherical TiO_2 particles were completely aged. These results indicate that the reaction time to form spherical TiO_2 particles would be 30 min at least to ensure the particles were completely aged in a mixed solvent of acetone-water system.

Reaction temperature had the most significant effect on the size, morphology, and reaction kinetics of the particles. TiO_2 particles that obtained from reaction at 70°C were spherical and discrete with narrow size distribution (~1 μm), while reaction at 80°C and 90°C were gradually changed to irregular shape and agglomerate. The crystalline structure of the spherical TiO_2 particles was examined by using XRD. Fig. 6 shows that a broad and small characteristic peak for anatase phase around 2θ of 25°C appeared in the as-synthesized sample and the phase of powders retained anatase below 400°C. If the calcination temperature increased up to 700°C for 2 h, anatase completely transformed to rutile and the calcined powders retained sphericity, but their size decreased slightly because of dehydration. In summary, The particles prepared at the condition of 0.1 M $TiCl_4$, R/H ratio of 3, HPC concentration of 0.001 g/cm^3, temperature of 70°C, and reaction time of 1 h exhibited the most uniform and spherical morphology for TiO_2 particles. These microspherical TiO_2 particles were used as the precursor to prepare barium titanate.

3.2. Synthesis of spherical $BaTiO_3$ particles

Spherical barium titanate particles were synthesized by using low-temperature (70–100°C) hydrothermal conversion of spherical titania particles. Fig. 7 shows the SEM micrographs of the sample prepared with an initial Ba/Ti ratio of 1.2, the hydrothermal conversion was carried out at 100°C for 24 h. As shown, the particles of barium titanate were near-monodispersed microspheres. The size and morphology of the converted particles remained the same as those of the titania particles, indicating that the formation of barium titanate was possible through the *in-situ* transformation mechanism [26, 27]. As *in-situ* model, it is believed to proceed by the diffusion of Ba^{2+} through the $BaTiO_3$ shell layer formed around the TiO_2 particles, followed by reaction with the TiO_2 core. The overall conversion rate could be controlled by either diffusion rate or reaction rate. On the basis of this model, it would be expected that the size and morphology of the converted $BaTiO_3$ particles should closely approximate those of the precursor TiO_2 particles.

The effects of reaction time was investigated by using four different reaction times (3 h, 6 h, 12 h and 24 h), while other process parameters remained the same (TiO_2 particles prepared from 0.1 M $TiCl_4$, Ba/Ti ratio of 1.2, 100°C). Fig. 8 shows the particles at four different reaction times. Fig. 8A and B show that the particles prepared in the shorter reaction times (3 h and 6 h) were spherical particles with some residual precursor chemicals (possibly $Ba(OH)_2$). As the reaction time increased to 12 h and above, the particles became more uniform and spherical (Fig. 8C and D). As shown in Fig. 8, the morphology of particles retained sphere

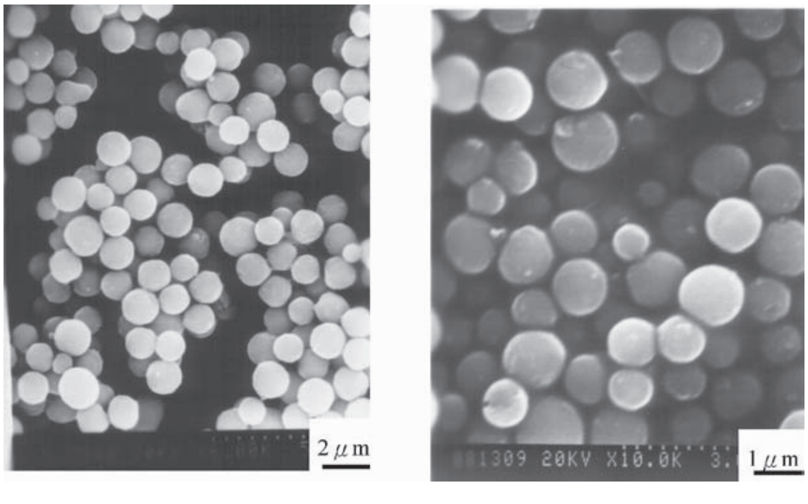

Figure 7 SEM micrographs of the $BaTiO_3$ particles after hydrothermal reaction.

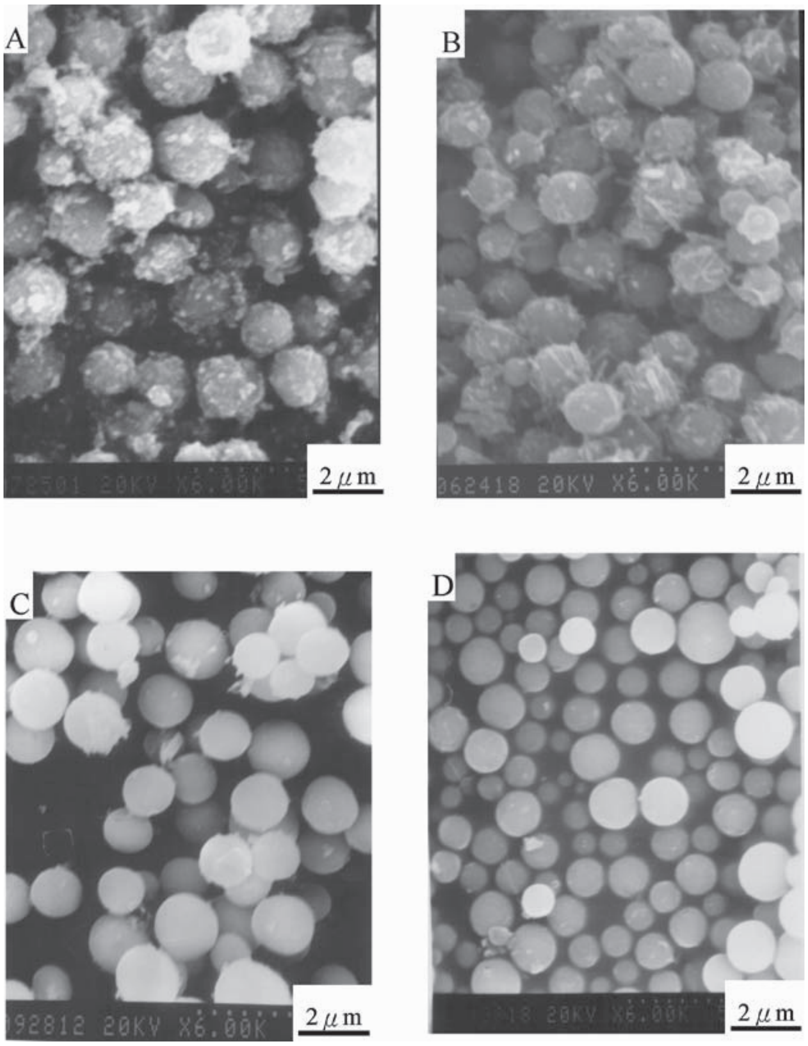

Figure 8 SEM micrographs of the $BaTiO_3$ particles after various reaction times (A) 3 h, (B) 6 h, (C) 12 h, and (D) 24 h.

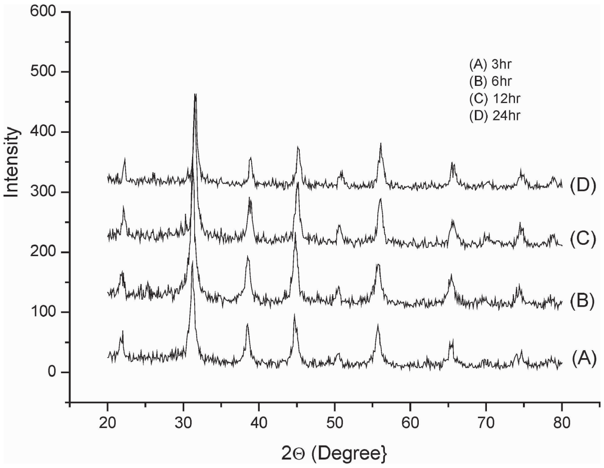

Figure 9 XRD patterns of spherical $BaTiO_3$ particles prepared with different reaction times.

through the overall reaction. These results reconfirm that the formation of spherical $BaTiO_3$ in hydrothermal conversion reaction was in situ transformation. Fig. 9 shows the XRD patterns of the spherical $BaTiO_3$ particles prepared with various reaction times. As can be seen in Fig. 9, the spherical $BaTiO_3$ particles with cubic phase occurred in a short time (3 h), a longer reaction time ensures that the uniform and spherical $BaTiO_3$ particles were completely aged. The $BaTiO_3$ crystalline phase prepared with 3 h and longer reaction times favored the future crystallization. These results indicate that the reaction time of spherical $BaTiO_3$ particles with cubic phase would be 12 h at least to ensure the particles were completely aged in a hydrothermal reaction.

Fig. 10 shows the XRD patterns of spherical $BaTiO_3$ particles prepared with various Ba/Ti ratios of 1.1–1.6, while other process parameters remained the same (TiO_2 particles prepared from 0.1 M $TiCl_4$, 100°C, 12 h). As shown in Fig. 10, the spherical $BaTiO_3$ particles with cubic phase were obtained with the Ba/Ti molar ratios in the range from 1.1 to 1.6 and a higher Ba/Ti molar ratio tented to give higher $BaCO_3$ peaks but not higher $BaTiO_3$ peaks.

The synthesis of spherical barium titanate particles was achieved by using low-temperature ($\leq 100°C$) hydrothermal conversion of spherical titania particles. Fig. 11 shows the XRD patterns of spherical $BaTiO_3$ particles prepared with various reaction temperatures in the range of 70–100°C, while other process parameters remained the same (TiO_2 particles prepared from 0.1 M $TiCl_4$, Ba/Ti ratio of 1.2, 12 h). Although $BaTiO_3$ with cubic phase could be obtained at the lowest temperature of 70°C, it tended to give higher $BaTiO_3$ and $BaCO_3$ concentrations when the reaction temperature increase. Higher reaction temperature favored the

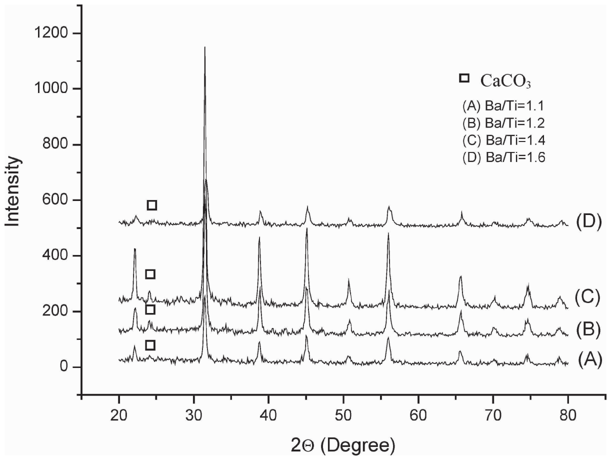

Figure 10 XRD patterns of spherical $BaTiO_3$ particles prepared with various Ba/Ti ratios.

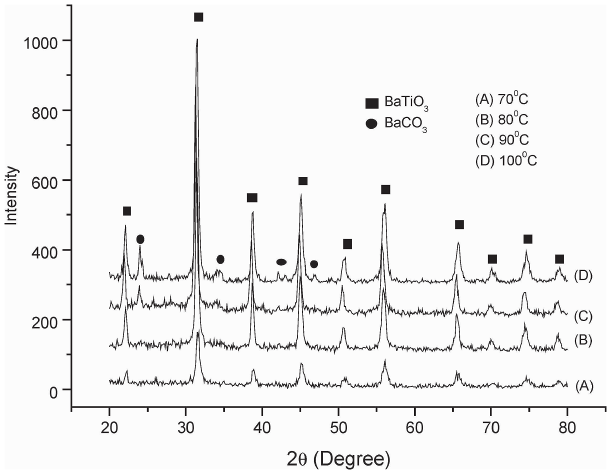

Figure 11 XRD patterns of spherical $BaTiO_3$ particles prepared with various reaction temperatures.

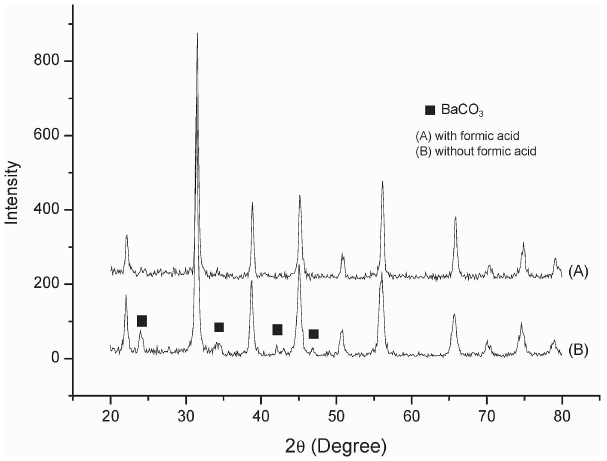

Figure 12 XRD patterns of spherical $BaTiO_3$ particles treated with and without formic acid.

further crystallization and also increase the concentration of unfavorable $BaCO_3$.

In order to obtain the high purity $BaTiO_3$, the samples should be washed with deionized water to remove the unreacted reactant ($Ba(OH)_2$), followed by washing with formic acid ($4\ mol \cdot dm^{-3}$) to remove $BaCO_3$. Fig. 12 shows the $BaTiO_3$ particles treated with and without formic acid, indicating the high purity $BaTiO_3$ could be obtained by the removal of $BaCO_3$.

4. Conclusions

An approach for the formation of spherical $BaTiO_3$ particles was developed by using a low-temperature ($\leq 100°C$) hydrothermal method from spherical titania particles. The change to dielectric constant of the liquid was used to produce spherical TiO_2 particles in submicrometer size from $TiCl_4$, followed by hydrothermal conversion in a barium hydroxide solution. The size and morphology of the TiO_2 particles was controlled by the volume ratio of acetone to water (RH ratio) in the mixed solvent. At the RH ratio of 3, the morphology of TiO_2 particles was very uniform and discrete. These spherical TiO_2 particles served as a precursor in the hydrothermal synthesis of spherical $BaTiO_3$ particles. In the hydrothermal process, the size and morphology of the $BaTiO_3$ particles were the same as those of the precursor TiO_2 particles. These evidences support the *in-situ* transformation mechanism for the conversion of TiO_2 to $BaTiO_3$. The $BaTiO_3$ particles prepared at the conditions of 0.1 M $TiCl_4$, Ba/Ti ratio of 1.2, temperature of 100°C and synthesis time of 12 h at least exhibited the most uniform and spherical shape. The mean density of the pellets sintered at 1300°C for 2 h were 5.47, 5.56, 5.72 and 5.86 g/cm^3 for 3 h, 6 h, 12 h and 24 h samples, respectively. These account for 90.86, 92.36, 95.02 and 97.34 % of the theoretical densities.

Acknowledgement

This research was supported by the National Science Council of the Republic of China.

References

1. M. Z.-C. HU, G. A. MILLER, E. A. PAYZANT and C. J. RAWN, *J. Mater. Sci.* **35** (2000) 2927.
2. G. J. CHOI, S. K. LEE, K. J. WOO, K. K. KOO and Y. S. CHO, *Chem. Mater.* **10** (1998) 4104.
3. S. WADA, T. SUZUKI and T. NOMA, *J. Ceram. Soc. Jpn.* **103** (1995) 1027.
4. B. HUYBRECHTS, K. ISHIZAKI and M. TAKATA, *J. Mater. Sci.* **30** (1995) 2463.
5. Y. SUYAMA and M. NAGASAWA, *J. Am. Ceram. Soc.* **77** (1994) 603.
6. A. BEAUGER, J. C. MUTIN and J. C. NIEPCE, *J. Mater. Sci.* **18** (1983) 3543.
7. A. AMIN, M. A. SPEARS and B. M. KULWICKY, *J. Am. Ceram. Soc.* **66** (1983) 733.
8. H. S. POTDAR, S. B. DESHPANDE and S. K. DATE, *Mater. Chem. Phys.* **58** (1999) 121.
9. S. G. KIM, M. H. LEE, T. Y. NOH and C. LEE, *J. Mater. Sci.* **31** (1996) 3643.
10. H. SHIMOOKA and M. KUWABARA, *J. Am. Ceram. Soc.* **78** (1995) 2849.
11. F. CHAPUT and J.-P. BOILOT, *ibid.* **73** (1990) 942.
12. P. K. DUTTA, R. ASIAIE, S. A. AKBAR and W. ZHU, *Chem. Mater.* **6** (1994) 1542.
13. K. KUMAZAWA, T. KAGIMOTO and A. KUWABARA, *J. Mater. Sci.* **31** (1996) 2599.
14. L. M. GAN, L. H. ZHANG, C. H. CHEW and B. H. LOO, *ibid.* **31** (1996) 1071.

15. P. GHERARDI and E. MATIJEVIC, *Colloids Surf.* **32** (1988) 257.
16. T. OGIHARA, N. MIZUTANI and M. KOTO, *Ceram. Int.* **13** (1987) 35.
17. C. SANCHEZ, J. LIVAGE, M. HENRY and F. BABONNEAU, *J. Non-Cryst. Solids* **100** (1988) 65.
18. H. T. HARRIS and C. H. BYERS, *ibid.* **103** (1988) 49.
19. H. K. PARK, Y. T. MOON, D. K. KIM and C. H. KIM, *J. Am. Ceram. Soc.* **79** (1996) 2727.
20. A. KATO, Y. TAKESHITA and Y. KATATAE, *Mater. Res. Soc. Symp. Proc.* **155** (1989) 13.
21. Y. T. MOON, H. K. PARK, D. K. KIM, I. S. SEOG and C. H. KIM, *J. Am. Ceram. Soc.* **78** (1995) 2690.
22. M. Z.-C. HW, V. KURIAN, E. A. PAYZANT, C. J. RAWN and R. D. HUNT, *Powder Technol.* **110** (2000) 2.
23. K. Y. CHEN and Y. W. CHEN, *ibid.* **141** (2004) 69.
24. F. FRANKS, “Water-A Comprehensive Treatise,” (Plenum Press, New York, 1973) Vol. 2, p. 405.
25. L. MEITES, “Handbook of Analytical Chemistry,” (McGraw-Hill Press, New York, 1982) p. 1–49.
26. J. O. ECKERT JR, C. C. HUNG-HOUSTON, B. L. GERSTEN, M. M. LENCKA and R. E. RIMAN, *J. Am. Ceram. Soc.* **79** (1996) 2929.
27. W. HERT, *ibid.* **71** (1988) 879.

Received 19 August 2003
and accepted 20 September 2004