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Homogeneous (co)precipitation of inorganic salts for synthesis of monodispersed barium titanate particles*

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Various processes of coprecipitation or crystallization of inorganic salts of barium and titanium from homogeneous solutions were studied in this work. In particular, barium hydroxide and barium chloride salt as well as titanium tetrachloride were used as the starting materials for dielectric-tuning homogeneous precipitation in mixed solvents of isopropanol and water. Hydroxypropylcellulose was used as a steric dispersant. Evaluations of size, shape, and composition of synthesized particles were made using scanning electron microscopy, high-temperature X-ray diffractometry, and differential thermal analysis. Results show that salt concentration, pH, and reaction time are important in determining the morphology and composition of the final powder. The titania particles from dielectric-tuning precipitation are perfect microspheres with narrow size distribution (near monodispersed), while the particles from barium salts are flake-like, irregular in shape and size. Instead of particles containing uniform compositions of barium and titanium compounds, dielectric-tuning coprecipitation yielded powders of two separated phases, i.e., monodispersed titania microspheres ($\sim$1 μm) coated on barium chloride salt flakes. Titanium-rich barium titanate was obtained after calcination of coprecipitated powders. However, preliminary results show that the titania particles obtained by dielectric-tuning precipitation can be hydrothermally converted to $BaTiO_3$ particles that are fully crystallized after calcination above 950°C. *© 2000 Kluwer Academic Publishers*

1. Introduction

Barium titanate ($BaTiO_3$), a perovskite-type electroceramic material, has been extensively studied and utilized due to its dielectric and ferroelectric properties. The cubic form of barium titanate exhibits a very high dielectric constant (1500–6000 at room temperature); meanwhile, the tetragonal polymorphs show ferroelectric, piezoelectric, and thermoelectric properties. The wide applications of barium titanates include multilayer capacitors in electronic circuits, electro-optical devices, thermistors, piezoelectric actuators, nonlinear resistors, thermal switches, passive memory storage devices, and transducers. In addition, barium titanate can be used for chemical sensors due to its surface sensitivity to gas adsorption [1].

Ultrafine barium titanate powders are important not only for preparation of monolith ceramics but also for fabrication of multiple-layer capacitors during which process aqueous dispersions of micrometer-size particles are generally used as a means of tape casting thin films of $BaTiO_3$ (thickness <100 μm). These applications demand high-purity particles that are aggregate free and have a high degree of compositional homogeneity, as well as controlled particle size (ideally

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submicrometer) [2], monodispersity, morphology, and crystallinity. Traditionally, barium titanate is prepared by the solid-state reaction at high temperatures around 1000°C: $BaCO_{3(s)} + TiO_{2(s)} \rightarrow BaTiO_{3(s)}$ [3], followed by grinding and further calcination. The resulting microstructure has a wide grain-size distribution and multiple phases, and is inevitably porous. These characteristics result from inadequate existing ball-milling operations that can introduce such impurities as alumina, silica, sulfur, and phosphorus etc. [4]. The lack of control over the physical and/or chemical characteristics of commercial barium titanate particles results in microstructural variations that lead to poor electrical property optimization and reproducibility [5]. Wet-chemical techniques for synthesizing ceramics offer promising approaches for preparing ultrafine, homogeneous, high-purity powders at temperatures far below those required for conventional powder preparation. Further, low-temperature processing and use of inexpensive inorganic salt precursors improve the cost-effectiveness of the powder production.

Table I summarizes various wet-chemical synthesis methods described in the literature for preparing barium titanate powders, which include homogeneous precipitation, coprecipitation, sol-gel, hydrothermal synthesis, sol-gel reactions coupled with microemulsion technique, and sol-gel reactions combined with hydrothermal processing. In particular, hydrothermal reactions between barium compounds and various forms of titanium, including hydrous titanium oxide [26, 36, 37, 43] or anatase and rutile [5, 26, 29, 43], are increasingly being used to prepare fine powders of barium titanate. Numerous ceramic powders can be conveniently synthesized by the hydrothermal processing, which makes it possible to prepare phase-pure products from inexpensive and easily accessible precursors in a single step. Also, the synthesis can be performed at moderate temperatures and pressures using a simple autoclave. The conditions of hydrothermal reactions can be optimized by varying the chemical process variables, such as reagent concentrations, temperature, pressure, and pH [5, 26].

TABLE I Methods for wet-chemical synthesis of barium titanate powders

Method	Brief description	References
Homogeneous precipitation	Precipitating precursor particles such as barium titanyl oxalate, then thermal decomposition to $BaTiO_3$	[7–9]
Coprecipitation	Polymerized complex method:	
	(1) using citrate—Pechini-type reaction route,	(1) [10, 11]
	(2) oxlate, or	(2) [8]
	(3) acetate gels (difficulty for doping; only good for Ba : Ti = 1 : 1)	(3) [12, 13]
Sol-gel method	Involving hydrolysis/condensation in solutions of	
	(1) mixed alkoxides,	(1) [14–17]
	(2) Ti-alkoxide–$Ba(OH)_2$,	(2) [2, 18–21]
	(3) bimetallic alkoxides, and	(3) [22, 23]
	(4) complex alkoxides.	(4) [24, 25]
Hydrothermal synthesis	e.g., Ti-precursor (gel or anatase) + $Ba(OH)_2 \rightarrow BaTiO_3$	
	(1) >100°C	(1) [5, 26–31]
	(2) low temperature (<100°C)	(2) [5, 26, 29, 30, 32–38]
	Typical conditions: CO_2-free environment, T>70°C, $pH \geq 13.4$, $[Ba^{2+}] = 0.2\ M$	
Combined approaches	(1) Microemulsion with sol-gel reaction	(1) [39, 40]
	(2) Sol-gel plus hydrothermal conversion	(2) [41]
	(3) Coprecipitation of oxalates plus inverse microemulsion	(3) [42]

Few of the above-mentioned methods really achieved the production of monodispersed microsphere particles. Gherardi and Matijevič [25] successfully prepared spherical colloidal (submicrometer size) $BaTiO_3$ particles of narrow size distribution by homogeneous precipitation involving a relatively expensive titanium alkoxide. They utilized complexes of Ti^{4+} and Ba^{2+} for designing appropriate solution species that would result in homogeneous nucleation and subsequent particle growth.

While the current wet-chemical methods show promise for producing barium titanate powder, further refinement of these methods is needed. The starting materials for metal alkoxide methods are restrictive due to high cost and moisture sensitivity. Some typical prices for barium and titanium alkoxides are, based on the Aldrich Catalog Handbook of Fine Chemicals [44]: titanium ethoxide (Ti ∼20%)–$92.60/250 g, titanium isopropoxide (99.999%)–$145.35/100 ml, and barium isopropoxide (99.9%)–$99.95/10 g. Inorganic salts of barium and titanium, however, are relatively inexpensive: titanium tetrachloride (99.9%)–$22.6/200 g, barium chloride dihydrate (99%)–$10.7/100 g, barium hydroxide octahydrate (98+%)–$13.70/100 g. Hydrothermal syntheses such as those conducted by Eckert Jr. *et al.* [5] and Wada *et al.* [36] were able to synthesize barium titanate from relatively inexpensive inorganic salt precursors. However, the particles formed in their experiments were not uniform in terms of size and shape and are usually aggregates. The $BaTiO_3$ particles prepared by Eckert Jr. *et al.* [5] appeared to form from a solid-state reaction between solid titanium oxide and Ba^{2+} that precipitates onto the surface of the titanium oxide. The barium titanate then grows inward from the point on the surface where barium first attaches. In the study by Wada *et al.* [36], a gel network of hydrous titania was formed by adding NH_4OH to a solution of $TiCl_4$. The barium hydroxide was then added to this "white gel solution," and $BaTiO_3$ was formed.

Recently, a so-called "dielectric-tuning" sol-gel method was developed for synthesis of monodispersed microsphere and nanosphere particles of oxides such as ZrO_2 and TiO_2 from inorganic salts [6, 45, 46]. This method is essentially a homogeneous precipitation process that is based on the use of mixed alcohol-water solutions of inorganic salts. The nucleation and growth of particles are controlled by adjusting the alcohol volume fractions and temperatures of the mixed solutions. In the work reported here, we attempted to explore the dielectric-tuning method for precipitation of single salt as well as coprecipitation of both barium and titanium precursor salts and, thus, the formation of barium titanate. Monodispersed microspheres of titanium oxide were successfully grown on the surfaces of barium chloride dihydrate crystal flakes via the coprecipitation of both titanium and barium inorganic salts in mixed isopropanol-water solvents. The effect of varying volume ratios of isopropanol to aqueous part on the particle/flake morphology was investigated. More importantly, we proposed a new synthesis route for producing monodispersed $BaTiO_3$ fine particles, i.e., dielectric-tuning precipitation of monodispersed titania microspheres coupled with hydrothermal conversion in $Ba(OH)_2$ solutions.

2. Materials and methods

2.1. Preparation of starting solutions

Titanium tetrachloride liquid (min. 99.0% $TiCl_4$, Johnson Matthey, USA) was added dropwise to ice-cold acidified deionized water. In a 50-ml volumetric flask, 2.85 ml of 1.0 N HCl was added to the deionized water prior to the addition of $TiCl_4$ in order to minimize the explosive generation of orthotitanic acid [$Ti(OH)_4$] [6]. The concentration of titanium in the prepared stock solution was 1.0 M. Barium chloride dihydrate (99.82% $BaCl_2{\cdot}2H_2O$, Fisher Scientific Co., USA) was added to distilled, deionized water at room temperature to generate a 1.0 M solution. Barium hydroxide octahydrate (min. 98% $Ba(OH)_2{\cdot}8H_2O$, Mallinckrodt Baker, Inc., USA) was added to solutions of titanium tetrachloride to make final mixed solutions containing 0.1 M titanium as well as 0.1, 0.2, and 1.0 M barium, respectively. Hydroxypropylcellulose (HPC, average molecular weight ~100,000 g/mol) was added to ice-cold distilled, deionized water to make a stock solution with a concentration of 0.1 g/cm^3. The HPC was used as a steric dispersing agent that adsorb on the surfaces of particles in a suspension.

2.2. Dielectric-tuning precipitation of single salt

A mixed-solvent approach was developed for dielectric-tuning precipitation of monodispersed titania microspheres with slight modifications from previous works [6, 46]. In this procedure we dissolved the inorganic salt ($TiCl_4$) and HPC in water and then added isopropanol, instead of *n*-propanol as was used in Park *et al.*'s work [6, 46]. The volume ratio of alcohol to aqueous part (RH), initial concentration of titanium salt, incubation time, and incubation temperature were controlled to allow for the rapid formation of uniform, well-dispersed microspheres of hydrous titania, which were then used as a good-quality precursor for the formation of barium titanate. Unless otherwise indicated, typical reaction conditions were 0.05 to 0.1 M titanium tetrachloride, RH = 1/1 to 5/1, 0.002 g/cm^3 HPC, and incubation at 80 to 100°C for 1 to 24 h. (Although precipitation may occur in short time, a longer incubation period ensures that the TiO_2 microspheres are completely aged.) After precipitation, the titania suspension was neutralized by the dropwise addition of 5 N NH_4OH under stirred conditions. As previously observed by Park *et al.* [6], the neutralization procedure helps to chemically stabilize the microspheres. Without neutralization the microspheres tend to dissolve into the water during any subsequent washing step to eliminate any impurities in particles, such as the chloride ion. The centrifugation and washing (with distilled, deionized water) steps were repeated twice. The washed white titania paste (containing equivalent 0.1 M titanium) was then redispersed into distilled, deionized water for hydrothermal synthesis of barium titanate.

To study the precipitation of barium precursor chemicals in mixed-solvents, similar procedure was used except for the use of barium salt (chloride or nitrate) to replace $TiCl_4$.

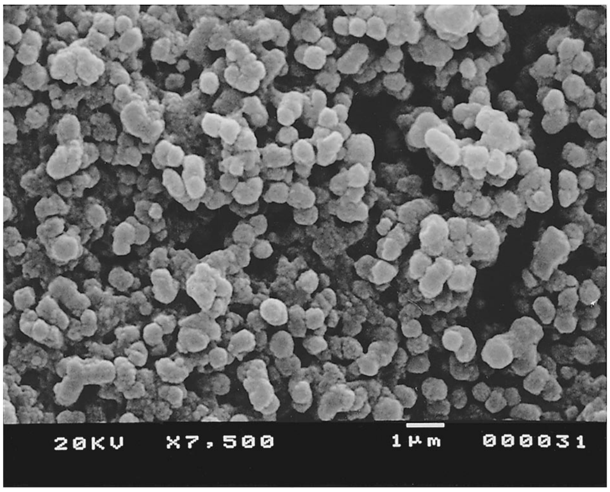


Figure 1 SEM photograph of titania particles prepared by dielectric-tuning precipitation at low RH values (1.0): 0.1 M $TiCl_4$ and 0.002 g/cm^3 HPC in isopropanol-water solution, incubated at 70°C for 1 h and then neutralized by 5 N ammonia.

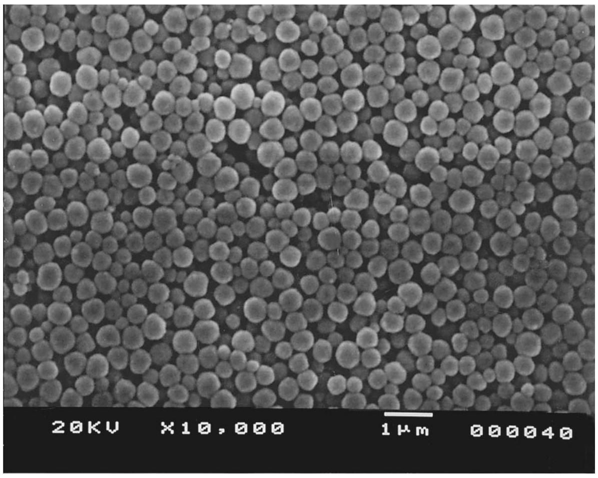


Figure 2 SEM photograph of titania particles prepared by dielectric-tuning precipitation at relatively high RH values (3.0): 0.1 M $TiCl_4$ and 0.002 g/cm^3 HPC in isopropanol-water solution, incubated at 70°C for 1 h and then neutralized by 5 N ammonia.

2.3. Coprecipitation from titanium and barium salt solutions

Appropriate amount of stock solutions of titanium tetrachloride, barium dichloride, and HPC were added in

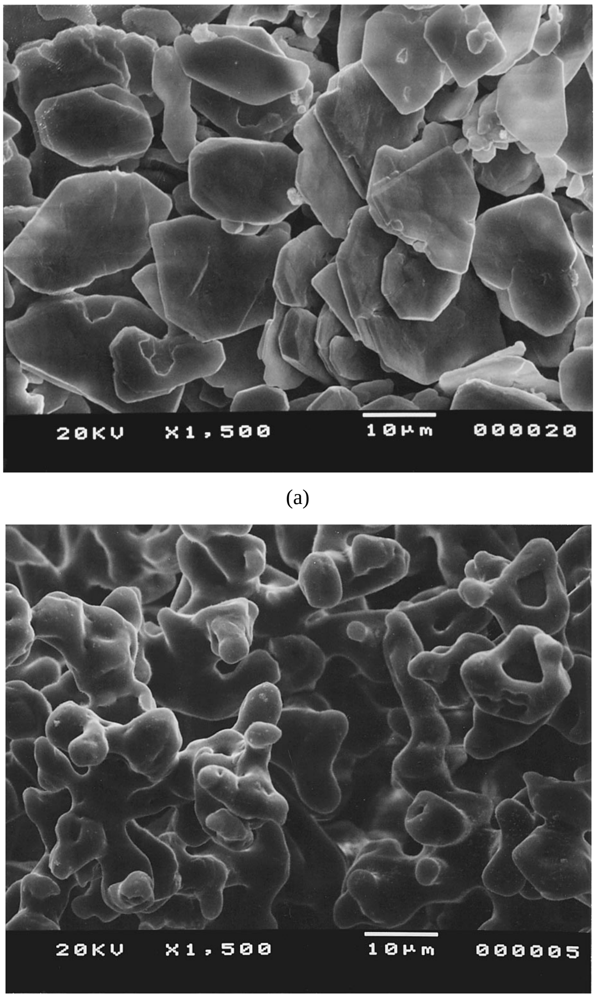


Figure 3 SEM photographs of barium precursor particles prepared by dielectric-tuning precipitation in barium salt solutions: (a) barium chloride (0.1 M $BaCl_2$, 0.002 g/cm^3 HPC, RH = 3, 100°C, 1 h, neutralized with 5 N ammonia); (b) barium nitrate (0.075 M $Ba(NO_3)_2$, 0.002 g/cm^3 HPC, RH = 3, 100°C, 1 h, neutralized with 5 N ammonia).

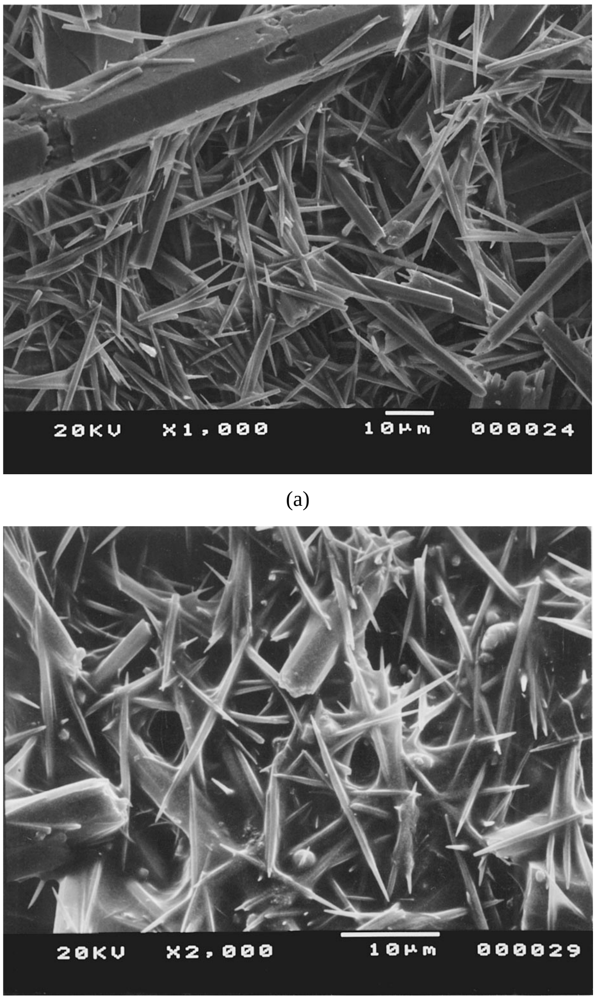


Figure 4 SEM photographs of barium precursor particles prepared by the urea hydrolysis method: (a) 0.1 M $BaCl_2$ in 2.0 M urea and 0.002 g/cm^3 HPC, incubated at 100°C for 1 h (mean particle size = 24.1 μm); (b) 0.5 M $BaCl_2$ in 1.0 M urea and 0.002 g/cm^3 HPC, incubated at 100°C for 1 h (mean particle size = 47.5 μm).

distilled, deionized water to form solutions that typically contain 0.05–0.2 M in barium salt, 0.05–0.2 M titanium salt, 0.002 g/cm^3 in HPC, and 1/1–5/1 in RH ratio. The final mixed solution (10 ml) was contained in a 20-ml glass scintillation vial, tightly capped, and then incubated at 100°C for 1 h. After precipitation, the suspension was neutralized with 5 N NH_4OH and subsequently analyzed by scanning electron microscopy (SEM). Heat treatment and characterization of the phase evolution were carried out using high-temperature X-ray diffraction (HTXRD).

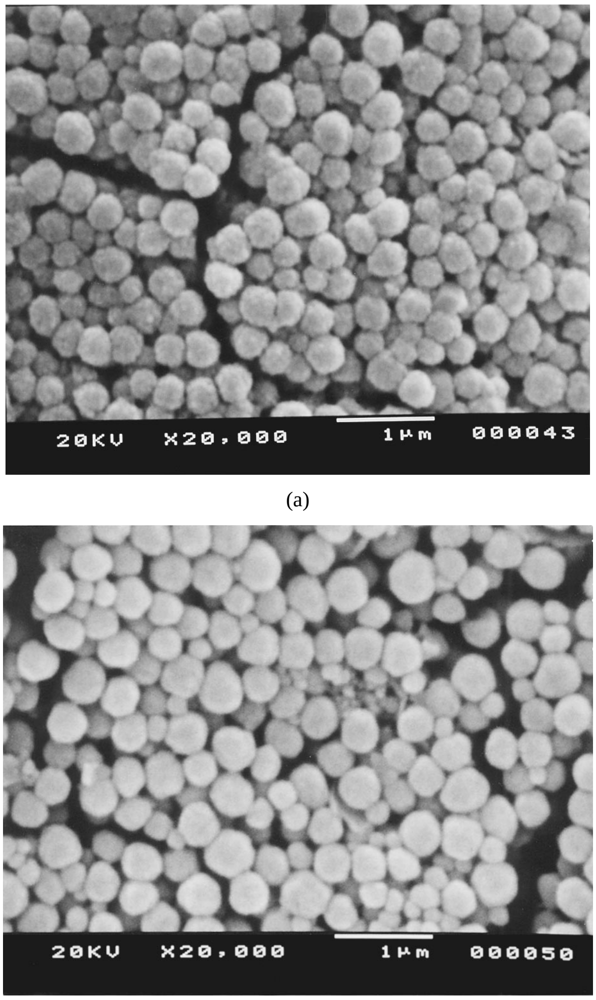
2.4. Hydrothermal synthesis of barium titanate particles

Titania microspheres (containing 0.1 M titanium equivalent) were prepared using the procedure described above. Then barium hydroxide octahydrate salt (0.95 g) was added to the aqueous slurry (30 ml) of titania microspheres until the barium concentration became 0.1 M (i.e., a Ba/Ti molar ratio of 1). After heating, the 0.1 M barium hydroxide was totally dissolved in the aqueous titania slurry, which had a pH about 12. Incubation at 70°C in tightly capped plastic centrifuge tubes for 72 h converted the slurry into a white precipitate in a light yellow-brown liquid. The precipitate was centrifuged, washed, and dried in an open-air oven at 100°C.

2.5. Characterization of the (co)precipitated particles

The particle size and morphology were analyzed by SEM (JSM–T220A, JEOL) prior to heat treatment. After precipitation (plus neutralization and washing steps, in some cases), 20 μl of the slurry was pipetted onto a carbon planchette that was glued onto a brass sample stub. After the sample had dried in air, a gold coating was applied on the surface of the powder via plasma sputtering (Hammer 6.2 Sputtering System, Anatech Ltd.) to create a conductive surface layer that is necessary for SEM imaging.

The X-ray diffraction measurements at room temperature (RTXRD, Scintag PAD V using Cu K_α radiation) were used for the phase determination of as-prepared samples without any heat treatment. Differential thermal analysis/thermal gravimetric analysis



(a)

(b)

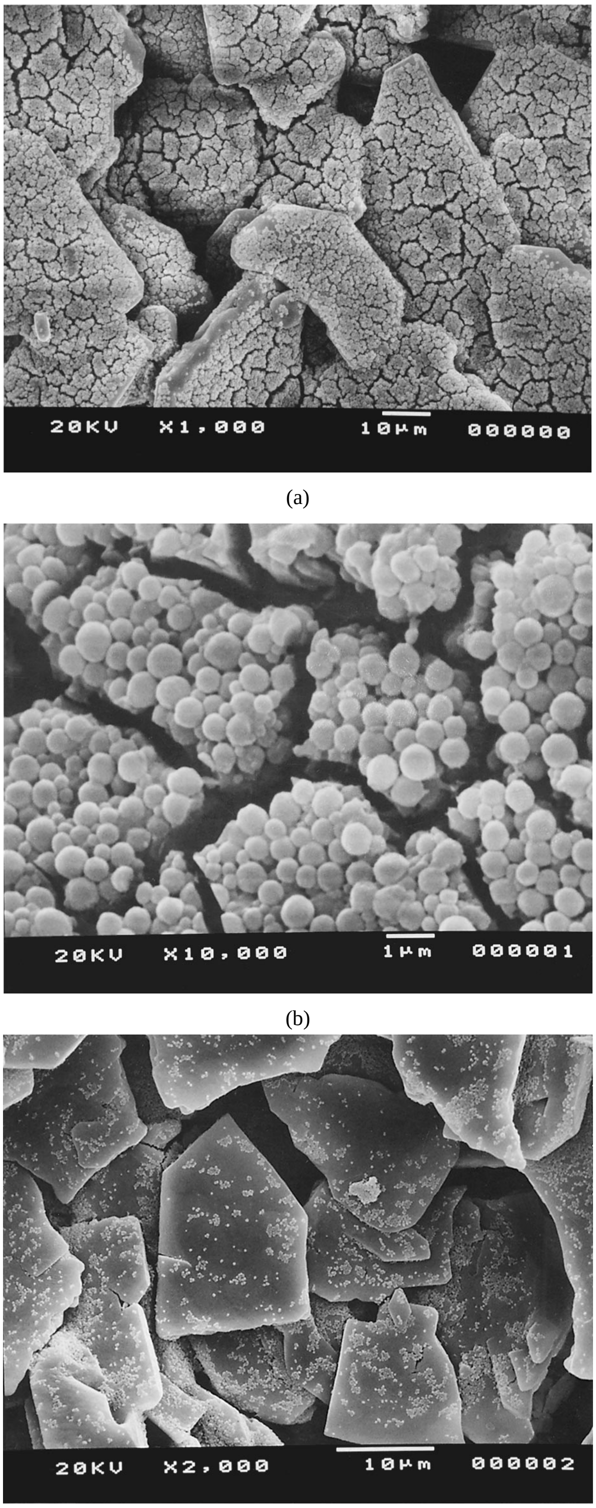
Figure 5 Ba-Ti particles obtained from dielectric-tuning coprecipitation in mixed solution of $BaCl_2$ and $TiCl_4$ (0.075 M for Ba^{2+} and Ti^{4+}, 0.002 g/cm^3 HPC, RH = 3, 100°C, 1 h): (a) no ammonia neutralization; (b) neutralized.

(DTA/TGA) (Harrop Model ST-736) of the $BaTiO_3$ particles revealed temperature ranges at which phase changes could take place. The DTA/TGA data were used to design a set of temperature ranges for X-ray diffraction scans to be run on the HTXRD instrument for the $BaTiO_3$ powders. The HTXRD (Scintag PAD X using Cu K_α radiation) measurements were carried out on powder samples to determine the phase composition at various temperatures from ambient to 1300°C. The detailed setup and analysis procedure for HTXRD has been described previously [47].

3. Results and discussion

3.1. Dielectric-tuning homogeneous precipitation of single inorganic salt

Monodispersed sub-micron sized titania microspheres were successfully produced by using isopropanol as a means of lowering the dielectric constant of the mixed alcohol/water medium. This mixed-solvent synthesis approach for homogeneous precipitation of inorganic salt(s) is adapted from a previous work conducted by Park *et al.* [6], who used a *n*-propanol/water mixture for the production of monodispersed titania microspheres. Isopropanol has a lower dielectric constant than *n*-propanol and thus, we believe, allows for faster precipitation kinetics. For the same period of incubation, the particles in an isopropanol system grew faster than those in a *n*-propanol system.



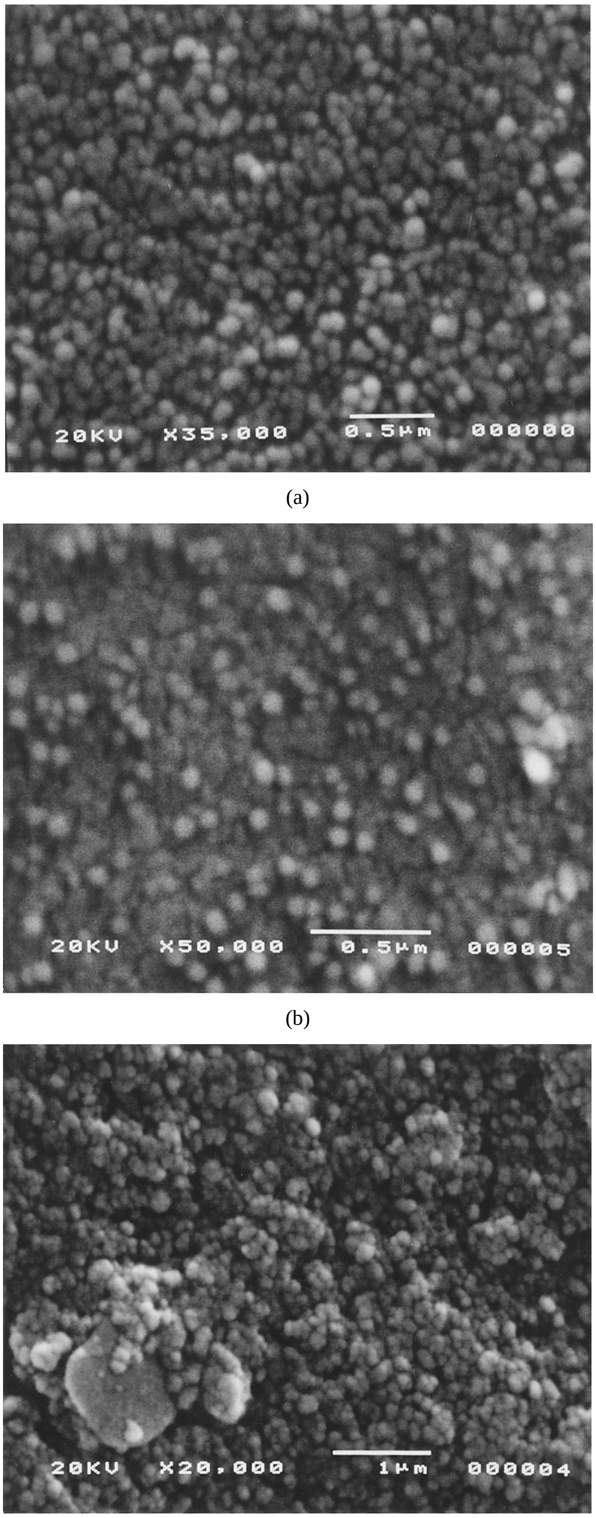
(a)

(b)

(c)

Figure 6 Ba-Ti particles obtained from dielectric-tuning coprecipitation in mixed solution of $BaCl_2$ and $TiCl_4$: (a) 0.1 M for Ba^{2+} and Ti^{4+}, 0.002 g/cm^3 HPC, RH = 3.55, 100°C, 1 h, no ammonia neutralization; (b) same as (a) except with higher magnification; (c) 0.075 M for Ba^{2+} and Ti^{4+}, 0.002 g/cm^3 HPC, RH = 5, 100°C, 1 h, no neutralization.

Dynamic light scattering (DLS) data revealed different growth dynamics for titania microspheres grown in the presence and in the absence of HPC as well as



(a)

(b)

(c)

Figure 7 Nanosized particles prepared by forced hydrolysis of aqueous solution of $TiCl_4$ in the presence of $Ba(OH)_2$ (0.1 M Ti, 0.1 M Ba, no isopropanol, 100°C, 4 days): (a) no ammonia neutralization and no washing by deionized water; (b) no neutralization but washed; (c) neutralized and washed.

under different RH conditions (data not shown; to be reported elsewhere). HPC addition tends to accelerate the initial stage of growth, perhaps due to the presence of many nucleation sites thought to be found on the HPC molecule. These nucleation sites may help to achieve a critical value of particles that leads to more rapid aggregation or flocculation.

SEM photographs revealed a trend toward decreasing titania particle size with increasing RH value. Restrictions of the stock solution concentration prevented the use of an RH value higher than 5/1, but particle diameter estimations based on SEM photographs for RH values between 4 and 5 are around 50–100 nm. When the RH was higher than 4, the nanoscale primary particles did not appear to aggregate into microspheres, which is in agreement with the observation by Park *et al.* [6]. The RH value also affects the surface properties and density of the microspheres. At low RH conditions (such as $RH = 1$), particles tend to stick together, forming aggregates and eventually producing a gel-type material after drying. Even the addition of HPC could not prevent the aggregation of the primary particles (Fig. 1). At higher RH conditions (such as $RH = 3$), well dispersed solid titania microspheres were formed (Fig. 2). The titania microspheres produced in this work were used to provide a high-quality precursor for later-stage hydrotermal synthesis of barium titanate particles. The characteristics of the titania microspheres in terms of monodispersity, size, and morphology directly affect or, at least, are related to similar characteristics of the barium titanate particles that are produced through hydrothermal conversion.

Unlike the homogeneous precipitation behavior of titanium tetrachloride in a mixed solvent such as isopropanol and water, the precipitation of barium salts (chlorides or nitrates) from mixed-solvent solutions tended to form irregular plate-shaped salt crystals with sizes ranging from 5 μm to tens of micrometers (Fig. 3). Other methods were also investigated to achieve the precipitation of ultrafine, uniform barium precursor particles, including urea hydrolysis (0.1 to 0.5 M $BaCl_2$, 1.0 to 2.0 M urea, and 0.002 g/cm^3 HPC incubated at 100°C for 1 h). Needles and hexagonal rod-shaped salt crystals were formed by the urea hydrolysis method (Fig. 4). No approach has yet been identified for producing uniform, ultrafine barium-compound particles from the precipitation of inorganic barium salts.

3.2. Co-precipitation for synthesis of barium titanate precursor powders

The composite particles or powders containing both barium and titanium compounds (at atomic- or molecular-level compositional homogeneity) can serve as good precursors for barium titanate phase formation under calcination conditions. The dielectric-tuning homogeneous precipitation method was also evaluated in the study presented here to simultaneously coprecipitate barium and titanium salts in mixed solvent (isopropanol-water) solutions. At relatively low concentrations of barium chloride (0.075 M) and titanium tetrachloride (0.075 M) under condition of a relatively low RH value ($RH = 3$), microsphere particles were obtained (Fig. 5). However, by adjusting the concentrations of both the barium and the titanium salts to 0.1 M and the RH value to 3.55, flakes of barium salt crystals coated with titania microspheres were produced (Fig. 6a and b). When the RH ratio is increased to 5, less amount of titania microspheres were produced anc

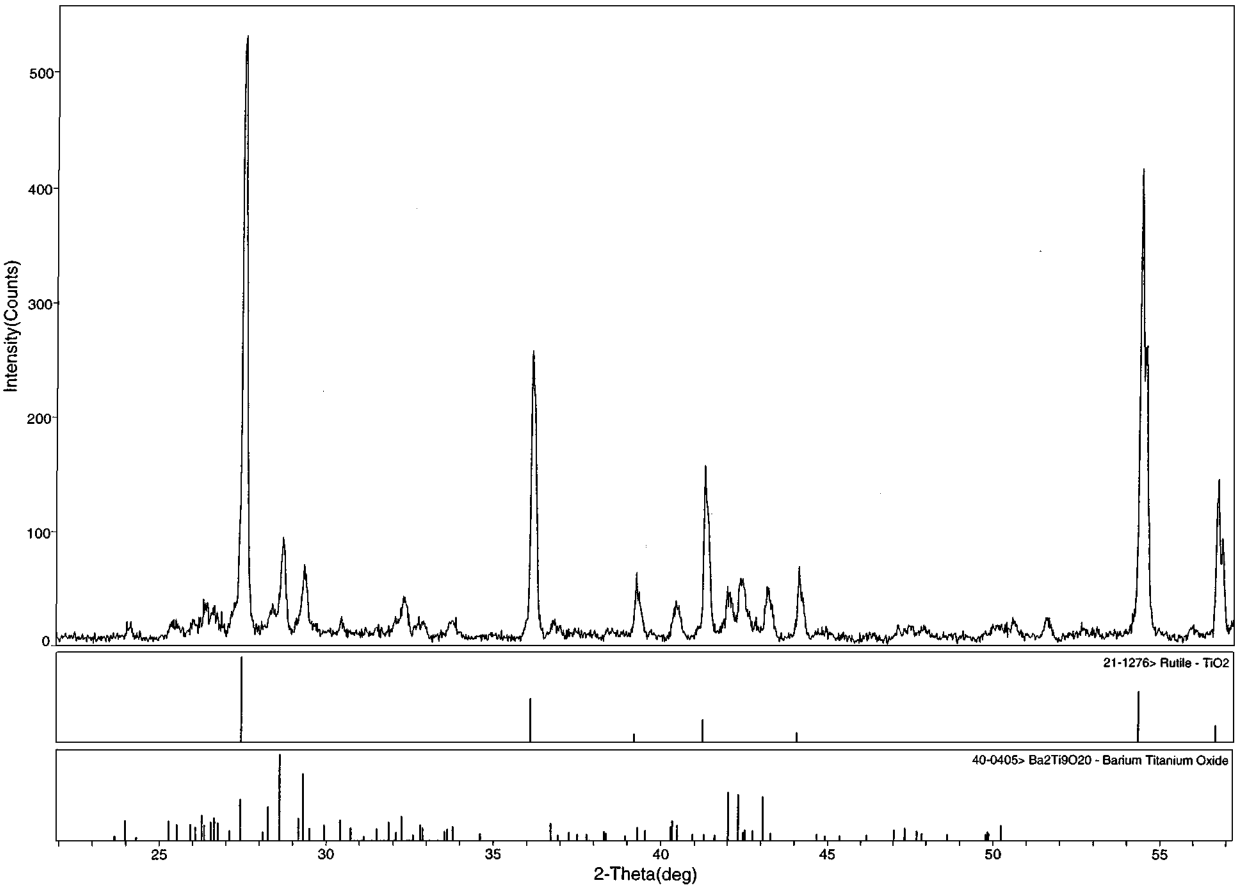


Figure 8 RTXRD spectrum for the nanosized particles shown in Fig. 7c after heat treatment at 1300°C for 2 h.

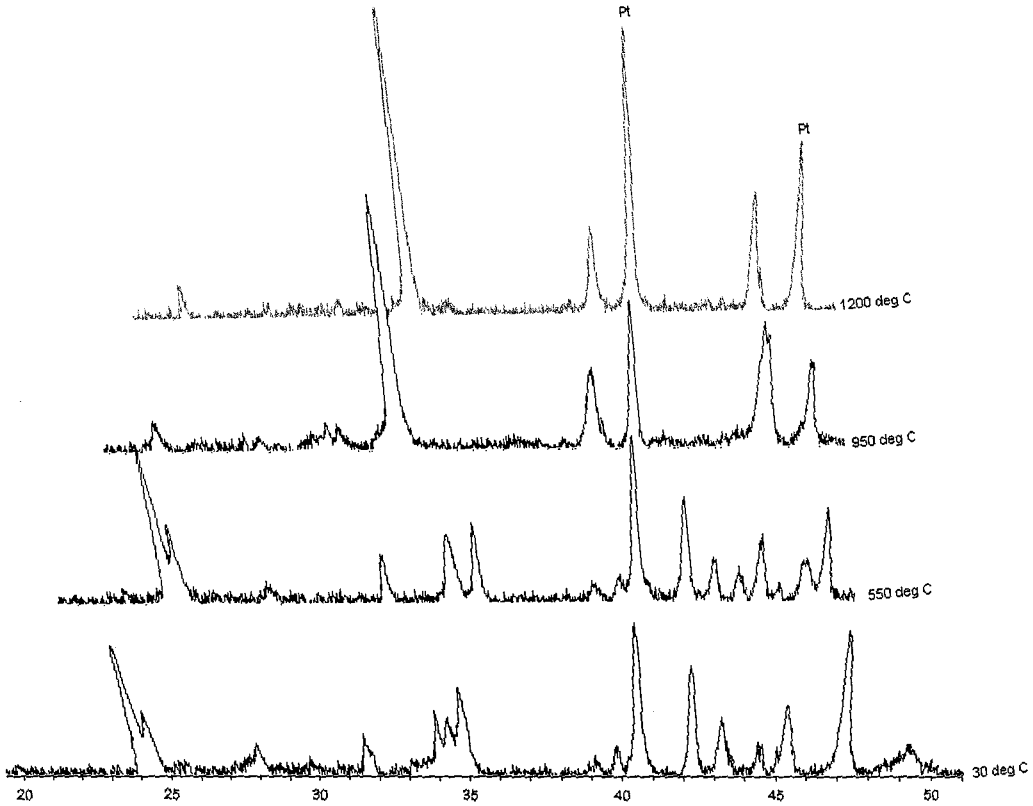


Figure 9 HTXRD data for particles obtained by hydrothermal conversion of titania microspheres (neutralized and washed) in aqueous $Ba(OH)_2$ solution. (0.1 M Ba, Ba/Ti = 1 : 1, pH ~12, 70°C, 3 days).

coated on the surfaces of barium-compound flakes. The titania-coated barium flake material as shown in Fig. 6a could serve as a good precursor for the formation of barium titanate through solid reactions at high temperatures because the thickness of the flake is below 1 μm, which matches the thickness of the titania microsphere coating.

In order to produce smaller-sized particles, a forced hydrolysis method employing titanium tetrachloride and barium hydroxide octahydrate was explored. Hydrothermal incubation of aqueous solutions containing both compounds at 100°C for four days produced uniform nanosized particles (below 100 nm) (Fig. 7). RTXRD results show the presence of $Ba_2Ti_9O_{20}$ and rutile for the nanoparticles that have been heat-treated at 1300°C for 2 h (Fig. 8).

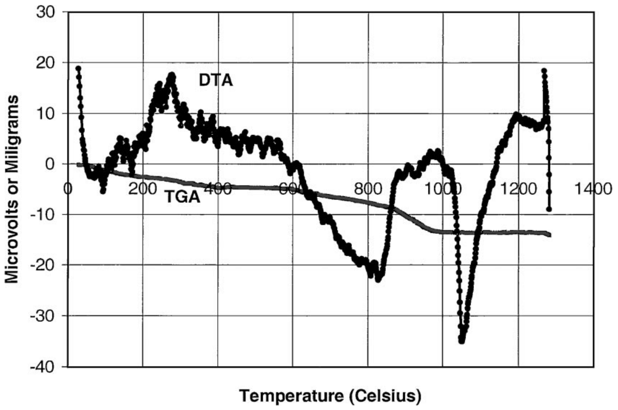


Figure 10 DTA/TGA analysis of the as-prepared powder sample from hydrothermal conversion of titania microspheres in aqueous $Ba(OH)_2$ solution.

3.3. Hydrothermal conversion to barium titanate

Preliminary studies were conducted for the hydrothermal conversion of titania to barium titanate, i.e., $TiO_2 + Ba(OH)_2 \rightarrow BaTiO_3$. This particular route has been previously utilized for the formation of barium titanate by several research groups (see references shown in Table I, under the category of hydrothermal synthesis). Previous work used commercially available titania particles (anatase) of relatively poor quality in terms of particle shape and size uniformity. In our work, however, we prepared barium titanate from the titania microspheres with well-controlled characteristics in terms of size, morphology, and monodispersity. It was discovered that the most important parameter affecting the barium titanate formation was pH. After the titania microspheres slurry had been mixed with barium hydroxide (0.1 M), there was no need to adjust the pH of the slurry because the pH was already greater than 12. Hydrothermal reactions at relatively high pH levels (above 10, based on the work by Eckert Jr. *et al.* [5] should induce the reactions between the Ba^{2+} and the titania, forming barium titanate. Our HTXRD data showed that the crystalline $BaTiO_3$ phase existed in the as-prepared sample obtained by hydrothermal treatment of the hydrous titania microspheres in aqueous $Ba(OH)_2$ solution (Fig. 9); however, minor impurity peaks (such as barium carbonate) were also present.

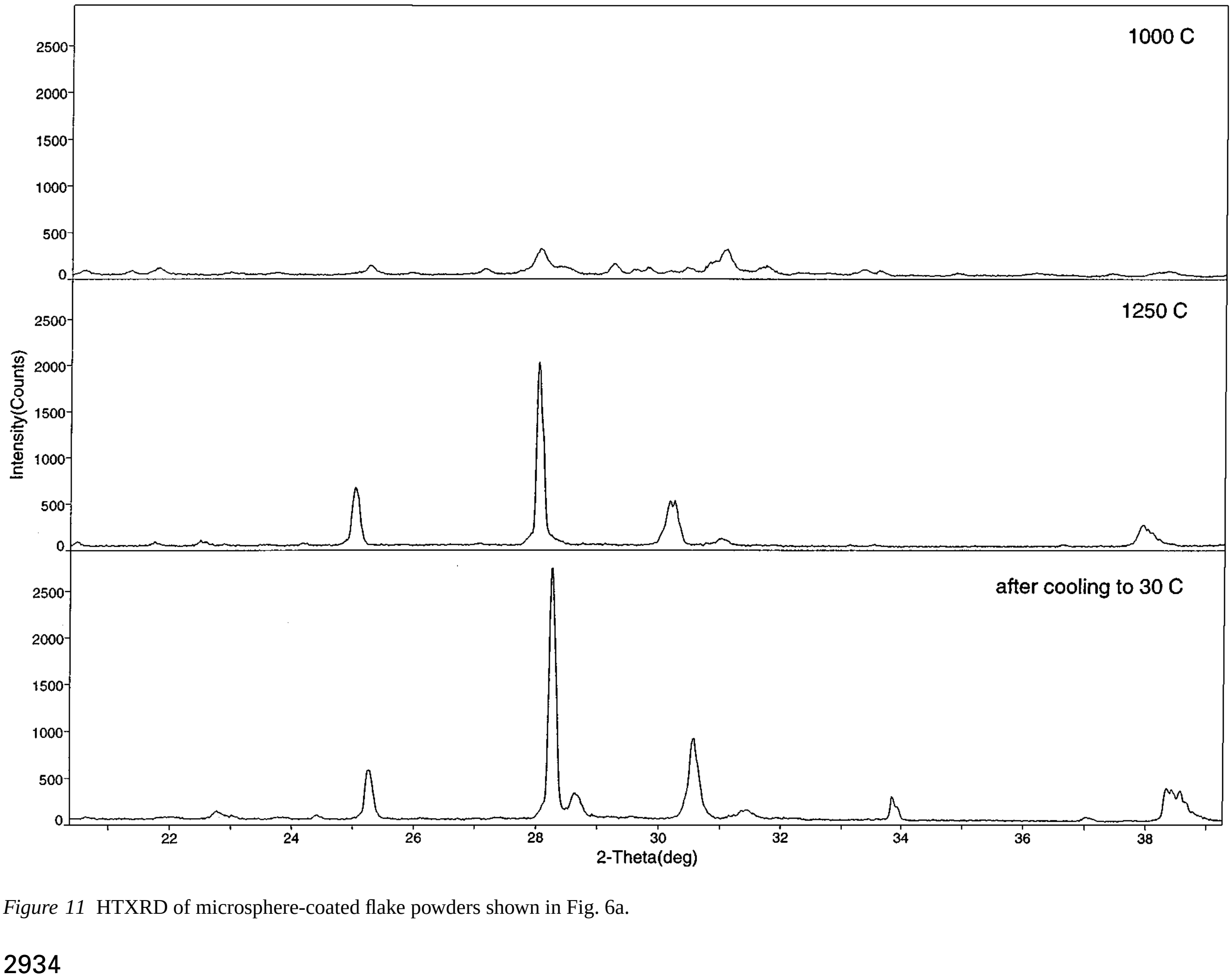


Figure 11 HTXRD of microsphere-coated flake powders shown in Fig. 6a.

The barium carbonate impurity may arise from the reaction between dissolved CO_2 and Ba^{2+} during solution incubation or from the reaction between CO_2 and the residual $Ba(OH)_2$ in the powder sample during drying at 100°C. In addition, with further heat treatment, more barium titanate crystallization occurred and eventually formed the relatively pure $BaTiO_3$ phase (from 950 to 1200°C) (Fig. 9). The DTA/TGA data (Fig. 10) show two major endothermic peaks: one between 600 and 900°C (corresponding to the formation of cubic phase barium titanate) and the other between 1000 and 1200°C (corresponding to phase transformation, possibly cubic to tetragonal). Furthermore, the HTXRD data for 950 and 1200°C (Fig. 9) show sharpening of a $BaTiO_3$ peak around 2θ of 45°, which possibly corresponds to a transformation from the cubic to the tetragonal phase. This is in agreement with the results obtained by Shi *et al.* [26].

Use of a washing procedure (with deionized water) after neutralization of the titania microspheres appeared to have no influence on the later conversion from TiO_2 to $BaTiO_3$. The impurities due to the presence of Cl^- and NH_4OH did not affect the formation of the barium titanate phase during the hydrothermal conversion.

It is interesting to note that in the dielectric-tuning precipitation of titania-coated barium salt flakes, the mixed solution contained both titanium source (salt or titania particles) and barium source (Ba^{2+}). This composition is similar to that of the solution for hydrothermal conversion of titania particles to barium titanate, except for the difference of the anionic species (OH^- versus Cl^-) and thus pH. The HTXRD data (Fig. 11) for the as-prepared powders of titania-coated flakes (shown in Fig. 6) did not show the $BaTiO_3$ crystalline phase, even after thermal treatment at various temperatures (1000, 1250, and cooled back to 30°C). This supports the claim that basicity of the reaction solution is responsible for the hydrothermal $BaTiO_3$-forming reaction between Ba^{2+} and titania. Additionally, the high-temperature (>1250°C) solid-state reactions between titania microspheres and the barium chloride salt flakes (Fig. 11) seemed to form more $BaTi_2O_5$, instead of $BaTiO_3$. Control of the phase formation in coprecipitated precursor particles would require additional investigation in the future. In addition, more detailed studies on the hydrothermal conversion process of titania microspheres (obtained by dielectric-tuning precipitation) will be reported elsewhere.

4. Conclusions

Various homogeneous precipitation schemes were explored for the production of uniform ultrafine Ti-, Ba-, and Ba-Ti-containing compound particles, which are potential precursors for preparing barium titanate powders. Special attention was focused on the dielectric-tuning precipitation and coprecipitation of inorganic salts in mixed isopropanol-water solutions. The dielectric tuning method has worked very well for producing ultrafine monodispersed titania microspheres (submicrometer size) from $TiCl_4$ but is somewhat problematic for the preparation of ultrafine barium-containing particles. The barium salt recrystallized into powders of flakes with irregular sizes in the range of tens of micrometers. Dielectric-tuning coprecipitation of titanium and barium inorganic salts formed composite powders that contain barium-compound flakes coated with submicrometer-sized titania microspheres. Finally, we devised a promising approach for the formation of monodispersed $BaTiO_3$-microspheres, i.e., dielectric-tuning precipitation of titania coupled with hydrothermal conversion in a barium hydroxide solution. Titania microspheres serve as an important precursor in the hydrothermal synthesis of $BaTiO_3$. Improvements in microsphere quality (such as smaller diameter, more spherical morphology, and improved monodispersity) as well as an understanding of the mechanisms and kinetics of hydrothermal conversion from titania to barium titanate, deserve to be the subjects of future studies.

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