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Preparation of $BaTiO_3$ by the Hydrothermal Method

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Abstract

The results of hydrothermal preparation of $BaTiO_3$ *fine powders are reported. The effects of the reaction temperature, the molar ratio of Ba/Ti in the precursors, the chemical form of the precursors on the phase composition, the size and the morphology of the products are presented. The higher the temperature, the higher the basicity and the greater the molar ratio of Ba/Ti in the precursor, the easier the formation of the perovskite type* $BaTiO_3$ *crystallite will be. It was found that* $BaTiO_3$ *microcrystals(150–300 nm) could be synthesized through the hydrothermal reaction of commercial* TiO_2 *with* $Ba(OH)_2$ *aqueous solution, while the hydrothermal reaction of the newly prepared* $Ti(OH)_4$ *gel with the* $Ba(OH)_2$ *solution produced highly crystallized, well dispersed perovskite type* $BaTiO_3$ *crystallites with very fine (<100 nm) particles. The newly prepared* $Ti(OH)_4$ *gel proved to be suitable precursor for the hydrothermal preparation of* $BaTiO_3$ *fine powders. X-ray diffraction (XRD) of the hydrothermal* $BaTiO_3$ *powders reveals a simple cubic perovskite structure. Above that, the lattice constant decreased with the increase of the reaction temperature. These abnormal crystallographic features are assumed to result from lattice defects, due to* OH^- *incorporation in the perovskite lattice.*

1 Introduction

$BaTiO_3$ is an ubiquitous electronic ceramic widely utilized in the manufacture of thermistors, multilayer capacitors (MLCs) and electro-optic devices.[1] $BaTiO_3$ powders are traditionally prepared via the calcination of $BaCO_3$ and TiO_2 or $BaTiO[C_2O_4]_2 \cdot 4H_2O$. As the temperature required is as high as 800–1100°C, the powders prepared are highly agglomerated and require extensive milling before they can be used in the various forming process. Low temperature, wet chemical routes offer an exciting possibility for the synthesis of high purity, homogeneous, ultrafine and multicomponent powders. Because of the possibility of producing highly crystallized, well dispersed and sintering active powders, the hydrothermal synthesis of ceramic powders is of great interest.

Christensen[2] and Kaneko[3] have shown that $BaTiO_3$ can be prepared from barium hydroxide solutions and oxide, esters or oxide gels of titanium, when temperatures from 380 to 500°C and pressures from 300 to 500 atm are applied. Recent work by Kutty and co-workers[4–6] demonstrates the synthesis of ultrafine $BaTiO_3$ powders at temperatures as low as 85°C and the pressures from 15 to 65 MPa. Hennings *et al.*[7] have reported the hydrothermal preparation of highly crystallized $BaTiO_3$ powders with a size of 200–300 nm from barium–titanium-acetate gel precursors.

We now report the results of the systematic study of the hydrothermal synthesis of $BaTiO_3$. The relation between the phase composition, size, morphology of the crystallites and the reaction temperature, the precursors, the molar ratio of Ba and Ti in the precursors have been found. The formation mechanism of $BaTiO_3$ under hydrothermal conditions has also been tentatively proposed.

2 Experimental Procedure

The precursors and the medium used in this study are shown in Table 1. The 160 ml reaction mixtures were charged into a Pt crucible of 200 ml capacity, which was then put into the autoclave and heated at 75–400°C for various durations. The pressure remained close to the vapour pressure curve of H_2O in this temperature range. The products were filtered and washed with dilute acetic acid to remove any excess $Ba(OH)_2$, and then washed with deionized water and alcohol and then air-dried at 120°C.

Identification of the phases was carried out by X-ray powder diffraction (XRD; Rigaku RAX-10). Transmission electron micrographs (TEM) were obtained from a JEOL JEM-2010 microscope. The extent of reaction was determined by analyzing the amount of OH^- in the residual solution.

Table 1. Precursors and solutions selected for hydrothermal synthesis of $BaTiO_3$ powders

No.	*Ba precursor*	*Ti precursor*	*Reaction medium*
1	$Ba(OH)_2{\cdot}8H_2O$	Commercial TiO_2	Aqueous solution
2	$Ba(CH_3COO)_2$ + NaOH	Commercial TiO_2	Aqueous solution
3	$Ba(OH)_2{\cdot}8H_2O$	Tetrabutyl titanate	Aqueous solution
4	$Ba(OH)_2{\cdot}8H_2O$	Tetrabutyl titanate	Ethanol 50 vol% aqueous solution

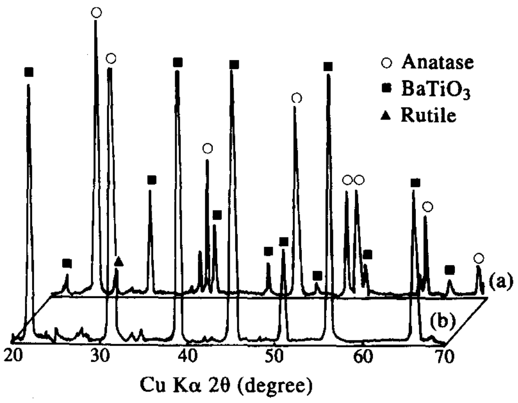

Fig. 1. XRD spectra of hydrothermal powders synthesized at (a) 75°C and (b) 400°C for 8 h using equimolar $Ba(OH)_2{\cdot}8H_2O$ and commercial TiO_2 powders.

3 Results and Discussion

3.1 The influence of temperature on the phase composition and morphology

Equimolar $Ba(OH)_2{\cdot}8H_2O$ and commercial TiO_2 powders (X-ray analysis showed that this titania consists principally of anatase with about 10–15% rutile) were hydrothermally processed at various temperatures for different durations. Figure 1(a) shows the XRD spectrum of the product of 75°C for 8 h. The $BaTiO_3$ peaks appeared besides the peaks of TiO_2, which means $BaTiO_3$ was formed. The products were nearly single phase $BaTiO_3$ when the precursors were treated at 400°C for 8 h (Fig. 1(b)). It was found by the analysis of the products synthesized at other temperatures (100, 150, 180, 200, 250 and 300°C) that the (101) peak of anatase was presented in all the products synthesized at the temperatures below 300°C.

Figure 2 illustrates the TEM morphologies of the powders prepared at different temperatures for 8 h. The morphologies of the powders were strongly dependent on the temperature. It can be easily seen from the photographs, that with an increase in temperature, the morphology of the powders changed from spheric cluster (Fig. 2(a)), to porous spheric cluster (Fig. 2(b, c)), and finally

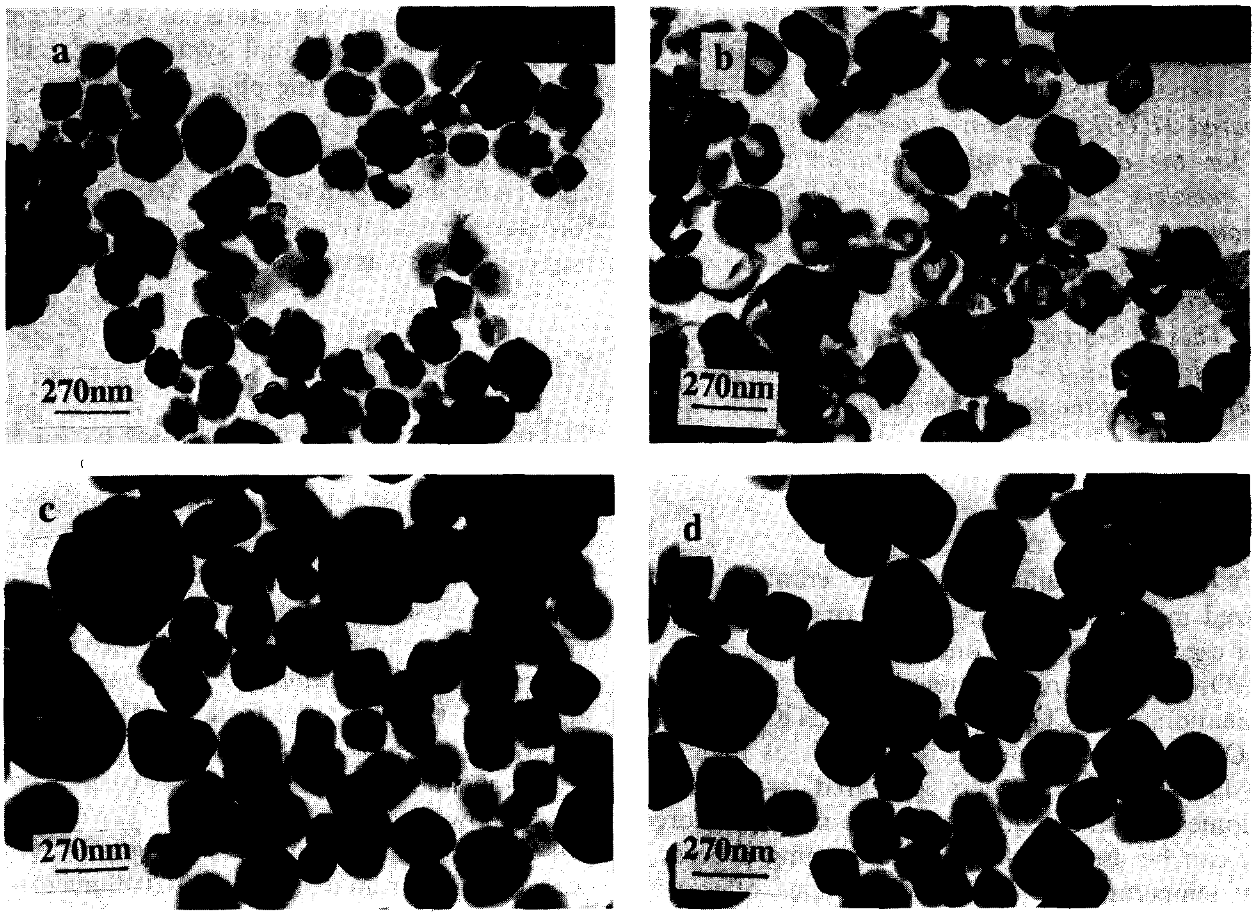

Fig. 2. TEM photographs of hydrothermal powders synthesized at (a) 75°C and (b) 400°C for 8 h using equimolar $Ba(OH)_2{\cdot}8H_2O$ and commercial TiO_2 powders.

Table 2. The relationship between reaction completeness and reaction temperature

Reaction temperature T(°C)	*Reaction completeness ρ(%)*
100	75·54
150	81·09
250	86·37
300	88·68
400	91·21

$Ba(OH)_2{\cdot}8H_2O + TiO_2$, m(Ba)/m(Ti)=1·0, 8 h.

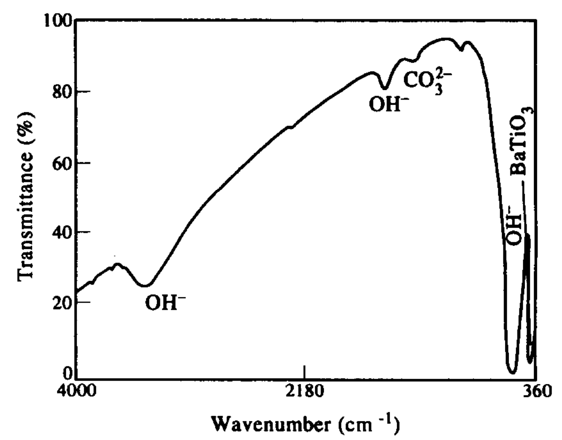

Fig. 3. IR spectrum of hydrothermal $BaTiO_3$ synthesized from $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 powders.

formed well crystallized cubes or spheres (Fig. 2(d)). It can also be seen that the size of the crystallites increased slightly with the increase of reaction temperature.

The following reaction took place in the system:

$$TiO_2 + Ba(OH)_2 \rightarrow BaTiO_3(\text{crystallite}) + H_2O.$$

Since the $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 used were of equal molar and there was no other OH^- source in the system, with the progress of the reaction, $BaTiO_3$ crystallites were formed and the amount of OH^- decreased. By defining

$$\rho = (1\text{–residual } OH^-/\text{initial } OH^-) \times 100\%,$$

the value of ρ can be approximately seen as the extent or the completeness of the reaction. Table 2 gives the ρ values for different temperatures. It can be clearly seen that the higher the reaction temperature, the greater the ρ value, which means the reaction took place more completely.

3.2 The relation between the lattice parameters and the reaction temperature

X-ray diffraction of hydrothermal $BaTiO_3$ revealed a simple cubic perovskite structure (Fig. 1) which is normally observed only at temperatures above the ferroelectric Curie point at 130°C or at very small crystallite size ($d<0{\cdot}15\ \mu m$). Above that, the lattice parameters changed with the change of reaction temperature as shown in Table 3. It can be seen from the table that the unit cell volume of the hydrothermal $BaTiO_3$ is larger than 'normal' coarse-grained $BaTiO_3$, moreover, with an increase in reaction temperature, the unit cell volume of the crystallites shrinks. When the temperature increased from 75 to 400°C, the unit cell volume shrank by about 2·08%. The unit cell volume of the crystallites prepared at 400°C for 8 h approached a value of 64 $\simeq$ $Å^3$,[8] which is the typical value of 'normal' coarse-grained $BaTiO_3$ by classical calcination.

Table 3. The relationship between the lattice parameters of the hydrothermal $BaTiO_3$ microcrystals and the reaction temperature

Reaction temperature T(°C)	75	100	150	250	300	400
Lattice constant a (Å)	4·031	4·025	4·016	4·012	4·008	4·003
Unit cell volume $Vc(Å^3)$	65·50	65·21	64·77	64·58	64·38	64·14

A typical IR spectrum (Fig. 3) of hydrothermal $BaTiO_3$ shows broad absorption in the region of 3200–3600 cm^{-1}, a shallow band around 1640 cm^{-1} and a strong band at 650 cm^{-1}. The 1640 cm^{-1} band (bending mode of H_2O) indicates that some H_2O is present. The strong band at 650 cm^{-1} is characteristic of the librational mode of OH^- groups and is more distinct than the OH^- stretching which is masked by the corresponding H_2O bands around 3600 cm^{-1}. A TG-DTA-MS study found that the samples gives out H and O when heated above 200°C. These phenomena suggest the OH^- is present in the lattice. Besides the $OH^{\bullet}$ defect, other defects may also form to meet the electroneutrality requisition. The presence of these defects suppressed the tetragonal distortion, so the crystallites can exist in cubic phase at room temperature. The defect concentration decreased when the reaction temperature increased, thus the unit cell volume of $BaTiO_3$ shrank.

3.3 The influence of Ba : Ti molar ratio in the precursors

With a fixed total amount of precursors (50 g), different Ba : Ti molar ratios of $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 were hydrothermally treated at 300°C for 8 h. Figure 4 shows the XRD spectra of the products. From the figure, we can see the anatase (101) peak appeared for the lower molar ratio (1·0) (Fig. 4(a)). But the peak disappeared for the higher molar ratio (Fig. 4(b, c)). Another interesting phenomenon is that the (002) (200) and (102) (210) peaks are split for the molar ratio of

2·0, which suggests that tetragonal $BaTiO_3$ was formed in this case. Further investigations have proved this suggestion (Figs 5 and 6). The product was easily contaminated with $BaCO_3$ when a high Ba : Ti molar ratio precursor was used.

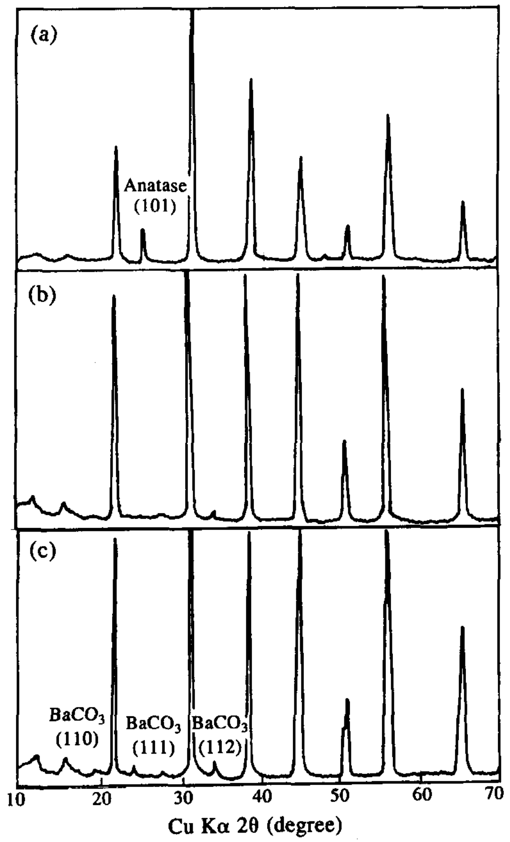

Fig. 4. XRD spectra of hydrothermal powders synthesized at 300°C for 8 h using different molar ratio of $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 powders. (a) m(Ba)/m(Ti) = 1·0, (b) m(Ba)/m(Ti) = 1·5, (c) m(Ba)/m(Ti) = 2·0.

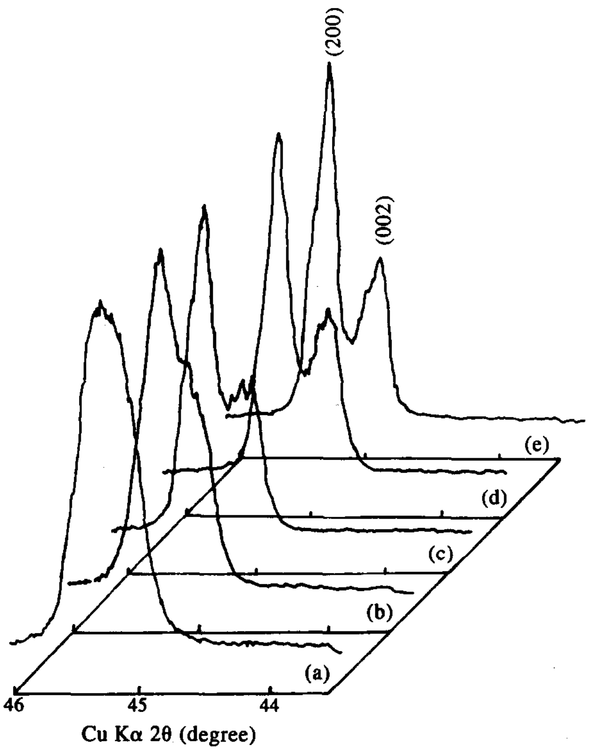

Fig. 5. X-ray diffraction traces of the (200) and (002) reflections for hydrothermal $BaTiO_3$ synthesized from different Ba/Ti molar ratio $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 at room temperature. (a) 1 : 1, (b) 1·5 : 1, (c) 2·0 : 1, (d) 2·5 : 1, (e) 3·0 : 1.

3.4 The influence of the kind of precursors on the size and morphology of the crystallites

Figure 7 shows the TEM photographs of the powders prepared from different precursors. Well-crystallized $BaTiO_3$ with a size of 80–100 mn was formed (Fig. 7(a)) when precursors in $Ba(OH)_2$ aqueous solution were hydrothermally treated at 300°C for 8 h, however from the photograph some organic residual can be seen. It was found that the organic residual disappeared when some alcohol was added to the reaction solution. Figure 7(b) is the TEM photograph of the powders prepared from newly prepared $Ti(OH)_4$ gel(hydrolysis product of tetrabutyl titanate) and $Ba(OH)_2{\cdot}8H_2O$. The powders are highly crystallized, well dispersed cubic or spheric $BaTiO_3$ crystalites with a size less than 100 nm.

In summary, the kind of precursors have a strong influence on the size and the morphology of the $BaTiO_3$ synthesized.

3.5 The influences of medium

Experiments show that when $Ba(OH)_2{\cdot}8H_2O$ and TiO_2 were used as precursors, the formation of $BaTiO_3$ under hydrothermal conditions could be facilitated by using an alkaline mineralizer (e.g. NaOH). Figure 8 shows the XRD spectra of the powders synthesized at 300°C for 8 h in pure water and 1 mol/l NaOH aqueous solution. The amount of the residual TiO_2 in powders synthesized in the NaOH aqueous solution was distinctly less than in pure water, which means the reaction was more complete in the former case. The crystallinity of the $BaTiO_3$ synthesized in the NaOH aqueous solution was also higher (Fig. 9(b)).

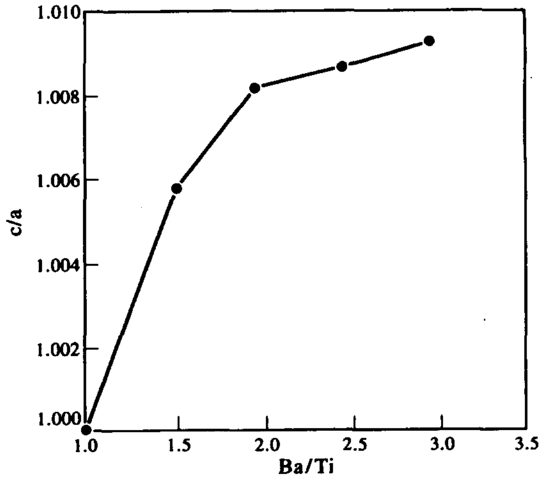

Fig. 6. The relationship between the *c/a* value of hydrothermal $BaTiO_3$ and the Ba:Ti molar ratio of $Ba(OH)_2{\cdot}8H_2O$ and TiO_2.

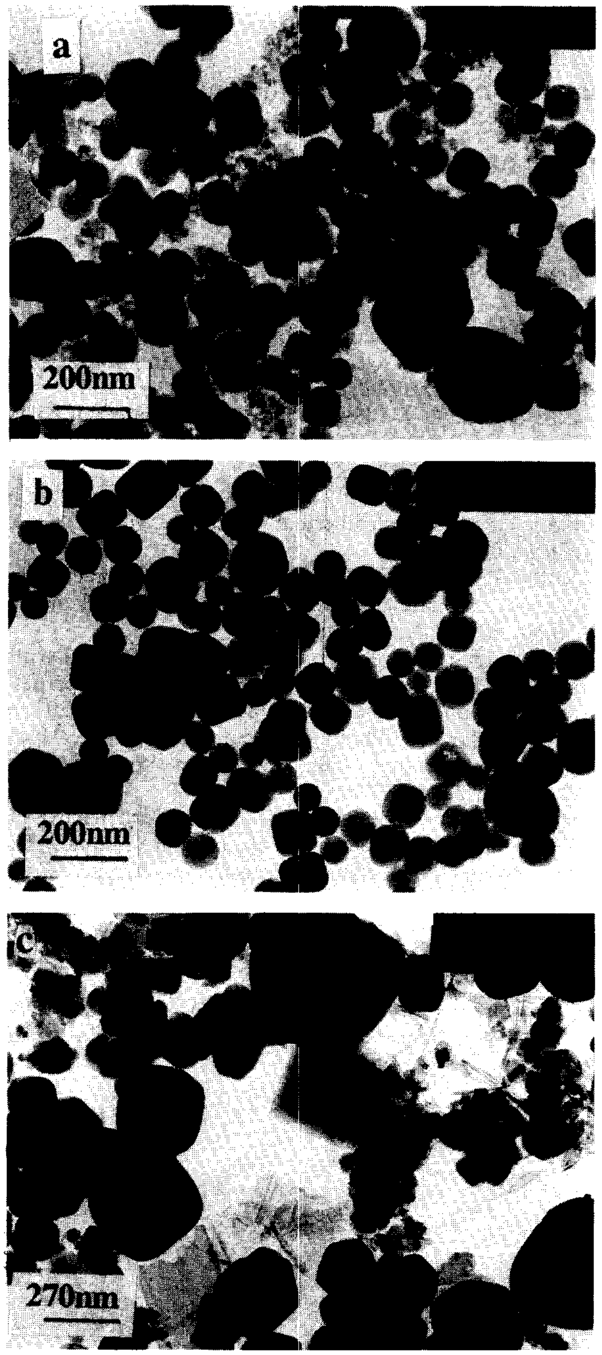

Fig. 7. TEM photographs of the powders prepared by (a) tetrabutyl titanate and $Ba(OH)_2$ aqueous solution; (b) newly prepared $Ti(OH)_4$ gel and $Ba(OH)_2$ aqueous solution; (c) commercial TiO_2 powder and $Ba(CH_3COO)_2$ in 1 mol/l NaOH aqueous solution.

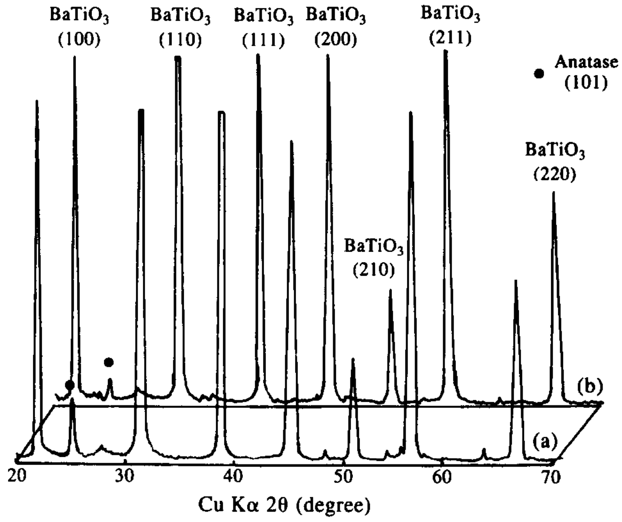

Fig. 8. XRD spectra of the powders synthesized at 300°C for 8 h in (a) pure water and (b) 1 mol/l NaOH aqueous solution.

The formation of ceramic powders under hydrothermal conditions is usually through a 'dissolution–crystallization' process.[9] The commercial TiO_2 powders are aggregates of particles with a primary size of 10–50 nm. When they are used as the Ti precursor, the interactions among these small particles are broken under the hydrothermal conditions. The powders are dissolved under the high temperature, high pressure and strong alkalinity of the system, and a variety of hydrated Ti–O ion groups are formed. These hydrated Ti–O ion groups are the growth units of $BaTiO_3$ crystallites. When the concentration of these growth units and Ba^{2+} reach or surpass the supersaturation for the formation of $BaTiO_3$ crystallites, the nucleation of $BaTiO_3$ begins and the crystallites grow. When freshly prepared $Ti(OH)_4$ gel is used as Ti precursor, the growth units are formed in a similar process, however, the growth units formed in these two systems are different in shape and size. Because the structure unit of TiO_2 is $Ti–O_6$ octahedron, so the growth units formed in this case are the linked $Ti(OH)_6$ octahedra units. The

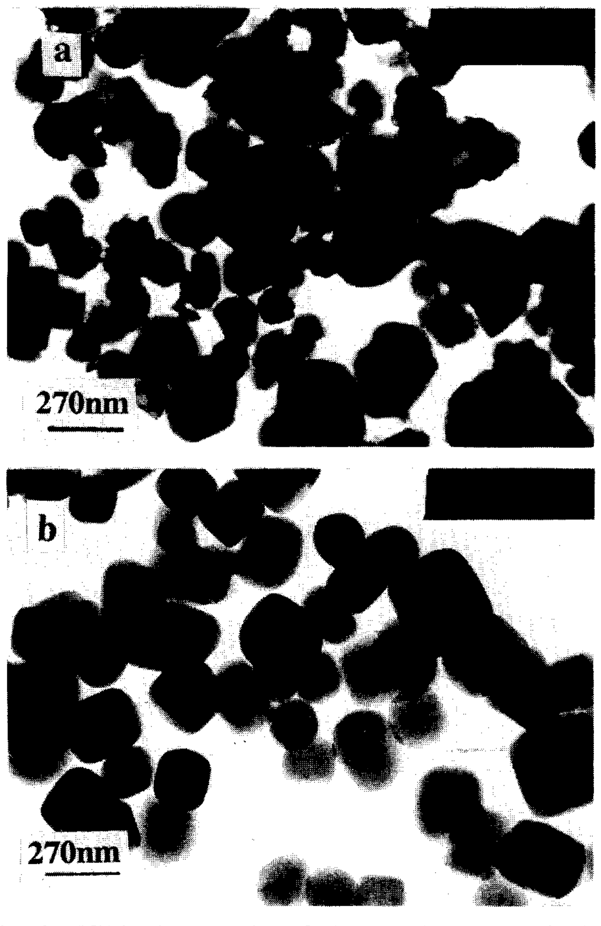

Fig. 9. TEM photographs of the powders synthesized at 300°C for 8 h in (a) pure water and (b) 1 mol/l NaOH aqueous solution.

structure similarity between these growth units and the $BaTiO_3$ crystal facilitate the nucleation and growth of the $BaTiO_3$ crystallites. On the contrary, the reticular structure of $Ti(OH)_4$ cause a slow nucleation and growth rate, so the $BaTiO_3$ produced from the reaction of the freshly prepared $Ti(OH)_4$ gel with the $Ba(OH)_2$ solution have a smaller size.

4 Conclusions

The main results of this study may be summarized as follows: (1) the higher the temperature, the higher the basicity and the greater the molar ratio of Ba/Ti in the precursor, the easier the formation of the perovskite type $BaTiO_3$ crystallite will be. (2) Hydrothermal reaction of the newly prepared $Ti(OH)_4$ gel with $Ba(OH)_2$ solution produced highly crystallized, well dispersed perovskite type $BaTiO_3$ crystallites with very fine (<100 nm) particles. The newly prepared $Ti(OH)_4$ gel turned out to be a suitable precursor for the hydrothermal preparation of $BaTiO_3$ fine powders. (3) X-ray diffraction of the hydrothermal $BaTiO_3$ powders reveals a simple cubic perovskite structure. The lattice constant (*a*) decreased with the increase of the reaction temperature. These abnormal crystallographic features are assumed to result from lattice defects, due to the OH^- incorporated in the perovskite lattice.

Acknowledgements

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