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The Hydrothermal Synthesis of BaTiO₃ Fine Particles from Hydroxide–Alkoxide Precursors

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Abstract

Fine powders of barium titanate were synthesized hydrothermally from aqueous barium acetate or barium hydroxide and titanium ethoxide solution, with different alkaline media; ammonia, hydrazine and tetramethylammonium hydroxide. Barium titanate powder prepared from $Ba(OH)_2$ after synthesis shows $BaCO_3$ impurities. On the other hand, powders prepared from $Ba(CH_3COO)_2$, $Ti(OC_2H_5)_4$ and tetramethylammonium hydroxide exhibit the smallest average grain size and did not contain $BaCO_3$ impurities. However, a relative by large amount of organic disintegration products which delay the sintering process were identified in the $BaTiO_3$ powders from Ba acetate. The $BaTiO_3$ powders were characterized by scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), thermogravimetric analysis (TGA), mass spectroscopy and dilatometric analyses. © 1998 Published by Elsevier Science Limited.

1 Introduction

The preparation of fine ceramic powders has become an important part of modern ceramic research. There is a strong trend toward the application of chemical methods for powder synthesis in electronic ceramics. In spite of a cost which is initially higher than powders prepared by conventional solid-state reaction of mechanically mixed and calcined materials, chemical methods, due to their improved performance and reproducibility, can save money and add value. There are various methods of fine powder preparation, including coreceptitation, spray drying, freeze drying, sol–gel and hydrothermal processes. Among these methods the hydrothermal process is very promising. It is a typical build-up method, where fine particles are preformed from much smaller particles, such as clusters, molecules, ions and atoms. With ever increasing energy costs, hydrothermal synthesis could possibly become very attractive for fine powder preparation because of the low temperatures involved and the good sinterability of the synthesized powder. The superiority of this process in respects such as the improved control of powder homogeneity and particle uniformity, could make its use dominant for electronic ceramics in the future.[1,2]

Barium titanate has been used for more than forty years as a basic material for electronic ceramics such as, for example, ceramic capacitors, multilayer capacitors and PTCR (positive temperature coefficient of resistivity) devices and others. The final microstructure and electrical properties of BaTiO₃ depend greatly on the powder characteristics. For this reason, many investigations were carried out on chemical synthesis of BaTiO₃ powders. Hydrothermal synthesis has been found to be a very promising route for preparation of well optimized and non-agglomerated powders.

In the beginning the hydrothermal synthesis of BaTiO₃ was performed at relatively elevated temperatures of 380–500°C and pressures of 300–500 atm.[3]

However, later the synthesis temperatures were drastically decreased to 85°C at equilibrium water vapour pressure (15–65 atm).[4–6] In general the hydrothermal method has the potential for producing extremely fine particles with high crystallinity, high purity and narrow size distribution. In this method an aqueous Ba(OH)₂ solution with suspended TiO₂ fine particles is hydrothermally treated and BaTiO₃ is formed through the dissolution–deposition route; i.e. Ba(OH)₂ reacts with titania under hydrothermal conditions to form BaTiO₃. During this process the concentrations of cations and hydroxide must increase to the supersaturation range where the nucleation products are stable.[7] Then the monodispersed grains are formed by subsequent uniform growth on the existing

nuclei, which were provided by adsorption of solute species, agglomeration and Ostwald ripening.[7] Thus, the dissolution of TiO_2 particles affects the supersaturation range, the nucleation and the growth of $BaTiO_3$ particles. The dissolution rate of titania and its constitution[8] to a great extent governs the formation of $BaTiO_3$ monodispersed grains. However, once the nuclei of $BaTiO_3$ from the supersaturation solution are formed, the aqueous suspension is only stable under strongly alkaline conditions at pH $\geq$ 13. Otherwise, due the thermodynamic instability of $BaTiO_3$ in water complete decomposition of $BaTiO_3$ to TiO_2 and $Ba(OH)_2$ can be expected. In practice, however, usually thin but water-impermeable layers of TiO_2 are formed on the surface of $BaTiO_3$ particles which prevents the $BaTiO_3$ grains from complete disintegration. In an aqueous suspension of hydrothermally processed $BaTiO_3$ particles dramatic Ba leaching is expected due to the higher surface area of smaller sized grains.

In this work we studied the processing of fine $BaTiO_3$ particles by hydrothermal synthesis of aqueous suspensions prepared from $Ba(OH)_2$ and $Ba(CH_3COO)_2$ salts and $Ti(OC_2H_5)_4$ with various organic hydroxides.

2 Experimental procedure

2.1 Preparation of barium titanate fine particles from $Ba(OH)_2$ precursor

Stock solutions containing Ba^{2+} and Ti^{4+} ions were prepared using $Ba(OH)_2*8H_2O$ (98% min., Alfa) and $Ti(OC_2H_5)_4$ (Alfa) as source materials. An appropriate amount of $Ba(OH)_2*8H_2O$ was dissolved in deionized water; the concentration of $Ba(OH)_2*8H_2O$ in all experiments was 1·1 mol litre^{-1}. Also an appropriate amount of $Ti(OC_2H_5)_4$ was diluted in abs. ethanol. The solutions of $Ba(OH)_2*8H_2O$ and $Ti(OC_2H_5)_4$ were mixed with different bases (NH_4OH, N_2H_5OH, $(CH_3)_4NOH$ (TMAH)) in order to prepare suspensions with the desired pH values.

When the desired pH value of the suspension had been obtained, the Teflon cup with the suspension was mounted in an autoclave (Model 4563M, Parr Instrument Co., Moline, IL) and heated at a rate of 3°C min^{-1}. Hydrothermal syntheses were conducted at temperatures of 150°C for 2 h. Table 1 shows the sample code, type of precursor used and the final pH values of suspensions, prior to hydrothermal synthesis.

After hydrothermal treatment, the pressure vessel was cooled and the product was washed free of organic radicals with boiling water, ethanol and methanol.

Table 1. Sample code, type of precursors used and the final pH values of suspensions, prior to hydrothermal synthesis

Sample code	Precursors	pH of suspension
BT	$Ba(OH)_2$ and $Ti(OC_2H_5)_4$	13·0
BTA	$Ba(OH)_2$, $Ti(OC_2H_5)_4$ and NH_4OH	13·4
BTH	$Ba(OH)_2$, $Ti(OC_2H_5)_4$ and N_2H_5OH	13·4
BTT	$Ba(OH)_2$, $Ti(OC_2H_5)_4$ and $(CH_3)_4NOH$	13·9

2.2 Preparation of barium titanate fine particles from $Ba(CH_3COO)_2$ precursor

Preparation of $BaTiO_3$ fine particles from $Ba(CH_3COO)_2$ (Alfa) and $Ti(OC_2H_5)_4$ (Alfa) was possible only when $(CH_3)_4NOH$ (TMAH) was added as an alkaline medium. Stock solutions containing Ba^{2+} and Ti^{4+} ions were prepared using $Ba(CH_3COO)_2$, which was dissolved in deionized water at a concentration of 1·1 mol litre^{-1} and the appropriate amount of $Ti(OC_2H_5)_4$ was diluted in abs. ethanol. TMAH as suspension medium was added to the reaction mixture to maintain the pH value during the reaction.

When the desired pH value was obtained, the Teflon cup was mounted in an autoclave and heated at a rate of 3°C min^{-1}. The hydrothermal syntheses were conducted at temperatures of 100, 150 and 230°C for 2 h.

After hydrothermal treatment, the pressure vessel was cooled and the product was washed free of organic contaminants with boiling water, ethanol and methanol.

2.3 Powder characterization

Particle size determination was performed using X-ray diffraction spectroscopy (XRD). Scanning electron microscopy (SEM) (Model JXA-840, JOEL, Tokyo, Japan) was used to observe the morphology of the powder. The gases evolved during heating of the powders were analyzed by mass spectroscopy. Thermogravimetric analysis (TGA) (Model STA 409, Netzsch, Inc., Exton, PA) was conducted in an air atmosphere at a heating rate of 5°C min^{-1}.

Green compacts of dimensions h = 5 mm and ø = 6 mm were obtained by pressing dry powder at 500 MPa; the green density of compacts was around 50% of theoretical density. The sintering of compacts was inspected by measuring shrinkage, and shrinkage rate spectra obtained by the use of a dilatometer (BÄHR–Gerätebau GmbH). The samples were sintered in a tube furnace at temperatures between 1250 and 1350°C for 2 h in air. The density of sintered samples was determined by Archimedes method. The microstructure of sintered samples was inspected by SEM on polished and thermally etched samples.
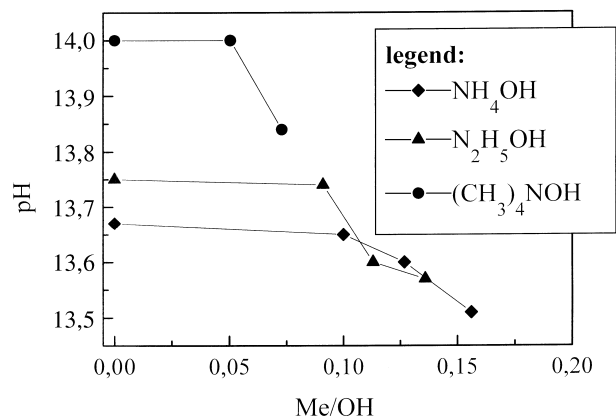
Fig. 1. Change in pH value with (Me/OH) ratio for suspensions prepared from Ba(OH)₂ + Ti(OC₂H₅)₄ + hydroxide (NH₄OH, N₂H₅OH, (CH₃)₄NOH), where (Me) is the total concentration of metal ions and OH is the concentration of hydroxyl ion.
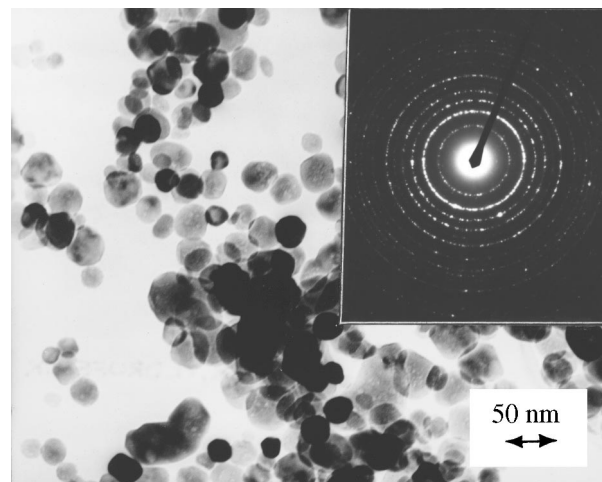

Fig. 2. Typical TEM image and electron diffraction of BaTiO₃ powder prepared from Ba(OH)₂ precursor. Syntheses were performed at 150°C for 2 h.

3 Results and Discussion

The pH value of the starting suspension and consequently the aqueous suspension of already formed BaTiO₃ nuclei after the hydrothermal synthesis are very important for the successful preparation of BaTiO₃ grains. After the formation of BaTiO₃ nuclei from supersaturated solution, the aqueous suspension of formed nuclei is stable only when the pH value exceeds 13.

The calculation of stability diagrams outlining that successful processing of BaTiO₃ required at least a pH > 12.[9]

3.1 Preparation of barium titanate fine particles from Ba(OH)₂

Figure 1 shows the pH values of the suspension formed when a stoichiometric amount of Ti(OC₂H₅)₄ and various amounts of different hydroxides, i.e. NH₄(OH), N₂H₅(OH) and (CH₃)₄NOH, were added to an aqueous solution of Ba(OH)₂.

According to the diagrams in Fig. 1, all the tested suspensions at (Me/OH) ratio < 0·16 show a sufficiently high pH value needed for the formation of a stable aqueous suspension of BaTiO₃ nuclei after synthesis. The suspension prepared by various hydroxides with a pH > 13 were hydrothermally treated at 150°C for 2 h. A typical TEM image of a synthesized powder and the corresponding electron diffraction is shown in Fig. 2.

The crystallite size of BaTiO₃ was estimated by the Scheerer eqn (1):

$$d_x = \frac{0·94\lambda}{\beta \cos \Theta} \qquad (1)$$

where d_x is the crystallite size, λ (1·5406) is the wavelength, β is the true half-peak width and is

half the diffraction angle of the centre of the peak (in degrees). The (200) peak was used to calculate the crystallite size. The XRD pattern in Fig. 3, besides BaTiO₃, also shows diffraction peaks which belong to BaCO₃. On leaching of the synthesized powders with diluted HNO₃ the amount of BaCO₃ can be decreased down to a level where BaCO₃ can no longer be detected by the XRD pattern. The morphological parameters of the synthesized powders are given in Table 2. The average particle size ($d_{(200)}$) of powders prepared from Ba(OH)₂ is similar irrespective of the hydroxide used during the syntheses. The crystallite size of BaTiO₃ obtained from the Scheerer equation is in general lower than that calculated from d_{BET} values. We believe that powders prepared from Ba(OH)₂ as precursor form hard agglomerates which consequently leads to a lower apparent specific surface area and thus to higher calculated particle size (d_{BET}).
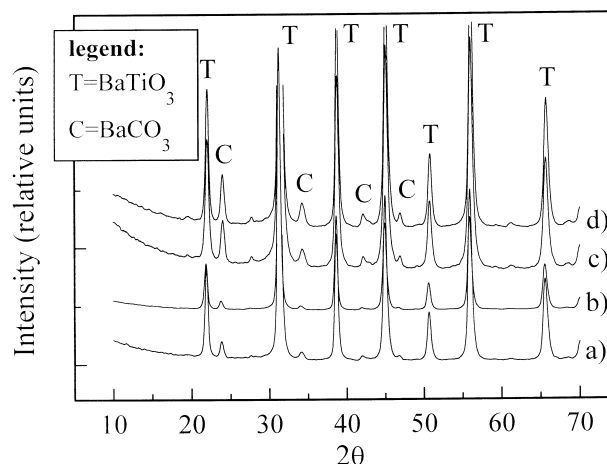

Fig. 3. X-ray powder diffraction patterns of nanosized BaTiO₃ powders, prepared from various hydroxides; a) BT, b) BTA, c) BTH and d) BTT.

Table 2. Specific surface area (A), average grain size, estimated from the X-ray diffraction peak (d_x) and average grain size (d_{BET}) estimated from the specific surface area by the use of the relation $d = 6/A\rho$, where A is the specific surface area and ρ is the theoretical density of $BaTiO_3$ ($6\cdot05$ g cm^{-3})

Sample code	A (m^2 g^{-1})	d_x (nm)	d_{BET} (nm)
BT	22·2	20·8	44·9
BTA	20·0	20·3	49·8
BTH	32·6	19·0	30·5
BTT	24·3	20·7	41·0

Fig. 5. TG analyses of $BaTiO_3$ powders obtained by hydrothermal synthesis: a) BT, b) BTA, c) BTH and d) BTT.

One of the reasons for the formation of hard agglomerates could be the presence of excess $Ba(OH)_2$ in the synthesized powders. Namely, $BaCO_3$ detected in the synthesized powders must be formed during processing. The starting $Ba(OH)_2$ solution used was filtered and did not contain $BaCO_3$ impurities. So during the hydrothermal synthesis retained $Ba(OH)_2$ can absorb CO_2 and form $BaCO_3$, which might contribute to the formation of strong agglomerates, thus decreasing the apparent specific surface area of the powders.

Figure 4 shows the mass spectra of these powders. Besides CO_2 the main disintegration products NO, CO and H_2O can be detected, though in much smaller amounts. Since the majority of organic compounds formed during hydrothermal synthesis are soluble and were leached out of the final hydrothermally treated suspension, the main disintegration product CO_2 identified at 800°C must come from $BaCO_3$ present in the synthesized powder, as indicated by the XRD pattern. From the TGA of powders (Fig. 5) it can be noted, that the amount of CO_2 released and the amount of $BaCO_3$ present in the synthesized powders decrease with increase in the pH value of the starting suspension (an exception is powder BT prepared without organic bases).
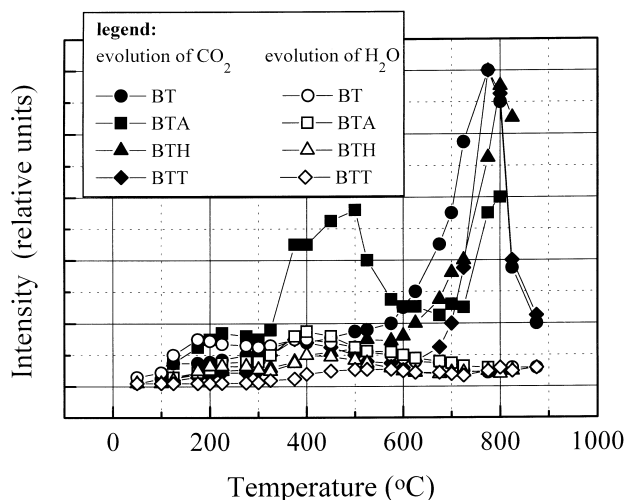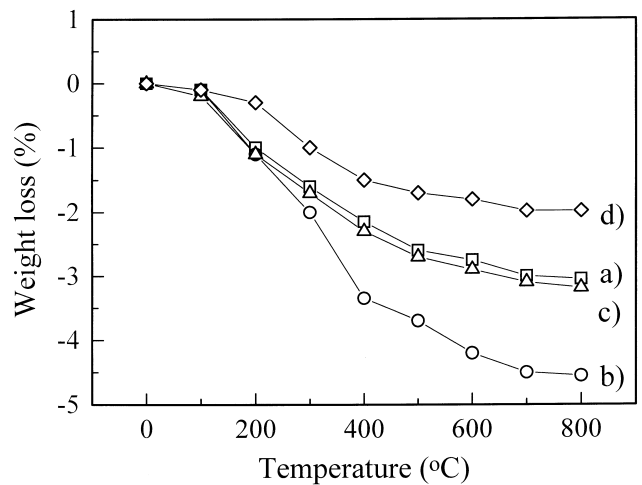
Since the preparation procedure of all powders was identical and the same stock solution of $Ba(OH)_2$ was used, we can assume that the decrease of the amount of CO_2 released from $BaTiO_3$ powders synthesized at higher pH value is due to less effective synthesis at lower pH values. The $Ba(OH)_2$ retained after hydrothermal treatment can easily be converted to $BaCO_3$ which can then be identified by mass spectroscopy and TGA. The stoichiometry of $BaTiO_3$ was maintained after the chemical analysis and an adequate change in the starting composition was made. The composition was kept constant close to $Ti/Ba \geq 1$ ($BaO/TiO_2 \approx 1\cdot02$).

The relative shrinkage spectra of samples BT, BTA, BTH and BTT showed a maximum between 800 and 900°C. The dilatometric curves of the samples are shown in Fig. 6.

The compacts prepared by pressing $BaTiO_3$ powder at 500 MPa with a green density of about 50% theoretical density were sintered at 1350°C for
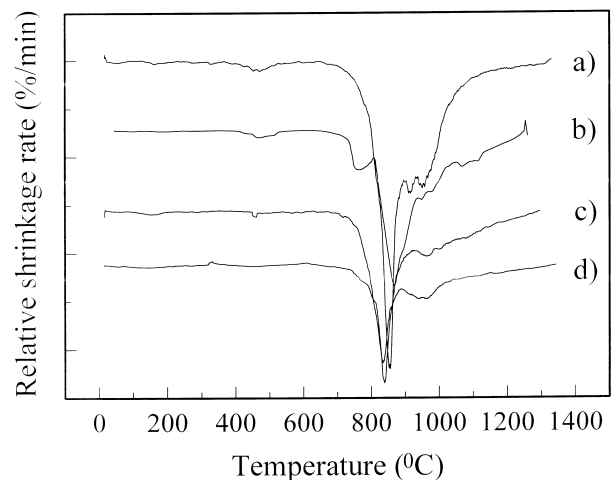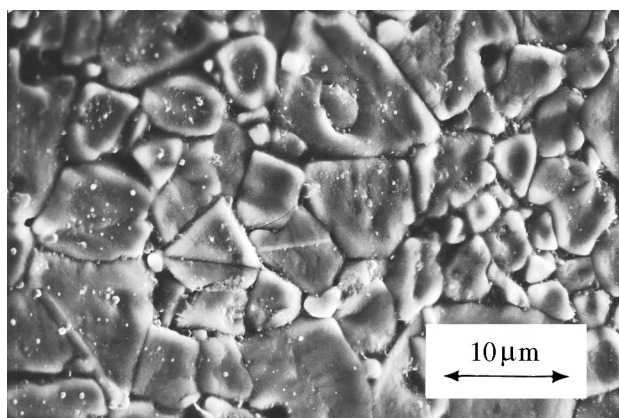

Fig. 4. Mass spectra of various $BaTiO_3$ powders prepared from different organic bases.

Fig. 6. Shrinkage rate spectra of samples a) BT, b) BTA, c) BTH and d) BTT.

Table 3. Sintered density (ρ), relative density (T.D.) and average grain size D of samples sintered at 1300°C (2 h)

Sample code	ρ (g cm^{-3})	T.D. (%)	D (μm)
BT	5·7	94·2	3·5
BTA	5·8	95·9	4·3
BTH	5·6	92·6	3·3
BTT	5·8	95·9	4·5

2 h. Table 3 shows the densities and average grain size of sintered samples, and typical microstructure of a sintered sample is shown in Fig. 7.
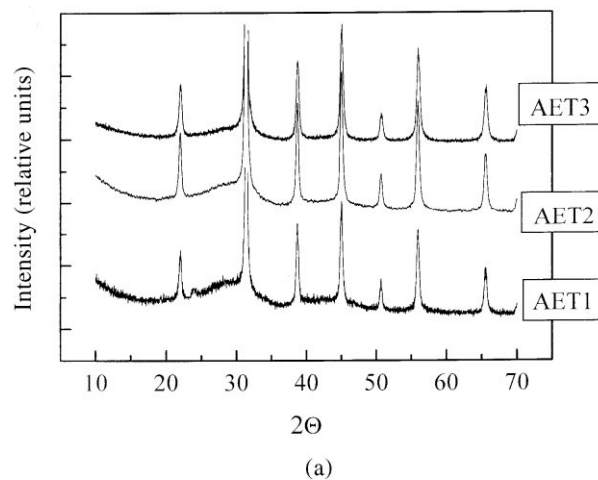
The hydrothermal synthesis of BaTiO₃ in strong alkaline media of Ba(OH)₂ and various ammonia-based hydroxides yielded fine grained BaTiO₃ powders which sinter to relative high density, depending on the hydroxide used during the preparation of the alkaline suspension. However, usually an excess of BaCO₃ accompanies the synthesis of BaTiO₃, which in the case of Ba/Ti > 1, converts to the Ba₂TiO₄ during sintering and can deteriorate the microstructure as well known. Otherwise, when the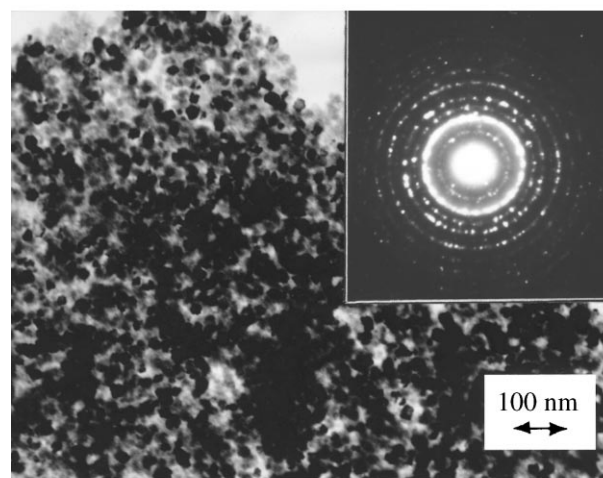 Ba/Ti ratio was kept < 1, no significant influence on microstructure formation could be noted. By the use of Ba(OH)₂ as precursor it is relatively easy to achieve the needed alkalinity to stabilise the BaTiO₃ nucleus during synthesis; however elimination of the additional BaCO₃ byproduct can be demanding and needs a careful experimental work.

3.2 Preparation of barium titanate fine particles from Ba(CH₃COO)₂

Figure 8 shows the pH values of a suspension prepared from Ba(CH₃COO)₂, Ti(OC₂H₅)₄ and (CH₃)₄NOH as a function of the ratio between the total molality of the metal ions and the (OH⁻) concentration. When the Me/OH ratio exceeds the value of 0·62, the pH value of the suspension exceeds ≥ 13, where the formation of BaTiO₃ can proceed. All other organic bases tested did not sufficiently increase the pH value of the suspension. Suspensions with pH > 13 were hydrothermally treated at temperatures of 100, 150 and 230°C for 2 h. A typical TEM image of a synthesized powder with its corresponding diffraction pattern is shown in Fig. 9(a). Powders obtained from Ba(CH₃COO)₂
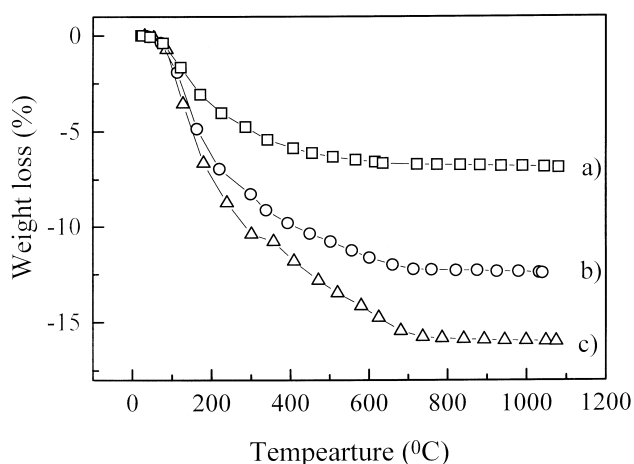

Fig. 7. Typical microstructure of a sample sintered at 1350°C, prepared from powder synthesized with Ba(OH)₂, Ti(OC₂H₅)₄ and TMAH precursors at a temperature of 150°C for 2 h.
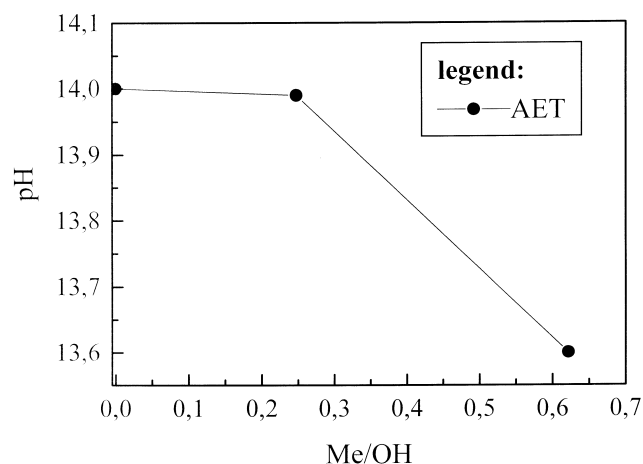
Fig. 8. pH value versus Me/OH ratio for suspensions prepared from Ba(CH₃COO)₂, Ti(OC₂H₅)₄ and (CH₃)₄NOH.

(a)

(b)

Fig. 9. (a) XRD patterns and (b) typical TEM image for a sample prepared from Ba(CH₃COO)₂, Ti(OC₂H₅)₄ and TMAH.

Table 4. Sample code, temperature of hydrothermal synthesis T_S, specific surface area (A), average grain size, estimated from the X-ray diffraction peak (d_x), average grain size (d_{BET}) estimated from the specific surface area and sintered density (ρ)

Sample code	T_S (°C)	A ($m^2\ g^{-1}$)	d_x (nm)	d_{BET} (nm)	ρ (g cm^{-3})
AET1	100	241	19·4	4·0	5·1
AET2	150	253	19·9	3·9	5·2
AET3	230	151	19·3	6·6	5·3

and $Ti(OC_2H_5)_4$ as precursors exhibited a fine particle size. No difference in particle size between powders synthesized at different temperatures could be noted from TEM images and XRD peak broadening ($d_{(200)}$), Table 4. However, when we calculate d_{BET} and assume a spherical shape, somewhat different values deviating by a factor of 3 from those obtained from the Scheerer method were achieved (Table 4). The much smaller average particle size d_{BET} calculated for these powders is due to the large measured specific surface areas of these powders. The relatively high amount of very fine disintegration products which could not be completely eliminated from the synthesized powder, and are deposited on the particle surface, increase the specific surface area determined by the BET method. For these reason, the calculated d_{BET} value is overestimated and the corresponding calculated d_{BET} is smaller than the $d_{(200)}$. At higher synthesis temperatures, when the concentration of organic disintegration products is lower, as can be observed from TG analysis, (Fig. 10), the measured specific surface area (A) is also lower and the corresponding calculated d_{BET} is larger. Powder a) synthesized at 230°C, for example, has a 100% lower weight loss in comparison to powder c) synthesized at 100°C.

Mass spectrometry indicates that the main disintegration products below 600°C are H_2O, CO_2, CO, NO, N_2O, amines and some organic radicals with masses of 28, 32, 43 and 44 g mol^{-1}. The main disintegration is at a temperature around 150°C,

when the decomposition of the base TMAH began.[5] At elevated temperatures > 600°C CO represents the main disintegration product.

Since no $BaCO_3$ could be detected by XRD (Fig. 9(b)) and no CO_2 release could be detected by mass spectrometry above 600°C where $BaCO_3$ starts to disintegrate, we concluded that the amount of $BaCO_3$ present in $BaTiO_3$ was below the detection limit. The shrinkage rate spectrum of this powder is different from the other powders prepared from $Ba(OH)_2$ as precursor. Besides a small peak at 800°C, the analysis of these powders show a larger peak at about 1300°C.

This powder has the smallest average grain size of all the powders synthesized during this work. Namely, synthesis of $BaTiO_3$ from $Ba(CH_3COO)_2$ and $Ti(OC_2H_5)_4$ precursors and TMAH as base results in the formation of amines, esters and organic radicals of relatively large molecules which stabilize the fine particles through the steric effect[10] of surface adsorbed molecules. This stabilization of fine particles during synthesis is very effective and an increase of the digestion temperature by more than 100% does not increase the average crystallite size during syntheses (Table 4). However, on the other hand, these large organic molecules cannot easily be eliminated and washed out of the large surface of the fine grained powder. TGA confirms the release of relatively large amount of organic impurities, which disintegrate up to 800°C in air. The weight losses decrease as the synthesis temperatures of the powders increase. At higher temperature the large organic molecules split into smaller parts which can be more easily eliminated during washing the powder. The mass spectra in Fig. 11 confirm the presence of organic impurities.

At temperatures around 750°C the release of CO was detected. We believe that CO is a product of incomplete oxidation of residual carbonized organic products. The relatively high amount of organic compounds, which cannot be completely removed during washing the synthesized powder, are deposited on the surface of $BaTiO_3$ grains and disintegrate during heating. Due to the limited access of oxygen to the carbonized disintegration products located on the grain boundary of a partially densified sample, carbon monoxide is formed, and can be detected by mass spectroscopy above 600°C (Fig. 11). Since direct contacts
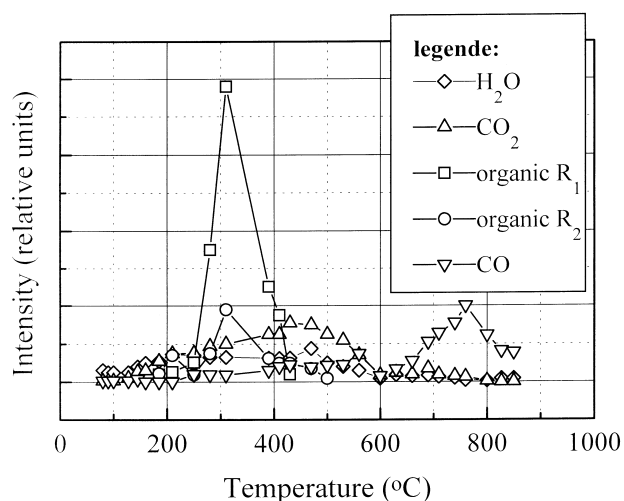
Fig. 10. TG analyzes of synthesized powders at a) 230°C, b) 150°C and c) 100°C.

Fig. 11. Mass spectra of BaTiO$_3$ powder AET2 synthesized at 150°C.

Fig. 13. Typical microstructure of a sample sintered at 1250°C, prepared from powder synthesized with Ba(CH$_3$COO)$_2$, Ti(OC$_2$H$_5$)$_4$ and TMAH precursors at a temperature of 230°C for 2 h, $\rho = 5\cdot3$ g cm^{-3}.

between grains are most probably prevented during an early stage of sintering due to disintegration products which are deposited on the grain boundary, the sintering process is very much delayed, as can be seen from the shrinkage rate spectra in Fig. 12.

The preparation of BaTiO$_3$ from Ba(CH$_3$COO)$_2$ as precursor is advantageous since the presence of

BaCO$_3$ in the synthesized powders can be effectively prevented due the lower affinity of Ba(CH$_3$COO)$_2$ for atmospheric CO$_2$ in comparison to that of Ba(OH)$_2$. However, of all the bases we tested, only TMAH was found to be sufficiently strong to maintain a suspension pH > 13, which stabilizes the aqueous suspension of BaTiO$_3$ nuclei during synthesis. Besides, the relatively large molecules of byproducts formed during digestion assist the formation of fine particles due to the steric effect. On the other hand, the powder obtained is less reactive due to the relatively larger amount of organic products which cover the grain surface and prevent contacts of grains during the early stage of sintering. Figure 13 shows a typical microstructure of a sample prepared from powder sintered at 1250°C.

4 Conclusions

The preparation of BaTiO$_3$ powders from hydroxide–alkoxide precursors is appropriate for the synthesis of nanocrystalline powder. Ba-hydroxide and Ti-ethoxide as precursors with addition of different alkaline media lead to the preparation of nanosized powder containing a certain amount of BaCO$_3$ which can deteriorate the microstructure of BaTiO$_3$ during sintering. However, during the synthesis of BaTiO$_3$ powder from Ba-acetate, Ti-ethoxide and TMAH, no BaCO$_3$ could be detected and powders with a higher specific surface can be prepared. Nanocrystalline powder prepared from Ba-acetate, Ti-ethoxide and TMAH contain a significant amount of organic impurities which are deposited on the grain surface, and retard the onset of sintering. An increase of synthesis temperature improves the sinterability of the powder; however, in general the powder prepared from Ba(CH$_3$COO)$_2$ and TMAH base exhibits a shrinkage rate maximum above 1200°C.
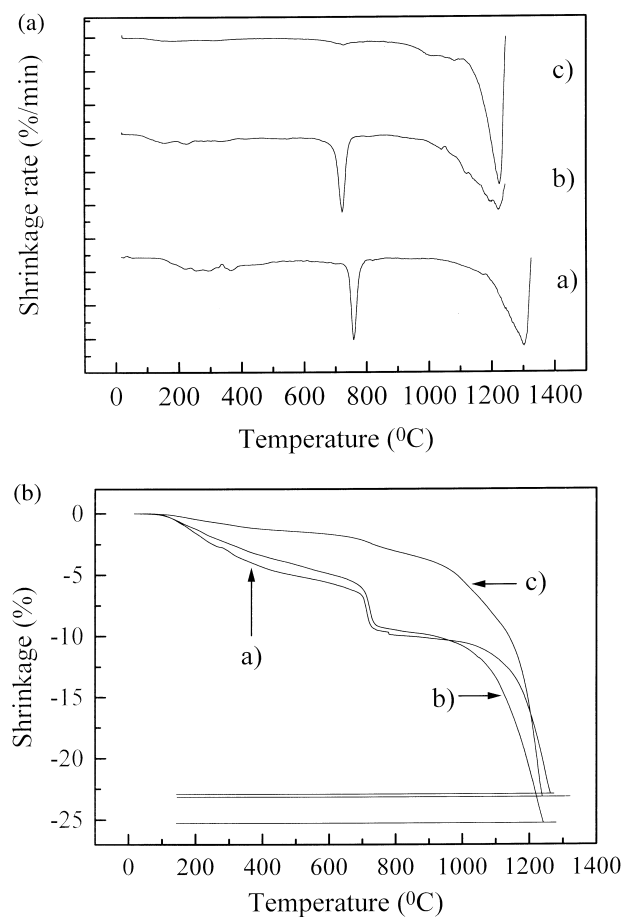

Fig. 12. (a) Shrinkage rate spectra and (b) dilatometric curves of hydrothermally prepared powders of BaTiO$_3$ synthesized at different temperatures a) 100°C (AET1), b) 150°C (AET2) and c) 230°C (AET3).
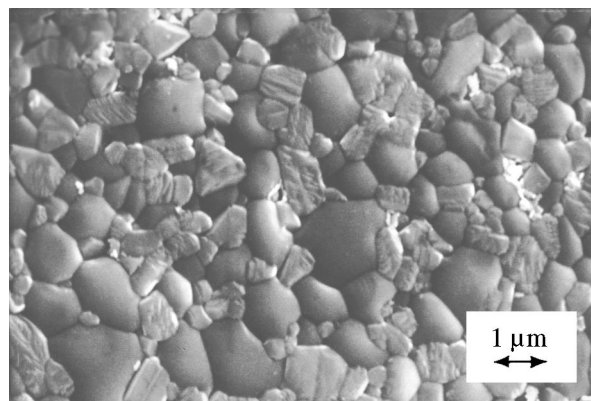
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