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Preparation of $BaTiO_3$ by Homogeneous Precipitation

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Abstract

Three different methods are studied for the preparation of fine-grained $BaTiO_3$ *by homogeneous precipitation: (1) Hydrolysis of barium and titanium alkoxide precursors, in which the required water is generated by an esterification reaction; (2) Precipitation of a barium–titanium complex as a result of thermal decomposition of Ba-EDTA; (3) Precipitation of a barium and titanium complex by the increase of pH caused by the hydrolysis of urea. The properties of powders, prepared via these methods, and their sintering behaviour are as follows: (1) The esterification method results in a powder with medium average aggregate size of about 3 μm and a sintered density of 90% which is higher than the value obtained with the other precipitation methods. The considerable differences, in hydrolysis rate between the barium and titanium precursors used, lead to second phase formation; (2) The complexation method gives the most promising results; 1 μm sized spherical aggregates were obtained which consist of smaller particles. Sintered densities obtained were up to 88% and the method can be optimised further to obtain values in excess of 95%; (3) The urea method results in large irregular aggregates and is found to be unsuitable for the preparation of* $BaTiO_3$ *ceramics.*

Keywords: homogeneous precipitation, powders: chemical preparation, sintering, sol-gel processes, $BaTiO_3$.

1 Introduction

The $BaTiO_3$ structure is based on the ideal perovskite structure and has small distortions leading to its interesting ferroelectric properties. Ceramics made from $BaTiO_3$ with specific dopants[†] have high dielectric constants, which strongly depend on grain size[1] and hence on the microstructure. Several preparation routes are described in literature[2] for the production of (doped) barium titanate powder, which is needed to prepare these ceramics. A distinction is made between mixed oxide and wet-chemical preparation processes. Mixed oxide processes contain less processing steps but generally result in less homogeneous powders and hence ceramics with a more irregular microstructure. If a more homogeneous, fine-grained ceramic microstructure and hence a better control of the powder morphology is required, the utilisation of wet-chemical powder preparation processes comes into scope. Most wet-chemical processes are based on precipitation of some precursor compound or mixture followed by calcination to obtain the proper $BaTiO_3$ phase. In this paper we distinguish between:

- *Heterogeneous precipitation* in which two different reactant solutions are mixed in solution so that a macroscopically heterogeneous liquid state is present for some time.
- *Homogeneous precipitation* in which nucleation and precipitation starts in an initially homogeneous liquid, containing all the reactants and the liquid state remains homogeneous during reaction.

In heterogeneous precipitation, which is most common, a precursor solution containing metal

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[†] In the present paper we ignore the dopants and may speak of $BaTiO_3$, even when dopants may be present.

ions is added to a second solution with e.g. special pH[3] or vice versa. Heterogeneous precipitation suffer from the following disadvantages:

- Even when the solution is stirred extremely vigorously. Considerable concentration gradients will be present in the solution for some time.
- Due to the required stirring action there is a high collision frequency between the particles, which result in the formation of large aggregates.[4] The collision frequency can be reduced to some extent by using special stirring rods[5] or very dilute systems.

The above-mentioned complications are not related to homogeneous precipitation processes. In such a process, one prepares a homogeneous solution that contains all metal ions and reactants but in such a way that, initially, no precipitation occurs. The actual precipitation, in this case is the result of a chemical reaction that becomes effective after a certain incubation period. The extent of this reaction can be adjusted by, e.g. controlling the solution temperature while gradients are avoided at the same time. In homogeneous precipitation, concentration gradients are prevented at all stages while the stirring speed can be reduced drastically to a level that particle sedimentation is just avoided and the solution temperature is kept homogeneous.

In the present paper a comparative study is presented, to our knowledge for the first time, of three different homogeneous precipitation methods for the preparation of $BaTiO_3$ powder by means of homogeneous precipitation. The quality of the calcined powders is evaluated by characterisation of particle morphology, average chemical composition as well as and compaction and sintering behaviour. The actual preparation methods investigated are presented below:

1.1 Esterification

In esterification homogeneous precipitation is accomplished by in situ formation of water. The reaction occurs at elevated temperatures in a solution containing an alcohol and a carboxylic acid:[6]

$$R'COOH + R''OH \xrightarrow{\Delta T} R'COOR'' + H_2O \quad (1)$$

According to Mazdiyasni[3] the water formed in eqn (2), reacts immediately with barium- and titanium alkoxides to form $BaTiO_3$:

$$\begin{aligned} &Ba(OR''')_2 + Ti(OR'''')_4 + 3H_2O \\ &\rightarrow BaTiO_3 2R'''OH + 4R''''OH \end{aligned} \quad (2)$$

1.2 Complexation method

The complexation method is based on the thermal decomposition of a Ba-EDTA complex, which is dissolved in aqueous solution. The Ba-EDTA complex decomposes above 40°C resulting in a gradual release of Ba^{2+} ions in the solution:

$$Ba(EDTA)^2 \xrightarrow{T>40^\circ C} Ba^{2+} + EDTA^{4-} \quad (3)$$

The homogeneously released barium ions reacts directly with a titanium peroxo complex at $pH = 9$ to form an insoluble complex:[7]

$$Ba^{2+} + TiO_2(OH)_4^{2-} \xrightarrow{pH=9} BaTiO_2(OH)_4 \quad (4)$$

The titanium complex is formed (at $pH = 9$) out of titaniumoxychloride and hydrogen peroxide before decomposition is performed. The $BaTi_2(OH)_4$ complex, formed by precipitation, is thermally converted to $BaTiO_3$ by calcination.

1.3 Urea method

The urea method is based on the pH-dependent structure of a titanium peroxo complex.[8] The general formula of this complex ion is $TiO_2(OH)_{n-2}^{4-n}$ in which n depends on the pH. $TiO_2(OH)_4^{2-}$, with $n = 6$ being the only titanium species that reacts with barium to form a salt-insoluble complex and is present at $pH > 9$ only. The precipitation reaction in the urea method is also based on reaction (4). Contrary to what is the case in the complexation process, in the urea process the barium atoms are already present while the titanium peroxo complex is formed gradually by changing the pH from 3 to 9. This increase in pH is accomplished by the thermal decomposition of urea that starts above 60°C[9] in aqueous solution according to:

$$(H_2N)_2CO + 3H_2O \xrightarrow{\Delta T} CO_2 \uparrow + 2NH_4OH \quad (5)$$

$BaTiO_3$ is finally obtained in the same way as in the complexation method, by thermal decomposition of the complex.

2 Experimental

2.1 Esterification method

Barium isopropoxide was freshly prepared by adding an excess of Na-dried isopropanol (Merck, p.a.) to Ba metal (Merck) in a molar ratio of 30:1 under purified nitrogen. This mixture was refluxed until all the metal had reacted. The barium isopropoxide/isopropanol mixture was mixed with titanium isopropoxide (Aldrich 97%) and an excess of 2-methoxy ethanol (Merck p.a.) and was refluxed for 2 h under a nitrogen atmosphere. The final reaction mixture had a composition, based on unreacted components, of [Ba]:[Ti]:[isopropanol]:[2-methoxy ethanol]:[acetic acid] = 1:1:15:5:10. The solution was cooled to 0°C and an excess of acetic acid (Merck p.a., 100%) was added slowly. The solution obtained was refluxed for approximately 8 h after which the precipitate was collected by filtration and calcined at 800°C for 10 h, using heating and cooling rates of $4°C.min^{-1}$. The calcined powder was ball-milled for 12 h in 2-propanol.

2.2 Complexation method

A titanium peroxo complex was prepared by mixing Ti-isopropoxide (Aldrich 97%), H_2O_2 (30%, Merck, medical extra pure) and HCl (Merck, p.a., 37%). The pH of this solution was raised from 1 to 9 by adding ammonia, followed by the addition of a second solution, consisting of a mixture of $BaCl_2$ and EDTA (Merck p.a.). This sequence was chosen to avoid premature oxidation of EDTA by H_2O_2 which causes blocking of the nitrogen lone pairs and hence diminishes complexation strength. In the final mixture, however, the presence of H_2O_2 may just have a favourable effect on the precipitation reaction because:

- The $Ti_2(EDTA)^{2-}$ complex is formed in equilibrium with $TiO_2(OH)^{2-}{}_4$ and $(EDTA)^{4-}$ and is decomposed by H_2O_2.[7]
- H_2O_2 may accelerate the breakdown of the $Ba(EDTA)^{2-}$ complex to form Ba^{2+}, needed in reaction (4) as well.

The composition of the reaction mixture, based on unreacted components was [Ba]:[Ti]:[H_2O_2]:[EDTA]:[H_2O] = 1:1:10:2:11·000, the barium concentration in the mixed solution was 10^{-2} mol 1^{-1}. The temperature of the reaction vessel was increased by heating on a hot plate at 50°C for 5 h or 2 l solution was placed in a microwave at 350 W for 2 h.[4] The precipitate was filtered and calcined at 700°C for 10 h, using heating and cooling rates of 4°C min^{-1}.

2.3 Urea method

The barium titanate prepared by the urea method was doped with small amounts of calcium and zirconium. It was expected, however, that these additions did not affect the morphological properties of the powder obtained. In the urea method $BaCl_2$, $CaCl_2$, $ZrCl_4$ and $TiOCl_2$ (Merck p.a.) were dissolved in the appropriate ratio. Hydrogen peroxide was added together with an excess compared to (5 times) of urea (Merck p.a.). The final reaction mixture had a composition, based on unreacted components, of [Ba + Ca]:[Ti + Zr]:[H_2O_2]:[urea]:[H_2O] = 1:1:10:5:16·000. The solution was heated on a hot plate under vigorous stirring. The precipitation started at 80°C and the mixture was kept for 3 h on 100°C. The precipitate was collected by filtration and washed and finally calcined at 900°C for 10 h, using a heating and cooling rate of 4°C min^{-1}.

2.4 Characterisation

The decomposition of the washed filtrates that were dried at 120°C overnight was followed by TGA (Stanton Redcraft STA 625). The TGA experiments were performed in normal air at atmospheric pressure; a flow rate of 20 ml min^{-1} (STP), a heating rate of 4°C min^{-1} and a temperature range of 25–1000°C was applied. The morphology of the calcined powder was studied with Scanning Electron Microscopy (Jeol JSM 35CF). The crystallite size of the powder was investigated with Transmission Electron Microscopy (Philips EM30). BET-surface area measurements were performed on a Micromeretics ASAP 2400. X-ray diffraction (XRD) measurements were performed using Philips PW1710 equipment and Ni-filtered Cu K_α radiation ($\lambda = 1{\cdot}5408$ Å). The chemical composition of the calcined 7 powders was determined by X-ray fluorescence (XRF) using a Philips PW 1480/10 X-ray spectrometer.

The volume distribution of the powder particles was measured by light scattering with a Microtrac X500 (Leeds and Northrup). Samples were made by pre-treating approximately 15 mg powder in 40 ml water with ultrasonic energy (30 W) 3× for 20 s, with a Branson Sonifier 450. For the interpretation of the measurements it was assumed that the powder particles were reflecting light and were spherical.

Ceramics discs with a diameter of 15 mm and a thickness of 5 mm were obtained by pre-pressing the powder uniaxially at 80 MPa and subsequently isostatic pressing at 400 MPa. All compacts were sintered at 1300°C for 10 h in an oxygen atmosphere using a heating rate of 2°C min^{-1} and a cooling rate of 4°C min^{-1}. Non-isothermal densification was studied on a Netzsch 410 dilatometer. Density measurements were performed by Archimedes technique using mercury. The relative density was based on a theoretical $BaTiO_3$ density of 6·02 g cm^{-3}. The microstructure of polished samples was revealed by thermal etching at a temperature, 10°C below the sintering temperature. The microstructure was studied with scanning electron microscopy (Jeol JSM 35C17).

3 Results and Discussion

3.1 Esterification method

Addition of acetic acid to the aqueous solution containing titanium and barium, initially results in the formation of some white precipitate, caused by traces of water in the acetic acid. Because of the low pH this precipitate redissolves after a few minutes and the actual precipitate starts to form after approximately 30 min of heating the clear solutions. The TGA results for the dried precipitate delpicted in Fig. 1 show significant weight losses at temperatures, just above 250 and 700°C. The weight loss below 350°C is due to loss of water and the decomposition of organic derivatives. At 350°C $Ba_2Ti_2O_5CO_3$ is formed out of $BaCO_3$ which is in turn a product of the reaction between Ba^2+ and the organic constituents. $Ba_2Ti_2O_5CO_3$ is stable up to 700°C.[10] The TGA results are not consistent with a zero weight loss according to reaction (2) and neither are they with the continuous weight loss of 10% up to 900°C as found by Mazdiyasni *et al.*[3] The latter is likely to be due to a continuous loss of absorbed water, CO_2 and remaining solvent. This implies that the precipitation mechanism in our case is different from the mechanism described by Mazdiyasni *et al.*[3] The rather high weight loss observed at 250°C may be ascribed to the possible exchange of acetate ions with the isopropyl groups of the alkoxides.[6] This exchange is likely to result in the formation of the organic fragments in the precipitate as mentioned.

XRD results of the calcined powders are presented in Fig. 2 in which it can be seen that the esterification-method results in the formation of cubic barium titanate with a small amount of $BaTi_2O_5$ second phase. Thus a small titanium excess is present in the precipitate which is confirmed by XRF measurements, (see Table 1). The titanium excess is probably caused by differences in hydrolysis kinetics of the single titanium and titanium- and Ba-precursors. The reactant combination barium isopropoxide, titanium isopropoxide, isopropanol and 2-methoxy ethanol lead to the best results to obtain a 1:1 Ba:Ti ratio. An exchange reaction takes place according to:

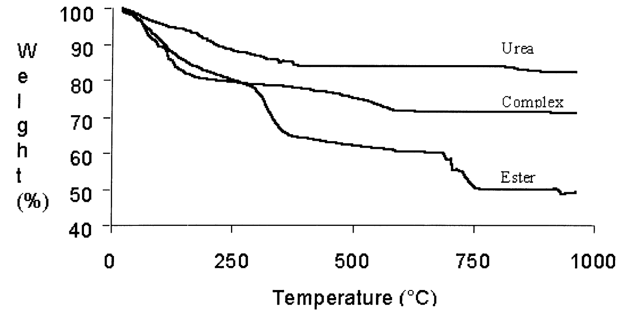

Fig. 1. TGA results, thermal decompostion of the dried precipitates.

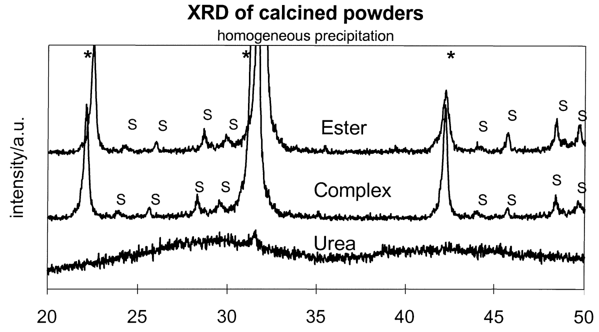

Fig. 2. XRD of the calcined powders. In this figure the cubic perovskite signals are marked with (*) and the second phases, $BaCO_3$ and $BaTi_2O_5$-with s.

$$Ti(OR)_4 + 4CH_3O[CH_2]_2OH \rightarrow Ti(OR)_{4-n}(O[CH_2]_2OCH_3)_n + nHOR + (4-n)CH_3O[CH_2]_2OH \qquad (6)$$

Because 2-methoxyethanol is more acidic than water, fast hydrolysis of titanium is avoided when water is added to the mixture. This should allow the proper polycondensation to take place and hence the formation of a Ba/Ti = 1 gel without precipitation of $Ti(OH)_4$.[11] Several other combinations of alcohol and carboxylic acid (e.g. 2-propanol and formic acid) were tested to address the problem of stoichiometry control. It was found, however, that the combination of 2-methoxy ethanol and acetic acid results in a ratio closest to Ba:Ti 1:1, the lowest amount of second phase and the highest sintered density. Interpretation of the results is complicated, however, by the occurrence of acetate exchange[6] mentioned before since this may reduce the hydrolysis rate as well. Hence the explanation for the titanium-excess in the precipitate can only be speculative in this stage:

- The ligand exchange mechanism may occur for barium too because barium is more electronegative, and the exchange may therefore be more efficient than for titanium. This, in turn, may lower the hydrolysis rate of the Ba-compound below that of the titanium-compound.
- Bariumhydroxide is well soluble in water, particularly at higher temperatures. Since the composition of the reaction mixture is such that a considerable excess amount of water can be formed, the liquid phase may contain a significant residual concentration of dissolved barium after precipitation. This barium is removed in the filtration step.

The latter explanation seems more reasonable. The particle size distribution of the calcined powder, which is determined by light scattering, is very broad: 50 vol of the particles has a size below

Table 1. XRF results of the calcined powders

Source	*[Ba]:[Ti]*
Ester method	0·79
Complexation method	0·87
Urea method	0·15
Theoretical	1·0

2·9 μm and 90 vol% of the particles has a size below 10·2 μm. A SEM picture of the powder exhibiting that the particles have a porous internal structure is shown in Fig. 3. SEM recordings at lower magnication showed aggregates with sizes, comparable to values obtained by light scattering. By means of TEM (Fig. 4) it was established that the aggregates consist of crystallites with a size of approximately 0·07 μm. This size was confirmed by XRD line-broadening and BET measurements.

During sintering densification of the green body starts at approximately 1150°C, after which the relative density increases rapidly. The maximum densification rate is reached at 1215°C and the final density is 90% (see Table 2). The microstructure of the sintered compact is given in Fig. 5 and reveals the occurrence of anomalous-grain growth. This can be explained by the presence of titanium-rich phases in the powder; these phases form, together with $BaTiO_3$ an eutectic melt at 1312°C.[12,13]

3.2 Complexation method

After complete mixing the barium-EDTA solution with the peroxo-oxalate solution, a clear yellow/green solution is obtained from which a yellow solid precipitates upon heating. The yellow colour is characteristic for the $BaTiO_2(OH)_4$, formed according to reaction (4). The TGA results for the dried precipitate in Fig. 1 show weight losses at two different temperatures. Below 200°C physically bound water is removed, whereas at approximately 550°C the peroxide groups decompose. XRD analysis of the calcined powder shows the cubic barium titanate phase, with a small amount of second phase ($BaTi_2O_5$). The excess of titanium is confirmed by XRF measurements of which the results are presented in Table 1. The composition of the powders is independent of the heating method (hot plate or microwave). The origin for the titanium-excess may be found in an incomplete decomposition of the Ba-EDTA complex so that a small amount of titanium and barium remain in solution. The unreacted $TiO_2(OH)_4^{2-}$ condensates then slowly to a large insoluble titanium–hydroxide complex[8] that is taken up in the precipitate while the barium remains in solution.

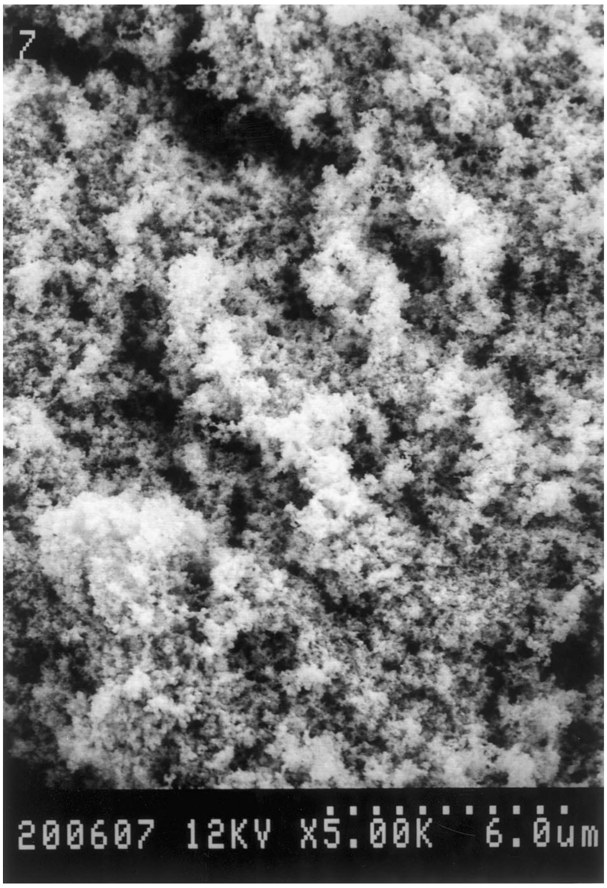

Fig. 3. SEM micrograph of the calcined powder prepared with the esterification method.

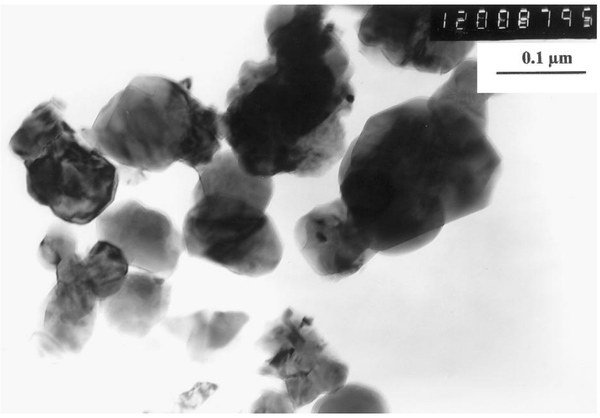

Fig. 4. TEM micrograph of powder prepared with the esterification method.

In Fig. 6 a SEM micrograph is depicted of the calcined powder, prepared by heating on a hot plate. Spherical aggregates with diamaters of about 1 μm are visible. The size is approximately the same as that determined by light scattering. Some neck-formation between the aggregates is visible as well. The morphology of powders prepared by microwave heating is similar to those prepared by hot plate heating. Hence in this case, the size of the aggregates does not depend significantly on the extent of inter particle collision during stirring. The aggregation process is more likely to occur due to the intimate interparticle contact during the filtra-

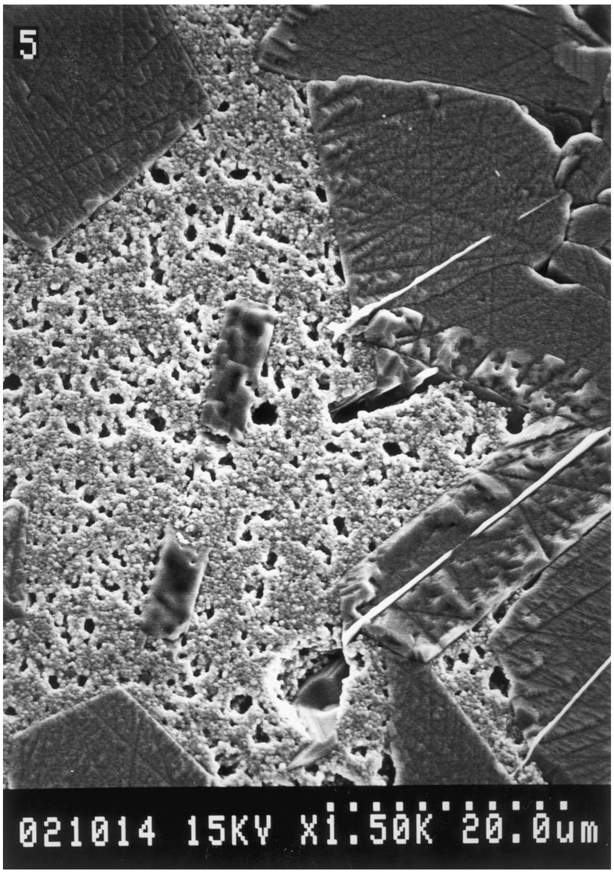

Fig. 5. Microstructure of thermally etched ceramic prepared with the esterification method.

Table 2. Green and final densities of the compacts

Method	*Green density*	*Final density (%)*
Ester	51	90
Complexation	53	88
Urea	58	65

tion step and the relatively long heating time for calcination. It was also found that the aggregate size of powders prepared by heating in a microwave does depend on the capacity of the microwave and therefore on the heating rate. Particle size measurements, performed directly after a temperature of 90°C was reached, showed that applying a microwave powder of 350 W resulted in an aggregate size of 2·2 μm, whereas increasing the powder to 1000 W gave grains of 4·6 μm (see Table 3).

The excess of titanium and possibly the presence of remaining chloride ions lead to exaggerated grain growth during sintering. After sintering the relative density of the sample had increased from 53 to 88%. This relatively low sintered density might also be the result of the formation of larger cohesive agglomerates by neck-formation (see also Fig. 4).

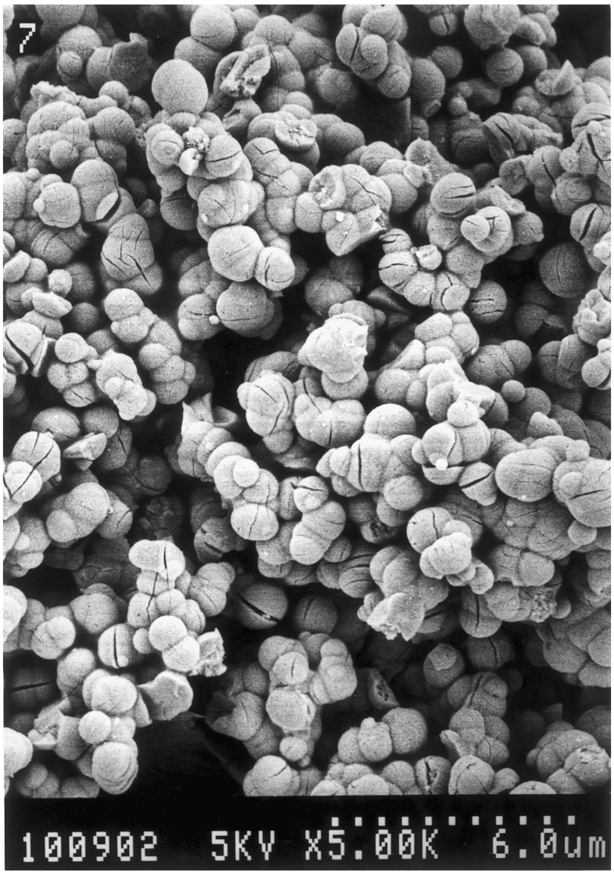

Fig. 6. SEM micrograph of powder prepared with the complexation method.

Table 3. Effect of microwave power on heating rate and particle size

Microwave power (W)	*Heating rate (Cmin^{-1})*	D$_{50}$ (μm)
160	3·75	—
350	7·25	2.2
500	10	2·7
650	12·75	4·6
750	15	3·9
1000	16·75	4·6

3.3 Urea method

After adding the hydrogen peroxide was added to the barium/titanium solution the solution is clear and red in colour. Upon refluxing of this solution an orange suspension was formed. The pH remains constant at 1 during refluxing. The formation of the suspension is accompanied by the release of small CO_2 gas bubbles, which is a reaction product of the hydrolysis of urea [see reaction (5)]. The TGA result of the dried precipitate in Fig. 1 shows three different weight-loss steps. Below 100°C water is removed and below 400°C crystal water is removed. The third weight loss at 800°C could be attributed by the conversion of $BaCO_3$ to BaO and, at the same time, of titaniumperoxo species to TiO_2.[14]

The precipitate was calcined at 900°C in air which resulted in the formation of an amorphous phase (see Fig. 2). As is shown in Table 1, the powder produced with the urea method mainly consists of titanium oxide. This implies that the expected formation of the insoluble barium titanium peroxo species ($BaTiO_2(OH)_4$) did not take place. An explanation may be found by the fact that, during decomposition of urea, the pH remains well below 7 so that the titanium peroxo complex will not or only partially be transformed into the $TiO_2(OH)_4^{2-}$ ions. As stated before, the latter ion represents the only complex-form for Ti^{4+} that is able to react with Ba^{2+} for the formation of an insoluble complex according to reaction (4). From a similar procedure for the precipitation of zirconia[15] in the presence of chloride and nitrate ions, it is known that the pH finally reaches a value of 7–8, but only after heating for more than 5 h. In that case, most of the released hydroxyl ions have reacted with zirconium to form a homologous series of $[Zr(OH)_n]_{4-n}$ complexes. The large titanium excess indicates that, in spite of the presence of hydrogen peroxide, the precipitation mechanism for titanium is similar to the one developed for zirconium. This mechanism presumably leads to the formation of a homologous series of species with the general formula $(Ti_2O_5)_m (OH)_n^{n-2m}$ that (Ref. 8) reacts further to $TiO_3 . xH_2O$ species (with $x \geq 1$).

The urea method results in a low-density powder with an aggregate size of approximately 3 μm. The sintering experiments with powders prepared from the urea method lead to ill-defined porous products which largely deviates from the perovskite stoichlometry and are as such not interesting.

4 Conclusions

The preparation of $BaTiO_3$ powders by different homogeneous precipitation techniques, results in powders with different morphologies (see Figs 3 and 6). Regardless of morphology, the three preparation methods are not yet applicable because the final chemical composition of the powders cannot be kept sufficiently under control. Possible improvements with the esterification method might be obtained if.

- A single precursor molecule is used, containing all metal ions in the proper ratio.
- The exchange reactions with the precursor can be sufficiently suppressed. This can possibly be accomplished by using bulky acid molecules for which the exchange reactions are sterically hindered.

In the urea method, the pH is too low for the formation of a titanium compound that can react with barium. The powder prepared by this method, consequently, contains a very large titanium-excess so that it is unlikely that the urea method, or any other similar method with controlled release of OH^- ions, will be suitable for the preparation of a high-quality barium titanate powder.

The sintering behaviour of the powder obtained with the complexation method can be improved further if.

- Neck formation between aggregates can be avoided by surface-chemical means or by a deagglomeration treatment afterwards.
- The titanium-excess can be avoided by the application of a less reactive precursor or titanium-complexation such that a more balanced precipitation is obtained.

The esterification method results in powders with the smallest aggregate size. The mechanism of precipitate formation in this process is not clear but it is obviously different from the one proposed by Mazdiyasni *et al.*[3] An important complication with the esterification method is that the water, which is released by the reaction between isopropanol and acetic acid, reacts differently with single titanium and barium precursor compounds. This easily results in the formation of a small amount of second phase in the final ceramic. In addition, the hydrolysis reaction may be unpredictably affected by the occurrence of exchange reactions between precursor ligands and ester forming reactants.

Despite the second phase formation and the fact that the sintered compact has a somewhat lower density than the compact formed by the ester method, the complexation method seems most suitable to prepare uniform spherical aggregates. The titanium excess in the powder prepared by the ester method results in the formation of a liquid phase during sintering. This liquid phase led to excessive grain growth accompanied by considerable pore entrapment hampering full densification.

To develop a suitable route for the homogeneous precipitation of $BaTiO_3$ powders further in a systematic way, more detailed insight is required to the chemistry of the complete hydrolysis and condensation mechanism, including ligand exchange reactions. The use of emulsion techniques or self-organising systems in the liquid phase, for instance, may lead to further improvements in powder composition and particle morphology. In the present paper all syntheses were performed in batch reactors in which the reaction conditions at the beginning and at the end of the precipitation are not entirely the same and this may influence the product properties. If, for instance, the ionic strength of the solution changes during the batch reaction, this may affect particle/aggregate size[4] in the product due to changes in colloid chemistry. Hence we expect that significant improvements in composition control and powder morphology could be achieved if the precipitation would be performed in the continuous mode.

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