

Hydrothermal Preparation of Barium Titanate from Barium–Titanium Acetate Gel Precursors

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Abstract

Clear, transparent gels of BaTi acetate have been prepared from titanium tetrabutylate (TBT), Ba acetate aqueous solution, isopropanol and acetic acid. Infrared spectroscopy and transmission electron microscopy (TEM) of such gels revealed linked clusters of polymer Ti oxyacetate with surface adsorbed Ba acetate. Spray dried Ti oxyacetate has been found to have the stoichiometric composition $Ti_2O_3[CH_3COO]_2$. Calcination of BaTi acetate gels to $BaTiO_3$ in air turned out to be a less favourable preparative route, because stable intermediate carbonate phases were formed. Corresponding to the high surface area and fine dispersion of Ba and Ti, BaTi acetate gels are highly reactive precursors for hydrothermal synthesis of $BaTiO_3$. Nearly quantitative (>99.7%) chemical reactions were obtained without using Ba excess at processing. TEM provided interesting information about the chemical mechanisms of hydrothermal processing.

Transparente Gele aus BaTi-Azetat wurden aus Mischungen von Titan-Tetrabutylat, Isopropanol, Essigsäure und wässrigen Lösungen von Ba-Azetat hergestellt. Infrarot-Spektroskopie und Transmissionselektronenmikroskopie (TEM) zeigten, daß die Gele aus verzweigten Aggregaten von polymerem Titan-oxyazetat und oberflächlich adsorbiertem Ba-Azetat bestanden. Die Zusammensetzung von sprühgetrocknetem Ti-oxyazetat entsprach genau der Formel $Ti_2O_3[CH_3COO]_2$. Die thermische Zersetzung von BaTi-Azetat Gelen in $BaTiO_3$ erwies sich wegen der Bildung thermisch stabiler Zwischenprodukte als eine ungünstige Präparationsroute. BaTi-Azetat Gele sind jedoch äußerst reaktive Vorprodukte für die hydrothermale Synthese von $BaTiO_3$. Nahezu quantitativer Umsatz (>99.7%) in

$BaTiO_3$ wurde ohne Verwendung von Ba-Überschuß in der Reaktion erreicht. Der Einsatz von TEM erbrachte interessante Einblicke in den Bildungsmechanismus von hydrothermale $BaTiO_3$.

On a préparé des gels transparents d'acétate de BaTi à partir de mélanges de tetrabutylate de titanium (TBT), de solutions aqueuses d'acétate de Ba, d'isopropanol et d'acide acétique. A l'aide de la spectroscopie infrarouge et de la microscopie électronique à transmission (TEM) on a pu mettre en évidence que ces gels étaient constitués d'aggrégats ramifiés d'oxyacétate de titane polymérisé et d'acétate de barium adsorbé en surface. La composition de l'oxyacétate de titane séché par atomisation correspond exactement à la formule stoechiométrique $Ti_2O_3(CH_3COO)_2$. La décomposition thermique des gels d'acétate en $BaTiO_3$ dans l'air apparaît comme une méthode de préparation moins favorable, du fait de la formation de phases carbonate intermédiaires stables. Les gels d'acétate de BaTi sont, grâce la surface spécifique élevée et à la fine dispersion de Ba et Ti, des précurseurs hautement réactifs pour la synthèse hydrothermique de $BaTiO_3$. Des réactions chimiques quasi quantitatives (>99.7%) ont été obtenues sans utilisation d'excès de Ba. La TEM a permis d'obtenir des informations intéressantes au sujet des mécanismes chimiques du processus hydrothermique.

1 Introduction

For more than 40 years barium titanate ($BaTiO_3$) has been used as a basic material for ceramic capacitors. Barium titanate powders are usually prepared by simple calcination of $BaCO_3$ and TiO_2 together with several additives. Nowadays the

classical preparative route ('Mix and fire') has been increasingly deserted and so-called 'wet chemical' routes are preferred. The increasing interest in thin dielectric layers for multilayer capacitors (MLCs) requires fine and poorly aggregated ceramic powders, which are more satisfactorily produced by employing wet chemical techniques.

The advantage of wet chemical preparative techniques is the quasi-atomic dispersion of Ba, Ti and dopants in liquid precursors. From this resulting lower calcination temperatures make production of fine and poorly aggregated powders possible. While most of the wet chemical preparative techniques, e.g. precipitation from BaTi alkoxides ('alkoxide route'¹), calcination of complex precursors ('oxalate route'², 'citrate route'³), spray-drying and roasting of solutions,^{4,5} and hydrothermal techniques^{6,7} have been already described in the literature, there is little known about sol-gel preparative routes to BaTiO₃.

In the following section preparation and characterization of BaTi acetate sols and gels are described and transformation of these precursors to BaTiO₃ is discussed. Special attention is paid to hydrothermal reactions of BaTi acetate gels and their possible use as precursors for hydrothermal processing of BaTiO₃.

1.1 Sol-gel techniques

The common technique of sol-gel processing is to convert colloidal sols, normally of oxides and hydroxides, by several means into semi-rigid gels. The gels then are dried and calcined to oxide ceramics. Shape and size of the final ceramic materials are substantially determined by the drying stage. The most convenient way of preparing sols is by peptization of freshly precipitated hydroxides with acids⁸ or by employing surfactants. The sols can be transferred into gels by neutralization or removal of stabilizing ions.

Sol-gel techniques have been successfully applied to monocomponent systems, such as SiO₂.⁹ In multicomponent systems problems often arise from the fact that certain components do not form gels. Not every ion is able to form a gel, e.g. the ions of alkali and alkaline earths. In the case of Ba(OH)₂-TiO(OH)₂ gels one has to expect that only the titanium component will readily form gels. Nevertheless, clear, transparent and rigid gels have been prepared in the system BaO-TiO(OH)₂-acetic acid,^{10,11} which can be used as possible precursors for production of fine BaTiO₃ powders.

Powders prepared from sols or gels by using thermal decomposition methods often suffer from

unfavourable morphologies, resulting from strong aggregation of fine particles. Whereas the very fine primary particles in the aggregates do readily sinter at relatively low temperatures, only rather poor densification is observed between the large aggregates. Hence, it is worthwhile looking for other and better processing methods for BaTi acetate gels to BaTiO₃ rather than to calcine these precursors in air.

1.2 Hydrothermal processing of gels

Hydrothermal syntheses of single oxides, e.g. Al₂O₃, γ -Fe₂O₃, and certain double oxides, are well known⁶ from the literature. The feasibility of hydrothermal preparations strongly depends on the nature of the precursors used. Important parameters determining the success of hydrothermal syntheses are morphology of the precursors, e.g. amorphous or crystalline structure, surface area, etc., processing temperature and pH. Precursors preferred for hydrothermal processing are hydroxides or hydrated oxide gels. Most hydrothermal syntheses have to be carried out at temperatures >100°C. Hence, closed pressure tubes or autoclaves are needed for these kinds of syntheses.

Hydrothermal syntheses of BaTiO₃ usually start from aqueous suspensions of TiO(OH)₂ (hydrated titanium oxide) and Ba(OH)₂ which are reacted to BaTiO₃ in autoclaves at temperatures of 150–200°C.¹²

2 Experimental

2.1 Preparation of BaTi acetate gels

Stable Ti acetate sols were prepared by mixing tetrabutyltitanate (TBT, Ti[C₄H₉O]₄), or tetraethyltitanate (TET, Ti[C₂H₅O]₄) (both from Dynamit Nobel, Troisdorf, Germany) with isopropanol and concentrated acetic acid (both from Merck, Darmstadt, Germany) in the molar ratios of 1/6/3. On storing in closed vessels, i.e. under the exclusion of water, TBT-based so-called 'Ti standard sols' were stable for more than one month at room temperature.

Ti standard sol was mixed with aqueous solutions of Ba acetate (Merck, Darmstadt, Germany) and concentrated acetic acid. The process of gelation of such prepared sols was rather slow; a continuous increase of viscosity usually took place. Depending on the water content and pH of the mixture, BaTi acetate sols were fluid for a maximum of 24 h at room temperature. With increasing temperatures the time of gelation was greatly reduced to a few minutes. Here, the 'time of gelation', t_{gel} , has been

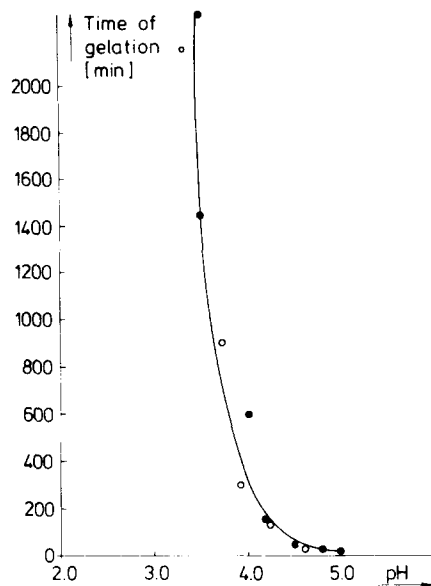


Fig. 1. Time of gelation as function of pH of BaTi acetate 'standard sol': ●, prepared from TBT; ○, prepared from TET.

empirically defined as the time after which a sol no longer flowed out of an inverted test tube.

In Fig. 1, t_{gel} is plotted as the function of pH. A strong decrease of t_{gel} was observed with increasing values of pH. The times of gelation of TBT- and TET-based gels were found to be similar. Clear, transparent gels have been observed only at $\text{pH} \approx 3.5$. At higher values of pH the gels became opaque or even contained segregated $\text{TiO}(\text{OH})_2$. BaTi acetate gels can be dried in air at temperatures of 80–150°C to form clear glassy lumps. On drying, strong shrinkage and formation of fissures took place.

2.1.1 Characterization of BaTi acetate gels

Since Ba ions do not belong to the gel-forming ions,⁹ it is hard to expect that Ba^{2+} ions participate in the formation of the BaTi acetate gel. It is thus an interesting question where the Ba^{2+} ions are located in the structure of hard, glassy lumps of transparent gel. The location of Ba in the gel has been studied by means of scanning transmission electron microscopy (STEM).

2.1.1.1 STEM microanalytical study of BaTi acetate.

Lumps of BaTi acetate gel have been dried at 60°C and cut into *c.* 50 nm thick slices employing an ultramicrotome. The intensities of Ba-L β_2 and (Ti – K α + L α) have been measured over scan lengths of 400 nm in a fine electron beam of *c.* 10 nm spot size, using an EDAX electron microbeam analyser.

The STEM micrograph (Fig. 2) displays irregularly formed agglomerates of light gel and dark, strongly electron-absorbing pores of 50–100 nm size.

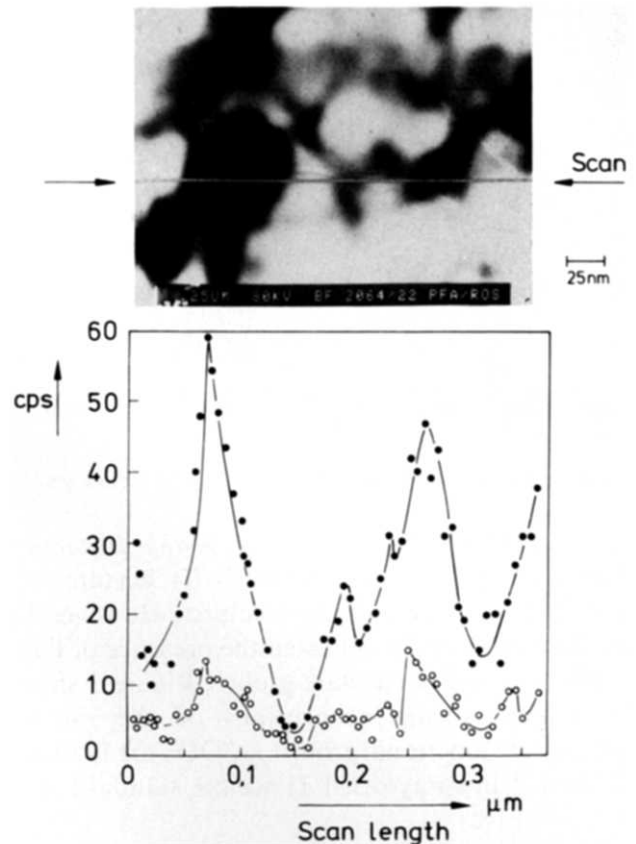


Fig. 2. Electron microbeam analysis of 60°C dried BaTi acetate gel: scanning transmission electron micrograph, line-scan spot size: 10 nm. ○, Ba-L β_2 ; ●, Ti-K α + Ba – L α .

It seems rather surprising that the strongest electron absorptions (dark regions) are just found in the pores of the gel. However, this effect can be explained by the results of the EDAX analysis. The measured X-ray intensities reveal that the heavy, strongly electron-absorbing ions of Ba are all located on the surface and pores of the Ti oxide gel. The light Ti ions produce only a small contrast in the electron beam.

Hence, the STEM–EDAX analyses confirm the well-known fact that Ba ions are not able to form polymer oxide gels and can accordingly not be incorporated as inorganic 'copolymer' into Ti hydroxide gels. BaTi acetate gels can be therefore considered as hydrated polymer titanium acetate with surface adsorbed Ba acetate.

2.1.2 Investigation of Ti oxyacetate gels

Since BaTi acetate gel has been found to consist of a 'skeleton' of polymer Ti oxyacetate with surface adsorbed Ba ions, the chemical composition and the structure of pure, Ba-free Ti oxyacetate were studied as a model system. These investigations have been carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), infrared (IR) spectroscopy and classical chemical analyses.

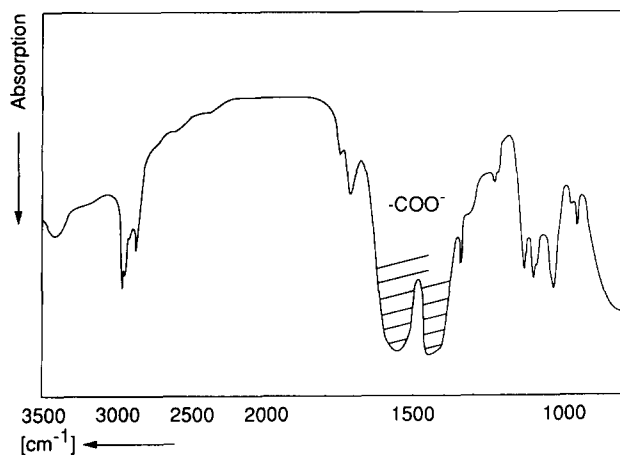
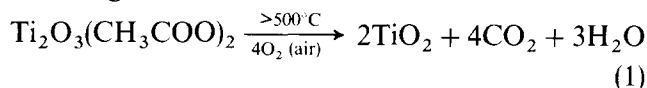


Fig. 3. Infrared spectrum of 110°C dried Ti acetate gel.

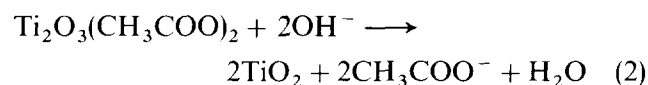
2.1.2.1 XRD, IR spectroscopy. X-ray diffraction (XRD) of spray-dried ($\approx 110^\circ\text{C}$) Ti acetate sols revealed X-ray amorphous structures. However, IR spectroscopy clearly indicated the presence of large numbers of ionized acetate groups. Figure 3 shows the typical strong absorptions of the ionized carboxylate functional group ($-\text{COO}^-$) at 1430 and 1570 cm^{-1} in spray-dried Ti acetate standard sol.

2.1.2.2 Chemical analysis. The chemical composition of Ti acetate gels has been determined by means of thermogravimetry (TGA) and classical titration analyses. Spray-dried Ti acetate gels were heated up to 1100°C in air in a thermobalance (Netzsch STA 429). For titration of the acetate content, spray-dried (60°C) gels were dried in N_2 flow over 60 h to release adsorbed residues of organic solvents, thereafter hydrolysed in excess KOH and then back-titrated with 0.1 M HCl , using phenolphthalein as indicator.

According to the results of TGA, the following reaction is proposed to occur on calcination of the Ti acetate gel:



The results of titration suggest the following chemical change:



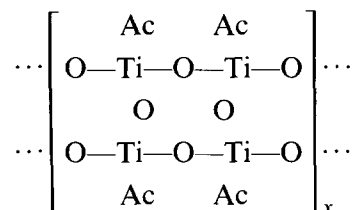
The theoretical and the observed weight loss and consumption of KOH for reactions (1) and (2) are shown in Table 1. The results of titrations and thermogravimetry of spray-dried Ti acetate sols both revealed the well-defined stoichiometrical composition of Ti oxyacetate, suggesting the formula ' $\text{Ti}_2\text{O}_3(\text{CH}_3\text{COO})_2$ '. This well-defined chemical composition has not been previously identified.

Table 1. Analytical Characterization of Ti-Acetate

Reaction	Expected	Observed
Weight loss, according to reaction (1), wt%	39	39.5
OH^- consumption of 1×10^{-2} mol $\text{Ti}_2\text{O}_3(\text{ac})_2$, according to reaction (2), mol	2×10^{-2}	1.99×10^{-2}

The agreement between calculated and measured results strongly confirms the proposed formula of the gel as $\text{Ti}_2\text{O}_3(\text{CH}_3\text{COO})_2$.

2.1.2.3 TEM investigation. The microstructure of dried BaTi acetate gels has been studied in TEM (Philips CM12). At very high magnification linked aggregates of fibrous polymer Ti oxyacetate can be seen in Fig. 4. The diameter of single $\text{Ti}_2\text{O}_3(\text{Ac})_2$ fibres is in the range of $d \approx 10\text{--}20\text{ nm}$. The proposed structure of the dried gel corresponds to polymer chains of Ti oxyacetate:



2.1.3 Thermal decomposition of BaTi acetate gels
On first glance, the relatively small average distance between Ba and Ti ions of $< 20\text{ nm}$ may suggest a strong reduction of the calcination temperature to



Fig. 4. Transmission electron micrograph of 110°C dried Ti acetate gel.

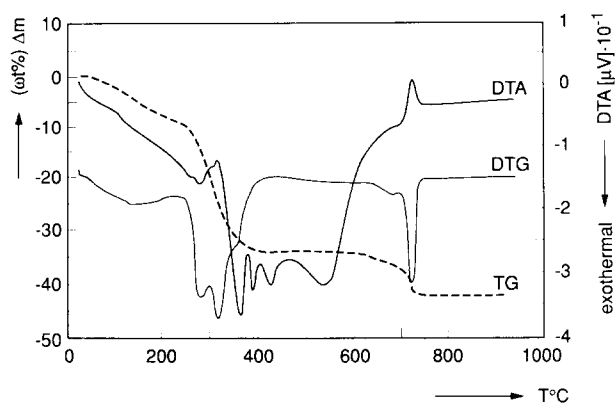


Fig. 5. Thermal decomposition (DTA/TGA) of spray-dried BaTi acetate gel; heating rate 5°C/min in air.

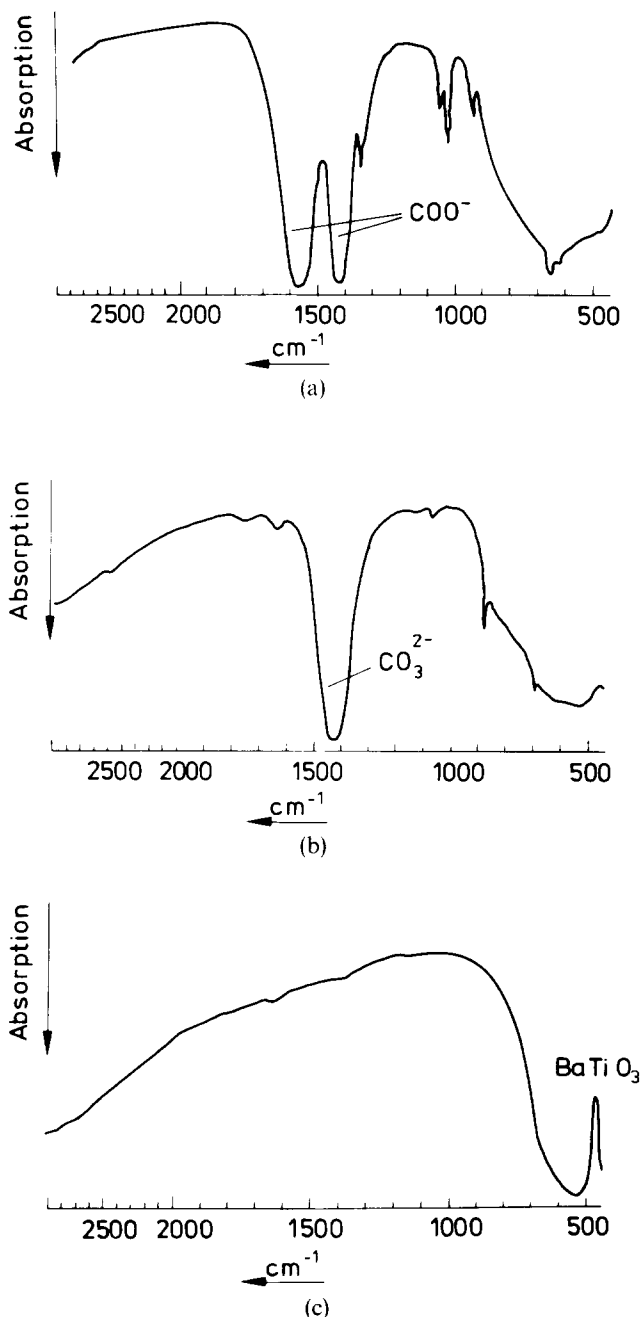


Fig. 6. IR spectroscopy of BaTi acetate gel, heated at various temperatures in air. (a) 340°C; (b) 700°C; (c) 850°C.

BaTiO₃, compared to the case of classical calcination of mixed oxides and carbonates. In mixed oxides the Ba and Ti ions have an average distance of approximately the powder particle size, i.e. 0.2–2 μm.

Thermal decomposition of spray-dried BaTi acetate gels to BaTiO₃ has been studied with DTA/TGA (Netzsch Thermoanalyser STA 429) in air at heating rates of 5°C/min. The DTA/TGA is shown in Fig. 5.

The total weight loss, observed at decomposition of the BaTi acetate gel to BaTiO₃, is *c.* ≈ 45%. Complete conversion into BaTiO₃ occurs at temperatures above 700°C. The relatively high formation temperature of BaTiO₃ is connected with the fact that BaCO₃ is formed on decomposition of acetate, and reacts to the intermediate phase Ba₂Ti₂O₅CO₃ (BTC) at about 400°C. The BTC phase is stable up to temperatures of 700°C.¹³ It becomes crystalline at $T \geq 650^\circ\text{C}$, then showing a number of X-ray reflexions.³ The presence of the carbonate (–CO₃) functional group in amorphous as well as crystallized BTC was detected with IR spectroscopy in gels which had been heated up to 750°C (Fig. 6). In samples annealed at ≈ 850°C IR spectroscopy revealed the absorptions of pure BaTiO₃.

Intermediate formation of BaCO₃, reacting to the thermally stable intermediate BTC phase, is a principle problem of the calcination of BaTiO₃ from organic precursors. The relatively high temperature of 700–750°C at which the BaTiO₃ perovskite phase appears makes thermal decomposition of BaTi acetate gels a less favourable route. BaTiO₃ calcined from BaTi acetate gels at 850°C consists of tough aggregates of very fine crystallites which need intensive milling before their use for dielectric preparations.

2.2 Hydrothermal processing of BaTi acetate gels

From a thermodynamical point of view aqueous suspensions of BaTiO₃ are only stable under strongly alkaline conditions,¹⁴ i.e. at pH ≥ 13. From this calculated instability of BaTiO₃ in water, it can be deduced that BaTiO₃ should completely decompose to TiO₂ and Ba(OH)₂ during washing or milling in water. In practice, thin but largely water-impermeable layers of TiO₂ are formed on the surface of BaTiO₃ particles, preventing the BaTiO₃ powder from total dissolution in water. However, corresponding to the rather high specific surface area of hydrothermal BaTiO₃ powder particles, strong Ba leaching¹⁴ and increased values of pH in aqueous suspensions of hydrothermal BaTiO₃ are in fact observed.

It is a severe disadvantage of the conventional hydrothermal route than an excess of $\text{Ba}(\text{OH})_2$ is necessary to achieve a complete reaction of $\text{TiO}(\text{OH})_2$ to BaTiO_3 . The unreacted $\text{Ba}(\text{OH})_2$ has to be washed out with water after processing. However, regarding the chemical instability of BaTiO_3 , it is rather difficult to wash out the excess $\text{Ba}(\text{OH})_2$ without simultaneous decomposition of the BaTiO_3 into $\text{TiO}_{2(\text{aq})}$.

The disadvantage of the conventional route can be avoided by using stoichiometric BaTi acetate gels. The intimate mixing of Ba and Ti on a scale of *c.* 20 nm makes BaTi acetate gels especially suitable precursors for hydrothermal processing of BaTiO_3 . Hence, it seems possible to yield quantitative chemical changes, starting from precursors with the Ba/Ti atomic ratio of 1:1.

2.2.1 Experimental

For all experiments the spray-dried ($\approx 120^\circ\text{C}$) BaTi acetate 'Standard precursor' (Section 2.1) has been used. According to the above-mentioned thermodynamic preconditions, a minimum value of $\text{pH} \geq 13$ had to be maintained during the whole course of processing. Since on the one hand ammonia is too weak a base and on the other hand contamination of BaTiO_3 with alkaline ions needs to be avoided, the strong organic base tetramethylammonium hydroxide, $\text{N}[\text{CH}_3]_4\text{OH}$ (Fluca, Buch, Switzerland), was used in 25 wt% aqueous solution.

Hydrothermal reactions have been carried out in a small, 250-cm³ laboratory autoclave (Berghof, Labortechnik, 7412 Eningen, Germany) which could be used at temperatures up to 200°C and pressures up to 150 bar. During the reaction the suspension was stirred at 250 rpm in the autoclave. Adequate reaction conditions were temperatures of 150°C and reaction times of 10–15 h. After processing the powders were decanted and washed out in methanol. For obtaining fluid powders, the BaTiO_3 was air-dried at 80°C and then weakly deaggregated in a plastic mortar.

2.2.2 Results

Ba/Ti-ratios (XRF analysis). The stoichiometry of hydrothermal BaTiO_3 powders was checked by means of X-ray fluorescence analysis (XRF) with an accuracy of $\pm 0.2\%$. For these analyses BaTiO_3 powder was dissolved in molten Li tetraborate glass. As a result, Ba/Ti atomic ratios between 1:1.005 and 1:0.995 were determined. Excess Ba in hydrothermal BaTiO_3 was usually caused by small amounts of BaCO_3 , which was precipitated by traces of CO_2 in the suspension. An excess of Ba in the precursor did

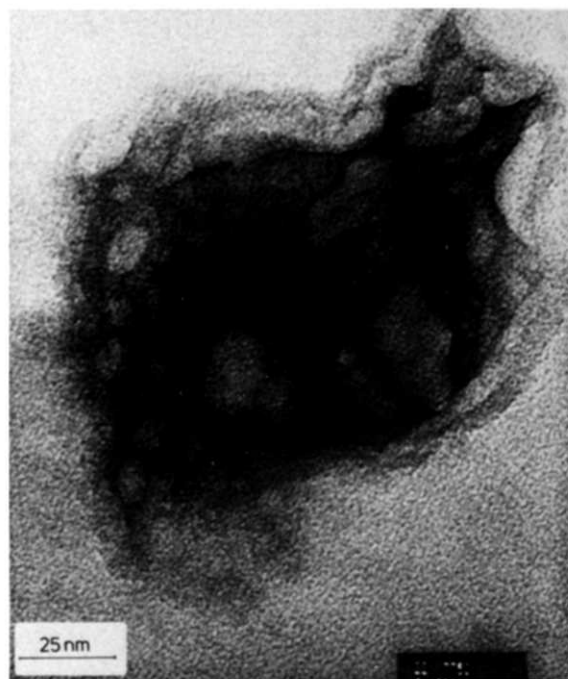


Fig. 7. Short time hydrothermally reacted BaTi acetate gel (TEM, 'initial state' of reaction).

not improve the observed scatter of the Ba/Ti atomic ratio.

At processing temperatures $> 150^\circ\text{C}$, thermal decomposition of the $\text{N}[\text{CH}_3]_4\text{OH}$ began which led to an unfavourable reduction of pH during reaction and, hence, to an incomplete chemical reaction.

2.2.3 TEM study of hydrothermal process

To get a better insight of the chemical mechanisms during hydrothermal synthesis of BaTiO_3 the course

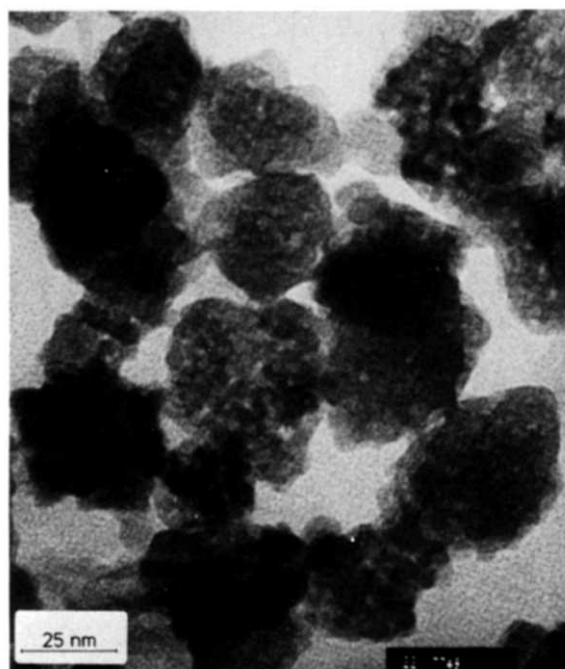


Fig. 8. Incompletely hydrothermally processed ($\approx 20\%$ BaTiO_3) BaTi acetate gel (TEM, 'nucleation of BaTiO_3 ').



Fig. 9. Incompletely hydrothermally processed BaTi acetate gel; fibrous character of gel precursor is still preserved (TEM, 'nucleation of BaTiO₃').

of the reaction was investigated with TEM at various states of incomplete reaction. The most convenient technique was to stop the reaction by decreasing the pH to < 10 and cooling the autoclave. After washing out the unreacted Ba²⁺, the actual extent of the chemical change was roughly estimated by use of XRF. Reaction products taken from the

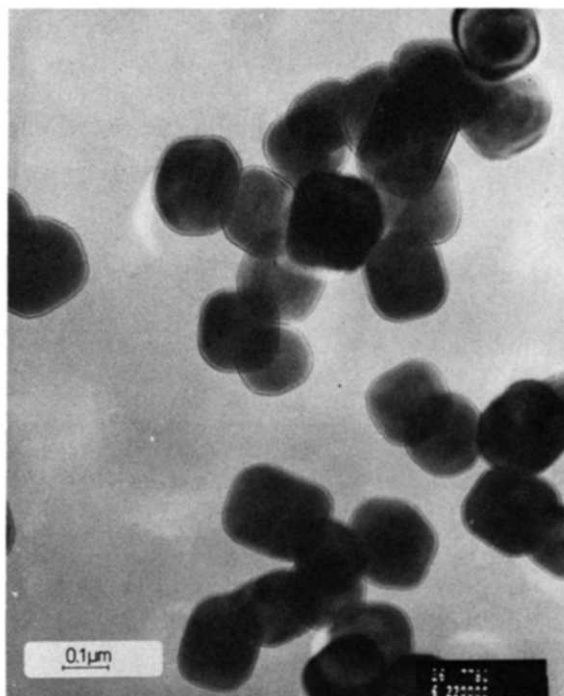


Fig. 10. Hydrothermal BaTiO₃ completely (99.7%) processed at 150°C, 10h (TEM, Ostwald ripening).

autoclave were dried and cut into < 50 nm thin slices, as described earlier. TEM micrographs, depicting various states incompletely reacted products, are shown in Figs 7–10.

2.2.3.1 Initial state of reaction (reaction time c. 5–10 min). The 'initial state' of the hydrothermal reaction process is obtained after a few minutes reaction time. This state is typically characterized by the TEM micrograph in Fig. 7. Reaction products of the initial state exhibit only an intense surface contrast, probably due to increased absorption or chemisorption of Ba²⁺ on the surface of the titanium oxide gel. The morphology of the gel has changed from fibrous into a lumpy structure. X-ray diffraction (Fig. 11) reveals amorphous structures. In

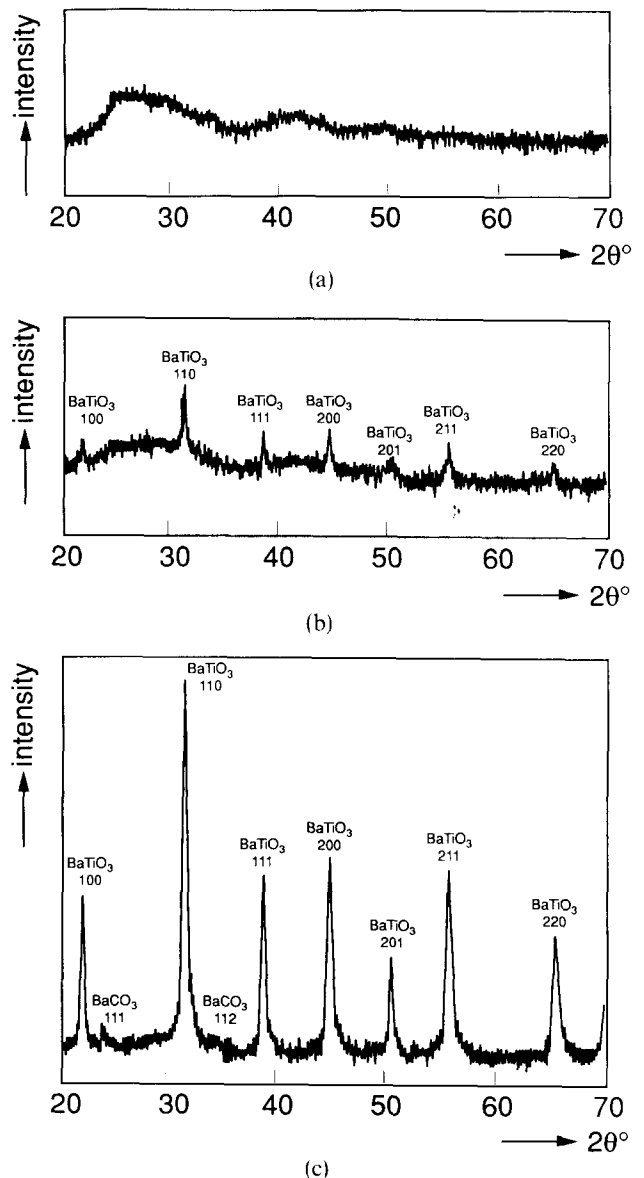


Fig. 11. XRD of BaTi acetate gel at various states of hydrothermal processing to BaTiO₃: (a) unreacted gel; (b) nucleation of BaTiO₃ (30 min reaction time); (c) final state of reaction (5–10h reaction time).

the initial state of reaction no actual chemical change into BaTiO_3 has taken place. All of the unreacted Ba can be easily washed out.

2.2.3.2 Nucleation of BaTiO_3 (reaction time c. 30 min). After c. 30 min reaction time roughly 15–20% of the gel has been changed into BaTiO_3 . Unreacted Ba ions can be easily washed out again. The process of BaTiO_3 formation is obviously still in a 'state of nucleation'. A large number of very small (<5 nm) crystallites of BaTiO_3 can be seen on the surface of the titanium oxide gel (Fig. 8). X-ray diffraction of these products provides the pattern of crystalline BaTiO_3 particles besides diffuse reflexions of amorphous products (Fig. 11).

The TEM micrograph of another sample of partly (c. 15% BaTiO_3) reacted BaTi acetate gel (Fig. 9) still displays the original fibrous character of the gel, forming long chains of small aligned particles. Particles, showing a stronger contrast in the electron beam, probably consist of nucleated BaTiO_3 .

2.2.3.3 Final state of reaction (reaction time 10 h). After 10 h reaction time at 150°C and pH > 13 the hydrothermal reaction process has been largely (99.7% BaTiO_3) completed. The TEM micrograph of reaction products for the 'final state' of hydrothermal processing shows a completely new picture (Fig. 10). The original fibrous structure of the gel has disappeared and nearly spherical particles of BaTiO_3 have been formed. The BaTiO_3 particles have grown to a fairly uniform size, 200–300 nm, while the crystallites seem to be only weakly agglomerated.

The strong growth of the BaTiO_3 crystallites from <5 nm to finally 200–300 nm in size is typical of a ripening process. During this process small unstable particles are dissolved. The dissolved BaTiO_3 is segregated at stable grains. However, it seems rather surprising that even the difficult to dissolve ions of TiO^{2+} participate in the transport process of Ostwald ripening. The process of particle ripening obviously stops at a final crystallite size of 200–300 nm. Even very extended processing times have no significant influence on the final crystallite size of the BaTiO_3 .

3 Results and Conclusions

Clear, transparent gels of BaTi acetate have been prepared which can be used as precursors for BaTiO_3 . BaTi acetate gels consist of linked clusters of polymer Ti oxyacetate with surface adsorbed

Ba ions. Spray-dried Ti oxyacetate has been found to have the stoichiometric composition $\text{Ti}_2\text{O}_3(\text{CH}_3\text{COO})_2$. On calcination in air, BaTi acetate gels do not form BaTiO_3 below 700°C. Formation of BaTiO_3 at lower temperatures is impeded by the stable intermediate phase $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ which is generally formed on decomposition of acetate or other organic groups. Hence, BaTi gels containing organic constituents are unfavourable precursors for calcination to BaTiO_3 .

BaTi acetate gels turned out to be suitable precursors for hydrothermal synthesis of BaTiO_3 . The following advantages of BaTi acetate precursors for hydrothermal processing of BaTiO_3 have been found:

- Stoichiometric BaTi (1:1) acetate precursors can be used to form stoichiometric BaTiO_3 .
- The fine dispersion of Ba and Ti on a scale of ≤ 20 nm strongly enhances the reactivity of the gel and enables complete hydrothermal reaction to BaTiO_3 .
- The well-defined stoichiometry of $\text{Ti}_2\text{O}_3(\text{CH}_3\text{COO})_2$, found in spray-dried precursors, facilitates the adjustment of pH to ≥ 13 , using the organic base $\text{N}[\text{CH}_3]_4\text{OH}$.

Transmission electron microscopy of partly reacted products revealed that hydrothermal reaction of BaTi acetate gels to BaTiO_3 starts with large numbers of very small (≤ 5 nm) BaTiO_3 nuclei formed on the surface of hydrolysed titanium oxide gel. In a subsequent process of Ostwald ripening the small BaTiO_3 nuclei disappear, forming widely monodispersed and equisized crystallite of BaTiO_3 of 200–300 nm in size. Even largely extended processing times have no significant influence on this final crystallite size.

References

1. Mazdiyasi, K. S., Preparation of high purity submicron BaTiO_3 powders. *J. Am. Ceram. Soc.*, **52** (1969) 523.
2. Clabaugh, W. S., Swiggard, E. M. & Gilchrist, J. R., Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of high purity. *J. Res. Natl. Bur. Standards* (1956) Research Paper No. 2677, p. 289.
3. Hennings, D. & Mayr, W., Thermal decomposition of (BaTi) citrates into barium titanate. *J. Solid State Chem.*, **26** (1978) 329.
4. O'Holleran, T. P., Neurogoanker, R. R., Roy, D. M. & Roy, R., EDS for the preparation of $\alpha\text{-Fe}_2\text{O}_3$. *Am. Ceram. Soc. Bull.*, **57** (1978) 459.
5. Messing, G. L., Gardner, T. J. & Ciminelli, R. R., Characteristics of EDS-derived powders. In *Science of Ceramics*, Vol. 12, ed. P. Vincencini. Ceramurgia s.r.l., Faenza, 1984, p. 117.

6. Dawson, W. J., Hydrothermal synthesis of advanced ceramic powders. *Am. Ceram. Soc. Bull.*, **67** (1988) 1673.
7. Vivekanandan, R., Philip, S. & Kutty, T. R., Preparation of CaTiO_3 fine powders by the hydrothermal method. *Mat. Res. Bull.*, **22** (1986) 99.
8. Brinker, C. J. & Scherer, G. W., Sol–gel–glass: I. Gelation and gel structure. *J. Non-Cryst. Solids*, **70** (1985) 301.
9. Segal, D. L., Sol–gel processing: Routes to oxide ceramics using colloidal dispersions of hydrous oxides and alkoxide intermediates. *J. Non-Cryst. Solids*, **63** (1984) 183.
10. Passing, G., Hennings, D. & Reynen, P., Resumes de Posters, IIème Conf. Franco–Allemande, Aachen, 4–6 March 1987, p. A-29.
11. Hennings, D., Evaluation of different industrial routes to synthesize barium titanate for capacitors. In *2nd International Conference on Passive Components: Materials, Technologies, Processing*, Paris, 18–20 November 1987, IP-5, p. 165.
12. Abe, K. I., Aoki, M. T., Rikimaru, H. N., Itoh, T. S., Hidaka, K. T., Segawa, K. & Ikema, N., Verfahren zur Herstellung einer Perowskitverbindungen enthaltenden Masse. German Patent Application De 3526647-A1, 25 July 1984.
13. Gopalakrishna Murthy, H. S., Subba Rao, M. S. & Kutty, R. T. N., Thermal decomposition of titanyl oxalates—II, kinetics of decomposition of barium titanyl oxalate. *J. Inorg. Nucl. Chem.*, **37** (1975) 891.
14. Utech, B. L., The effect of solution chemistry on barium titanate ceramics. Doctoral Thesis, Materials Research Laboratory, Pennsylvania State University, University Park, PA, May 1990.