

A New Ultrafine Titanium Oxide Raw Material for the Manufacturing of Fine-Particulate Barium Titanate Dielectrics

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Abstract

Following the roadmap of the electroceramics industry, the shrinking feature size of dielectrics requires very fine ceramic powders as starting materials. With respect to fine-particulate barium titanate (BT), typical requirements to this material in demanding applications such as multi-layer ceramic capacitors (MLCCs) include homogeneous composition and cation distribution, high purity, uniform particle size and shape, and weak agglomeration.

Whereas conventional solid-state reaction of barium carbonate and titanium dioxide reveals usually strongly aggregated, coarse-grained powders and requires intensive milling, we have identified a novel manufacturing approach: The use of a highly reactive and fine-particulate titanium hydrate precursor (TH) with optimized particle size and morphology allows lowering the temperature for titanate formation and providing finer barium titanate (BT). In comparison with standard titanium dioxide, TH has been shown to produce much finer barium titanate when employing the standard carbonate solid-state reaction at 1100 °C. Furthermore, reaction of TH with barium hydroxide allowed lowering the temperature of calcination down to even 400 °C. These very fine particles show physical properties similar to material synthesized by sol-gel processes.

With this new approach, we are able to combine a simple powder processing technology (in contrast to expensive hydrothermal or sol-gel technology) with outstanding properties of the resulting BT. Besides obtaining barium titanate by direct calcination, the TH raw material also allows to produce a ready-to-use dry BT precursor (“pre-calcined” BT). Physical and chemical properties of the precursor materials and of the resulting barium titanate are discussed.

Introduction

Ceramics on the basis of alkaline-earth titanates, particularly barium titanate (BaTiO_3) are among the most important electroceramics for application in electronics and microelectronics owing to their excellent ferroelectric and dielectric properties. They are widely used as the main components in many types of electroceramic devices such as multilayer capacitors (MLCC) and positive temperature coefficient resistors (PTCR) [1,2]. Alkaline-earth titanates may be produced by synthesis methods which employ solid state reactions such as the classical mixed oxide method as well as wet chemical methods [3]. The conventional solid state reaction between barium carbonate BaCO_3 and titanium dioxide TiO_2 to BaTiO_3 at temperatures of 1000 to 1200 °C represents an

economical method to prepare large quantities of barium titanate ceramics. However, well-known disadvantages of this method include low purity, chemical inhomogeneity, or large BaTiO₃ grain size accompanied by broad particle size distribution. This is especially true when conventional TiO₂ raw materials are used consisting of quite coarse particles such as those grades that are used for TiO₂ pigment applications (large particle size, small surface area of 5 to 10 m²/g).

Following the roadmap of the electroceramics industry, the shrinking feature size of dielectrics requires very fine ceramic powders as starting materials. Therefore, numerous approaches to fine-particulate barium titanate have been made, involving also finer titaniferous raw materials. From studies on the BaTiO₃ solid state formation mechanism, it is known that the reaction takes place mainly by diffusion of Ba²⁺ and O²⁻ ions into the TiO₂ particles, i.e. the morphology of the BaTiO₃ particles is primarily determined by the morphology of the TiO₂ particles [4,5,6]. Consequently, even if fine-particulate BaCO₃ is used in the solid state reaction with TiO₂ having a particle size of 200 nm, calcination at 900 to 1200° C gives a BaTiO₃ that is highly agglomerated with crystallite sizes of 200 nm to 1 µm and that has to be disintegrated by milling [6].

Wet chemical processes are another approach for producing BaTiO₃, such as the co-precipitation of barium and titanium compounds and subsequent calcination [7]. This method is very time-consuming and expensive as is the hydrothermal production of BaTiO₃ from Ba(OH)₂ or soluble barium compounds and TiO₂ using mineralisers, e.g. KOH, NaOH [8,9]. Due to the high cost of precursors, the large shrinkage during processing and now and then long processing times, industrial application of these processes has been difficult. Reproducing constant quality and physical properties of the final product to ensure reliability in MLCC manufacturing has been a very complex issue with many new and alternative synthetic routes to BaTiO₃ in mass production [10].

We have identified a novel manufacturing approach to provide fine-particle, high-purity and economically viable alkaline-earth titanates and especially barium titanate. Compared to prior art, it has been one objective to provide a method for the titanate production using available and cost efficient titaniferous raw materials. Accordingly, we would like to present and discuss the properties and use of a highly reactive and fine-particulate titanium hydrate precursor (TH) for titanate manufacturing. With an optimized particle size and morphology, TH allows lowering the temperature for titanate formation and providing finer barium titanate. In comparison with standard titanium dioxide, TH has been shown to produce much finer barium titanate when employing the standard carbonate solid-state route. Furthermore, reaction of TH with barium hydroxide allowed lowering the calcination temperature even more down to 400 °C. The resulting very fine BaTiO₃ particles show physical properties similar to material synthesized by sol-gel processes. With this new approach, we are able to combine a simple powder processing technology (in contrast to expensive hydrothermal or sol-gel technology) with outstanding properties of the resulting BaTiO₃. Besides obtaining barium titanate by direct calcination, the TH raw material also allows to produce a ready-to-use dry BT precursor (“pre-calcined” BT). Physical and chemical properties of the precursor materials and of the resulting barium titanate will be presented in the following.

Results and Discussion

Titanium hydrate (TH) - a highly reactive and fine-particulate raw material for titanate manufacturing

In contrast to conventional TiO_2 raw materials consisting of quite coarse particles and showing a small surface area of 5 to 10 m^2/g , we have developed a fine-particle, high-purity titanium oxide hydrate material (TH) and evaluated its use for electroceramic titanate manufacturing. We will shortly discuss some properties of the TH material and in the following sections present the results of several reaction pathways to barium titanate using TH. Typically, the titanium hydrate material used has a BET surface area greater than 200 m^2/g , preferably 250 to 350 m^2/g . The surface area can easily be adjusted according to the application needs. A comparison of selected properties of TH with a conventional coarse-grained rutile TiO_2 (R) and conventional fine-particle anatase TiO_2 (A) is given in Table 1. TH can be described as a fine-particulate, microcrystalline anatase material that is used in a hydrated form, i.e. the particles contain chemisorbed water. The nanoparticulate, microcrystalline character can be seen in the X-ray powder diffraction pattern (Figure 1, comparison of XRD shown for A, R, and TH).

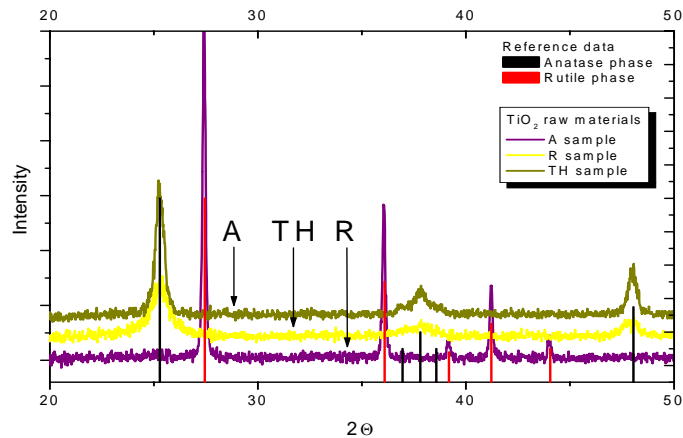


Figure 1: X-ray diffraction data of TiO_2 raw materials (A: fine particle anatase; TH: ultrafine titanium hydrate; R: coarse conventional rutile).

The primary particles are small, approximately spherical microcrystalline particles with a lattice-defective anatase structure. The particle size may be determined by calculation from the BET surface area assuming a monomodal grain size distribution of spherical particles. Accordingly, primary particles of TH show an average particle size of 3 to 15 nm. The material exists in a remarkable structure that can be characterized by scanning electron and transmission electron microscopy (SEM and TEM). The primary particles are agglomerating, resulting in secondary particles of approx. 30 to 50 nm in diameter, which in turn are forming tertiary particles of approx. 1 μm in diameter [11]. The nature of these agglomerates is relatively soft. Electron micrographs of TH are shown in Figure 2.

TiO_2 may be obtained by hydrolysis of inorganic or organic titanium compounds. Depending on the titanium compound and the reaction conditions, the titanium dioxides obtained in the process have different properties. In the case of TH, which is obtained by hydrolysing titanyl sulphate solution according to the sulphate method, there is a

particularly advantageous combination of properties, that is to say a high specific surface area and a microcrystalline anatase structure [12]. Preferably, TH is freed from adherent contaminants by filtering and washing and, if necessary, by subjecting additionally to a chemical treatment with reduction agents after obtained by hydrolysis. Commercial production of TH based on the sulphate method for the production of titanium dioxide also has the advantage of consistent product quality and continuous availability. Of particular advantage with the titanium oxide hydrate obtained from titanyl sulphate is its high purity in respect of iron, aluminium and other metals as well as its extremely low contents of chloride and carbon. For example, the chloride content of the particles is preferably less than 20 ppm in relation to TiO_2 , the iron content preferably less than 10 ppm.

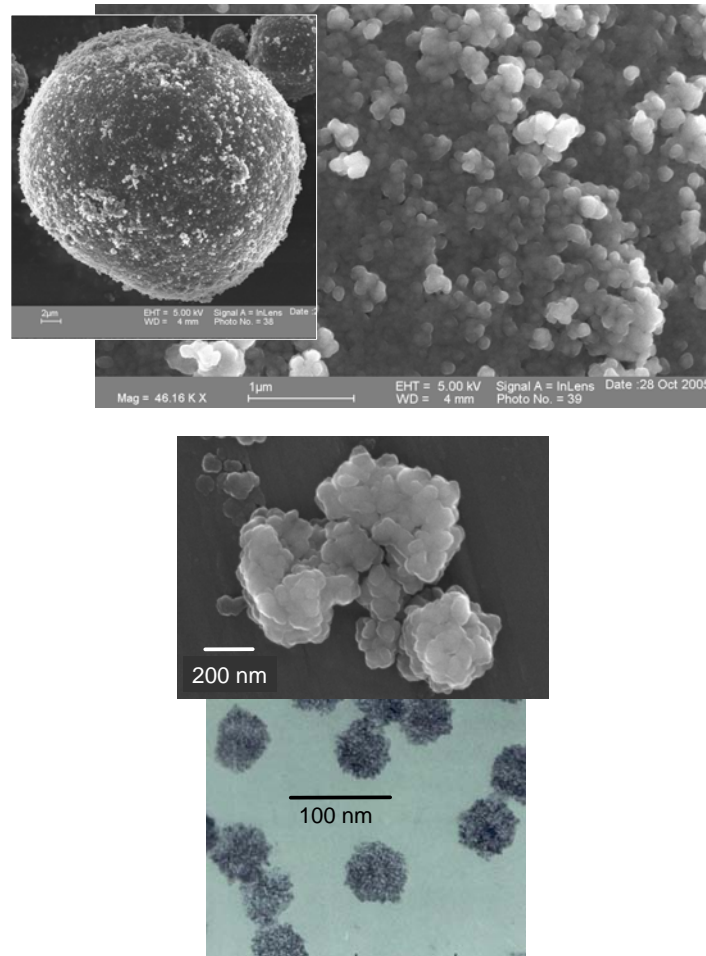


Figure 2: Electron micrographs (SEM top and bottom left, TEM bottom right) of titanium hydrate (TH). The material can be obtained conveniently as a spray-dried powder with homogeneous fine-particle agglomerates (top images). At higher magnification, the ultrafine agglomerates as well as the primary particles can be characterized.

Table 1: Selected data of TiO₂ raw materials

	<i>Specific surface area BET (m²/g)</i>	<i>Mean particle size calculated from BET surface area (nm)</i>
R (reference rutile)	5,7	247
A (reference fine-particulate anatase)	73	21
TH (new ultrafine raw material)	271	6

Reactivity of TH towards barium compounds

To evaluate the suitability of TH for electroceramic titanate manufacturing, we have screened the reactivity towards alkaline-earth metal compounds. With a focus on barium titanate manufacturing, we will discuss the evaluation of TH and reference compounds in the solid-state reactions with barium carbonates, oxalates, and nitrates, as well as in a modified solid-state reaction with barium hydroxide. In addition, we will present the evaluation of TH in hydrothermal BaTiO₃ synthesis using barium hydroxide.

Preparation of BaTiO₃ via the carbonate route comparing TH and conventional TiO₂

For comparison the carbonate route, a classical ceramic technology, was used for BaTiO₃ preparation starting from TH as well as from the two reference compounds described in Table 1. Starting materials were used according to their absolute TiO₂ content to account for weight loss due to humidity or dehydration during annealing. Barium carbonate BaCO₃ (Solvay, Sabel VL 600) and the corresponding titanium dioxide fine anatase A, coarse rutile R, or ultrafine TH were mixed/ground for 24 hours in distilled water with PVC-coated steel balls in a PVC drum. After suction extraction and drying, the powder mixtures were calcined. Temperatures of approx. 950 °C are necessary for complete reaction of the BaCO₃ with TiO₂ with the formation of BaTiO₃: From thermal analyses of TH/BaCO₃ reaction mixtures (not shown here) it is known that BaCO₃ decomposition reaches a maximum at 930 °C, also the phase transition from γ -BaCO₃ to β -BaCO₃ modification can be observed at 830 °C. Above 930 °C a significant exothermic effect can be seen due to reaction with TiO₂ and crystallization. XRD data of TH/BaCO₃ samples after 2 h at 830 °C reveal a crystalline mixture of BaCO₃, tetragonal BaTiO₃, and minor amounts of anatase TiO₂ and the Ba-deficient titanate BaTi₄O₉. After 2 h at 950 °C, only tetragonal BaTiO₃ can be detected. To follow usual manufacturing procedures, calcination was performed for 2 h at 1100 °C. XRD data for the resulting BaTiO₃ materials are shown in Figure 3.

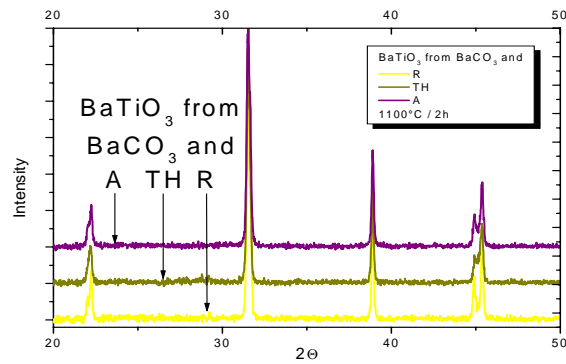


Figure 3: X-ray diffraction data of BaTiO_3 starting from the solid-state reaction of BaCO_3 and different TiO_2 raw materials (A: fine particle anatase; TH: ultrafine titanium hydrate; R: coarse conventional rutile).

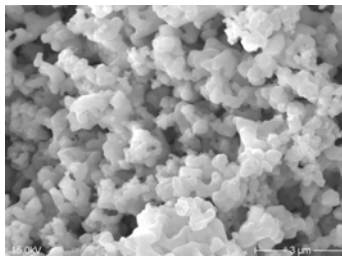


Figure 4: Electron micrograph of BaTiO_3 prepared via the carbonate route from TH at 1000°C , 2 h.

This classic approach yields in the case of coarse rutile R after calcination at 1000°C for 2 h a BaTiO_3 with a BET surface area of $2.0\text{ m}^2/\text{g}$, corresponding to a BaTiO_3 crystallite size d_{BET} of 500 nm. In case of the ultrafine TH, after calcination with BaCO_3 under the same conditions, a similar BaTiO_3 material is obtained with a BET surface area of $2.2\text{ m}^2/\text{g}$ and a corresponding BaTiO_3 crystallite size d_{BET} of 450 nm. Although TH therefore is suited to obtain a state-of-the-art high-purity BaTiO_3 , the ultrafine character has negligible effect on the particle size of the resulting titanate, since the Ba raw material requires very high calcination temperatures to be decomposed and to enter the reaction via the BaO intermediate. Figure 4 shows an electron micrograph of BaTiO_3 prepared via the carbonate route from TH at 1000°C , 2 h. Dielectric properties in a frequency range of 0.12 to 100 kHz were determined of barium titanate samples synthesized from TH, A, and R, sintered at 1300°C or 1350°C . Dielectric constants as well as the dissipation factor $\tan \delta$ are in the typical range of BaTiO_3 ceramics. The data show the typical maximum at the phase transition temperature of 120°C from tetragonal to cubic. Values for ϵ_r' are around 360 to 400 at 120°C and 170 to 230 at 75°C for samples sintered at 1300°C , and 900 to 1000 as well as 110 to 150, respectively, for samples sintered at 1350°C . The dissipation factor $\tan \delta$ was determined to be $1.4 \cdot 10^{-1}$ to $1.3 \cdot 10^{-3}$ depending on reaction conditions. A clear advantage of TH can be seen in the sintering performance, since already TH reaches a sufficient density at 1300°C that A as well as R derived samples only reach at 1350°C treatment. Accordingly, for the dielectric application a TH derived barium titanate powder is recommended since a high density can be realized at lower temperatures and with smaller grain size.

Preparation of BaTiO₃ via the oxalate route

Similar to the carbonate route experimental scheme, barium oxalate BaC₂O₄ (Alfa Aesar) and ultrafine TH were mixed/ground with distilled water and PVC-coated steel balls for 24 hours in a PVC drum. After suction extraction and drying, the powder mixture was subjected to thermal analyses and, finally, to calcination. The results of the thermal analyses (differential scanning calorimetry and thermal gravimetry) are shown in Figure 5. It can be seen that the reaction mixture of TH and BaC₂O₄ shows a two-step decomposition mechanism of the oxalate, involving a first decomposition according to BaC₂O₄ → BaCO₃ + CO at around 550 °C, followed by phase transitions of the resulting barium carbonate at 820 °C and 970 °C (γ → β modification and β → α modification, respectively) as well as barium carbonate decomposition according to BaCO₃ → BaO + CO₂. Therefore, reaction temperatures above 950 °C are necessary for a complete reaction to BaTiO₃. After calcining the TH/oxalate mixture at 1000 °C for 2 h, the BET surface area of the resulting BaTiO₃ is 2.8 m²/g, corresponding to a calculated crystallite size d_{BET} of 350 nm. The SEM image of this calcined barium titanate is shown in Figure 5.

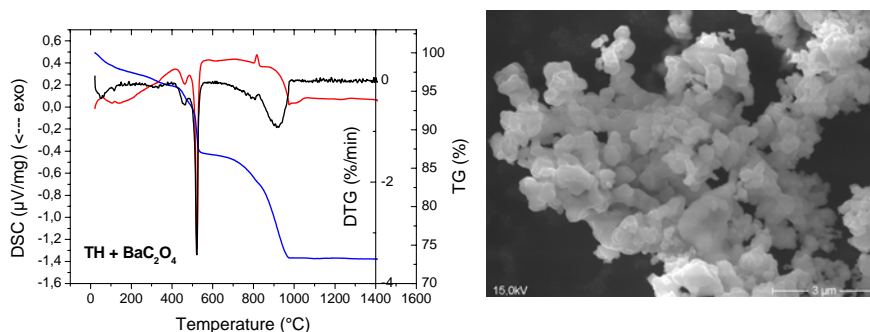


Figure 5: Thermal analysis of a reaction mixture of TH/BaC₂O₄ (left) and electron micrograph (right) of BaTiO₃ prepared via the oxalate route from TH at 1000 °C, 2 h.

Use of ultrafine TH in classical solid state reactions

When using alkaline-earth compounds with high decomposition temperatures such as carbonates or oxalates, there is not taken full advantage of the potential inherent in the fine-particle nature of the titanium component: sintering and coarsening of the titanium component has already taken place at the temperatures necessary for decomposition of the alkaline-earth compound. Nevertheless, even when using alkaline-earth compounds which only decompose at high temperatures (e.g. alkaline-earth carbonates), it is possible to achieve a certain improvement in the fine-particle nature of the alkaline-earth titanates by means of fine-particle titanium components [6]. This applies in particular if the carbonates are wet ground together with the TH as a result of which very homogeneous and reactive mixtures are formed. In addition, the high purity of TH is beneficial.

A novel manufacturing approach: Modified solid-state reaction of TH with barium hydroxide

To obtain fine-particulate barium titanate in an economically and technically viable and workable way, one approach is to aim for a solid-state reaction with highly reactive raw materials that can be performed at relatively low temperatures, e.g. below 700 °C or even more preferably below 600 °C or less. A solid state reaction is understood to be a chemical reaction between two or more solids in the absence of a solvent such as water, for example. This contrasts with wet chemical and also hydrothermal methods in which, for example, solutions containing barium ions are initially produced. We have developed an approach using ultrafine TH in combination with alkaline-earth metal compounds that decompose at low temperatures, e.g. with formation of alkaline-earth metal oxides. Thus, amongst the barium salts, barium hydroxide, barium nitrate and other easily decomposable barium compounds and mixtures thereof are preferred.

Experimentally, Ba(OH)₂·8 H₂O (Fluka, p.a.) and the corresponding titanium dioxide fine anatase A, coarse rutile R, or ultrafine TH were placed in outgassed, distilled water. The mixture is dissolved or suspended whilst stirring for 1 h at 50 °C. Subsequently, the solvent water is removed on the rotary evaporator under vacuum. The powder obtained is dried in the desiccator. The production steps are carried out in a protecting gas atmosphere to prevent the formation of BaCO₃ due to the reaction of Ba(OH)₂ with CO₂ in the air.

In case of ultrafine TH, following heat treatment of the reaction mixture for 2 h at 400 °C, a product with a specific surface area of $S_{\text{BET}} = 27.6 \text{ m}^2/\text{g}$ is obtained; following heat treatment for 2 h at 600 °C, a product with a specific surface area of $S_{\text{BET}} = 12.8 \text{ m}^2/\text{g}$ is produced. In each case, only BaTiO₃ is detected as the crystalline phase by X-ray powder diffraction. The BaTiO₃ crystallite sizes calculated from the specific surface areas are 36 and 78 nm respectively. After calcining at 1000 °C, the BET surface area is 3.2 m²/g, corresponding to a crystallite size of 310 nm, due to particle growth with increasing calcination temperature. After bead grinding of a product suspension calcined at 600 °C, the ground and dried barium titanate obtained has a BET surface area of 32.5 m²/g.

In case of the conventional titanium dioxide raw materials R or A, the fine-particulate BaTiO₃ is not found, since specific surface area is too low and crystallite sizes are too large. Reaction mixtures of R or A, respectively, with Ba(OH)₂ result in low BaTiO₃ yields even at 1000 °C in connection with the formation of unwanted orthotitanate Ba₂TiO₄ and unreacted TiO₂ starting material.

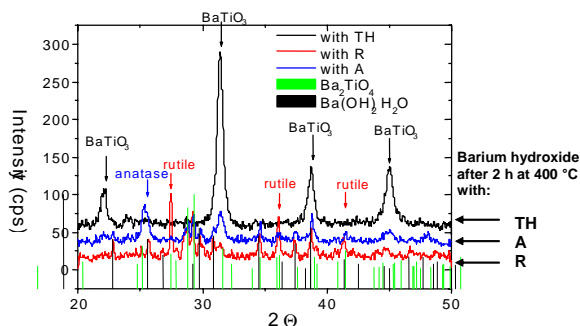


Figure 6: X-ray powder diffraction data for reaction mixtures of barium hydroxide and different TiO₂ raw materials calcined for 2 h at 400 °C (A: fine particle anatase; TH: ultrafine titanium hydrate; R: coarse conventional rutile).

For conventional rutile R, calcination of the reaction mixture for 2 h at 400 °C gives a material with a specific surface area of 2.5 m²/g, at 600 °C 2.2 m²/g, and treatment for at 1000 °C results in a product with a specific surface area of 1.9 m²/g. Unlike with TH, the main phase after calcination at 400 °C is rutile, along with Ba₂TiO₄ and BaTiO₃ in addition to reacted or reverse-reacted Ba(OH)₂·xH₂O. There is likewise no complete reaction to BaTiO₃ to be ascertained after tempering at 600 °C and 1000 °C. Rutile and Ba₂TiO₄ occur as subsidiary phases. A comparison of phase analyses by XRD is shown in Figure 6 for reaction mixtures of barium hydroxide with fine anatase A, coarse rutile R, and ultrafine TH.

The high reactivity of TH and resulting small BaTiO₃ particle size of d_{BET} 36 nm after calcining the TH derived BaTiO₃ precursor at 400 °C represents a dimension of physical properties that commonly has not been achieved by solid-state reactions but only via wet chemical titanate syntheses involving hydrothermal reactions or molecular precursor materials. A summary is given in

Table 2.

Table 2: Summary of BaTiO₃ properties depending on different solid-state manufacturing approaches.

<i>TiO₂ source</i>	<i>Synthetic pathway to BaTiO₃, Ba raw material</i>	<i>Reaction temperature (°C) for 2 h</i>	<i>Specific surface area of reaction product S_{BET} (m²/g)</i>	<i>Mean particle size calculated from BET (nm)</i>
TH	carbonate route, BaCO ₃	1000	2.2	450
TH	oxalate route, BaC ₂ O ₄	1000	2.8	350
TH	novel approach, Ba(OH)₂·xH₂O	400	27.6	36
TH	novel approach, Ba(OH)₂·xH₂O	600	12.8	78
TH	novel approach, Ba(OH) ₂ ·xH ₂ O	1000	3.2	310

Typically for this new approach, oxidic alkaline-earth metal compounds or alkaline-earth compounds are preferred, which decompose at a temperature below 600 °C (e.g. with formation of alkaline-earth metal oxide). Thus, amongst the barium salts, barium hydroxide, barium nitrate and other easily decomposable barium compounds and mixtures thereof are particularly preferred. Barium carbonate, however, only forms barium oxide at higher temperatures (approx. 1000 °C). Barium oxalate and barium acetate are also less preferred as they initially decompose to barium carbonate. Surprisingly, it has also been observed that calcination can be realized at a temperature which lies below the decomposition temperature of the pure alkaline-earth metal compound. With regard to the fineness of the titanate obtained, it is possible to carry out the calcination at a temperature which is in the range between 50 °C and 200 °C below the temperature at which the alkaline-earth metal compound used decomposes to the oxide.

Additionally, a barium and titanium containing precursor to BaTiO_3 has been developed, which can also be described as pre-calcined BaTiO_3 , and is available in dried form. In the production of this material as an intermediate product for the titanate it is possible, if necessary, to add doping compounds. Semi-conducting doped alkaline-earth titanates obtained therefrom by calcination are the essential components of temperature-dependent resistors.

Particularly advantageous at the low calcination temperatures facilitated by this method is the low fusion of the alkaline-earth titanate particles obtained. Hence the alkaline-earth titanate particles calcined at low temperatures are particularly easily *pulverised* or it may even be possible to disperse completely with *pulverisation* prior to further processing. Regarding the novel approach described in this contribution, a patent application has been filed for fine-particle alkaline-earth titanates, their production involving ultrafine titanium oxide raw materials, and their use in micro-electronic components [13].

The following SEM, TEM, and EDX data displayed in Figure 7 to Figure 9 give an impression of the versatility of this new synthetic approach. Several examples of different barium titanate samples prepared under varied process conditions are shown and underline the versatile use of high-purity ultrafine TH as raw material for titanate electroceramics.

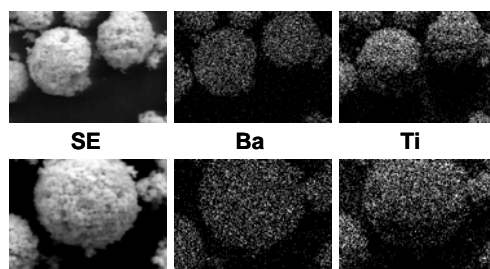


Figure 7: EDX mapping of spray-dried TH-derived BaTiO_3 precursor showing the homogeneous Ti/Ba distribution prior to BaTiO_3 formation.

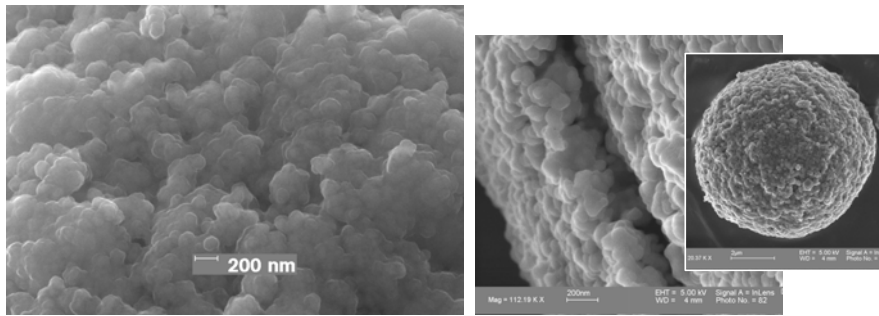


Figure 8: High-resolution SEM images showing details of a fine-particulate BaTiO_3 powder sample (left) derived from TH and $\text{Ba}(\text{OH})_2$ in the modified solid-state approach, and of a spray-dried, granulated sample (right).

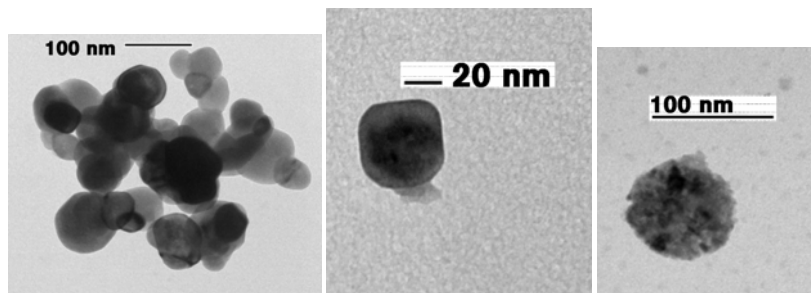


Figure 9: TEM images of different fine-particulate BaTiO_3 powder samples derived from TH and $\text{Ba}(\text{OH})_2$ in the modified solid-state approach (left, middle) and detail of a TH-derived BaTiO_3 precursor material (right).

Barium titanate from titanium oxide hydrate and barium nitrate

To investigate another barium source with a lower decomposition temperature than carbonates and related compounds, barium nitrate $\text{Ba}(\text{NO}_3)_2$ was dissolved or suspended with TH in distilled water whilst stirring for 10 min. at 50 °C. Subsequently, the solvent water was removed on the rotary evaporator and the powder obtained oven dried at 120 °C. Calcination of the powder with formation of BaTiO_3 takes already place at 600 °C and crystalline a product with a specific surface area S_{BET} of 3.6 m^2/g is obtained, calcination at 800 °C leads to a product with S_{BET} of 2.7 m^2/g , corresponding to particle sizes of d_{BET} 277 and 369 nm, respectively. After 2 h at 1000 °C the BET value decreases to 1.5 m^2/g , however, after bead grinding, the BET surface areas of all samples are above 5 m^2/g . Surprisingly, the decomposition processes of $\text{Ba}(\text{NO}_3)_2$ when mixed with TH takes place in a significantly smaller temperature range than in the pure substance, as shown by thermal analyses and XRD (not shown here). At approx. 600 °C, the decomposition is almost completely finished after one step. In contrast, pure barium nitrate does not react completely, but via the intermediate stage $\text{Ba}(\text{NO}_2)_2$ until approx. 750 °C. This underlines the high reactivity of ultrafine TH that even stimulates the Ba compounds to higher reactivity.

Hydrothermal BaTiO₃ synthesis using TH

To evaluate the suitability of TH for hydrothermal synthesis of BaTiO₃, the reactivity was tested and compared with different TiO₂ materials: Ba(OH)₂·8H₂O (Fluka) was placed with the titaniferous raw material (TH, or A or R for reference purpose, cf. Table 1) and 150 ml distilled and outgassed water in a Teflon beaker. The molar Ti/Ba starting ratio was 1.0. Reaction was carried out at 100 °C or 150 °C whilst stirring the reaction mixture in a laboratory autoclave with a hold time of one hour. Outgassed, CO₂-free water was used in order to prevent possible formation of barium carbonate. A pH value of 13.7 was adjusted by the Ba(OH)₂/solvent water ratio selected. After the reaction, the solid was suction filtered via a G4 filter frit, washed several times with distilled water until a pH value of 9 resulted and subsequently oven dried for 24 hours at 120° C. The set of experiments is summarized in

Table 3.

In case of the ultrafine raw material TH, the reaction product obtained at 100 °C treatment has a specific surface area S_{BET} of 20.7 m²/g and is unambiguously characterized as BaTiO₃ by means of X-ray diffractometry, no by-products or starting materials were detected. The BET surface area corresponds to a particle size of 48 nm. Treatment at 150 °C gives BaTiO₃ with a surface area of $S_{\text{BET}} = 15.9 \text{ m}^2/\text{g}$ ($d_{\text{BET}} = 63 \text{ nm}$). The material was not treated with additives or surfactants, so that the particles are softly agglomerated as can be seen from electron microscopy (shown for BaTiO₃ synthesized from TH at 100 °C in Figure 10). However, smaller features in the size of approx. 50 nm can be seen that correspond well with the particle size of 48 nm calculated from BET.

In comparison, the conventional rutile TiO₂ (sample R) does not react at all at 100 °C. XRD, BET, PDS data show only the starting material, a coarse rutile phase with S_{BET} of 6 m²/g. Treatment at 150 °C gives a reaction mixture of unreacted rutile TiO₂ and trace amounts of BaTiO₃. The specific surface area is even worse with 4 m²/g. Even the conventional fine-particle anatase TiO₂ (sample A) with a BET surface area of 73 m²/g does not form a clean BaTiO₃ product at 150 °C hydrothermal treatment. Apart from BaTiO₃, unreacted anatase is still present, as shown by XRD. Furthermore, the resulting barium titanate is quite coarse with a BET of 7 m²/g (

Table 3).

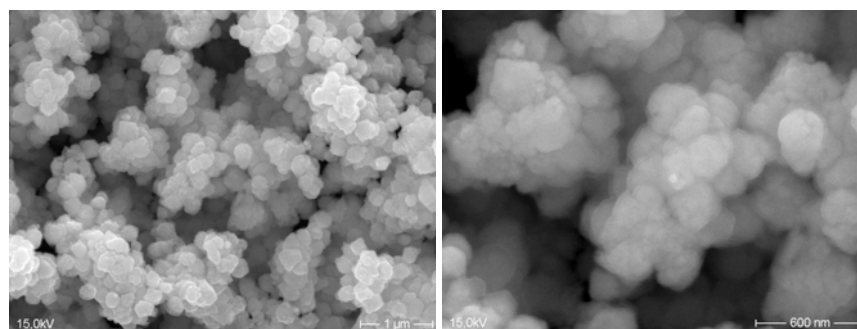


Figure 10: Electron micrographs of hydrothermal BaTiO₃ prepared from ultrafine TH and barium hydroxide.

Table 3: Summary of hydrothermal reactions involving ultrafine TH and reference TiO₂ materials.

<i>TiO₂ source</i>	<i>Temperature (°C)</i>	<i>Product</i>	<i>Specific surface area of reaction product S_{BET} (m²/g)</i>	<i>Mean particle size calculated from BET (nm)</i>
TH	100	BaTiO ₃	20.7	48
TH	150	BaTiO ₃	15.9	63
A	150	BaTiO ₃ Ba-deficient, trace of TiO ₂ anatase	7.0	143
R	100	TiO ₂ rutile	6.2	228
R	150	TiO ₂ rutile, trace of BaTiO ₃ Ba-deficient	4.2	236

Hydrothermal syntheses involving a variety of different TiO₂ starting materials show that a finer titania powder enables a higher yield and finer titanate product. The high surface area of ultrafine TH allows an efficient dissolution-reaction rate and mechanism in the reaction with Ba²⁺ ions under strong alkaline conditions. Only TH shows an almost quantitative yield, even at 100 °C, whereas the conventional powders do not react satisfactorily even at 150 °C. For the hydrothermal reaction version, a low sulphate content is of particular importance since in this reaction version the formation of the alkaline-earth titanate takes place by way of soluble intermediate stages and thus the presence of sulphate could lead to the formation of alkaline-earth sulphates.

Conclusion

A novel manufacturing approach for fine-particle barium titanate and a highly reactive and fine-particulate titanium hydrate (TH) has been presented. With its optimized particle size and morphology, TH allows lowering the temperature for titanate formation and thereby providing finer barium titanate (BaTiO₃). In the new approach, reaction of TH with barium hydroxide allowed lowering the temperature of calcination down to even 400 °C. The resulting very fine particles show physical properties similar to material synthesized by sol-gel processes. This is enabling the combination of a simple powder processing technology (in contrast to expensive hydrothermal or sol-gel technology) with outstanding properties of the resulting BaTiO₃. Besides obtaining barium titanate by direct calcination, the TH raw material also allows to produce a ready-to-use dry precursor (“pre-calcined” BT).

TH titanium dioxide has significant advantages in respect of its suitability for the production of alkaline-earth titanates over conventional commercially available titanium dioxides. Fine-particle titanates are obtained because of the high specific surface area, the small particle size of titanium oxide hydrate and the high reactivity during reaction with alkaline-earth compounds. Moreover, the low chloride and carbon content of the titanium oxide hydrate particles have a positive effect on the titanate properties. The small content of chloride and metallic trace elements has a favourable effect on the electrical properties of the titanates produced from TH whilst the low content of carbon

ensures that there is no intermediate reduction of TiO_2 and no intermediate formation of alkaline-earth carbonates and, therefore, particularly fine-particle alkaline-earth titanates may be obtained. The presence of halides or carbon is disruptive particularly at low reaction temperatures to the alkaline-earth titanate - this is avoided by use of TH. Underlining the versatility of TH, the advantageous application of TH has also been demonstrated for hydrothermal reactions as well as for the standard carbonate solid-state reaction.

Barium titanate obtained according to the TH/ $\text{Ba}(\text{OH})_2$ approach preferably has a BET surface area of 10 to $60 \text{ m}^2/\text{g}$, depending on process conditions and application demands. Due to the fine-particle character, the resulting BaTiO_3 , may be used for the manufacture of microelectronic components, e.g. of a capacitive or PTC component. It is possible to realise particularly thin layers and thus particularly small component dimensions. Application in multi-layer ceramic capacitors (MLCC) is a particular consideration where it is possible to obtain particularly thin layers (less than $2.5 \mu\text{m}$, particularly preferred 0.1 to $1 \mu\text{m}$).

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References

- 1 *Ceramic Materials for Electronics*, 3rd ed., R. C. Buchanan (ed.), Marcel Dekker, Inc. (2004).
- 2 M. Rössel, S. Gablenz, T. Müller, A. Röder, H.-P. Abicht, *Anal. Bioanal. Chem.* 375 (2003) 310.
- 3 C. Pithan, D. Hennings, R. Waser, *Int. J. Appl. Ceram. Technol.* 2 (2005)1.
- 4 A. Beauger, J. C. Mutin, J. C. Niepce, *J. Mater. Sci.* 18 (1983) 3543.
- 5 J. C. Niepce, G. Thomas, *Solid State Ionics* 43 (1990) 69.
- 6 D. F. Hennings, B. S. Schreinemacher, H. Schreinemacher, *J. Am. Ceram. Soc.* 84 (2001) 2777.
- 7 D. Hennings, H. Schreinemacher, DE 3635532.
- 8 J. H. Lee, H. H. Nersiyian, C. W. Won, *J. Mater. Sci.* 39 (2004) 1397.
- 9 J. Moon, J. A. Kerchner, H. Karup, J. H. Adair, *J. Mater. Res.* 14 (1999) 425.
- 10 F. J. Gotor, L. A. Perez-Maqueda, J. M. Criado, *J. Eur. Ceram. Soc.* 23 (2003) 505.
- 11 *Synthesis, Functionalization and Surface Treatment of Nanoparticles*, M.-I. Baraton (ed.), American Scientific Publishers (2003).
- 12 *Industrial Inorganic Pigments*, 3rd ed., G. Buxbaum, G. Pfaff (eds.), Wiley-VCH (2005).
- 13 WO 2006/029834.