

# Wet forming of concentrated nano-BaTiO<sub>3</sub> suspensions

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## Abstract

Nanostructured materials are currently being studied extensively due to their unusual physical and mechanical properties. One of the most important dielectric materials is barium titanate (BaTiO<sub>3</sub>). Capacitors made of this material offer excellent frequency characteristics, high reliability, high breakdown voltage and excellent volumetric efficiency. It is believed that these properties may be significantly improved by achieving a structure at the nano-scale.

In this work, nano-BaTiO<sub>3</sub> powders have been formed into complex-shaped green bodies using gelcasting as colloidal forming route. This procedure has been demonstrated to be very effective for shaping submicron-sized powders and in this manuscript the achievement of this technique for the shaping of nanosized powders is evaluated. The first step was the preparation of stable concentrated suspensions of the nanopowders through the optimization of the quantity of dispersant and time of homogenization. This was found to depend on the method of manufacture of the different commercial nanopowders investigated. Bulk components were then manufactured using aqueous gelcasting involving polysaccharides that gel on cooling. The performance of this consolidation technique for obtaining dense green bodies from the BaTiO<sub>3</sub> nanopowders will be discussed.

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## 1. Introduction

The recent interest in nanostructured materials is due to their unusual properties. Colloidal processing allows the production of complex-shaped parts with decreased number and size of pores and higher reliability. Gelcasting is a bulk fabrication process for manufacturing near-net shaped components.

Thermogelling polysaccharides like agar, agarose and carrageenan have demonstrated a high efficiency at low concentration<sup>1</sup> when they are dissolved into a warm slurry, which is then cast or injected in a mould cavity cooled below the glass transition temperature,  $T_g$ .<sup>2</sup>

Barium titanate (BaTiO<sub>3</sub> or BT) is used extensively in the production of multilayer ceramic capacitors. It has been reported that barium titanate is not thermodynamically stable in acidic

aqueous solutions<sup>3,4</sup> because Ba<sup>2+</sup> ions are leached out of the powder, which results in a titanium enriched surface layer. The Ba<sup>2+</sup> present in the solution also arises from impurities of BaCO<sub>3</sub> present in the BaTiO<sub>3</sub> powder. The concentration of dissolved Ba<sup>2+</sup> ions increases as the pH decreases below 7.<sup>5</sup> Due to the complexity of the system, some authors prefer to use organic BaTiO<sub>3</sub> suspensions.<sup>6</sup>

The current interest in using different types of ultrafine, nanosized powders puts a high demand on the suspension processing and control of the forming process. Ammonium polyacrylates have been found to be very useful in the stabilization of micron, submicron<sup>7–9</sup> and nanosized BaTiO<sub>3</sub> suspensions<sup>10,11</sup> at basic values of pH. Recently, Boschini et al.<sup>12</sup> found that the combination of both an acrylic polyelectrolyte and a strong quaternary base, viz. tetramethylammonium hydroxide, TMAH, yielded greater stability to concentrated BaZrO<sub>3</sub> suspensions than the polyelectrolyte or base on their own.

This work aims to study the dispersion of commercial nanosized powders of BaTiO<sub>3</sub> and the preparation and characterization of concentrated suspensions for shape forming pieces by gelcasting with thermogelling polysaccharides.

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Table 1  
Properties of the powders

Powder	$S_s$ (m <sup>2</sup> /g)	$\rho$ (g/cm <sup>3</sup> )	$d_{\text{BET}}$ (nm)	Wt loss (TG) 600 °C	Ba/Ti*
P1	17.0	5.5	64	~0.7%	0.996–1.004
P2	31.2	4.3	45	~5%	0.995–1.010

\* Data provided by the manufacturer.

## 2. Experimental procedure

### 2.1. Powder characterization

Two commercial nanosized BaTiO<sub>3</sub> powders (HPB-1000, TPL Inc., USA, and Nanostructured & Amorphous Materials, Inc., USA) were used as starting materials. They are referred to as P1 and P2, respectively. The characteristics of the powders are shown in Table 1.

The surface area was measured by one point N<sub>2</sub> adsorption (Monosorb, Quantachrome, USA), and the density with a He picnometer (Quantachrome, USA). The particle size values shown in the table were calculated using the values obtained by BET and were confirmed using a field emission gun scanning electron microscope (Leo 1530 VP, Elektronenmikroskopie GmbH, Germany). The zeta potential of BT in aqueous suspensions without any dispersant was measured as a function of pH with an AcoustoSizer II (Colloidal Dynamics, Australia). Thermogravimetric, TGA, and X-ray diffraction analysis were performed on both powders.

### 2.2. Suspensions preparation

Aqueous suspensions were prepared by adding tetramethylammonium hydroxide,<sup>12</sup> TMAH, supplied by Aldrich-Chemie (Germany) as a 25 wt% aqueous solution to distilled water generating a pH up to 11.0. Subsequently 2.0 and 3.0 wt% of an ammonium salt of polyacrylic acid (Duramax D3005, Rohm & Haas, USA) was added as deflocculant prior to the addition of the powder in concentrations of 70 and 80 wt% (28 and 40 vol%). Suspensions were prepared by mechanical agitation with helices and then ultrasonically homogenized using a 400 W sonication probe, UP400S (Hielscher Ultrasonics GmbH, Germany), for up to 10 min.

A commercially available agar (Grand Agar, Hispanagar S.A., Burgos, Spain) was used as the gelling agent. Solutions of agar were prepared to concentrations of 6 wt% by heating in a pressure vessel in order to achieve the high temperatures, 110 °C, required for its full dissolution.<sup>2</sup> The rheological behavior of the suspensions was studied through control rate measurements using a rheometer (Haake RS50, Germany) with a double-cone and plate system.

The influence of the volume fraction of solids, the dispersant concentration and the time of ultrasonic mixing on the flow behavior were studied.

### 2.3. Green samples

Barium titanate green bodies were obtained by gelcasting. For preparing the gelcasting suspensions, the well-dispersed BT suspensions (80 wt%, 40 vol%) were heated to 50 °C where the rheological properties were not affected by significant evaporation. The agar solution was then added at this temperature in a concentration of 0.5 wt% with regard to dry solids. The green densities were measured by the Archimedes' method using mercury. The green fracture surfaces were observed by scanning electron microscopy, SEM (Zeiss DSM40, Germany).

## 3. Results and discussion

### 3.1. Powder characterization

The properties of the precursor powders such as agglomeration, binder content and Ba/Ti ratio, which are key aspects in the preparation of the aqueous BT suspensions and determine the quality of the final samples, result from the powder synthesis method. Fig. 1 shows the micrographs of the two as-received powders. P1 consists of hard spherical granules with diameters ranging from 5 to 40 μm, typical of a spray-dried

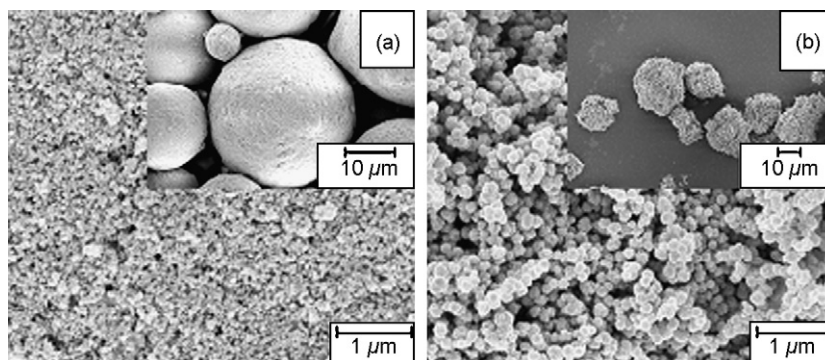


Fig. 1. Micrographs of the as-received P1 (a) and P2 (b) powders.

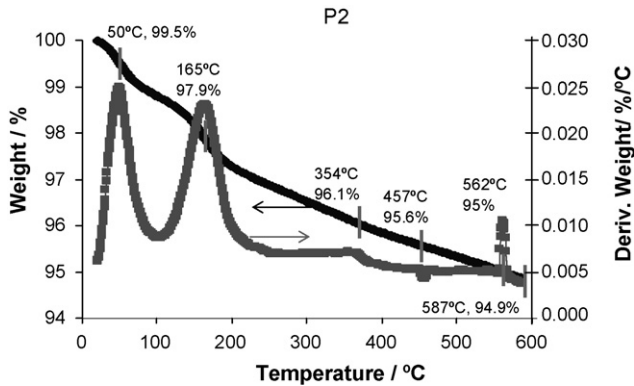


Fig. 2. TGA curves from P2 powder.

powder. The primary particle size is about 50–60 nm. P2 has similarly sized primary particles but consists of smaller and more irregularly shaped agglomerates that are more loosely formed.

The TG analysis of P2, Fig. 2, shows a larger binder content than for P1, ~5 and ~0.5 wt%, respectively, Table 1. The same table shows an unusually low-density value for powder P2. Since the same value was obtained for the powder as-received and after calcination at 350 °C for 0.5 h, the value was clearly independent of the binder content. X-ray diffraction experiments were performed on the calcined P2, Fig. 3, in order to understand why the density is so low. This revealed a cubic BaTiO<sub>3</sub> structure with displaced peaks<sup>13</sup> that indicate larger lattice parameters and hence confirm the open structure, which explains the lower density.

### 3.2. Suspensions preparation

The variation of zeta potential with pH was measured via continuous titration from their initial pH values, 9 and 8.5 for P1 and P2, respectively, to pH 12, and from there on to pH 2 using dilute P1 and P2 suspensions prepared in 0.01 M KCl solutions without any dispersant. Isoelectric points of the powders were found to occur at pH 9.5 and 8.3 for P1 and P2, respectively. This difference is probably due to the slight differences in the Ba/Ti ratio.<sup>14</sup> The IEP values for BaTiO<sub>3</sub> reported in the literature differ widely, from ~4 to ~10, although a “true” isoelectric point

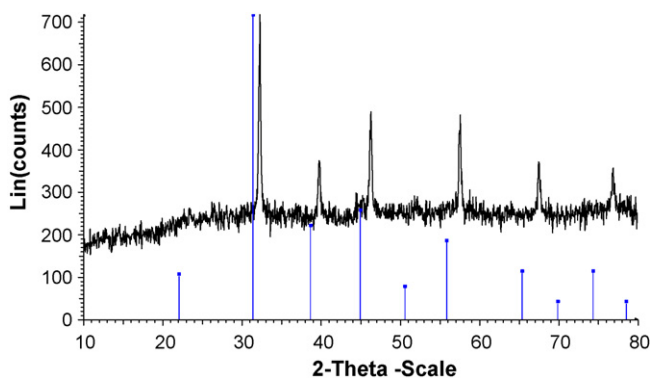


Fig. 3. X-ray diffraction of calcined P2 powder.

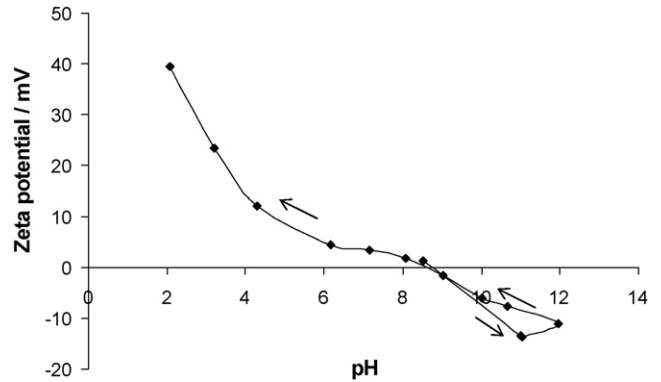


Fig. 4. Evolution of the zeta potential of P2 with pH.

was found at 6.5 by extrapolation to zero BaCO<sub>3</sub> in BaTiO<sub>3</sub>.<sup>14</sup> The results for P2 powder are plotted in Fig. 4. At basic pH values the absolute value of zeta potential is not large enough to stabilize the suspension, hence the addition of some deflocculant is required.

In the case of acidic pH values, higher zeta potential values were observed as a result of the electrostatic repulsion force created by the large positive zeta potential developed at the particle–solution interface. Since BaTiO<sub>3</sub> powder behaves like both a simple insoluble oxide and partially soluble inorganic salt, the zeta potential was determined both by the H<sup>+</sup> and Ba<sup>2+</sup>, where the contribution made by Ba<sup>2+</sup> to the surface charge was considerable and was most marked at lower pH values.<sup>14</sup> Since the concentration of dissolved Ba<sup>2+</sup> ions increases as pH decreases at < 7, changing the surface chemistry of BaTiO<sub>3</sub> and increasing the pH of resulting suspension, it is not recommended to work in the acidic pH range.

Concentrated suspensions, 70 wt%, were prepared from both powders using TMAH<sup>12</sup> and ammonium polyacrylate (2.0 wt% active matter). The rheological behavior of both suspensions without ultrasound treatment was quite similar, being slightly thixotropic for P1 suspension, as shown in Fig. 5. When these suspensions were homogenized by using an ultrasound probe for a few minutes, their rheological behavior became very different; in the case of the P1 suspension, the viscosity decreased as expected, due to the better stabilization achieved when the agglomerates were broken down. However, in the case of P2,

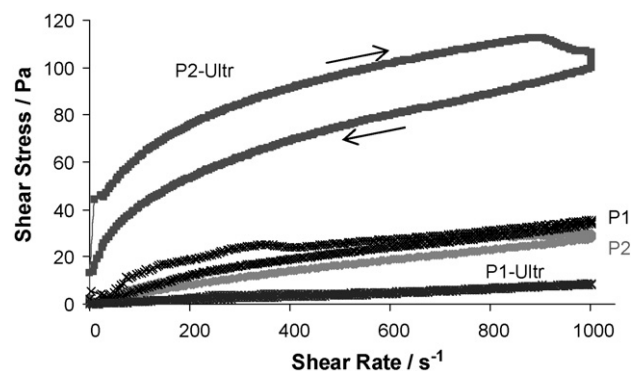


Fig. 5. Flow curves of 70 wt% P1 and P2 suspensions with and without ultrasound.

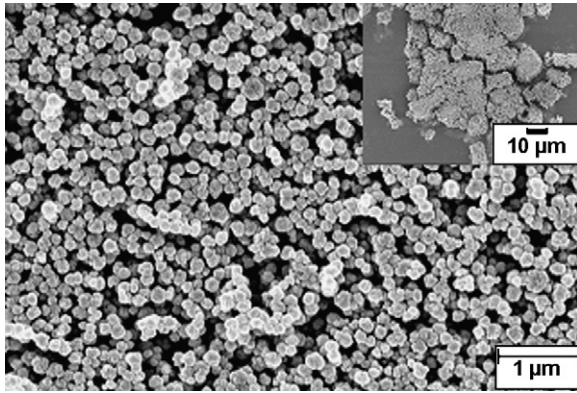


Fig. 6. Micrographs of the calcined P2 powders.

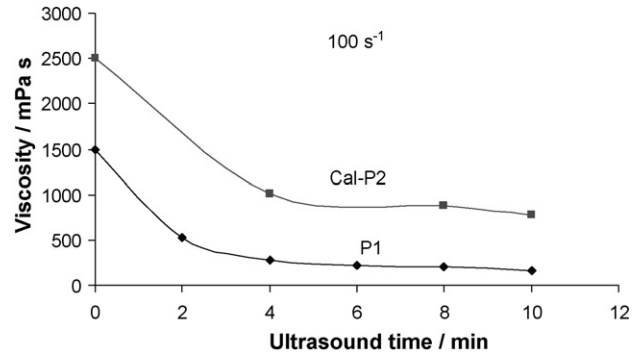


Fig. 8. Viscosity of 80 wt% P1 and P2 suspensions as a function of ultrasound time.

the viscosity and the thixotropy of the suspension increased and the suspension became very viscous.

It is believed that this behavior is related to the presence of a significant amount of organics, which makes it difficult to achieve stabilization as a result of poor dispersant adsorption. Hence the preparation of more concentrated P2 suspensions was limited. These organics are very sensitive to the strong heating and diffusion effects of the ultrasound probe. For this reason and according to the TG curve, Fig. 2, P2 was calcined at 350 °C for 0.5 h before the preparation of further suspensions. To be sure that no large agglomerates were formed after the heat treatment, the calcined P2 powder was observed by FEG-SEM, Fig. 6. Although a similar image to the as-received powder was observed, the calcined P2 powder allowed the preparation of more concentrated suspensions, 80 wt%, which were impossible to obtain without calcination.

The dispersant content was optimized for both powders. For P1 and P2, maximum values of zeta potential were found when 2.0 and 3.0 wt% of polyacrylate, respectively, were added to the suspensions. The flow curves of the 80 wt% P1 suspensions with different dispersant contents prepared with TMAH and without ultrasound are plotted in Fig. 7. The lowest shear stress values were found at any shear rate when 2.0 and 3.0 wt% deflocculant, respectively, was added.

A decrease in pH was also found for P2 suspensions with TMAH when increasing the dispersant content in the suspen-

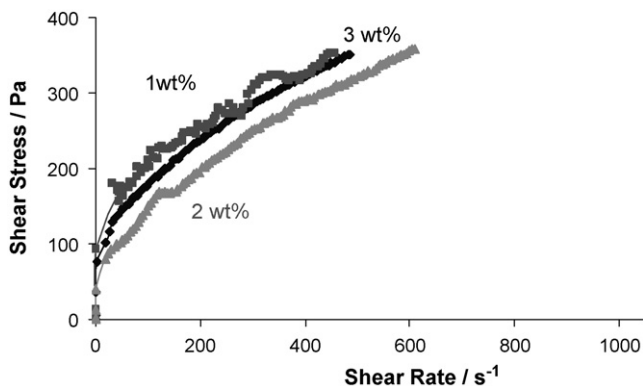


Fig. 7. Flow curves of 80 wt% P1 suspensions with different polyacrylate contents.

sion, viz. pH values of 10.1, 9.8 and  $9.6 \pm 0.1$  were measured for 1.0, 2.0 and 3.0 wt% polyacrylate additions, respectively. Similar values were found for P1.

Since the ultrasound probe was demonstrated to be very effective in the stabilization of suspensions, different ultrasound times were applied to the same volume of 80 wt% suspensions of either P1 or P2 dispersed with 2.0 and 3.0 wt% dispersant, respectively. Flow curves were measured for both P1 and calcined P2 suspensions. The viscosity values of the up-curves taken at a shear rate of  $100 \text{ s}^{-1}$  are plotted in Fig. 8. It can be seen that longer times of ultrasonic mixing produce lower viscosity suspensions and hence increased stability, with a lowest value after 10 min. For calcined P2 suspensions, the viscosity was reduced by more than a factor of 3 after 10 min of ultrasound meanwhile for P1 suspensions the viscosity was reduced by more than a factor of 7 after 8 min of ultrasound. Also, it can be observed that the suspension prepared from P1 displays a lower viscosity than the calcined P2 suspension at any ultrasound time. The presence of the remaining agglomerates of P1 suggests that they are hard enough to remain unbroken after ultrasonication, indicating that they may be retained in the green samples.

### 3.3. Green samples

Green samples were obtained by gel casting from stable suspensions of the P1 and calcined P2 powders prepared at 80 wt% solids loading after 10 min of ultrasonication. Green fracture surfaces of the samples at different magnifications are shown in Fig. 9. Spherical agglomerates similar to those observed in the as-received powder can be seen in Fig. 9a and b, confirming that they could not be broken after 10 min of ultrasonication. The green density was 56% of the measured powder density. A previous study demonstrated that these P1 agglomerates also persist in die pressed samples, even after micronizing the powder for several minutes and applying 500 MPa of pressure.<sup>15</sup> On the other hand, the gelcast samples prepared from the calcined P2 powder had a higher green density, 60% of measured density of powder, and a homogeneous microstructure without large agglomerates, Fig. 9c and d, as observed previously for the gelcasting of other ceramic powders.<sup>16</sup>

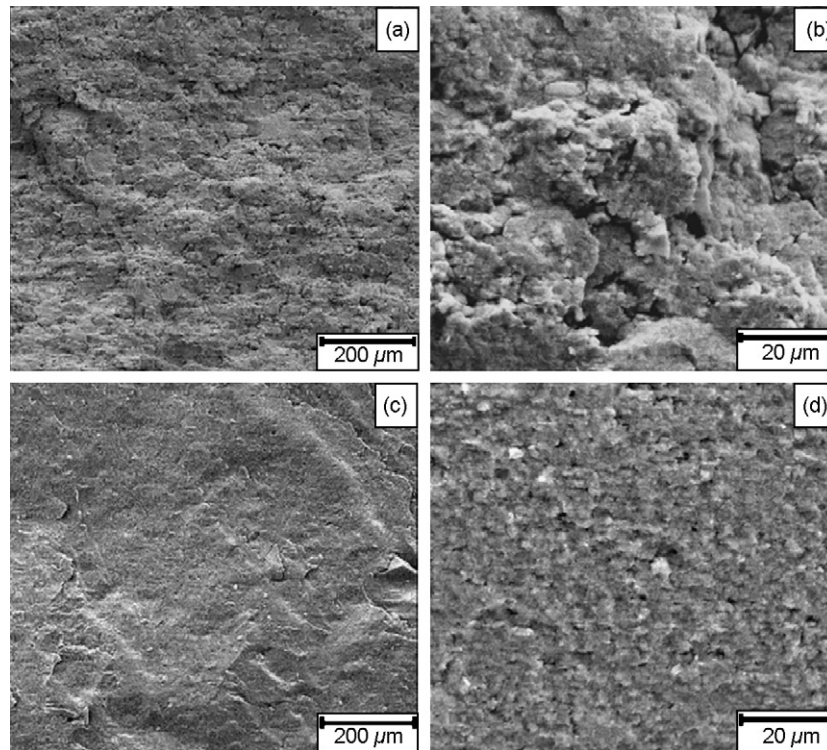


Fig. 9. Microstructures of the green samples prepared by gel casting from 80 wt% P1 (a and b) and P2 (c and d) suspensions.

#### 4. Conclusion

Stable nano-BaTiO<sub>3</sub> suspensions have been prepared with solids loadings as high as 80 wt% by dispersing nanopowders with 2.0 and 3.0 wt% of ammonium polyelectrolyte (active content), for P1 and P2, respectively, in combination with TMAH and the use of an ultrasound probe for mixing times of up to 10 min. In the case of powder P2, the use of ultrasound leads to a higher viscosity as a result of a high binder content, so the powder needed to be calcined if concentrated suspensions were to be prepared successfully.

Bulk components were manufactured by aqueous gelcasting using concentrated agar solutions (6 wt%) up to a final content of agar of 0.5 wt% on a dry solids basis. Unbroken agglomerates, similar to those observed in the as-received powder, were present in the green samples manufactured with powder P1, whereas homogeneous green bodies without large agglomerates were obtained for the calcined P2 powder, according to the green density results.

Gelcasting of polysaccharides resulted an excellent alternative to avoid the extremely slow rates and size limitations which appear in the slip casting of nanoceramics.

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