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Low-Temperature Aqueous Preparation of Barium Metatitanate Powders

P. Nanni

Istituto di Chimica, Facoltà di Ingegneria, Università di Genova, Fiera del Mare, Pad. D, Piazzale Kennedy, I-16129 Genoa, Italy

M. Leoni, V. Buscaglia

Istituto di Chimica Fisica Applicata dei Materiali, CNR, Via De Marini 6, I-16149 Genoa, Italy

&

G. Aliprandi

Istituto di Scienze e Tecnologie dell'Ingegneria Chimica, Via Opera Pia, I-16145 Genoa, Italy

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Abstract

Submicron $BaTiO_3$ powders have been prepared at 85°C under atmospheric pressure starting from $TiCl_4$ and $Ba(OH)_2$ in NaOH aqueous solution. Characterisation by BET, thermal analysis, differential dilatometry, X-ray diffraction and SEM/TEM microscopy has been performed. The powders, with high specific surface area, show a cubic lattice and a quasi-spherical morphology. A slight deviation from stoichiometry and a low level of residual carbonate have also been observed. Sintering tests on isostatically pressed samples without binders have been carried out. A 15 h thermal treatment at 950°C upon firing results in improved final density ($\approx$96% of the theoretical density) and in very fine grain size (1·1 μm). Washing with dilute (0·1 M) acetic or hydrochloric acid to eliminate $BaCO_3$ is detrimental to a high final density and gives rise to polytitanate formation.

Aus $TiCl_4$ und $Ba(OH)_2$ in wässriger NaOH Lösung wurde bei Atmosphärendruck und 85°C submikrometer $BaTiO_3$ Pulver hergestellt. Die Charakterisierung der Pulver erfolgte mittels BET, thermischer Analyse, Differentialdilatometrie, Röntgenbeugung und SEM/TEM. Die Pulver mit einer hohen spezifischen Oberfläche haben ein kubisches Kristallgitter und besitzen eine quasi sphärische Morphologie. Desweiteren konnte eine leichte Abweichung von der Stöchiometrie und ein geringer Anteil von restlichem Karbonat festgestellt werden. Sintertests an isostatisch gepreßten Proben ohne Zugabe von Binder wurden durchgeführt. Eine 15 h Wärmebehandlung bei 950°C nach dem Feuern verbesserte die Dichte ($\approx$96% der theoretischen Dichte) und ergab eine kleine Korngröße (1·1 μm). Das Reinigen mit verdünnter Essig- oder Salzsäure (0·1 M) um $BaCO_3$ zu eliminieren, ist der Erzielung einer hohen Dichte entgegengesetzt und führt zur Bildung von Polytitanat.

Des poudres submicroniques de $BaTiO_3$ ont été préparées à 85°C sous pression atmosphérique à partir de $TiCl_4$ et $Ba(OH)_2$ en solution aqueuse de NaOH. Les poudres ont été caractérisées par BET, analyse thermique, dilatométrie différentielle, diffraction de rayons-X et microscopie électronique à transmission et à balayage. Les poudres, qui présentent une aire spécifique de surface bien élévée, montrent une structure cubique et une morphologie presque sphérique. Elles ont révélé une petite déviation de la stoechiométrie et un certain degré de carbonatation. Des épreuves de frittage sur des poudrees pressées isostatiquement sans liens ont été aussi réalisées. Si l'on soumet les echantillons à un traitement thermique de 15 h à 950°C pendant la cuisson, la densité atteint presque le 96% de la densité théorique et la croissance des grains est interdite (1·1 μm). Des lavages avec acide acétique ou chloridrique dilués (0·1 M) à fin d'éliminer le $BaCO_3$ présent dans les poudres, se sont demontrés négatifs pour la densification et ont donné lieu à la formation de polytitanates.

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1 Introduction

Barium metatitanate is one of the most extensively employed materials for ceramic capacitors. Possible applications for very compact devices make it of great industrial interest. For this purpose, however, a very small average grain size is required and therefore the traditional preparation[1] of this compound through solid-state reaction between $BaCO_3$ and TiO_2 at 1100–1200°C is progressively losing favour, due to the unsatisfactory microstructural control for the final application requirements.

Alternative methods have been set up, such as those based upon metallo-organic compounds,[2–10] but they generally result in rather complex procedures; severe safety regulations have also to be fulfilled in the case of industrial applications.

In the last few years, an increasing interest has been given to some innovative synthesis methods and chemical procedures have been developed accordingly. Among them, the so-called aqueous processes[11–13] have received a particular emphasis related to the possibility of producing several high purity ceramic materials, with very fine particles. This procedure also allows an easy mixing of particular dopants with the main product and avoids the contamination and the high energetic consumption associated with milling which is always needed when $BaTiO_3$ is produced by solid-state reaction.

2 Experimental Procedures

Unlike other aqueous methods used to prepare $BaTiO_3$,[11–13] in the present work an extremely simplified route has been followed, which permits the use of chemical reactants which are rather easy to manipulate. The procedure followed requires relatively low temperature and can be carried out under atmospheric pressure either in air or under an inert gas.

The method is based upon the following reaction:

$$Ba(OH)_2 + TiCl_4 + 4\,NaOH = BaTiO_3 + 4\,NaCl + 3\,H_2O \qquad (1)$$

Accordingly, a quantity of $Ba(OH)_2.H_2O$ (Aldrich, 99%) corresponding to 40 cm^3 of $TiCl_4$ was dissolved in 1150 cm^3 of fresh distilled water and kept at 85°C. A 1·5 to 1 molar stoichiometric excess of NaOH (Fluka, 99%) was added in order to neutralise HCl formed from $TiCl_4$ hydrolysis and to keep the batch to a high pH value (>13), to exceed $BaTiO_3$ solubility and let it precipitate.[14] Subsequently $TiCl_4$ (Aldrich, 99%) was slowly dropped into the solution, while keeping it stirred.

After 6 h digestion at temperature, the suspension was cooled down and washed with distilled water by decantation until the neutrality was reached. The powders, dried in an oven at 90°C, were eventually isostatically pressed (wet bag) at 150–175 MPa and sintered for 2 h at 1225 and 1300°C.

In general, as the experiments were performed in air, a partial carbonation was observed: in this case the effect of acid treatment with 0·1 M dilute CH_3COOH or HCl on $BaTiO_3$ powders was studied.

Specific surface area was determined by the BET method using He and N_2 (Carlo Erba Sorpty 1750). Chemical analyses were carried out on the powders by plasma spectrometry (ICP) after disgregation in $Li_2B_4O_7$. The morphological characterisation was performed by ordinary electron microscopy techniques (SEM, Philips 515-EDAX PV9900, TEM, Siemens Elmiskop 102), while the lattice constants were determined by X-ray powder diffraction (Philips PW 1710 system). The powders also underwent thermal analysis (Mettler, TAl) in the temperature range 25–1250°C and dilatometric tests (Setaram DHT, DSC2000K) up to 1350°C. After sintering, the densities were measured by Archimede's method.

3 Results

The chemical composition of $BaTiO_3$ obtained with the present aqueous method indicates a Ti to Ba ratio of 1·04 and a Na content as low as 400–600 ppm. Other impurities, mainly Sr (4·7 mol %), arise from the starting chemical reactants used for the preparation.

Under TEM observation, even if the powders exhibit a certain degree of agglomeration ($\leq 0{\cdot}2$ μm), it is however possible to identify isolated, almost spherical particles, with $\phi < 0{\cdot}03$ μm (Fig. 1). The

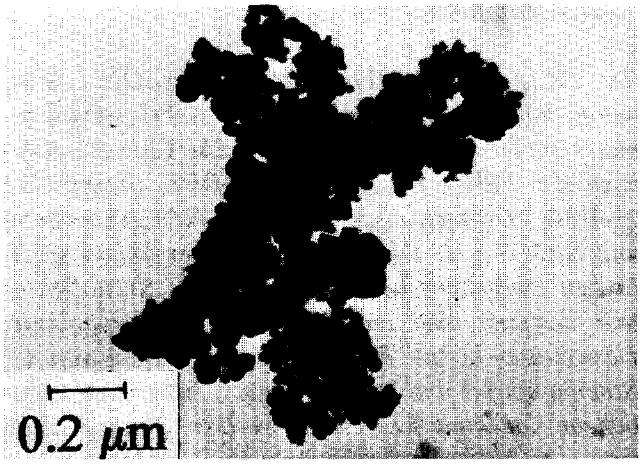


Fig. 1. TEM image of as-obtained $BaTiO_3$ powder.

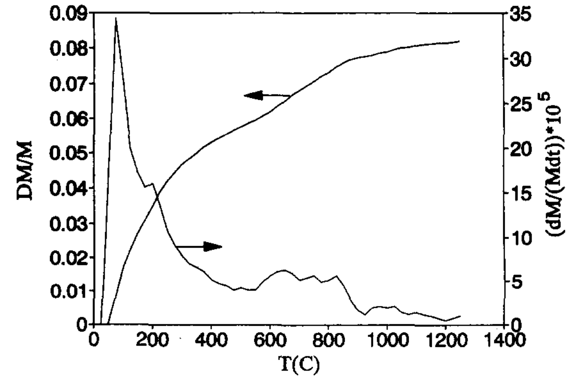


Fig. 2. Weight loss percentage and derivative curve versus temperature for as-obtained $BaTiO_3$.

corresponding specific surface area is 39·15 m^2 g^{-1} as obtained by BET measurements.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in air on small cylinders of $BaTiO_3$ isostatically pressed without binders at 175 MPa, with a heating rate of 1°C min^{-1}. The results (Fig. 2) show main weight losses at 100, 200 and ≈650°C, whereas in the range 800–1000°C some minor losses are observed. No thermal effects were revealed by DTA.

The X-ray diffraction pattern collected from the as-obtained $BaTiO_3$ powders by 0·05° 2θ, 5 s step-by-step scanning is reported in Fig 3. The lattice can be assigned to the cubic phase with a crystal edge a_0 = 0·403 61 nm calculated by the least squares procedure, using Si as an internal standard. Small quantities of $BaCO_3$, estimated to less than 1·5%, have been observed. The treatment with 0·1 M dilute acetic[14] or hydrochloric acid results in a strong amorphization, especially when performed before powder drying.

Linear shrinkage (%) and shrinkage rate (% min^{-1}) for the as-obtained powders are reported in Fig. 4(a). The maximum rate is found at ≈1110°C, whereas a complex trend is observed between ≈950 and ≈1100°C.

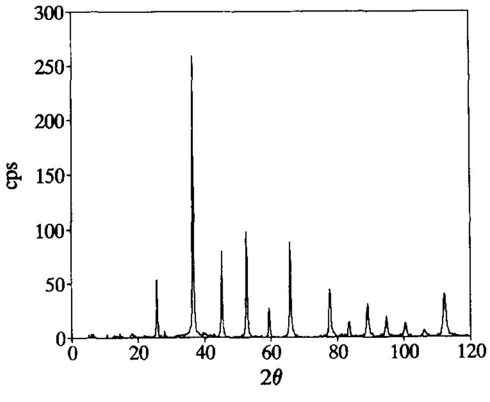


Fig. 3. X-Ray diffraction pattern of as-obtained $BaTiO_3$ powder.

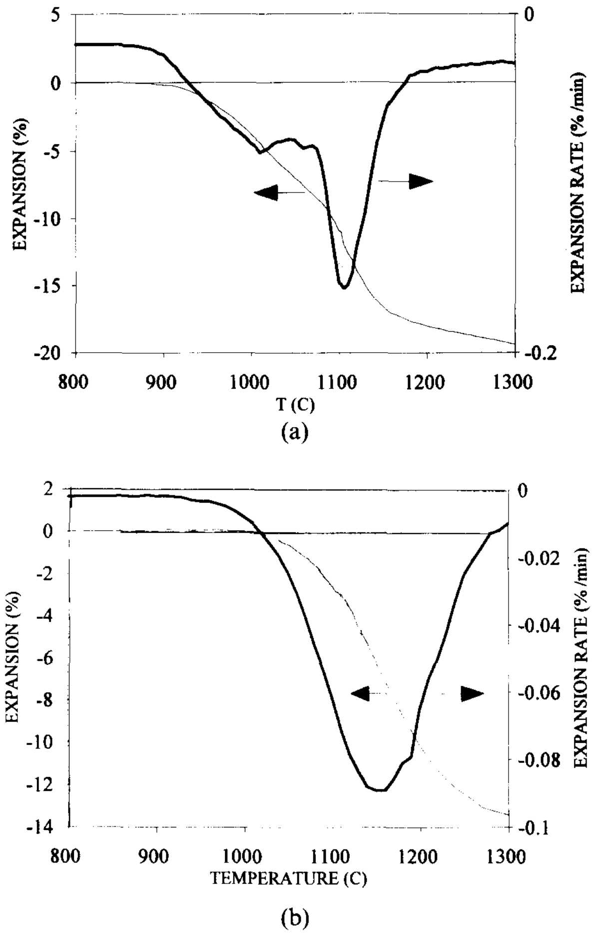
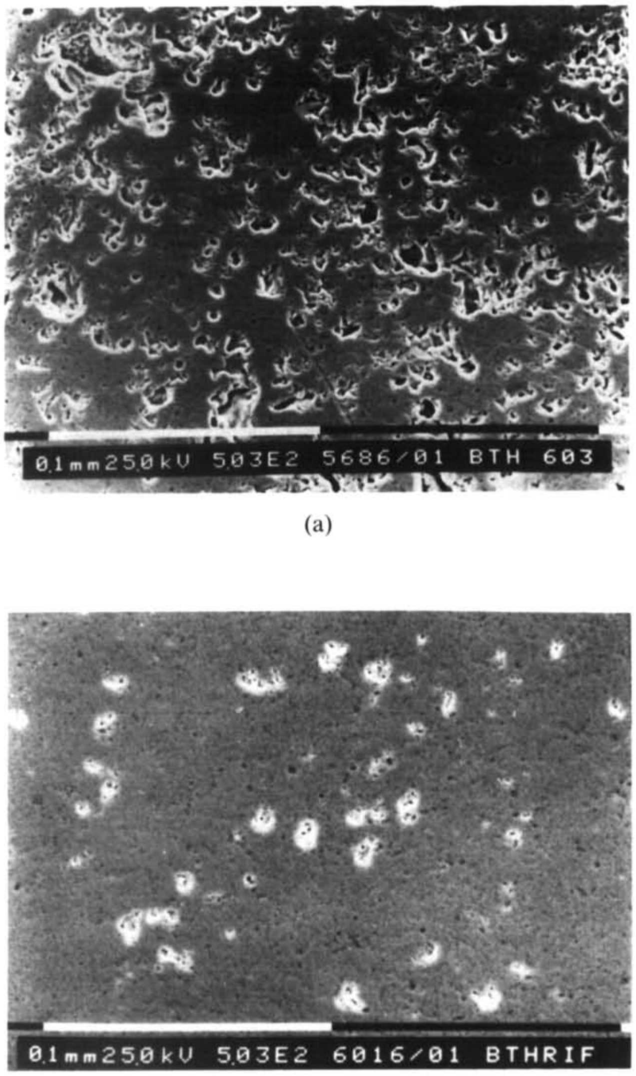


Fig. 4. Expansion (%) and expansion rate (%min^{-1}) versus temperature at the heating of 1°C min^{-1} for (a) as-obtained $BaTiO_3$ powder, and (b) $BaTiO_3$ powder after 15 h thermal treatment at 950°C.

In order to test the powder sinterability, small cylinders isostatically pressed to ≈55% of the theoretical density (6·012 g cm^{-3})[15] were fired for 2 h at 1225 and 1300°C obtaining a final density which was measured as 5·25 g cm^{-3} (87·3%). X-Ray diffraction analysis shows that the lattice of the sintered bodies is tetragonal, with the crystal edges a_0 = 0·399 16 nm and c_0 = 0·402 86 nm.

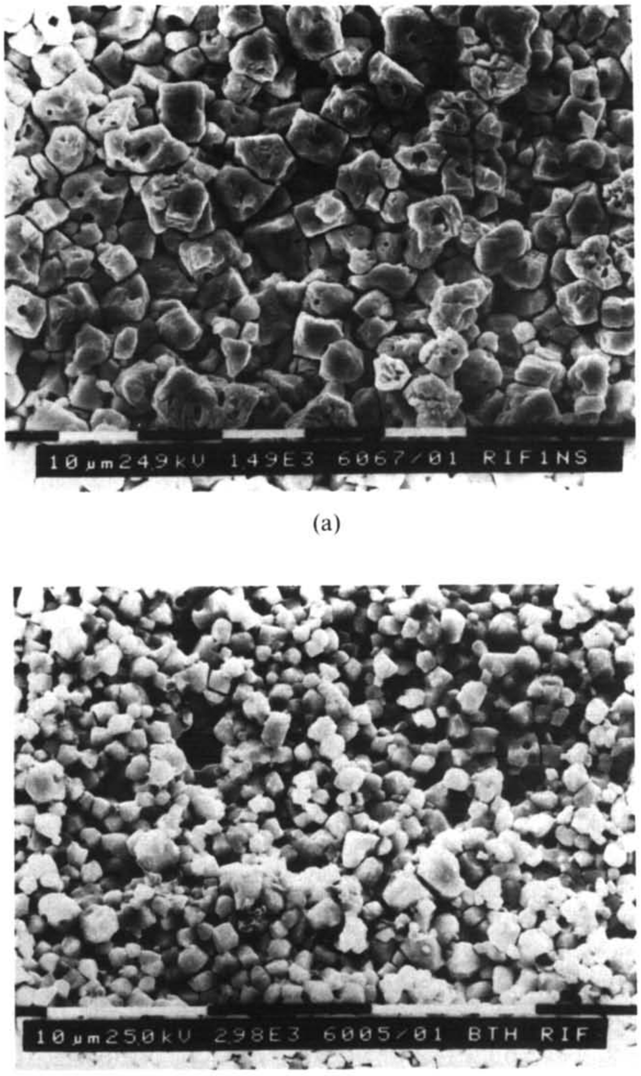
As these densities are unsatisfactory in spite of the small crystallite size of the powders, an attempt was made to increase them. The powders were heated at 950°C for 15 h in order to modify both the surface and the structure of the powders and to stabilise the tetragonal cell. A more regular dilatometric behaviour was observed with maximum shrinkage rate at ≈1150°C (Fig. 4(b)). After pressing, the samples were sintered for 2 h at 1225°C obtaining 5·77 g cm^{-3} (95·7%) as the final density. Figure 5(a) and (b) show the cross-sections of two samples sintered for 2 h respectively at 1300°C, starting from the as-obtained powders, and at 1225°C, after the thermal treatment at 950°C. The samples were also etched to evaluate the grain size. As the thermal etching is scarcely effective, due to the small grain sizes, the samples underwent a chemical treatment with an aqueous solution containing 1% of a 1 : 2 mixture of concentrated HF and HNO_3, i.e. a slight modi-



(a)

(b)

Fig. 5. Microstructure (SEM image) of (a) as-obtained $BaTiO_3$ powder sintered for 2 h at 1300°C and (b) $BaTiO_3$ powder sintered for 2h at 1225°C, after 15 h thermal treatment at 950°C.



(a)

(b)

Fig. 6. Microstructure (SEM image) after chemical etching of (a) as-obtained $BaTiO_3$ powder sintered for 2 h at 1300°C, and (b) $BaTiO_3$ powder sintered for 2 h at 1225°C, after 15 h thermal treatment at 950°C.

fication of the literature report.[16] Figure 6(a) and (b) show the grain structure after the chemical etching of the same samples reported in Fig. 5 (a) and (b) respectively.

The same final microstructure and enhanced densification can be equally obtained performing the mentioned thermal treatment during the heating up of the samples to the sintering temperature.

4 Discussion

The reaction followed for the preparation of $BaTiO_3$ is extremely simple to carry out. Although this method has already been reported in the general outlines,[14,17] the real operational parameters have not been described in full detail. Thus, the time required at this temperature for the transformation to metatitanate has been determined by analogy with other similar systems such as, for instance, the reaction between $Ba(OH)_2 . 8H_2O$ and amorphous TiO_2, where the transformation to $BaTiO_3$ is almost completely achieved after about 4–5 h at 85°C and about 3·5 h at 90°C.[18] Even if in the present case the reaction kinetics have not yet been studied, a time of 6 h has been found adequate for the experiments, as barium hydrate and possible compounds from $TiCl_4$ hydrolysis have not been detected in the X-ray diffraction patterns of the final product. The temperature of reaction is surely the most important operational parameter and its influence has to be determined. The dependence of the external pressure on the process, performed here at 10^5 Pa, has not been investigated so far, although it would play a less relevant role.

X-Ray diffraction patterns indicate the presence of one single-phase cubic compound: only small amounts of an amorphous unidentified phase and $BaCO_3$ ($\leq 1{\cdot}5\%$) are present. This result is confirmed by DTA where thermal effects have not been detected, excluding therefore relevant presence of secondary phases in the system. The relatively small amount of $BaCO_3$ observed depends on the washing time, which, even if performed with freshly distilled water, always implies a certain amount of carbonation as several treatments are required to eliminate Na^+ and Cl^- ions and to allow the system to reach neutrality.

The Ti to Ba ratio in the final product shows a slight deviation from the stoichiometry, although the determination of some relevant electric properties, such as the dielectric constant and the ferroelectric transition temperature, has proved that no appreciable effect can be detected.[19] The possibility of obtaining a stoichiometric ratio closer to 1 has been considered. The main factor in reducing the Ba amount in $BaTiO_3$ is probably a certain degree of carbonation both in Na and Ba hydrates, which prevents reaction (1), but it is also possible that some amorphous by-products can be formed.

These undesired effects can be reduced or eliminated using higher purity starting hydrates and a closed batch reactor where the atmosphere control and $TiCl_4$ introduction can be realised with more accuracy. Minor corrections on the stoichiometric initial reactants ratio could also be made in order to adjust the final product stoichiometry. The reduction or elimination of the amorphous compounds appears instead more difficult and, at the moment, the authors cannot present any adequate solution to this problem. A further possible reason for deviation from the stoichiometric composition has been considered, related to the solubility of $BaTiO_3$: although at pH 7 it has not been measured, it seems however low, in that no Ba^{2+} ions have been revealed with ordinary analytical techniques during the final washing treatment.

The powders heated up to 1225°C have shown a rather important weight loss up to 500°C ($\approx$6 wt%), while some 2% additional loss has been observed between 500 and 980°C and another 0·2% between 980 and 1225°C. Even if a detailed study has not been carried out, surely the decomposition of some $BaCO_3$, always present in the powders, must play a role, as well as the elimination of H^+ and OH^- which in fact contribute to the cubic structure stabilisation;[20] release of oxygen, as observed in pure TiO_2-excess $BaTiO_3$,[21] seems to be of minor importance. Further investigations on this point are presently in progress.

Following the present route, $BaTiO_3$ has been obtained as very fine, high purity powders: the small crystallite sizes suggest a possible high reactivity and also the possibility to obtain sintered bodies with small grained microstructure. The powders however present a rather strong degree of agglomeration which can result from the interactions of OH^- groups probably present at the surface.[20] This can produce forming defects during isostatic pressing with subsequent macroporosity in the sintered bodies. It is necessary therefore to improve the green formation procedure, reducing powder agglomeration and internal friction during the forming step.

The samples sintered for 2 h at 1225 and 1300°C exhibit high porosity when prepared from the as-obtained $BaTiO_3$ (Fig. 5(a)). The thermal treatment results in higher final density (Fig. 5(b)), although the sintered bodies still present several pressing defects as no binder has been used to avoid further possible contamination effects. However, this treatment seems to be very effective in enhancing density and it is possible to forecast a density close to the theoretical if higher green densities could be obtained in the forming step. The grain sizes, both in the as-obtained and in the thermally treated samples, seem homogeneous, as observed after the chemical etching which is nevertheless rather difficult to control and implies a deep attack along the grain boundaries. A comparison with the grain size measured on fracture surfaces confirm this result. It seems important to state that the thermal treatment at 950°C produces also a remarkable reduction in the average grain size which drops from 3·8 to 1·1 μm (Fig. 6 (a) and (b)). A strong reduction of the internal porosity of the grains, which is particularly evident in Fig. 6(a), is also observed.

The unexpected low density measured for the as-obtained powders after sintering could be related to the $BaTiO_3$ crystal lattice which remains cubic up to $\approx$950°C. Samples heated at the rate of 1°C min^{-1} to this temperature and immediately quenched in air in fact retain the cubic structure. It is likely that the complex dilatometric behaviour (Fig. 4(a)) in the temperature range 1010–1100°C, where some expansion mechanism seems to compete with shrinkage, could be related to the cubic–tetragonal transition.

If the system instead is allowed to change to tetragonal before sintering, the lattice change can strongly modify the defective state of the system and improve the sinterability of the powders, as already observed for the γ- to α-Al_2O_3 transition.[22] The contemporary modification of the powder surface can also play a positive role in achieving a better densification.

The samples sintered for 2 h at 1225°C after dilute acid treatment of the powders, both with CH_3COOH and HCl, have shown a very low density (71 to 77%) and the presence of large amounts of polytitanates like $BaTi_2O_5$ and $Ba_4Ti_{13}O_{30}$. The carbonate formation therefore has to be prevented in the reaction phase, because the $BaCO_3$ elimination, at least by the acid treatment used here, seems to cause very negative side effects.

5 Conclusions

It has been proven that it is possible to obtain $BaTiO_3$ as submicron powder following a very simple route from easy to manipulate reactants. The powders, which can be prepared at high purity according to the starting materials, show high specific surface area and high reactivity. It is possible to achieve high density by sintering at relatively low temperatures with short firing times, obtaining at the same time very fine grain sizes. The present method can be improved to reduce the carbonation and to make the Ba/Ti ratio closer to unity.

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