

Strategies for the Structure and Morphology Control of BaTiO₃ Nanoparticles

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Abstract. This review provides insights regarding synthesis strategies for simultaneous control of tetragonality, size and shape in barium titanate. Details concerning the understanding of structure, size and shape effect on BaTiO₃ properties will be considered in the first part. Then a revision of the most reported BaTiO₃ particles solution-based synthesis approaches for the control of its structure and morphology will be presented. In the final section, a description of the contribution of the authors to the topic is presented and demonstrates that low-temperature hydrothermal synthesis using suitable titanium precursors is a suitable approach to simultaneously control structure and morphology in BaTiO₃.

1. Introduction

Control of the shape and size in multifunctional materials is a great interest because they play very important roles in determining magnetic, electrical, and optical properties due to the spatial geometry effect [1]. In this view, notable advancement has been made for the controlled synthesis and self-organization of inorganic materials with regular geometrical shapes, whether in the dimensions of nanoscale or micrometer scale [2].

The ferroelectric materials with perovskite structure have found widespread applications as sensors, microactuators, infrared detectors, microwave phase filters and non-volatile memories, for which their functional properties such as switchable polarization, piezoelectricity, high non-linear optical activity, pyroelectricity, and non-linear dielectric behavior are indispensable [3–7].

BaTiO₃ is a typical ferroelectric material, subject to fundamental research since WWII due to its high permittivity and low losses properties suitable for many applications. According to Haertling [8] the discovery of non-linear dielectric properties in barium titanate associated with very high values of the dielectric permittivity, was crucial for the development of the new generation of materials for electronic and microelectronic devices. Hence, BaTiO₃ is among the most systematically studied and widely used ferroelectrics and considered as the prototype lead-free ferroelectric ceramic. BaTiO₃ was firstly used as piezoelectric ceramic transducers. However, due to the discovery of better piezoelectric properties in other materials, namely the solid solution between lead titanate and lead zirconate, BaTiO₃ found its main use as high permittivity dielectric in multilayer ceramic capacitors (MLCC) [9]. Barium titanate based ceramics show dielectric constant values as high as 15,000 as compared to 5 or 10 for common ceramic and polymer materials. The high dielectric constant BaTiO₃ ceramic based disk capacitors are simple to be manufactured and have captured more than 50% of the ceramic capacitor market [10]. The advances in tape casting technology have made it possible to make dielectric layers < 20 μm thick. This combined with the use of a high dielectric constant ceramic like BaTiO₃ allows large capacitance values to be achieved in relatively small volume capacitor devices. Good reviews have been written on the state of the art of the MLCC technology and the technical challenges it faces [10–12].

Devices miniaturization or scaling down, in one word the nanotechnology, is the strategy for improved resources efficiency in energy devices, as has been highlighted in the FP7 Observatory NANO report, European Nanotechnology Landscape, released in November 2011 [13]. In nanotechnology the concept “smaller” means greater performance in less space. A performing capacitor is the one that can store a large amount of electrical charge (high capacitance density) and then discharge that charge to give a significant amount of power (high operating voltage) with maximum efficiency (low losses as leakage current or power dissipation). In order to guarantee the good performance of a capacitor high surface area electrodes and high dielectric constant materials are required. In 2006 the International Technology Roadmap for Semiconductors (ITRS) suggested that the capacitors structure must become three-dimensional (3D) by 2010 to accommodate requisite storage density [14]. The 3D architecture capacitors refer to vertically stackable cell arrays in monolithic integration, with acceptable yield and performance. Their use is a requirement for the dynamic random access memories (DRAM) scaling down, as has been highlighted in the last report of ITRS [15].

The present review is divided in three parts. In the first section the explanation regarding the necessity of understanding the size and shape effect on the barium titanate properties is provided. The second part is a revision of the most common barium titanate particles synthesis approaches for the control of its structure, size and morphology. Finally, some original results reported by the authors during the

last 8 years are presented and discussed. It is demonstrated that the low temperature hydrothermal synthesis using suitable titanium precursors is a very good strategy for the simultaneous control of structure, size and shape in BaTiO₃.

2. Effect of Structure, Size and Shape on the Barium Titanate Application

This section will answer the following questions:

- Why is needed tetragonal structured barium titanate?
- Why small size of BaTiO₃ particles is required?
- Why are looked-for different BaTiO₃ particles shapes?

BaTiO₃ is one of the complex oxides within the perovskite family and a typical ferroelectric material. The ideal perovskite structure adopted by many oxides has the general formula ABO_3 [16]. Based on the tolerance factor (t) [17], which takes into account the sizes of the O , A and B ions, the ideal perovskite structure adopts the cubic space group $Pm\bar{3}m$. But factors other than the ionic size, *e.g.* degree of covalency, metal-metal interactions, Jahn-Teller and ion pair effects play a role in determining the space group [18]. At room temperature and atmospheric pressure barium titanate BaTiO₃ adopts a tetragonal structure with a space group $P4mm$ [19]. For pure barium titanate, the tolerance factor equals 1.06. Here the tolerance factor is greater than 1 (ideal) because Ti⁴⁺ is smaller than its cavity and/or Ba²⁺ is larger than its cavity. During several years the room temperature tetragonal structure of barium titanate was controversial. Based on the studies of Evans [19, 20] and Megaw [21], the structure of barium titanate is now well known and the room temperature tetragonal structure of the BaTiO₃ is explained by ionic displacement of the Ti ions regarding to the oxygen ions. This structural feature induces a spontaneous electric polarization that can be reversed by the application of an external electric field, the fingerprint of the ferroelectric materials.

It was observed that the ferroelectricity of BaTiO₃ disappears in particles smaller than 120 nm [22]. Further, the dielectric constant, although it increases with decreasing size, reaches a maximum at a grain size near the nanometer scale below which it rapidly decreases [23]. These observations have stimulated an exponential growth on research aiming to understand the phenomena [24–28]. By then, one of the explanations was related to the stabilization of the cubic paraelectric polymorph of BaTiO₃ at room temperature, rather than the ferroelectric tetragonal structure for particles with size in the nanoscale [25]. Besides the size it has been theoretical demonstrated that the shape of the BaTiO₃ nanoparticles can also influence its tetragonality [29]. According to Morozovska BaTiO₃ ferroelectricity seems to be independent of the particle size in the case of anisotropic *cylindrical* shaped nanoferroelectrics or one-dimension (1D) nanostructures, such as nanotubes, nanorods and nanowires. It was theoretically demonstrated that 1D BaTiO₃ particles preserve the tetragonality even at very low

dimensions (2.5 nm) and an enhancement of the ferroelectricity is expected due to the effective surface tensions and minimal depolarization field influence in the cylindrical nanoparticles [29]. This theoretical prediction of the absence of a critical size for 1D nanoferroelectrics introduced a new variable in the discussion of dimensionality in ferroelectrics, and, besides the size, the dependence on the shape gained importance [30]. It is therefore important to establish from the experimental point of view the relations between synthesis–structure–morphology–properties in ferroelectric nanostructures, namely in BaTiO₃.

3. Solution-Based Methods for Simultaneous Control of Structure, Size and Shape in BaTiO₃

The ferroelectric tetragonal structure of BaTiO₃ is mostly reported for materials synthesized at relatively high temperatures, above 600°C [31–33], where grain growth and aggregation are inevitable. On the other hand, syntheses at lower temperatures mostly led to the formation of BaTiO₃ non-ferroelectric cubic structure [34, 35]. With the need of preparing materials at very low temperatures that could be compatible with polymeric materials of low melting point, as required by the microelectronic industry, hydrothermal and related methods have been gaining importance [36]. The common BaTiO₃ structure obtained by hydrothermal synthesis is cubic. However several reports describe the hydrothermal synthesis of tetragonal BaTiO₃ powders. Asiaie *et al.* obtained tetragonal BaTiO₃ nanopowders of 90, 300 and 500 nm particle sizes by hydrothermal crystallization at 240°C starting from BaCl₂ and hydrated titanium oxide with a varying concentration of NaOH in the reaction medium [37]. In this work only the larger particles were pure barium titanate, whereas the powder with smallest particle sizes (90 nm) contained unreacted titanium dioxide [37]. At the same hydrothermal treatment temperature, 240°C, Xu *et al.* prepared tetragonal BT powders with an average particle size of 80 nm [38]. At even lower temperature, 220°C, Jung *et al.* obtained tetragonal BaTiO₃ particles through glycothermal reaction for 12 h using Ba(OH)₂ and amorphous titanium hydrous gel as precursors and 1,4-butanediol and water as solvent [39]. High purity tetragonal BaTiO₃ powders with an average size of 150 nm in diameter were synthesized by a hydrothermal reaction at temperatures of around 200°C by Xie *et al.* [40]. Tetragonal BaTiO₃ was hydrothermally obtained at 200°C [41] or higher than this temperature [42] from titanium butoxide and Ba(OH)₂ [41] or Ba(NO₃)₂ in the presence of KOH [42]. The influence of the particles shape on the BaTiO₃ tetragonality has also been verified by hydrothermal synthesis. Cube-shaped and highly crystalline tetragonal BaTiO₃ was obtained from amorphous peroxo-precursor prepared by mixing BaCl₂, TiCl₄, H₂O₂, NH₄OH which was hydrothermally treated in a 10 M NaOH solution at 200°C for 24 h [43]. BaTiO₃ nanowires obtained at 170°C hydrothermal temperature [44] present high tetragonality and, in consequence, good ferroelectric and dielectric properties [45].

4. Structure and Morphology Control of BaTiO₃ by Hydrothermal Synthesis

The present authors demonstrated that tetragonal BaTiO₃ particles can be obtained at temperatures lower than 170°C by hydrothermal synthesis [46, 47]. We established the relations between the precursor chemistry and the final structure of barium titanate compound. In this section our results obtained using different titanium precursors for the hydrothermal synthesis of barium titanate are revised and discussed in terms of structural and morphological characterization of the obtained powder.

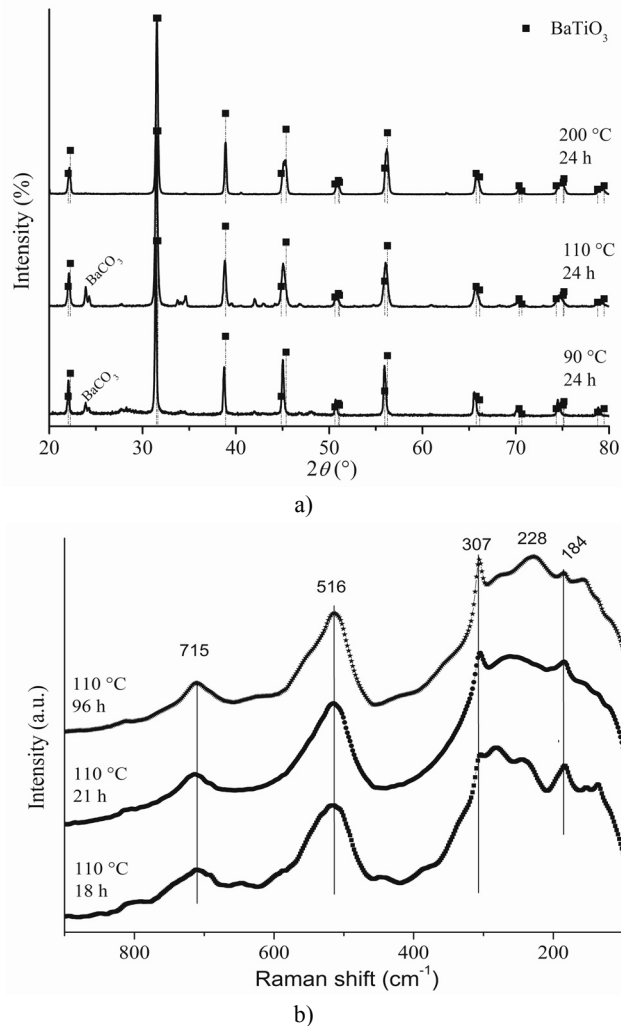


Fig. 1. XRD and Raman spectra of samples obtained from dry TiNTs and Ba(OH)₂.

(a) The first approach consists in a chemical template method. For this we used dry powder of layered sodium titanate nanotubes (TiNTs), prepared by hydrothermal synthesis [48], as both titanium precursors and growth directing agents [49, 50]. The structural analysis was conducted by X-ray diffraction (XRD) and Raman spectroscopy (Fig. 1) and the morphological evaluation was done by scanning and transmission electron microscopy (SEM and TEM) (Fig. 2 and Fig. 3).

It was observed that when dry TiNTs powder was hydrothermal treated with aqueous solution of $\text{Ba}(\text{OH})_2$ at various temperatures (90, 110 and 200°C) for different reaction times, the structure and the morphology of the barium titanate product is changing as follows:

➤ At low temperature and low time pseudo-cubic structured (Fig. 1) *wild* type dendritic (Fig. 2a and 3a) BaTiO_3 particles have been formed by a phase boundary topotactic reaction on the TiNTs surface [49, 50].

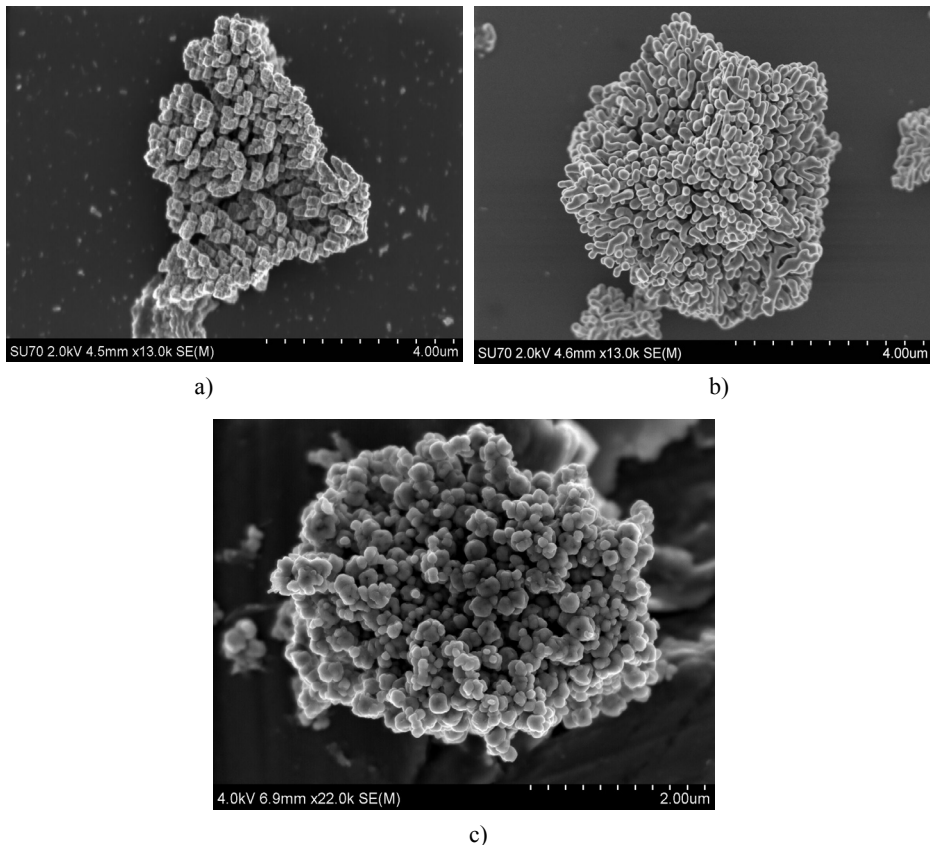


Fig. 2. SEM images of BaTiO_3 powders obtained starting from dry TiNTs and $\text{Ba}(\text{OH})_2$; the images are presented in the order of reaction stages showing the formation of “wild”-type dendrites to round shaped particles and “seaweed” dendrites

➤ At intermediate temperature and time of reaction round shaped particles of BaTiO₃ (Fig. 2b) were formed [49].

➤ Finally, at high temperature and longer time ‘seaweed’ type dendrites with predominately tetragonal structure were obtained, the BaTiO₃ crystallization process being controlled by a dissolution precipitation mechanism [49, 50].

The gradual transition from pseudocubic to tetragonal barium titanate with the reaction temperature and time is indicated by the reflections around 2θ of 45° [(200) and (002)] in the X-Ray patterns which became broader as the temperature (Fig. 1a) and time of reaction increases [49, 50]. The splitting of the reflection at $2\theta \approx 45^\circ$ is characteristic of the tetragonal distortion of the BaTiO₃ structure. This cell distortion is reflected also in the Raman spectra [49, 50] by the appearance of the sharp band at $\sim 307 \text{ cm}^{-1}$ (Fig. 1b). We postulate therefore, that at the early stages of crystallization cubic BaTiO₃ is more likely to form, whereas at later stages predominately tetragonal BaTiO₃ particles are obtained [49, 50]. In SEM (Fig. 2) and TEM (Fig. 3) micrographs, we observed that the transition from pseudocubic to tetragonal is accompanied by a change in the particle morphology from “wild”-type dendrites to round shaped particles and “seaweed” dendrites. At low synthesis temperature (90°C) and short reaction times “wild” type dendrites with a rough defective surface are formed (Fig. 2a and 3a). As the crystallized BaTiO₃ fraction increases with the temperature and time, round shaped particles are observed (Fig. 2b) followed by defect free dendritic particles with smooth surface called “seaweed” type (Fig. 2c and 3b).

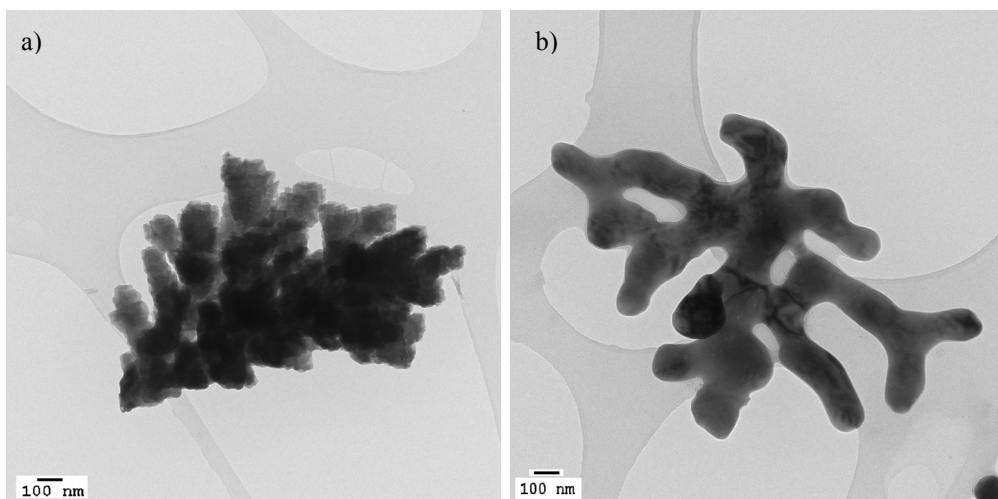


Fig. 3. TEM micrographs of a) wild-type and b) seaweed dendrites.

Our previously work [49, 50] clearly shows that dry TiNTs can not easily act as directing growth agents for hydrothermal synthesis of BaTiO₃ but influence the anisotropic growth of this perovskite compound.

(b) In our subsequent investigations, the effect of titanium alkoxides as titanium precursors on the hydrothermal synthesis of BaTiO₃ was assessed [46, 51]. This approach is based on sol-gel processes knowing that the sol-gel based methods have the advantage of good mixing of the reagents which induce a controllable structure, stoichiometry, size and shape of the final product. The sol-gel process is a versatile, solution-based process for producing various ceramic and glass materials in the form of nanoparticles, thin-film coatings, or fibers and involves the transition of a liquid, colloidal “sol” into a solid “gel” phase [52]. It is, furthermore, a cheap technique that allows fine control of chemical composition. Typical starting materials for the preparation of the sol include metal salts or metal organic compounds, such as metal alkoxides, which undergo a series of hydrolysis and condensation reactions to form a colloidal or polymeric sol. One of the major drawbacks is that the product typically consists of an amorphous phase rather than defined crystals and, thus, requires crystallization and postannealing steps at high temperatures. Therefore in our study the sol-gel processes were combined with hydrothermal synthesis methods. The hydrothermal method enables the formation of crystalline particles or films without the need for postannealing and calcinations [49–51, 53].

For this approach titanium butoxide [Ti(OBu)₄] and titanium iso-propoxide [Ti(OⁱPr)₄] were used as titanium sources. The barium and titanium reagents sol was precipitated in aqueous solution of NaOH and hydrothermally treated at various temperatures for different times [46, 51].

The structural analysis by XRD and Raman (Fig. 4) of the samples prepared from different titanium alkoxides revealed that tetragonal in average but orthorhombic at local scale BaTiO₃ is obtained from Ti(OⁱPr)₄. Cubic in average but tetragonal at local scale barium titanate was obtained instead with Ti(OBu)₄ as titanium precursor. It was considered that the stabilization of different BaTiO₃ phases under hydrothermal conditions is depending on the Ti coordination in the titanium aqueous species [54], but this speculation has not been experimentally proved before our work. In our experimental conditions, Ti(OⁱPr)₄ is likely to form monomeric species in which the titanium atom is 4-fold coordinated (tetrahedric). Differently the Ti(OBu)₄ forms oligomers in the same experimental conditions in which each titanium atom is in 5-fold coordination [55]. This difference can be responsible for the formation of distinct barium titanate structures when starting from different titanium alkoxides precursors [46].

The effect of some additives on the hydrothermal synthesis of BaTiO₃ starting from Ti(OBu)₄ was studied [51]. There are syntheses procedures in which the modification of the crystal growth may occur if the growth on some of the crystal faces will be restricted. This may be achieved by reducing the supply of material to

a particular crystal face or by modifying the specific surface energy, that is, in the presence of some additives, named crystal habit modifiers [56] and classified as additive-assisted syntheses.

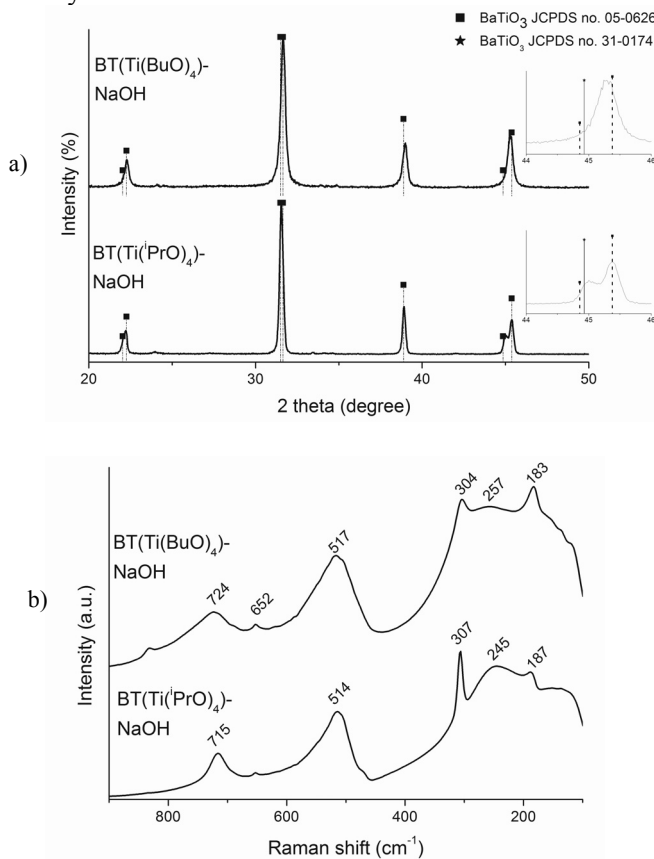


Fig. 4. XRD and Raman spectra of the samples obtained from different titanium alkoxides.

We reported that although the tested additives influenced the growth of BaTiO₃, their behaviour varied [51]. For instance, the poly(acrylic acid) (PAA) adsorbed on specific crystallographic faces changing the growth kinetics. PAA influences BaTiO₃ nucleation by modifying the quantity of the Ba²⁺ in solution. The direct aggregation observed when PAA is used (Fig. 5b) indicates that this additive also influences the growth of BaTiO₃. These results suggest that the growth process is controlled by an aggregation mechanism called oriented attachment [57, 58]. It is then suggested that in the present study PAA could preferentially adsorb on high energy BaTiO₃ crystallographic faces, decreasing the growth rate of these faces and inducing the oriented attachment of BaTiO₃ particles. It can be therefore stated that

PAA limits the growth kinetics of BaTiO_3 by decreasing the surface energy and so decreasing the growth rates of specific crystallographic faces. So PAA both adsorbs onto high energy surfaces and is trapped during the precipitation [51].

The hydroxypropylmethylcellulose (HPMC) is growth inhibitor and also crystal habit modifier (Fig. 5c) [51]. HPMC is a polysaccharide chemically derived from cellulose by insertion of hydrophobic moieties such as hydroxypropyl and methyl. Despite the introduction of these hydrophobic groups, HPMC presents a linear polymeric chain with a high hydrophilic character due to the presence of polyhydroxy groups on the molecular chains, which make the polymer water-soluble [59]. The hydrophobic parts of HPMC are important for its surface activity (as in a polysoap) and unique hydration-dehydration characteristics.

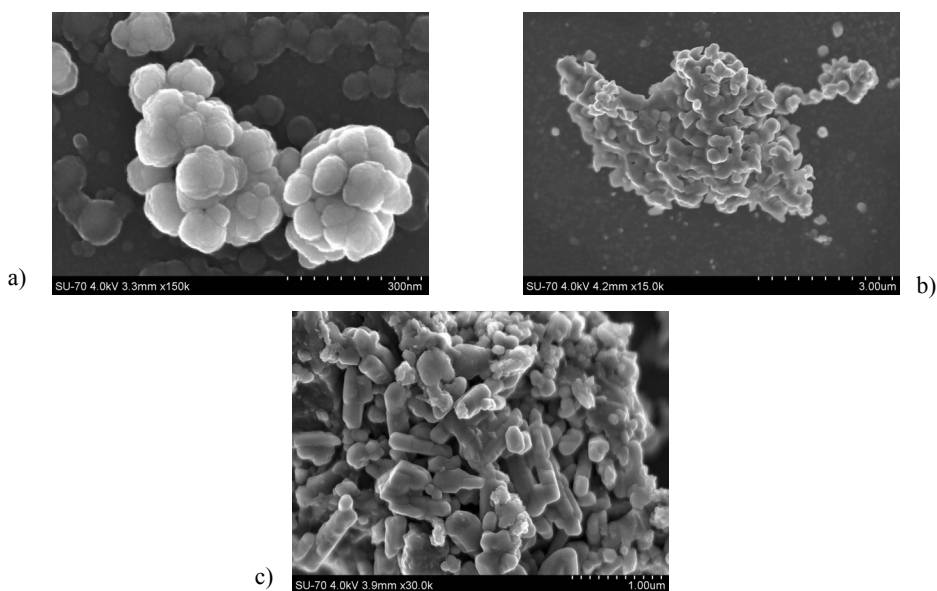


Fig. 5. SEM images of the samples obtained from $\text{Ti}(\text{BuO})_4$ in the presence of additives: a) blank; b) PAA; c) HPMC.

In our experimental conditions [51] HPMC acts as both growth inhibitor and crystal growth modifier. HPMC can act as a growth inhibitor as the crystal growth can be regulated and restricted by the three-dimensional network structure of HPMC gel formed when increasing the synthesis temperature and additive concentration [51].

When using titanium isopropoxide $\text{Ti}(\text{O}^i\text{Pr})_4$ as titanium source, the obtained results lead to the following key aspects [46]:

- At the hydrothermal synthesis temperature as low as 110°C tetragonal cube like (Fig. 6a) BaTiO_3 nanoparticles are formed;

- When increasing the NaOH concentration the tetragonal BaTiO₃ faceted cuboids-shaped (Fig. 6b) particle size increases. Moreover, at high concentrations of the NaOH barium titanate (111) twins growth appear (Fig. 6c);
- Monophasic crystalline BT is formed when using NaOH as mineralizer, compared to the sample obtained in the presence of N(CH₃)₄OH in which amorphous TiO₂ NRs are formed as a secondary product.

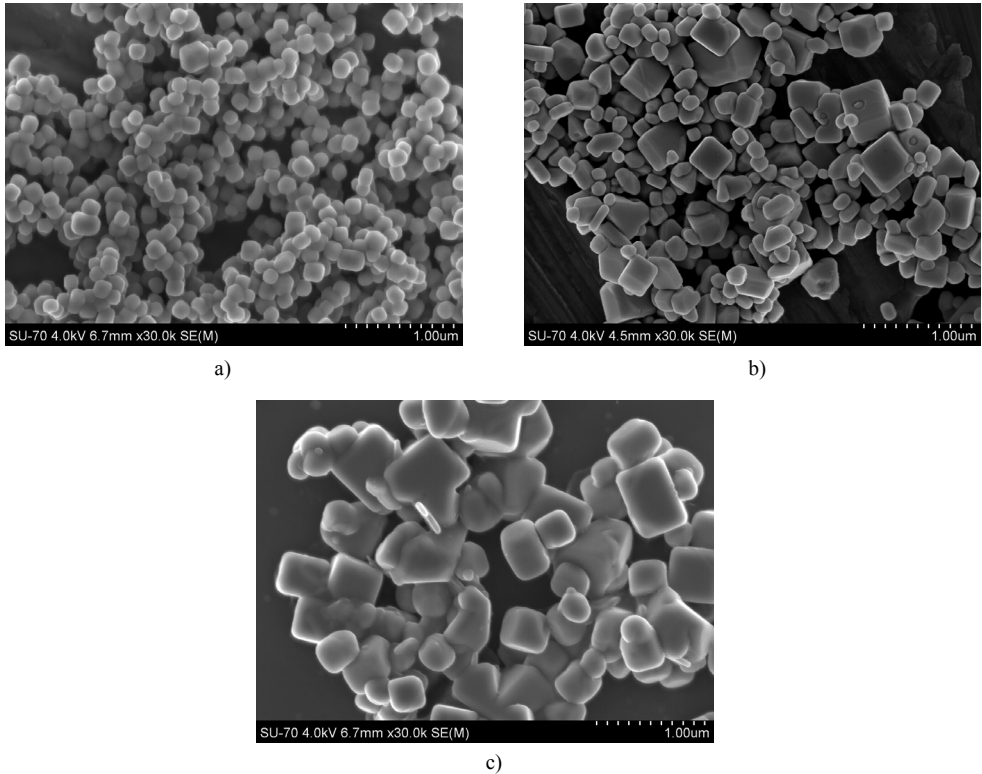


Fig. 6. SEM micrographs of the BaTiO₃ samples obtained from Ti(OⁱPr)₄.

It was reported that the (111) crystallographic plane twins of barium titanate can only be formed at high temperatures (higher than 1300°C) and in samples containing an excess amount of TiO₂ [60, 61]. They play an important role in the abnormal grain growth in BaTiO₃ ceramics due to the singular grain boundaries formed along the {111} flat faces of the BaTiO₃ grains [62, 63]. Although well-documented the role of (111) twins in the abnormal grain growth of ceramics, their formation mechanism in BaTiO₃ powders is still under debate. We demonstrated that the formation of (111) BaTiO₃ growth twins is influenced by the increased

concentration of sodium ions, which act as growth modifiers [46], and it is not influenced by the titanium surplus as reported before [64, 65].

5. Conclusions

The present revision provides good insights of finding low temperature synthesis strategies for structure and morphology control of BaTiO₃ nanoparticles. It is demonstrated that the structural transformation of barium titanate is accompanied by morphological changing in accordance with the characteristics of the titanium precursor. In the reported studies we confirmed that the hydrothermal synthesis, at temperatures not higher than 200°C, is suitable for the preparation of:

➤ Tetragonal structured BaTiO₃ with “seaweed” dendritic morphology which was obtained at late stage reaction of dry TiNTs powders hydrothermally treated with Ba(OH)₂. At early stages of barium titanate crystallization, “wild” type dendritic particles with cubic structure were obtained by a phase-boundary mechanism using dry TiNTs as titanium precursors.

➤ Tetragonal cube-shaped with uniform size distribution and dimension of ~ 70 nm BaTiO₃ obtained starting from titanium isopropoxide and barium acetate in the presence of NaOH. Instead, round shape barium titanate particles with predominantly cubic structure were formed when titanium butoxide was used as titanium precursor. This result is the first experimental proof that the stabilization of different barium titanate phases under hydrothermal conditions is depending on the Ti coordination in the titanium aqueous species.

This work is an unquestionable experimental proof of the barium titanate structural and morphological control obtained by tuning the titanium precursor’s chemistry at low temperature hydrothermal crystallization.

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