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Influence of the synthesis method on the preparation of barium titanate nanoparticles

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ABSTRACT

Dielectric barium titanate nanoparticles are essential to develop reliable microelectronic devices. However, their dielectric properties largely depend on the synthesis method used. Hence, we developed $BaTiO_3$ nanoparticles by various synthesis methods seeking to compare and evaluate their crystal structure, size, and homogeneity. Syntheses were carried out by four distinct synthesis methods: polymeric precursor (Pechini), electrochemical, hydrothermal and microwave-assisted hydrothermal. X-ray diffraction and Raman spectroscopy analysis revealed the formation of barium titanate in cubic and tetragonal structures. The nanoparticles synthesized have BET superficial areas varying in the range 10–15 $m^2 g^{-1}$. Pechini method propitiated the formation of smaller particles than the other methods, *i.e.* 44.0 ± 15 nm. By the electrochemical synthesis method the particles were obtained with 67.0 ± 20 nm of diameter, with large distribution in particle size. The use of hydrothermal methods conducted to various particle size distributions; while particles of 180.0 ± 60 nm were formed using conventional hydrothermal synthesis, smaller particles (66.0 ± 16 nm) were formed using the microwave-assisted hydrothermal synthesis in lower reaction times (six fold). All four methods were effective to synthesize crystalline $BaTiO_3$ nanoparticles, with different sizes and structural characteristics. Thus, the choice of the suitable synthesis method will depend on the desired properties of the $BaTiO_3$ nanoparticles.

1. Introduction

Barium titanate ($BaTiO_3$) was discovered in the 40s when its high dielectric constant was reported worldwide [1]. The $BaTiO_3$belongs to the perovskite family, of the ABO_3 type [2] and its structure has a low Curie temperature of nearly 120 °C, which attributes to this material an elevated dielectric constant at environmental temperature ($\varepsilon = 3600$ at 25 °C and 10^5 Hz). This feature allows their use in high-capacity charge storage capacitors [3,4]. The $BaTiO_3$ presents different crystallographic structures which frequently present distinctive dielectric properties. Three phase transitions are possible in the $BaTiO_3$, according to temperature: rhombohedral to orthorhombic, transition that occurs around −90 °C; from orthorhombic to tetragonal, phase transition that occurs around 5 °C; and from tetragonal to cubic in temperatures around 120 °C [5].

Due to excellent piezoelectric properties (polarization occurs after applying pressure), $BaTiO_3$ is used in developments of counters, data collectors, sound detectors, as well as in microelectronic devices fabrication [6]. Moreover, the dielectric characteristics of this material are important in the electronic industry for the fabrication of multilayer ceramic condensation devices, ceramic capacitors, supercapacitors, among other applications [1,3,6]. $BaTiO_3$ crystalline nanoparticles with high purity are necessary for the fabrication of reliable microelectronic devices. This application highly depends on the grain size, the smaller the better, besides the good distribution and uniformity of the particles [6,7].

Staedler et al. [8] developed $BaTiO_3$ nanoparticles of particle size 123 nm, with non-linear optical properties applied to fluorescent probes for biological applications and multiphoton microscopy. Biocompatibility studies of particles of barium titanate, with sizes of 150 nm, on stem cells demonstrated the possibility of application as nanovectors and enhancement of osteogenic potential of mesenchymal stem cells (MSCs) for bone regeneration [9,10].

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Dielectric properties mainly depend on crystal structure, size, stoichiometry, and homogeneity, and surface properties of $BaTiO_3$, that strongly depend on the synthesis method [11]. Conventional barium titanate synthesis involves high temperatures (~1200 °C) for the calcination of $BaCO_3$ and TiO_2 powders, that commonly results in low purity and forms large particles (>1 μm) with non-uniform distribution, which is due to both the high temperatures and the reaction in heterogeneous solid phase [12,13].

However, researchers have focused on new synthesis methods to prepare $BaTiO_3$ particles with various sizes and morphologies, using low temperatures [14]. Among them, hydrothermal synthesis of crystalline $BaTiO_3$ involves chemical reactions among a concentrate solution of barium hydroxide and TiO_2, or gels of Ba–Ti acetate mixtures, at relatively low temperatures (<1200 °C). This method received attention due to the possibility to produce small particles (1–1000 nm) with a more uniform size distribution [11]. Solid–fluid phase interaction allows control of the particle size through tailoring of synthesis parameters, such as pH, reaction temperature and heating time. Control of these parameters can stabilize $BaTiO_3$ particle formation and delay impurity formation. Besides, the precursors for the $BaTiO_3$ preparation by hydrothermal route are low cost and easy management, which establishes this method as a simple and efficient route for $BaTiO_3$ preparation [11].

In this context, heating technologies by microwaves have been applied in organic reactions since late 80s [15]. However, they are scarcely used in material synthesis laboratories. Heating by microwaves differ from those that occur by bath or heating plates, where heating is done through conduction, irradiation and convection. The action mechanisms of microwaves are the dielectric heating, by dipole rotation and/or ionic conduction [16]. The microwaves application to heating in the hydrothermal synthesis occurs by interaction between microwaves and polar substances of the reaction medium: radiation is absorbed by reagent and the electromagnetic energy is converted into thermal energy. Thus, heat is generated from the interior of the material, which allows a reduction in process time and energy cost [17].

On the other hand, electrochemical route for nanoparticles synthesis is of considerable interest due to the particle size control obtained by adjusting the current density or the applied potential, which is considered the most attractive goal for the synthesis in this field. Extensive investigations were concentrated on metallic particles electrochemically synthesized, particularly noble metal particles. However, few studies were carried out for a synthesis of inorganic compounds [18]. This method was used in the formation of $BaTiO_3$ film and $BaTiO_3$ nanoparticles over metallic titanium by the reaction of $Ba(OH)_2$ or $Ba(CH_3COO)_2$ in alkaline aqueous solution (NaOH) with pH 13. The process can be thermally activated at moderate temperatures ($T < 200$ °C, $P < 106$ Pa), or activated by electric current between a titanium anode and a platinum cathode [19].

The Pechini method, also known as a polymeric precursor method, was proposed by Pechini in the 60s. This method involves the formation of chelates from some hydro carboxylic organic acids, on which the metalcations incorporated are homogeneously distributed. The salt solution, in acid media, is mixed with a polyhydroxilated alcohol, under heating and agitation, leading to the formation of an ester due to the condensation of alcohol and acid chelate. The chelation reaction results from the capacity of some carboxylic acids (as citric acid) to form polybasic chelates with various cations, such as, titanium, zirconium, chrome, lead, cobalt, nickel, barium, among others. In this method, the carboxylic acid is esterified by alcohol molecules, producing water. These are polyfunctional reactant, in the formation of a polymeric resin with chelated cations divided by the entire length of the molecular structure of the resin [20]. The thermal treatment of the resin is carried out in atmospheric air normally in temperature over 500 °C generating metallic oxide crystallites, by oxidation, which is adequate for the organic part elimination and achievement of the desired stage. Some advantages of the Pechini method are, it allows good chemical homogeneity, and presents a direct and precise control of the stoichiometry in complex systems [21–23].

In this context, the goal of this study was to synthesize barium titanate nanoparticles by four different routes: Pechini method, electrochemical synthesis, hydrothermal synthesis and microwave-assisted hydrothermal synthesis. These methods allowed the achievement of materials with different particle size, granulometric distribution, as well as structural characteristics.

2. Experimental

2.1. $BaTiO_3$ synthesis by electrochemical method

Barium titanate synthesis by electrochemical method [24,25] was conducted in a 200 mL electrochemical cell coupled to a thermostatic bath (Nova Ética, Ultrathermostatic Bath) maintaining a constant reaction temperature of 50 °C, since the reaction is exothermic. The reaction inside the cell was maintained under magnetic agitation with electrodes connected to a double power supply source 0–30 V, 3 A (ICEL Manaus PS-5000), working in series, reaching a maximum potential of 60 V and a current of around 3.25 A. These high potentials are needed to detach titanium from the electrode and then form $BaTiO_3$ in a 2 h reaction.

To prepare the electrolytic solution, 300 mL of ultrapure water was previously boiled during 30 min to remove CO_2 dissolved in water, thus seeking to avoid barium carbonate formation as an undesired byproduct. 200 mL of a 0.1 mol L^{-1} octohydrated barium ($Ba(OH)_2{\cdot}8H_2O$, from Synth®) solution and a 0.1 mol L^{-1} sodium hydroxide 99% (NaOH, from Vetec®) solution were used as electrolyte. Firstly, $Ba(OH)_2$ was dissolved and then NaOH was added under constant agitation. Afterwards, titanium electrodes (7 cm length × 2 cm width) were sanded, washed with acetone and rinsed with distilled water.

Once the reaction completed, the solid particles precipitated and the excess liquid (supernatant) was removed. The particles were washed with distilled water and then vacuum filtered. Some particles were also washed with 0.1 mol L^{-1} nitric acid (HNO_3, Vetec®) aqueous solution to remove barium carbonate probably formed in the synthesis. Finally, particles were washed again with ultrapure water and dried at 120 °C.

2.2. $BaTiO_3$ synthesis by Pechini method

Citric acid ($C_6H_8O_7$) and barium acetate ($BaC_4H_6O_4$), both from Synth®, and ethylene glycol ($C_2H_6O_2$) from Vetec®, were used for the precursor solution preparation.

2.2.1. Barium citrate preparation with ethylene glycol

Initially 10.98 g of barium acetate was dissolved in 400 mL of ultrapure water; simultaneously, 24.8 g of citric acid was dissolved in ultrapure water. So both solutions were mixed and 16.5 g of ethylene glycol were added, leaving the mixture under agitation until complete dissolution.

2.2.2. Titanium citrate preparation with ethylene glycol

The titanium citrate solution was prepared dissolving 80.6946 g of citric acid in 400 mL of distilled water. After this procedure, 20 g of titanium isopropoxide was slowly added, with further addition of 53.8 g of ethylene glycol under constant agitation until complete dissolution. Finally, both prepared complexes were mixed and pH adjusted to 9 using NH_4OH. The mixture was left under magnetic agitation and heated at 200 °C, to form a yellow solution with