

## Structural studies of $\text{BaTiO}_3:\text{Er}^{3+}$ and $\text{BaTiO}_3:\text{Yb}^{3+}$ powders synthesized by hydrothermal method

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**Abstract:** Erbium and ytterbium doped barium titanate nanopowders were prepared using the hydrothermal method. A barium titanate structure doped with rare earth ions manifested new characteristics and improved the field of application of optical devices such as trichromatic tubes, LCD displays, lamps, and infrared lasers. In this work,  $\text{BaTiO}_3:\text{Er}^{3+}$  and  $\text{BaTiO}_3:\text{Yb}^{3+}$  were prepared using barium chloride [ $\text{BaCl}_2$ ], titanium butoxide [ $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ], erbium chloride [ $\text{ErCl}_3$ ] and ytterbium chloride [ $\text{YbCl}_3$ ] as precursors. Anhydrous methanol was employed as a solvent. Metallic potassium was used to promote solubility in the system and increase the pH to 13. This method yielded the formation of a predominantly cubic structure in both  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\text{BaTiO}_3$  powders. Characteristic bondings of  $\text{BaTiO}_3$  were observed with FT-IR spectroscopy. The predominantly cubic structure was confirmed by X-ray diffraction and micro-Raman analyses. The particle size (~30 nm) was estimated using the Scherrer equation and X-ray diffraction data. The results were presented and discussed.

**Keywords:** nanopowders; hydrothermal;  $\text{BaTiO}_3:\text{Er}^{3+}$ ;  $\text{BaTiO}_3:\text{Yb}^{3+}$ ; rare earths

$\text{BaTiO}_3$  is a ceramic material with ferroelectric, dielectric and piezoelectric properties. Barium titanate has been thoroughly studied due to specific characteristics (dielectric tunability, high dielectric constant and piezoelectricity<sup>[1,2]</sup>) that enable it to be widely applied in the electronics industry, such as in multilayer ceramic capacitors, piezoelectric transducers, wireless communication, pyroelectric elements and positive temperature coefficient (PTC) sensors, microphones and opto-electronic devices. The structure of  $\text{BaTiO}_3$  structure is important because its properties depend on its crystallographic phase. For example, the cubic phase has paraelectric properties, while the tetragonal phase does not exhibit these properties. The barium titanate structure acquired optic properties after doping with rare earths<sup>[3,4]</sup>. A luminescent effect is provoked by the dopant ion insertion into the  $\text{BaTiO}_3$  structure; thus, the different emissions observed in the electromagnetic spectrum depend on the characteristics ion dopant. Therefore, barium titanate nanopowders doped with rare earth ions could be used in imaging devices (LCD displays, trichromatic tubes) and optoelectronic devices<sup>[5]</sup>. Furthermore, promising up-

conversion properties of barium titanate nanopowders doped with  $\text{Er}^{6+}$ ,  $\text{Er-Yb}^{7+}$  or  $\text{Yb-Er-Tm}^{8+}$  were presented<sup>[8]</sup>. However, the final properties of  $\text{BaTiO}_3$  depend on the characteristics of the particles. The method of synthesis of barium titanate is very important for controlling the shape, size, ion particle distribution, and crystallographic structure<sup>[9,10]</sup>.

Barium titanate powders have been prepared by different methods; micron-size  $\text{BaTiO}_3$  powder is generally prepared by solid-state reaction<sup>[11]</sup>, using high temperature ranges (1000–1300 °C);  $\text{BaTiO}_3$  nanopowders can be synthesized by chemical methods such as the co-precipitation method<sup>[12]</sup>, sol-gel process<sup>[13,14]</sup>, and the hydrothermal method<sup>[15,16]</sup>. With chemical methods, the nanopowders obtained present a cubic<sup>[17]</sup> or tetragonal<sup>[18]</sup> structure.  $\text{BaTiO}_3$  powders, albeit with large-grained particles with uncontrolled and irregular morphology, were obtained by the microwave sintering method.

Investigations into the size of  $\text{BaTiO}_3$  particles are of great interest in relation on their dielectric and ferroelectric properties. When the hydrothermal method is used for the sintering of  $\text{BaTiO}_3$  nanopowders, a small particle

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size can be obtained<sup>[19]</sup>. When the particle size of BaTiO<sub>3</sub> is sufficiently small, the paraelectric-ferroelectric phase transition vanishes, and the cubic phase can be stabilized at room temperature, in contrast to the ferroelectric tetragonal form. Recent studies have shown the possibility of stabilizing the cubic phase to yield particles under 30 nm<sup>[20,21]</sup>.

Some researchers have offered hypotheses to explain the effects of grain size on ceramics, which describe the presence of electric fields of depolarization in the compound and tensions in the grain. Arlt et al.<sup>[22]</sup> suggest that the effect of grain size on the ferroelectric-paraelectric temperature transition is due to tensions present in the grains.

In the present work, structural studies of BaTiO<sub>3</sub>:Er<sup>3+</sup> and BaTiO<sub>3</sub>:Yb<sup>3+</sup> nanopowders synthesized by hydrothermal method were discussed. The samples were characterized by X-ray diffraction (XRD), FTIR and Raman spectroscopies as well as high resolution transmission electron microscopies (HRTEM).

## 1 Material and methods

Erbium and ytterbium doped BaTiO<sub>3</sub> nanopowders were synthesized by the hydrothermal method, using barium chloride [BaCl<sub>2</sub>], titanium butoxide [C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti], erbium chloride [ErCl<sub>3</sub>] and ytterbium chloride [YbCl<sub>3</sub>] as precursors. Anhydrous methanol was used as a solvent. Metallic potassium promoted the solubility in the system and increased the pH to 13. This hydrothermal method allows the formation of a predominantly cubic structure in both Er<sup>3+</sup>- and Yb<sup>3+</sup>-doped BaTiO<sub>3</sub> powders. For this method, a stainless autoclave of 45 mL was used; the hydrothermal process took place inside the autoclave due to temperature and pressure conditions. The temperature and time were varied during the synthesis of nanoparticles. In order to perform the synthesis, 0.35 g of barium chloride were added to 13 mL of anhydride methanol; while in another container, the ytterbium was dissolved in 2 mL of anhydride methanol. The potassium was dissolved in a controlled atmosphere to avoid the humidity. Finally, to obtain the final dissolution, the above mixtures were combined. The molar ratio used was Ba/Ti=1.6, to promote barium vacancy. After the synthesis of barium titanate, the obtained powders of barium titanate were cleaned to remove impurities, and after washing, the powders were dried at 90 °C.

The IR spectra were recorded using a Perkin Elmer 2000 FT-IR; the range was 2500–400 cm<sup>-1</sup>. Raman spectroscopy analysis was conducted with Horiba-Jobin Yvon equipment and a LabRAM HR800 model with 1 cm<sup>-1</sup> resolution; the studied range was 150–1000 cm<sup>-1</sup>. The crystallographic phase of BaTiO<sub>3</sub> was identified using a diffractometer Bruker AXS D8 Advance; the scan was 0.05 (°)/s, and the 2θ range was 0° to 90°. The Ba-

TiO<sub>3</sub> micrographs of the obtained powders were obtained by HRTEM (JEM-2299FS), operating at 200 kV.

## 2 Results and discussion

### 2.1 Infrared spectroscopy

The infrared spectra presented in Fig. 1 show absorption peaks at ~1630 cm<sup>-1</sup>, corresponding to the bending vibrations of O–H corresponding to coordinated H<sub>2</sub>O, as well as Ti–OH.

The presence of OH<sup>-</sup> groups was originated by hydrolysis of the nanoparticles surface with alcohol and water compounds. The synthesis performed at 180 °C and 36 h produced high quality powders. Fig. 1 shows the fingerprint absorption bands relating to BaTiO<sub>3</sub>, situated at ~545 and ~410 cm<sup>-1</sup><sup>[23,24]</sup>. The absorption bands correspond to Ti–O<sub>I</sub> stretching vibrations and O<sub>I</sub>–Ti–O<sub>II</sub> torsion vibrations, related to the Ti–O<sub>6</sub> octahedron<sup>[25]</sup>. From the synthesis conditions used, it can be observed that the CO<sub>3</sub><sup>2-</sup> group is characterized by absorption bands in the region 1080–1250 cm<sup>-1</sup>. BaCO<sub>3</sub> compound present in the crystallite was probably due to the reaction of residual Ba<sup>2+</sup> with CO<sub>2</sub> in the air, mixed into the crystallite after thermal treatment<sup>[26]</sup>. The BaTiO<sub>3</sub> matrix is composed of Ti–O<sub>6</sub> octahedrons, and the Ba<sup>2+</sup> is located at the center of eight Ti–O<sub>6</sub> octahedrons. The so-called OH defect is formed by one proton with an oxygen molecule of the octahedron<sup>[27]</sup>. It requires a charge compensator to maintain the neutrality of the crystallites. The negatively charged cation vacancy could act as the compensator. The Ti–O<sub>6</sub> octahedron is the most stable form of Ti<sup>4+</sup> and is the basic structural element in perovskite BaTiO<sub>3</sub>. Thus, the Ba<sup>2+</sup> vacancy is proposed as the most probable compensator.

### 2.2 XRD analysis

The X-ray diffraction patterns of BaTiO<sub>3</sub>:Er<sup>3+</sup> and BaTiO<sub>3</sub>:Yb<sup>3+</sup> nanopowders are presented in Fig. 2. The pat-

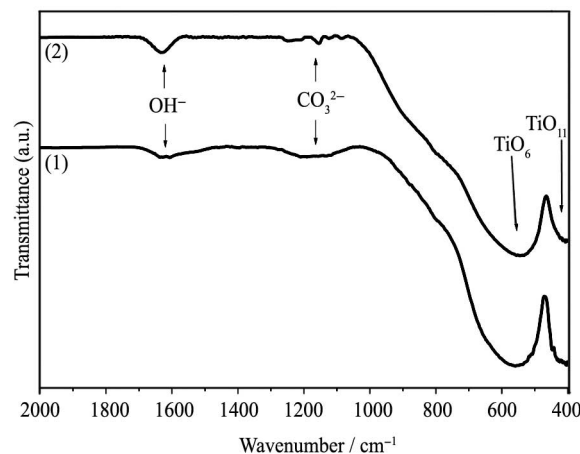


Fig. 1 IR spectra of BaTiO<sub>3</sub>:Er<sup>3+</sup> (5 mol.%) (1) and BaTiO<sub>3</sub>:Yb<sup>3+</sup> (6 mol.%) (2) nanopowders obtained by hydrothermal method

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