

## Nanofibers Obtained by Electrospinning of BaTiO<sub>3</sub> Particles Dispersed in Polyvinyl Alcohol and Ethylcellulose

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Received: September 17, 2012; Revised: January 03, 2013

Barium titanate particles (100-300 nm) synthesized by hydrothermal method were dispersed in both polyvinyl alcohol (PVA) and ethylcellulose (EC) solutions. These suspensions were processed by electrospinning. When no particles were added, homogeneous polymeric nanofibers were obtained. Under certain conditions, polymeric suspensions of barium titanate particles were electrospun generating polymeric fibers with BT particles. The effect of a surfactant was also assessed over the formation of nanofibers. The BaTiO<sub>3</sub> particles synthesized by hydrothermal method were characterized by X-Ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and Raman spectroscopy. Fibers were characterized by scanning electron microscopy (SEM).

**Keywords:** BaTiO<sub>3</sub>, electrospinning, ethylcellulose, polyvinyl alcohol, hydrothermal

### 1. Introduction

Barium titanate (BaTiO<sub>3</sub> or BT) is widely used as dielectric material in ceramics capacitors<sup>1</sup>. Among the many crystallographic forms, the tetragonal phase is ferroelectric and it has a high dielectric constant at about 130 °C, above which, the unit cell transforms into a paraelectric cubic structure<sup>2,3</sup>.

Material properties are affected by the different synthesis routes. Many methods have been used to prepare BT powders such as sol-gel<sup>4-6</sup>, hydrothermal<sup>7-9</sup> and mechanochemical activation<sup>10</sup>. The hydrothermal method may give an alternative route to synthesize oxide powder with controlled characteristics in one-step process, by means of an aqueous systems and relatively low temperatures. Nevertheless, BT powder synthesized under hydrothermal conditions with good crystallinity has ultrafine particle size and narrow size distributions<sup>11</sup>. However, BT powders prepared by conventional hydrothermal method, often exhibit a higher degree of tetragonality than that of BT obtained by other aqueous chemical methods<sup>8,12</sup>. Dutta et al. reported that barium chloride favors tetragonal phase compared with other barium precursors<sup>9</sup> and Pinceloup et al. studied the mechanism of BT formation starting from titanium alcoxides dissolved in organic solvents<sup>7</sup>. Alternative solvothermal methods have strong influence on the crystal growth and dispersability of particles by using organic solvents instead of water solvent<sup>13</sup>. Based on these studies, the hydro-solvothermal may be a proper method for the synthesis of BT particles.

On the other hand, electrospinning has been recognized as an efficient technique to make polymeric nanofibers<sup>14</sup>. In the last decade, materials based on organic and inorganic

species at a nanoscale have been developed by many researchers, among them, Shao et al. reported the preparation of nanofibers of poly(vinyl alcohol)/silica composite<sup>15</sup>, and Bai et al. obtained composite nanofibers of PVA and gold nanoparticles by electrospinning<sup>16</sup>. Highly magnetic composite nanofibers (Fe<sub>3</sub>O<sub>4</sub>/PVA) were also prepared by this technique<sup>17</sup>. In this work ethylcellulose was used because of its solubility in several organic solvents, easy burn and harmless as well as its little abrasiveness during processing<sup>18</sup>. Also, functional groups on the surface of BT particles surface interact through hydrogen bonds with this polymer. The other selected polymer was PVA. In addition, the surfactant effect on dispersions is assessed by using Triton, a non-ionic-surfactant.

### 2. Experimental Procedure

#### 2.1. Hydrothermal Synthesis (HT)

The barium titanate synthesis was carried out according to previous work<sup>3</sup>. Briefly, titanium isopropoxide (TIP, 97%, Aldrich) was dissolved in absolute ethanol and stabilized with anhydrous acetic acid (Cicarelli, 99.5%). The TIP sol was added to a BaCl<sub>2</sub>·2H<sub>2</sub>O (Mathson Colem & Bell, 99%) aqueous solution with the Ba/Ti ratio equal to 1.1. The pH was fixed at 14 by the addition of a KOH solution. The mixture was transferred into a PTFE-lined stainless steel vessel for hydrothermal treatment at 180 °C in a silicon oil bath with constant stirring. After 24 hours, the reactor was left to naturally cool to room temperature inside the oil bath. The resulting dispersions were washed with acetic acid in order to remove barium excess. After washing several times

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with water, powders were left overnight at 60 °C for drying. The final product was characterized by X-ray diffraction (XRD, PANalytical X'Pert), field-emission scanning electron microscopy (FE-SEM, Zeiss Supra 35), Raman spectroscopy (Renishaw in Via, 514 nm Ar-ion laser) and transmission electron microscopy (TEM).

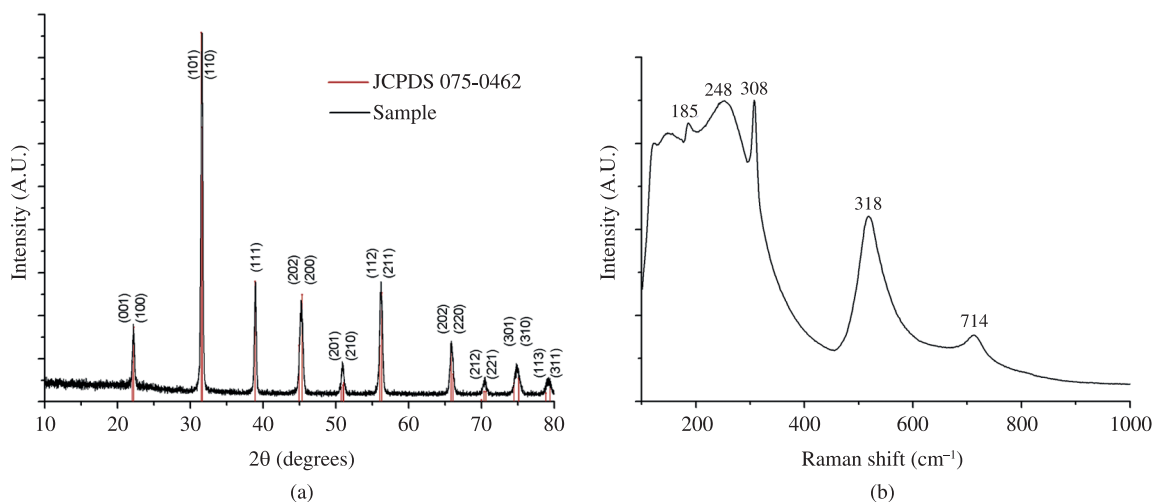
## 2.2. BT dispersions for electrospinning

The obtained BT dry powders were dispersed in polyvinyl alcohol (PVA) and ethylcellulose solutions. A polyvinyl alcohol (PVA 77-79 kDa, J.T. Baker, 99-99.8%) 10% wt./v solution was prepared in distilled water at 80 °C with constant stirring to promote dissolution. Once cooled to room temperature, BT was added in 4-5.5% wt. to the polymeric solution under vigorous stirring.

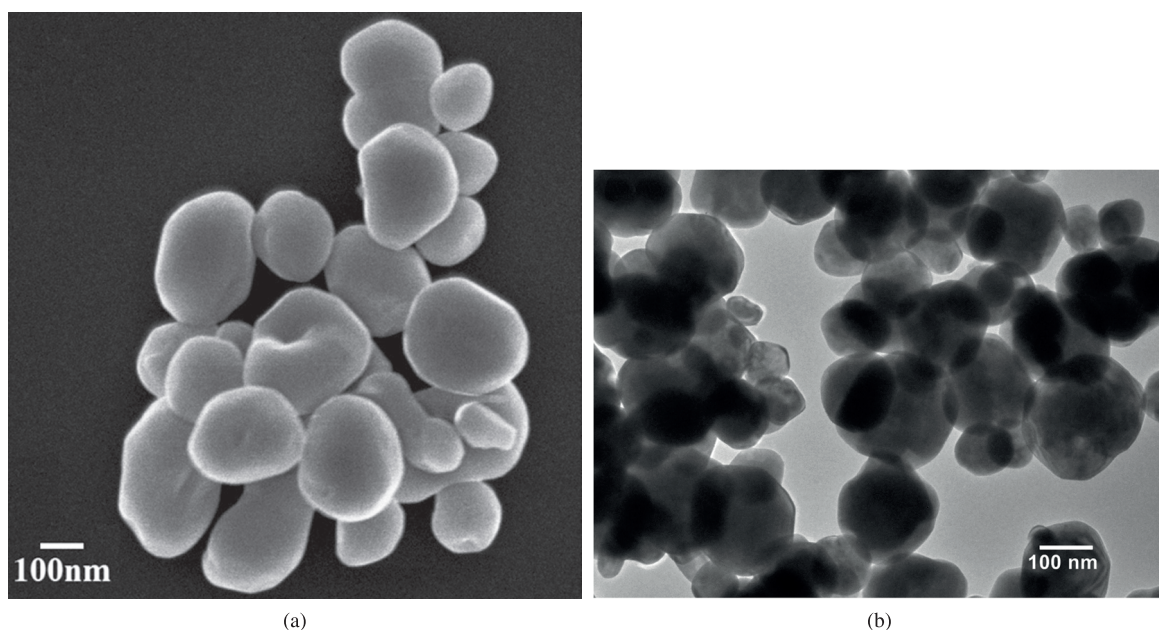
Simultaneously, an ethylcellulose (EC, Fluka, 48-49.5% ethoxyl groups) 13% wt./v solution was prepared in a solvent mixture of tetrahydrofuran (THF, Anedra, 99.9%) and N,N-dimethylformamide (DMF, Cicarelli, 99.8%) in a 20:80 ratio. BT particles were added to this solution in a 29.5% wt./v under stirring. Both PVA and ethylcellulose dispersions were treated with an ultrasonic probe at 300 W and 24 kHz for 30 minutes to ensure mixing. The effect of dispersing Triton X-100 (Aldrich) was also studied.

## 2.3. Electrospinning procedure

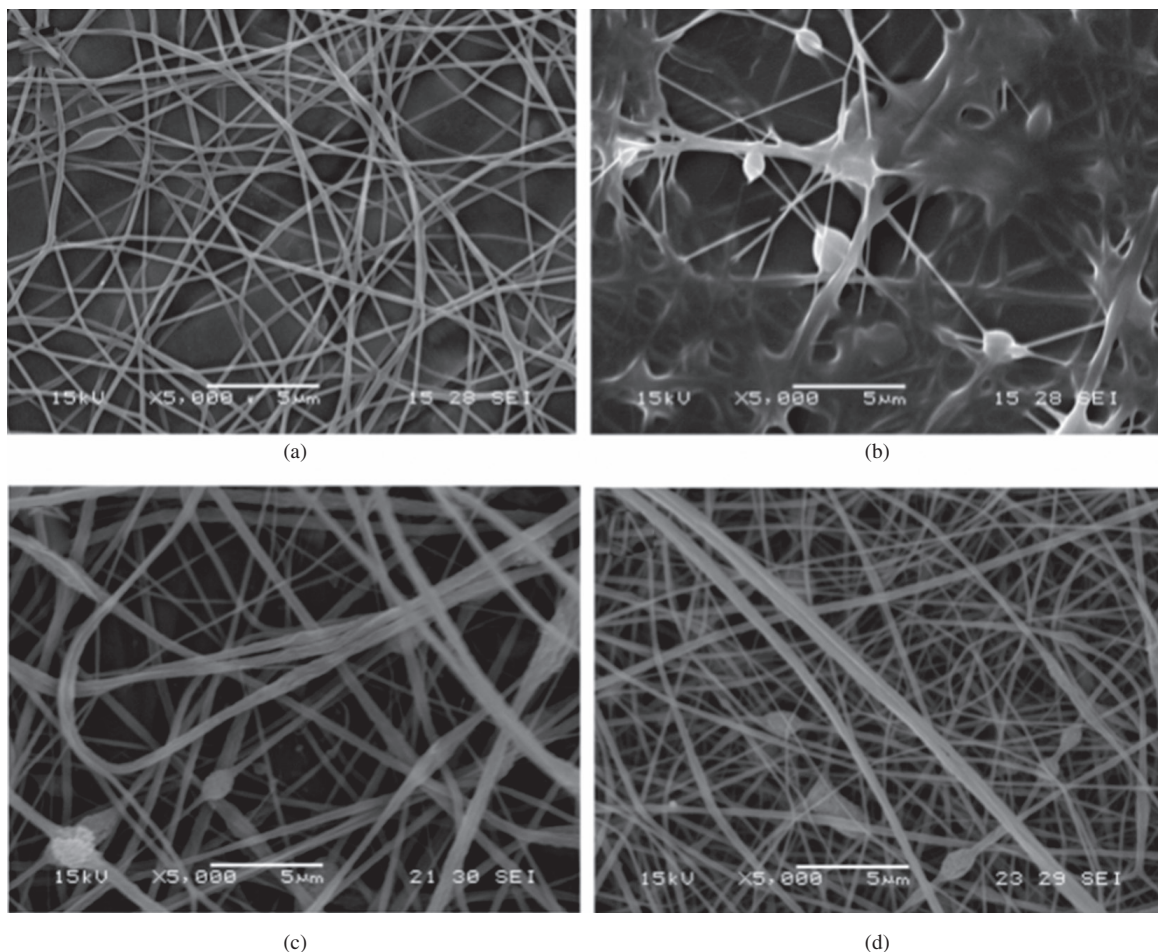
A Gamma High Voltage Research (0-30 kV) power supply was connected to a stainless steel needle attached to a plastic syringe containing the BT-PVP or BT-EC dispersions. The applied voltage between the needle and the metallic



**Figure 1.** a) X-ray diffraction pattern of the synthesized BT powder, and b) corresponding Raman spectrum.



**Figure 2.** a) FE-SEM and b) TEM images of BaTiO<sub>3</sub> particles as obtained by HT synthesis.

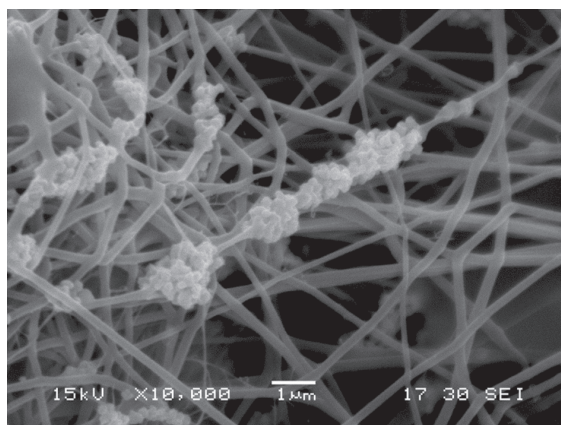


**Figure 3.** SEM images of a) PVA/H<sub>2</sub>O; voltage: 18 kV; flow rate: 0.2 mL/h; distance: 12 cm; without Triton. b) Idem with Triton. c) EC/THF/DMF; 13 kV; 0.5 mL/h; 10 cm without Triton. d) Idem with Triton. Notice that the electrospinning conditions for fiber forming are different for each polymeric system.

collector was 10-20 kV with a constant distance between them of 10-12 cm. The dispersion flow was controlled by means of a syringe pump (AcTIVA Prestige-equipment) which fed the mixture at rates from 0.2 to 0.5 mL/h.

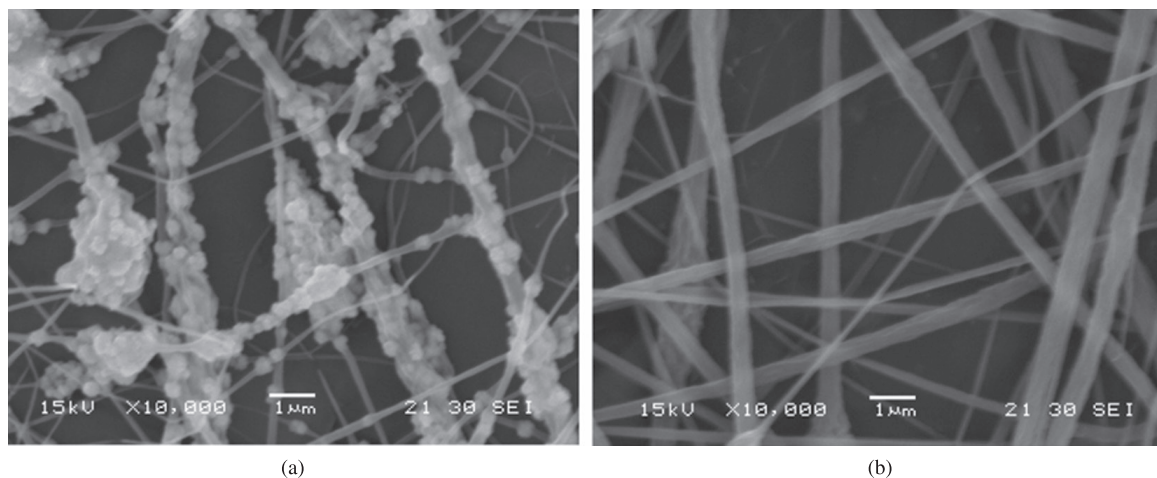
### 3. Results and Discussions

Figure 1(a) shows the X-ray diffraction pattern of the BT powder obtained by hydrothermal synthesis at 180 °C for 24 hours. The characteristic split of the (200) peak is not observed, which indicates that the material did not crystallize in the tetragonal phase. This figure also shows the matching with the JCPDS 075-0212 file from cubic BaTiO<sub>3</sub>. On the other hand, the results from Raman spectroscopy shown in Figure 1b, revealed certain degree of tetragonality. The narrow bands at 185 cm<sup>-1</sup> [A<sub>1</sub>(TO), E(LO)] and 308 cm<sup>-1</sup> [B<sub>1</sub>, E(TO + LO)], and the broad bands at 248 cm<sup>-1</sup>, 518 cm<sup>-1</sup> and 714 cm<sup>-1</sup>, associated with vibration modes [A<sub>1</sub>(TO)], [A<sub>1</sub>, E(TO)] and [A<sub>1</sub>, E(LO)], respectively<sup>19,20</sup>, confirmed the presence of the BT tetragonal phase. The phase purity is also confirmed in this spectrum, in which only the characteristic bands of BaTiO<sub>3</sub> are observed.



**Figure 4.** SEM images of PVA/H<sub>2</sub>O; voltage: 18 kV; flow rate: 0.2-0.5 mL/h; distance: 10 cm; BT content: 4,7% wt.

Figure 2 shows the FE-SEM and TEM images of the synthesized powder. The BT particles are almost spherical with sizes in the 100-300 nm range. However, some particles exhibit slightly beveled edges which can be explained by



**Figure 5.** SEM images of a) EC/THF/DMF 20/80; voltage: 13 kV; flow rate: 0.2-0.4 mL/h; distance: 10 cm; BT content: 29,5% wt., b) without BT.

the preferred formation of frame cubic growth units of BT in a solution with 1.1:1 Ba/Ti molar ratio<sup>21</sup>. Also, most of particles have smooth surfaces and slight depressions, which were originated by the particle formation mechanism after the fusion of former smaller particles during the synthesis process as discussed in<sup>3</sup>.

Figure 3 shows the effect of Triton on the PVA and EC fibers (without BT particles). The surfactant had a deleterious effect on PVA fiber forming. Among other causes, fibers remained wet when reaching the collector. On the other hand, Triton did not modify significantly the EC fibers.

The addition of BT powder to PVA solution, Figure 4, shows that particles are not uniformly distributed within the polymeric matrix, generating few interconnected agglomerates supported by polymer fibers.

Figure 5 (a) shows EC fibers with BT particles. Although particles are agglomerated, they are well distributed in the fiber mat. A higher amount of particles (29.5% wt.)

was added to this system with respect to the PVA fibers. Figure 5 (b) shows EC fibers without BT particles obtained under the same processing conditions.

Further work is needed in order to obtain fibers with particles not agglomerated and aligned in the fiber direction.

#### 4. Conclusions

The hydrothermal method produced crystalline tetragonal barium titanate as determined by Raman spectroscopy. The powder consisted of particles with spheroidal morphology and homogeneous size. Electrospinning is an effective process for the formation of nanofibers of different polymers. PVA and EC nanofibers were obtained without and with the addition of BT particles. The addition of Triton X-100 was deleterious for PVA fibers, whereas it did not modify the EC fibers. Barium Titanate-Ethylcellulose fibers, with ceramic content of about 30% wt., showed the presence of particles dispersed in the fiber mat.

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