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Synthesis and Characterization Of Pure and Mn-Doped $BaTiO_3$ Nanofibers

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Over the last few decades, one dimensional nanomaterials such as nanotubes and nanofibers, have attracted great attention due to their unique structure and properties, i.e. large specific surface area and chemical/mechanical stabilities. Thus nanofibers can be used as building blocks in nanotechnology [1,2]. Previously, several ceramic nanofibers have been synthesized by various processes, e.g. solution method, laser ablation, chemical vapor deposition (CVD), sol-gel, hydrothermal method and mechanochemical activation. On the other hand, electrospinning has been recognized as an efficient technique to make polymeric nanofibers [3]. Recently, there has been an intense research effort on electrospinning of ceramics since it is a straightforward way to synthesize nanostructures.

Barium titanate, $BaTiO_3$ (BT) is widely used as dielectric material in ceramic capacitors [4], it is also one of the extensively studied ferroelectric material with wide range of applications in non-volatile ferroelectric random access memories, as transducers, sensors and actuators, etc [5].

The synthesis of pure and Mn-doped $BaTiO_3$ nanofibers, were synthesized by the electro-spinning technique. A detailed description of the procedure can be found in the literature [6]. In this work, the precursor solution was composed by poly(vinylpyrrolidone) (PVP), barium acetate $Ba(C_2H_3O_2)_2$, titanium isopropoxide $Ti[OCH(CH_3)2]_4$ and manganese acetate $Mn(C_2H_3O_2)_2$ dissolved in ethanol/acetic acid. The solution was heated at 25°C with stirring for 5 hours and then delivered into a metallic needle at a constant flow rate of 0.3 mL/h by a syringe pump. The metallic needle was connected to a high-voltage power supply and a grounded aluminum foil was placed 15 cm from the needle tip.

With an applied high-voltage of 15 kV, the precursor solution jet was accelerated toward the aluminum foil, leading to the formation of $Ba(C_2H_3O_2)_2/Ti[OCH(CH_3)_2]_4/Mn(C_2H_3O_2)_2$/PVP fiber composite, together with a rapid evaporation of the ethanol. The composite nanofibers were then annealed 2 h at 850 °C, with a heating rate of 3°C/min, at the end of the thermal cycle, $BaTiO_3$ and $BaTi_{1-x}Mn_xO_3$ nanofibers were obtained.

The presence of a pure phase is confirmed by XRD analysis, as shown in Fig. 1, for calcined fibers, showing the formation of crystalline $BaTiO_3$. Figs. 2 and 3 show the XRD patterns from $BaTi_{0.95}Mn_{0.05}O_3$ and $BaTi_{0.95}Mn_{0.05}O_3$, respectively. In these patterns was observed the presence of additional signal from (103) and (203) planes, it is expected that they are from a Mn compound.
Fig. 4 shows a SEM micrograph of as-spun fibers. Cylindrical and randomly oriented fibers with diameter about 30-250 nm were obtained. Fig. 5 shows a TEM micrograph from isolated and calcined $BaTiO_3$ nanofibers. In this Figure, it can be observed fibers with few µm in length and an irregular morphology. Fig. 6 shows TEM micrograph from doped sample, different surface morphology is evident. Deeper characterization by TEM on fiber with different concentration are carried-out

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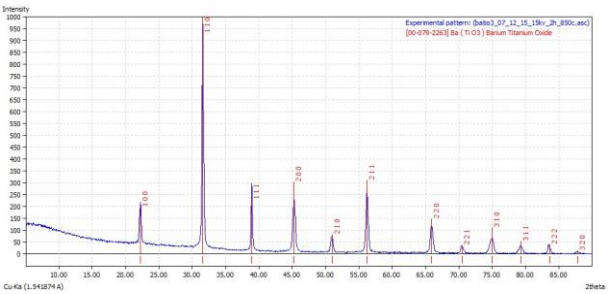

Figure 1. XRD pattern $BaTiO_3$

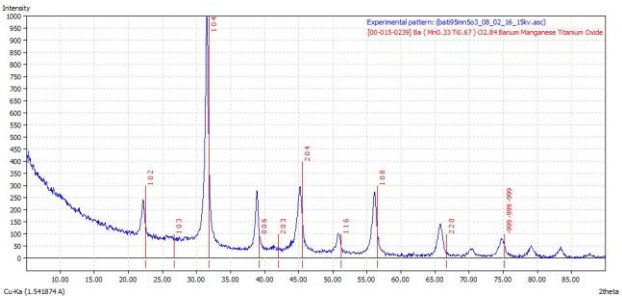

Figure 2. XRD pattern $BaTi_{0.95}Mn_{0.05}O_3$

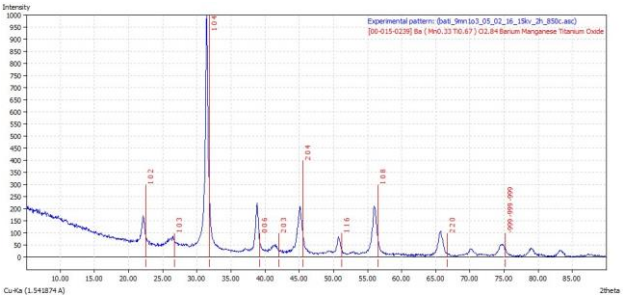

Figure 3. XRD pattern $BaTi_{0.90}Mn_{0.1}O_3$

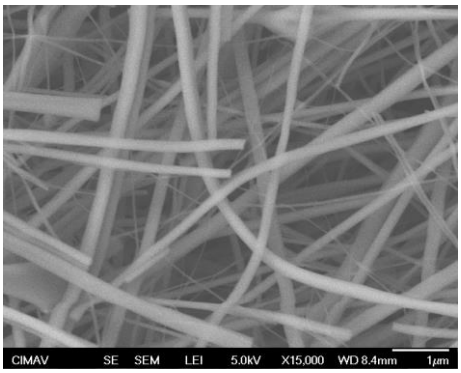

Figure 4. SEM images of as-spun $VOSO_4/Nb(OCH_2CH_3)_5/LiOH/Mn(C_2H_3O_2)2/PVP$ composite.

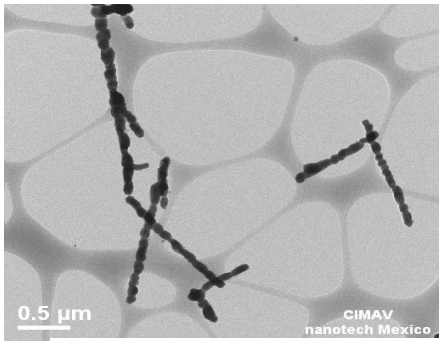

Figure 5. TEM image of a $BaTiO_3$ nanofiber.

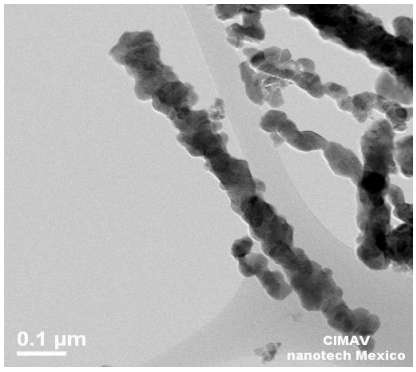

Figure 6. TEM image of $BaTi_{0.90}Mn_{0.1}O_3$ nanofibers.