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Morphology Control of $BaTiO_3$ Nanoparticles Prepared by Sol-gel Hydrothermal Method

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Barium titanate (BT), a typical ferroelectric material with a tetragonal structure bellow $T_C \approx 125$ ºC has found widespread applications especially in electronic devices. However, modern electronics demand very small functional structures and, as a consequence nanostructures of ferroeletrics are being considered. However it was observed that there is a critical size for BT nanostructures below which T_C decreases, the paraelectric cubic phase is stabilized at room temperature and then ferroelectricity may no longer exist [1]. These observations have stimulated an exponential growth of research aiming to understand the effect of scaling on the ferroelectric properties. In addition some theoretical studies predicted the enhancement of ferroelectricity in anisotropic "cylindrical" shaped nanoparticles [2]. Therefore, the morphology control and fabrication of ferroelectric nanostructures with different size and shapes are of key importance. Within this context, we demonstrated that the control of the morphology of BT nanoparticulates can be achieved by hydrothermal method [3].

In this work the influence of titanium precursors and the nature and concentration of mineraliser on the morphology of BT nanoparticles prepared by sol-gel hydrothermal synthesis at 200 ºC is investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM micrographs of BT nanopowders obtained starting from titanium butoxide ($Ti(OBu)_4$) reveal the formation of round shaped particles of ~60 nm size (Fig 1a). When titanium isopropoxide ($Ti(O^iPr)_4$) was used as titanium source faceted BT particles of ~ 250 nm were formed (Fig. 1b). Combination of X-ray diffraction (XRD), Raman spectroscopy and high resolution TEM (Fig. 1c) suggested that the BT faceted particles have pure tetragonal structure and present ferroelectric switching as verified by Piezoresponse Force Microscopy (PFM) (Fig. 1d). In the round shaped BT particles a local tetragonal structure rather than cubic structure exists.

Regarding the influence of the nature of mineraliser SEM analysis reveal the formation of cuboid shaped particles when using aqueous solution of sodium hydroxide (NaOH) (Fig. 2a). In the presence of tetramethyllammonium hydroxide ($N(CH_3)_4OH$) the coexistence of small nanorods (NRs) and round shaped nanoparticles is observed by SEM (Fig 2b). Combination of XRD, Raman, and HRTEM (Fig. 2c) demonstrated that the round particles are crystalline BT and the NRs are amorphous anatase.

Another important result of this study is the increasing of BT particles size with cuboid morphology as the concentration of NaOH is increased from 5 M to 10 M (Fig. 3a and b). Various shapes of faceted BT particles (rods, cubes, tetrahedral, rectangle) are obtained when increasing the NaOH concentration to 12 M and 20 M, respectively (Fig. 3c and d).

This work proves that defect free tetragonal BT can be obtained at low temperatures by tuning the precursor's chemistry.

References

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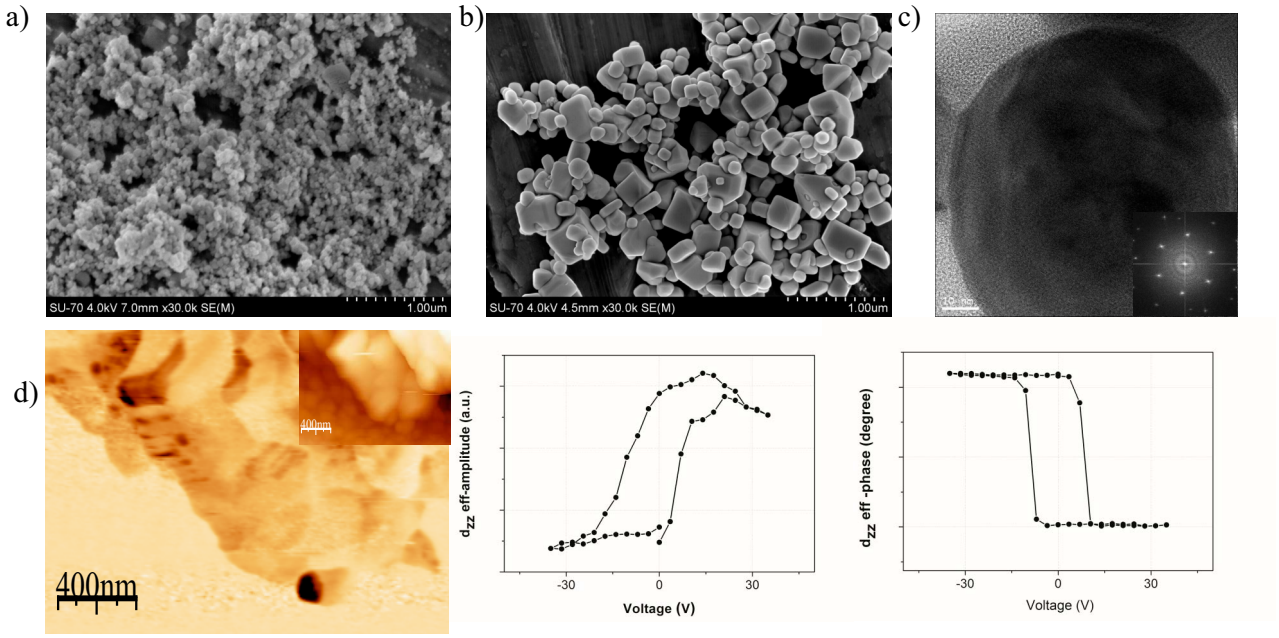

Figure 1. The influence of titanium precursor: a) SEM of BT-Ti(OBu)4 sample, b) SEM, c) HRTEM and d) PFM of BT-Ti(OiPr)4 sample.

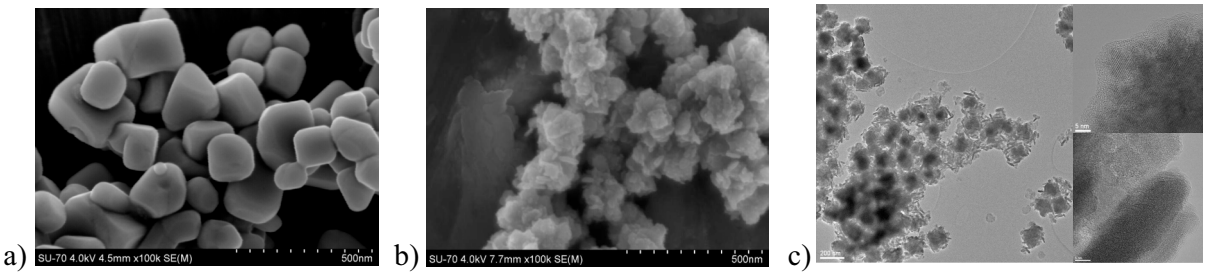

Figure 2. The influence of the mineraliser: a) SEM of BT-NaOH sample, b) SEM and c) TEM of BT-N(CH3)4OH.

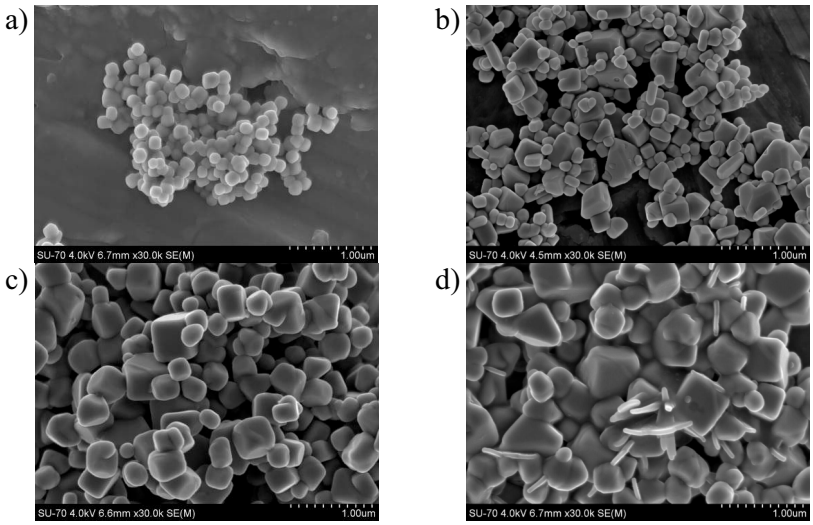

Figure 3. The influence of mineralizer concentration: SEM of a) BT-NaOH 5M, b) BT-NaOH 10M, c) BT-NaOH 12M, and d) BT-NaOH 20M.

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