NANOTUBES OF $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ PREPARED BY SOL-GEL CHEMISTRY

Marin CERNEA[1], Adelina Carmen IANCULESCU[2], Bogdan Stefan VASILE[3], Catalina Andreea VASILESCU[4]

Nanotubes of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ with an average diameter of 80 nm and wall thickness of ~8 nm were prepared from the precursor sol using as template a polycarbonate membrane with the pores diameter size of 100 nm. The Ce doped-$BaTiO_3$ nanotubes calcined at 700 ºC, 1h in air crystallized on the lattice of $BaTiO_3$ cubic phase as indicated the high resolution transmission electron microscopy and selected area electron diffraction analyses. The nanotubes showed a polycrystalline structure with crystallites of 3-5 nm size. The results prove that we can prepare $BaTiO_3$ doped with 5 at.% Ce nanotubes for future capacitor applications.

Keywords: Nanotubes; Sol-gel preparation; Microstructure; Spectroscopy.

1. Introduction

Barium titanate ($BaTiO_3$, abbreviated as BT) has been widely used in the ceramic capacitors industry [1]. Based on its functional properties such as switchable polarization, piezoelectricity, non-linear optical activity, pyroelectricity and non-linear dielectric behavior, BT has applications as sensors, microactuators, infrared detectors, microwave phase filters and non-volatile memories [2,3]. Pure barium titanate is a high insulating material. By adding dopants, very interesting characteristics for various applications can be obtained [4]. The effect of substitution on dielectric relaxation, ferroelectric phase transition and electrical properties of $BaTiO_3$ has been extensively studied [5,6]. Doping $BaTiO_3$ with cerium is interesting because of their high endurance under dc field stress, grain growth inhibition, and the effective Curie temperature shift [7-10]. In order to reduce the size of microelectronics devices, many efforts have been dedicated to the development of new fabrication strategies of micro- and

[1] National Institute of Materials Physics, P.O. Box MG-7, Bucharest-Magurele, Romania
[2] Department of Oxide Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania
[3] Department of Oxide Materials Science and Engineering, University POLITEHNICA of Bucharest, Romania
[4] Department of Oxide Materials Science and Engineering, University POLITEHNICA of Bucharest, and National Institute for Lasers, Plasma and Radiation Physics, P.O. Box MG54, Magurele, Romania, e-mail: katyvasilescu85@yahoo.com

nanoscale ferroelectric structures. Ferroelectric nanotubes with different external and internal electrodes are useful for memory application [11]. In the recent years, the nanotubes and nanowires show a great scientific and applied interest. The ferroelectric and piezoelectric properties of $BaTiO_3$ with one-dimensional form depend on their size (length and diameter). These materials have applications in nanoscale devices including memory, transducers, sensors, etc. [12-17]. Also, due to the enhanced dielectric and optical properties observed in ferroelectric nanotubes, these may be used in microwave devices. $BaTiO_3$ nanowires of 10 nm diameter still retain their ferroelectric properties, and nonvolatile polarization domains with dimensions as small as 100 nm^2 can be induced in these nanowires [18]. This suggests the possibility of fabricating $BaTiO_3$ nanowire-based nonvolatile memory devices with an integration density approaching 1 terabit/cm^2 [12,16,19,20]. Particularly, oxide nanotubes exhibiting ferroelectric or piezoelectric properties can serve as components or nano-electromechanical systems (NEMS) [21]. $BaTiO_3$ nanotubes and nanowires were prepared using a porous alumina or macroporous silicon templates [22,23] or by a controlled hydrothermal synthesis method [18]. The fabrication of Ce doped-$BaTiO_3$ nanowires is not reported in literature, until now.

In this paper, we report on the preparation procedure of 5 mol % Ce doped-$BaTiO_3$ ($Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$) nanotubes using sol-gel method and porous polycarbonate membrane template with 100 nm pores diameter. Also, we investigated their structure and micro-structure.

2. Materials and methods

In order to prepare nanotubes of barium titanate doped with cerium, a sol-gel method and a polycarbonate membrane were used. Precursor sol of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ was prepared starting from barium acetate ($Ba(CH_3COO)_2$, 99%, Aldrich), titanium (IV) isopropoxide, 97% solution in 2-propanol ($Ti\{OCH(CH_3)_2\}_4$, Aldrich) and cerium acetate ($Ce(CH_3CO_2)_3$, 99,9%, Aldrich). Barium and cerium acetates were dissolved in acetic acid, at 70 °C, under continuous stirring. As stabilizer for the sol, 2-methoxyethanol and acetylacetone in 2:1 volume ratio were used. A sol with the concentration of 0.3 M and pH=2-2.5 as-prepared it has proved to be optimal for making cerium doped $BaTiO_3$ nanotubes using a polycarbonate membrane with thickness of 20 µm, pore diameter of 100 nm and 10^8 cm^{-2} pore density. The sol precursor was poured on the membrane and centrifuged with 3000 rpm for 20 seconds using a spinner. The sol wets the pore walls of porous membrane and fills the pores. The prevention of surface film formation on one side of the membrane was achieved by washing the surface of the membrane with propanol. Then, the membrane with sol was kept for two days in air to complete transformation of the sol to a gel. Such nanotubes that reinforced polycarbonate membranes were separated by dissolving the membrane in chloroform. The tubes were separated from the solution by repeated centrifugation and washing with isopropanol.

It should be noted that the sol passes through the membrane pores without spinning, only if the concentration is low. The nanotubes were deposited from isopropanol suspension on $Pt/TiO_2/SiO_2/Si$ substrates, then dried at 100 °C and calcined at 700 °C, 1 h in air. The as-obtained cerium doped $BaTiO_3$ nanotubes shown a policrystalline perovskite structure.

The structure and microstructure of the Ce doped-$BaTiO_3$ nanotubes was investigated by electronic microscopies SEM and TEM using a FEI Quanta Inspect F scanning electron microscope and, a Tecnai^{TM} G^2 F30 S-TWIN transmission electron microscope with a line resolution of 1Å, in high resolution transmission electron microscopy (HR-TEM) mode and selected area electron diffraction (SAED).

3. Results and discussion

3.1. Microstructure

The SEM micro-graphs of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ dried nanotubes are presented in Fig. 1.

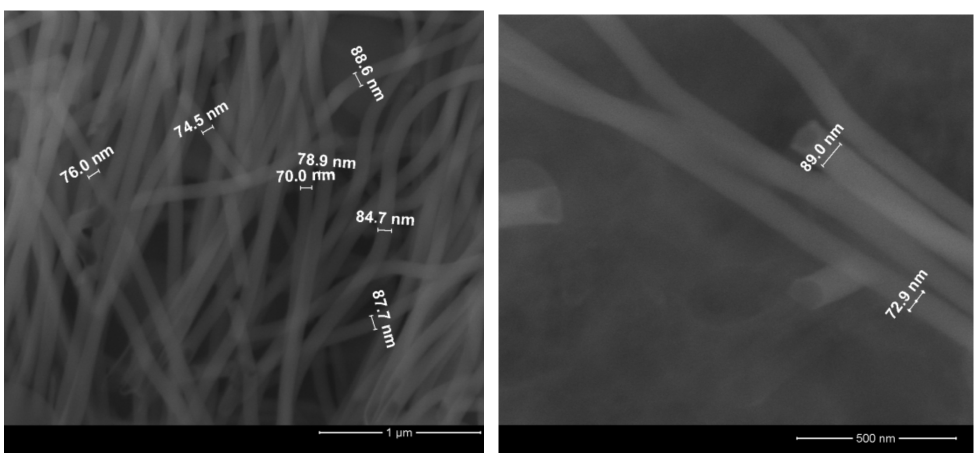

Fig.1. SEM images of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ as-prepared nanotubes: (a) and (b)

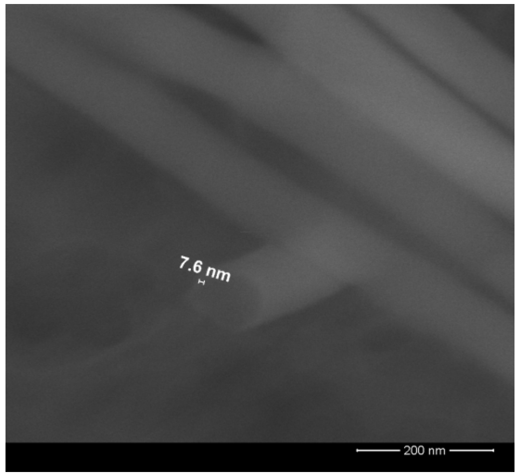

Fig.1. SEM images of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ as-prepared nanotubes: (c) details

As it can be seen in Fig. 1, the nanotubes dried at 100 °C show an average diameter size of 80 nm (Fig. 1(a)) and a wall thickness of ~8 nm (Fig. 1(b)). The SEM images of the $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ calcined nanotubes presented in Fig. 2 indicate an average diameter size of 65 nm.

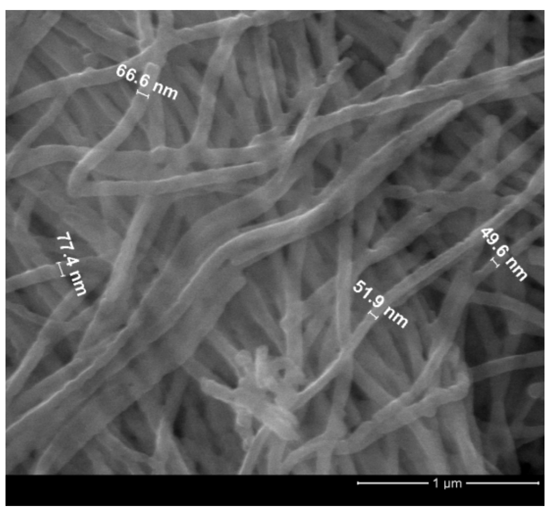

Fig. 2. SEM images of $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes calcined at 700 °C, 1h

During the calcinations stage, the dried $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes undergo processes of densification and shrinkage and results tubes with diameter smaller than of un-calcined ones. The TEM images (Fig.3) of

$Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ calcined nanotubes indicate that the nanotubes contain grains with crystallites and amorphous zones among crystallites.

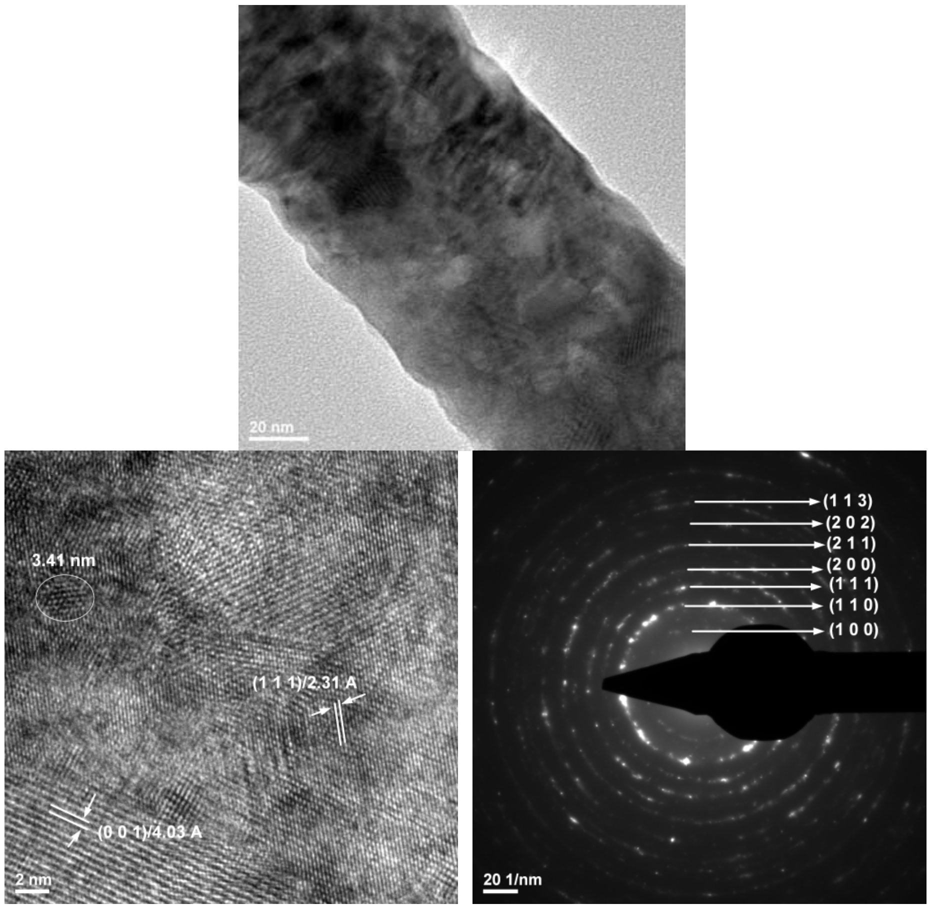

Fig. 3. TEM (a), HR-TEM (b) images and SAED spectra (c) for $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes calcined at 700 °C, 1h

The nanotubes have grains of 15-20 nm, consisting of crystallite of 3-5 nm (Fig. 3(a)-(b)). The high-resolution TEM image (Fig. 3(b)) indicates the lattice planes (111) and (001) corresponding to the interplanar space d = 2.31 Å and d = 4.03 Å, respectively. The SAED spectra (Fig. 3(c)) show the lattice planes (100), (110), (111), (200), (211), (202) and (113). The HR-TEM image and the SAED spectra indicate well crystallized $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes on the cubic structure of $BaTiO_3$ (pattern PDF 79-2263) [24].

4. Conclusions

Sol-gel method and a porous polycarbonate membrane template were successfully used to prepare cerium doped-$BaTiO_3$ nanotubes. The main parameters for preparation of these nanotubes are pH=2-2.5 and 0.3 M concentration of the precursor sol and centrifugation with 3000 rpm for 20 seconds. The as-prepared $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ nanotubes show < 20 μm length, an average diameter of 80 nm and wall thickness of ~ 8 nm. After calcinations at 700 °C, 1h in air, the nanotubes show a polycrystalline structure with grains size of 15 - 20 nm and crystallites of 3 - 5 nm. The tubes show as single phase, the cubic $BaTiO_3$ phase. This work can potentially be used to develop one-dimensional dielectric and ferroelectric nanostructures for various electric applications.

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