Preparation and Ferroelectric Properties of Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) Nanotubes

Juntai Chen\(^a\), Qiqi Zhou\(^b\), Yang Liu\(^c\), Youming Dong\(^d\), Mengen Ma\(^e\), Xiangyun Deng\(^f\)*

College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China
Email: \(^a\)1015323770@qq.com, \(^b\)294766425@qq.com, \(^c\)1412311964@qq.com, \(^d\)1759099527@qq.com, \(^e\)1031950727@qq.com, \(^f\)xiangyundtj@126.com

Abstract. In this paper, the microstructure and ferroelectric properties of Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes were prepared by hydrothermal method using TiO\(_2\) nanotube as templates. Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes at different concentration of Ca(CH\(_3\)COO)\(_2\)•H\(_2\)O and (CH\(_3\)CO\(_2\))\(_3\)Ce•xH\(_2\)O were investigated. The experimental results show that increasing the concentration of (CH\(_3\)CO\(_2\))\(_3\)Ce•xH\(_2\)O and Ca(CH\(_3\)COO)\(_2\)•H\(_2\)O are beneficial to the transition of TiO\(_2\) nanotubes to Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes and improve ferroelectricity, and the results show that in the Ca(CH\(_3\)COO)\(_2\)•H\(_2\)O, (CH\(_3\)CO\(_2\))\(_3\)Ce•xH\(_2\)O doping concentration of 0.032mol/L, 0.008mol/L, respectively, the surface morphology of Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes is the best. Typical hysteresis loops with remanent polarization and coercive field are 0.33 μC/cm\(^2\), and 33 kV/cm, respectively.

1. Introduction

Ferroelectric materials have been increasingly used in actuators and sensors [1]. The barium titanate is one of the most important ABO\(_3\)-type ferroelectric materials [2]. BaTiO\(_3\)-based materials therefore exhibit many kinds of useful properties and applications [3]. The A and B sites of barium titanate can be doped with other ions, the properties and structure of the doped barium titanate will be changed and the dopants will have a great effect on the polarization response of the ferroelectrics [4, 5]. Ca\(^{2+}\) can diffuse into BaTiO\(_3\) lattice, then shift the orthorhombic-tetragonal phase transition temperature of BaTiO\(_3\) [6]. Ca, Ce co-doped BaTiO\(_3\) ceramic has clear hysteresis loop [7]. Most of these are the study of powders or bulk materials, calcium and cerium doped barium titanate films or nanotubes are rarely reported.

In addition, nanotubes are one-dimensional nanostructured materials with unique high specific surface area and BaTiO\(_3\) nanotubes have been successfully prepared by hydrothermal method [8].

In this paper, Ba\((1-x-y)\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes are prepared by hydrothermal synthesis method using TiO\(_2\) nanotube as templates. The morphology, element composition and the ferroelectric properties were tested by SEM, XRD and TF Analyzer.

2. Experimental

The size of titanium foil after cutting is about 2×1.5cm, then titanium foils were cleaned with acetone, methanol, isopropanol and distilled water by ultrasonic cleaning. Each cleaning process lasts 10 minutes. Prepared titanium foils were anodized in the electrolyte containing 0.5 wt % NH\(_4\)F +150mL HOCH\(_2\)-CH\(_2\)OH +15mL deionized water with electrode distance 2cm, oxidation voltage 50V, oxidation time 6h. Titanium foils were placed on anode, the cathode electrode is platinum. Then the TiO\(_2\) nanotube templates were vertically placed in the hydrothermal reaction vessel. There were Ba(OH)\(_2\),...
Ca(CH₃COO)₂•H₂O , (CH₃CO₂)₃Ce•xH₂O and deionized water in the vessel. Then the reaction vessel was heated in the oven at 180°C for 2h. After cooling to room temperature, samples are cleaned with a large amount of deionized water. Then the samples are ready for testing. XRD (D/MAX-2500) was performed to examine the phase constitution of Ba(1-x-y)CaₓCe₂/₃TiO₃ nanotubes at room temperature. Morphology features of the specimens were investigated using SEM(SU8010,Hitachi,Japan) . The hysteresis loops of the samples were obtained by a TF Analyzer (TF2000 analyzer, aixACCT, Germany).

![Reaction process diagram](image)

**Figure 1.** Ba(1-x-y)CaₓCe₂/₃TiO₃ nanotubes preparation process.

**Table 1.** Preparation parameters of Ba(1-x-y)CaₓCe₂/₃TiO₃ nanotubes.

| Number | Ba(OH)₂ concentration [mol/L] | Ca(CH₃COO)₂•H₂O concentration [mol/L] | (CH₃CO₂)₃Ce•xH₂O concentration [mol/L] |
|--------|-------------------------------|--------------------------------------|----------------------------------------|
| 1      | 0.18                          | 0.016                                | 0.004                                  |
| 2      | 0.16                          | 0.032                                | 0.008                                  |
| 3      | 0.14                          | 0.048                                | 0.012                                  |

3. Results and Discussion

Scanning electron microscopy (SEM) images of samples with different doping concentrations show that all the samples after hydrothermal reaction are nanotube-like structures. The nanotubes after hydrothermal reaction are different from the template. Compared with the templates, the tube walls become thicker and the boundaries become blurred. Titanium dioxide nanotubes have smooth walls, but Ba(1-x-y)CaₓCe₂/₃TiO₃ nanotubes are composed of numerous nanoparticles. With the increase of doping content, the nozzle of nanotubes will be blocked, and the columnar structure will become more and more obvious.
Figure 2. Scanning electron micrographs (SEM) of the resulting samples, (a)x=0.08,y=0.02 (b)x=0.16,y=0.04 (c) x=0.24,y=0.06.

Figure 3 shows the XRD figures of Ba\((1-x-y)\)Ca\(x\)Ce\(2y/3\)TiO\(3\) nanotubes. The X-ray diffraction patterns show no other phase except perovskite structure. Meanwhile the XRD data indicate that the Ce, Ca doping causes the XRD peaks to broaden. It is important that we notice that the peaks shift to the right, this is because the ionic radius of cerium ion and calcium ion is less than that of Ba ion. We can draw a conclusion that cerium ions and calcium ions have successfully entered the parent lattice after hydrothermal reaction.
Figure 4. Hysteresis loops of the Ba\(_{1-x-y}\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes.

Figure 4 shows the hysteresis loops of Ba\(_{1-x-y}\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes measured at room temperature at 1 Hz, the applied voltage is 25 V. The P–E hysteresis loops confirm the ferroelectricity of the Ba\(_{1-x-y}\)Ca\(_x\)Ce\(_{2y/3}\)TiO\(_3\) nanotubes. With the increase of doping concentration, the residual polarization increases first and then decreases. This may because calcium and cerium ions will replace barium ions at suitable doping concentrations, however, too high doping concentration will lead to the substitution of titanium ions.

4. Acknowledgements
This project was funded by Tianjin Normal University (Grant No. 53H14049).

5. References
[1] Fang F, Yang W W, and Zhang F C Fatigue crack growth for BaTiO\(_3\) ferroelectric single crystals under cyclic electric loading 2005 J. Am. Ceram. Soc 88 2491
[2] Lou Q W, Shi X, Ruan X Z, et al Ferroelectric properties of Li-doped BaTiO\(_3\) ceramics 2018 J. Am. Ceram. Soc 101 3597
[3] Huang Y C , Chen S S, and Tuan W H, et al. Process window of BaTiO\(_3\)-Ni ferroelectric-ferromagnetic composites 2007 J. Am. Ceram. Soc 90 1438
[4] Yang Y , Hao H , Zhang L, et al Structure, electrical and dielectric properties of Ca substituted BaTiO\(_3\) ceramics 2018 Ceramics International 44 11109
[5] Liu S J , Xie Q D, Zhang L X, et al Tunable electrocaloric and energy storage behavior in the Ce, Mn hybrid doped BaTiO\(_3\) ceramics 2018 Journal of the European Ceramic Society 38 4664
[6] Chen Z h , Li Z W, et al Dielectric and ferroelectric properties of Ba\(_{0.87}\)Ca\(_{0.10}\)La\(_{0.03}\)Ti\(_{1-x}\)Sn\(_x\)O\(_3\) lead-free ceramics 2017 Journal of Physics and Chemistry of Solids 111 311
[7] Liu S J, Zhang L X , Wang J P et al Structure, dielectric, ferroelectric and diffuse phase transition properties of the Ce, Ca hybrid doped BaTiO3 ceramics 2017 Journal of the European Ceramic Society 43 36
[8] Chen D, Zhang H T, Chen R K et al Well-ordered arrays of ferroelectric single-crystalline BaTiO\(_3\) nanostructures 2012 Phys. Status Solidi A 209 714-717