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Original Research Paper

Synthesis and crystallization of lead–zirconium–titanate (PZT) nanotubes at the low temperature using carbon nanotubes (CNTs) as sacrificial templates

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$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) nanotubes with diameters of 80–100 nm and a wall thickness of 15–20 nm were prepared by sol–gel template technique and using multi-walled carbon nanotubes (MWCNT) as sacrificial templates. The coating process of MWCNT with PZT precursor sol and removal of the carbon nanotubes by an interrupt heat treatment were discussed and studied by Raman spectroscopy. Simultaneous thermal analysis (STA) revealed that PZT nanotube crystallized at the low temperature of 410 °C by the significantly low activation energy of crystallization of 103.7 kJ/mol. Moreover, based on the X-ray diffraction (XRD) pattern and selected area electron diffraction pattern the crystal structure of the PZT nanotube was determined as perovskite. High resolution transmission electron microscope (HRTEM) and field-emission scanning electron microscope (FE-SEM) images proved that the final PZT had a tubular structure.

1. Introduction

Lead zirconium titanate (PZT), a solid solution of the perovskites lead zirconate and lead titanate, is a prominent ferroelectric material that has stimulated tremendous fundamental and applied research due to its high spontaneous polarization abilities, piezoelectric coefficient, dielectric permittivity and pyroelectricity [1,2]. The highest values for both, the piezoelectric coupling coefficient (k_p) and the permittivity (ε_r) have been observed for chemical composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$, the so-called morphotropic phase boundary (MPB), at which the rhombohedral and tetragonal phases coexist [3,4]. The reason for this behaviour is currently believed to be the relatively large ionic displacements associated with stress, although various other mechanisms have also been proposed.

One-dimensional (1D) nanostructures of ferroelectric materials exhibit significant properties which recently motivated many in-depth researches on potential applications [5–7]. Synthesis of 1D PZT nanostructures has attracted significant attention due to the ferroelectric properties of the material. The presence of ferroelectric properties and domains in the nano dimension is the key of having such modern applications since usually decreasing the size of most ferroelectrics leads in vanishing of the ferroelectric properties [8]. Determining the ferroelectric properties of 1D nanostructures needs developing modeling theories and piezoresponse force microscopy measurements. Applications of PZT nanotubes include tunable photonic crystals, ferroelectric random access memories, terahertz emission, fluidic delivery, nanosensors and NEMS [9–12]. Arrays of PZT nanotubes could be exploited in ferroelectric random access memory (FRAM) devices [13] due to a unique polar axis of each tube in the array that can be inversed in direction by application of external electric field. In addition, the significant need of miniaturization of electronic devices leads to more extensive usage of PZT FRAMs based on nanotubes.

Amongst many suitable methods for the preparation of nanostructured PZT materials, including magnetron sputtering, pulsed laser deposition, chemical vapor deposition (CVD), photochemical deposition [14–17], sol–gel process is one of the promising routes, as it leads to materials with high chemical homogeneity and purity at comparably low temperatures [18–21]. PZT nanotubes have only been produced so far by using anodic aluminum oxide (AAO) templates, which was coated by a sol–gel process and subsequently removed with concentrated NaOH, [9,21,22]. This technique provides vertically aligned pores, rather than individual tubes, requires high temperature processing and in addition allows little control over pore width and wall thickness. Therefore, in the present work we demonstrate how CNTs can be used as templates to produce PZT nanotubes at the low temperature with good control of morphology and dimensions.

MWCNTs have been frequently used as sacrificial templates for the preparation of metal oxide nanowires and nanotubes, such as

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