Materials Research Bulletin 45 (2010) 717–721

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Fabrication of lead-free $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ piezoelectric nanofiber by electrospinning

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ARTICLE INFO

Article history:
Received 24 September 2009
Received in revised form 21 January 2010
Accepted 9 February 2010
Available online 13 February 2010

Keywords:
A. Nanostructure
B. Sol–gel chemistry
C. Atomic force microscopy
D. Piezoelectricity

ABSTRACT

$(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ nanofibers were synthesized by sol–gel process and electrospinning. Scanning electron microscopy was used to verify that the diameters and lengths are in the range of 150–600 nm and several hundreds of micrometer. Perovskite structure and grain size (20–70 nm) were verified by X-ray diffraction and transmission electron microscopy. The high effective piezoelectric coefficient d_{33} (96 pm/V) was measured by scanning force microscopy. It may be attributed to easily tilting the polar vector of domain for an electric field and the increase in the number of possible spontaneous polarization direction near the rhombohedral–tetragonal morphotropic phase boundary. The research shows that there are potential applications for $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ nanofiber in nanoscale lead-free piezoelectric devices.

1. Introduction

Low-dimensional nanostructures have attracted extensive interest due to their unique physical and chemical properties different from their bulk counterparts [1,2]. One-dimensional (1D) nanostructures, such as nanowires, nanotubes, and nanofibers, represent the smallest dimension for efficient transport of electrons and excitons, and thus are ideal building blocks for hierarchical assembly of functional nanoscale electronic and photonic structures [3]. For the synthesis of 1D nanostructure, there are various methods, e.g., sol–gel electrophoresis, sol–gel alumina template method, solution phase decomposition, and electrospinning [4–6]. Among these methods, electrospinning is the most attractive because of its convenience, simplicity, and low cost, which can also spin a variety of ultra-fine fibers at micro- and even nanoscale [7,8]. Several previous studies have been focused on the syntheses and properties of various nanofibers by electrospinning technique, such as Nd-substituted bismuth titanate ferroelectric nanofibers [9], and multiferroic $CoFe_2O_4$–$PbZr_{0.52}Ti_{0.48}O_3$ nanofibers [10].

For the sake of environmental protection and biocompatibility, lead-free $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is considered to be an excellent candidate for piezoelectric materials because of its strong piezoelectric properties with relatively large remanent polarization $P_r = 38\ \mu c/cm^2$ at room temperature [11]. In contrast with pure NBT, NBT-based solid solutions shows improved piezoelectric properties because of the existent rhombohedral–tetragonal morphotropic phase boundary (MPB) [12] and the phase transition induced by symmetry-allowed polarization rotation [13]. Generally, single crystals and ceramics of $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ are focused on the ferroelectric, dielectric and piezoelectric properties [11,14], and NKBT thin films are focused on the ferroelectric and dielectric properties [15,16]. Piezoelectric materials, especially in the form of low-dimensional nanostructures, own a number of advantages in micro-electro-mechanical systems (MEMS), such as low hysteresis, high available energy density, high sensitivity with wide dynamic range, and low power requirement, therefore it is worth considering the impetus for integrating piezoelectric nanostructures into MEMS devices [17]. As NBT-based relaxor ferroelectric materials, $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ ceramics at a composition around $x = 0.16$–0.2 are near the MPB and own high ferroelectric, dielectric and piezoelectric properties [18]. However, to the best of our knowledge, the fabrication and piezoelectric properties of $(Na_{0.82}K_{0.18})_{0.5}Bi_{0.5}TiO_3$ (NKBT) nanofibers near the MPB have not been reported.

Here, we reported the piezoelectric properties of NKBT nanofibers by sol–gel process and electrospinning technique. The morphology, crystallized phase, crystal structure, and grain size were investigated by scanning electron microscopy (SEM), X-ray diffractometer (XRD), transmission electron microscopy (TEM),

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doi:10.1016/j.materresbull.2010.02.013

and high resolution transmission electron microscopy respectively (HRTEM). To characterize the piezoelectricity, the effective piezoelectric coefficient d_{33} of NKBT nanofibers has been investigated by scanning force microscopy (SPM), and the mechanism of the high piezoelectricity was discussed. We expect that the research can offer useful guidelines to the design of 1D NKBT nanostructure lead-free piezoelectric devices in the MEMS application.

2. Experimental details

2.1. Fabrication of NKBT nanofibers

NKBT nanofibers were synthesized by sol-gel process and electrospinning technique as follows. At first, NKBT precursor solution was prepared by dissolving appropriate proportions of bismuth nitrate, potassium nitrate, natrium acetum and titanium butoxide in glacial acetic at room temperature, with an appropriate amount of acetylacetone added to stabilize the solution. A 10% excess of bismuth nitrate was added to compensate for possible bismuth loss during the high temperature process. Secondly, an ethanol solution containing poly (vinylpyrrolidone) (PVP) (MW = 1,300,000) was then added to the NKBT solution, with the concentration of PVP controlled around 0.035 g/ml, and the NKBT/PVP composite solution was stirred continuously to form a homogeneous polymer solution. At last, the homogeneous NKBT/PVP composite solution was loaded into a plastic syringe equipped with a needle, and then electrospun using a high voltage system (Spellman, model SL300, USA). In the electrospinning process, the NKBT/PVP composite nanofibers were collected on Pt/Ti/SiO_2/Si substrate with the electric field 1.5 kV/cm. After electrospinning, the as-spun nanofibers were dried at 120 °C for 8 h, followed by heating at 400 °C for 1 h and then calcining at 700 °C. According to Ref. [19], NBT film annealed at low temperature 600 °C for 1 h exhibits rather low crystallinity, and it indicates the onset of crystallization for NBT and the existence of $Bi_2Ti_2O_7$ as a secondary phase. A single well-established crystalline NBT phase was observed for that annealed at 700 °C. Its crystallinity is reduced when the film is annealed at 750 °C due to excess loss of bismuth at high annealed temperature. Besides, the NBT film annealed at 700 °C for 1 h exhibits a dense film structure, with few pores being observed at the grain boundaries and junctions. Analogously, we deduce NKBT nanofibers calcined at 700 °C should be of good crystallinity and piezoelectric properties as a kind of NBT-based 1D materials, therefore it was only used to investigate the size and morphology effects on the piezoelectric response in our experiment.

2.2. Characterization of NKBT nanofibers

The surface morphologies of as-synthesized products were characterized by SEM (Stereoscan 360, Leica Cambridge, UK). Phase identification and degree of crystallinity were investigated by XRD (D500, Siemens, Germany) with Cu Kα radiation, and crystalline structure was examined by TEM and HRTEM (JEM-2000CX, JEOL, Japan). Piezoelectric properties of NKBT individual nanofibers were characterized by SPM (SPI4000&SPA300HV, Seiko, Japan). The d_{33} was achieved by keeping the SPM tip fixed above the interesting point and applying a dc voltage from −10 to 10 V, while the displacement–voltage (D–V) "butterfly" curve was recorded. Considering the SPM characterization is a local method [20], the piezoelectric measurements for NKBT nanofibers were conducted repeatedly on different points, and the d_{33} was expressed by average value of 20 measurements. To characterize the piezoelectric property, the d_{33}–voltage (d_{33}–V) loops could be indirectly calculated from the corresponding D–V "butterfly" curves via the modified equation of converse piezoelectric effect [20]:

$$d_{33} = \frac{D - D_I}{V - V_I}, \qquad (1)$$

where D, V, D_I and V_I are the measured values of piezoelectric displacement, the applied voltage for each point on the D–V curve, the piezoelectric displacement and applied voltage of the intersection, respectively.

3. Results and discussion

3.1. Microstructure, surface profile and crystalline structure

Fig. 1 shows XRD patterns of as-spun NKBT/PVP composite nanofibers without being calcined and NKBT nanofibers calcined at 700 °C, and the diffraction peaks were indexed according to standard diffraction pattern data of NBT phase compiled in the JCPDS card. For the as-spun composite nanofibers without being calcined, no diffraction peaks could be observed, and it indicates that no crystal phase was formed. In the case of the nanofibers calcined at 700 °C, diffraction peaks could be observed obviously, and the NKBT nanofibers exhibit perovskite phase. They are polycrystalline nanofibers without any obvious preferred orientation, and it is consistent with the existences of perovskite phase for NKBT thin films [14]. Thus, it indicates that the as-synthesized products are NKBT nanofibers with fine crystallization after being calcined at 700 °C.

Fig. 2(a) shows the SEM image of as-synthesized NKBT/PVP composite nanofibers without being calcined, and the SEM images of NKBT nanofibers calcined at 700 °C are displayed in Fig. 2(b) and (c). From Fig. 2(a), it could be obviously seen that the as-synthesized nanofibers have smooth surfaces and large uniform diameters around 300–900 nm along its entire length. After being calcined at 700 °C for 1 h shown as Fig. 2(b), the diameters of nanofibers decrease to 150–600 nm, and the reason is due to the removal of organic components and crystallization of perovskite phase during the calcined process. As selected individual nanofiber shown as Fig. 2(c), the diameter is about 370 nm and uniform along its entire length. Although the diameters of nanofibers calcined at 700 °C are smaller than that of nanofibers without being calcined, the NKBT nanofibers remain to be dense and robust.

As shown in Fig. 3, the microstructure, and crystalline structure of the NKBT nanofibers were further confirmed by TEM and HRTEM. From Fig. 3(a), the microstructure of the individual nanofiber can be hardly visualized, and it indicates that the NKBT individual nanofiber is very dense in morphology. The perovskite structure of NKBT nanofiber was also confirmed as shown in Fig. 3(b), in which the lattice space is measured to be 0.27 nm along

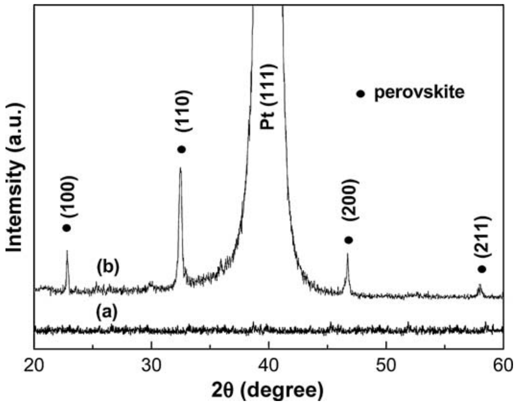

Fig. 1. XRD patterns of NKBT/PVP nanofibers: (a) without being calcined, and (b) calcined at 700 °C, displaying perovskite phase.