Solid State Sciences 13 (2011) 934–937

Contents lists available at ScienceDirect

Solid State Sciences

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

Electric properties of high strain textured $Na_{0.5}Bi_{0.5}TiO_3$–$BaTiO_3$–$K_{0.5}Na_{0.5}NbO_3$ thick films

Fang Fu [a], Jiwei Zhai [a,*], Zhengkui Xu [b], Wangfeng Bai [a], Xi Yao [a]

[a] Functional Materials Research Laboratory, Tongji University, No. 67 Chifeng Road, Shanghai 200092, China
[b] Department of Physics and Materials Science, City University of Hong Kong, Hong Kong

ARTICLE INFO

Article history:
Received 11 March 2010
Received in revised form
19 January 2011
Accepted 26 February 2011
Available online 9 March 2011

Keywords:
Textured thick film
Electric properties
High strain

ABSTRACT

Textured $(1-x)(0.94Na_{0.5}Bi_{0.5}TiO_3-0.06BaTiO_3)-xK_{0.5}Na_{0.5}NbO_3$ (abbreviated as NBT–BT–KNN) thick film on platinum substrate was prepared via tape casting method. The structure and electrical properties of the thick films were investigated. The results show that the thick films possess typical polycrystalline perovskite structures and the orientation degree reached to 75%. The remnant polarization (P_r) and coercive field (E_c) were optimized to 11.2 μC/cm^2 and 12.8 kV/cm for $x=0.02$ thick film. The dielectric properties of NBT–BT–KNN thick films as a function of temperature were also investigated. With the addition of KNN, the T_d (depolarization temperature) and T_C (Curie temperature) are all decreased. Meanwhile, the dielectric constant is increased with the addition of the KNN at room temperature. The piezoelectric constant of the thick film was calculated from unipolar electric field-induced strain curve. With the addition of KNN, the d_{33} value increased and reached to the maximum value of 349 pm/V for $x=0.02$ thick film.

1. Introduction

PZT-based materials have been commercially applied for almost half a century. However, these lead-containing materials contain at least 60 wt% of lead oxides and induce to serious problems to the environment during manufacturing at high temperature or disposal after usage. A lot of attempts thus have been concentrated on the research and development of high performance lead-free piezoelectric materials.

$Na_{0.5}Bi_{0.5}TiO_3$ (NBT) and $Na_{0.5}K_{0.5}NbO_3$ (NKN) are two dominant lead-free piezoelectric compositions with perovskite structures at present. The NBT materials possess a relatively mature processing and stable electrical properties. S. H. Choy [1,2] and his co-workers studied the NBT-based materials and suggested that the properties of NBT-based materials are good enough to replace PZT in certain applications such as ultrasonic wire-bonding transducers and accelerometers. NBT is strongly ferroelectric with relatively large remanent polarization $P_r=38$ μC/cm^2. But the coercive field $E_c=73$ kV/cm and the large current leakage of the NBT materials make the polarization difficult and then lead to weak piezoelectric properties [3,4]. These problems improved by forming solid solutions with $BaTiO_3$ (BT), $Bi_{0.5}K_{0.5}TiO_3$, $KNbO_3$, $NaNbO_3$, $BiFeO_3$, $BiScO_3$, etc [5–11]. A morphotropic phase boundary (MPB) was found out in the system at about 6 mol% BT, where the materials show enhanced electric performances. Our work based on this composition formulated at the MPB between rhombohedral and tetragonal phases. The NBT–BT ceramics substituted with small amounts of orthorhombic KNN was studied by Shan-Tao Zhang [12] and his co-worker. They obtained very promising results, since its large signal d_{33} value is as high as 560 pm/V which is comparable to that of PZT.

In recent years, the interest in thick film is driven by various applications including microactuators, micro-electro-mechanical systems (MEMS), high-frequency transducers, pyroelectric infrared sensors, and surface acoustic wave devices for its miniaturization, high power sensitivity and system integration [13–15].

Furthermore, grain orientation technique is considered to be an effective method to enhance the piezoelectric properties of ceramics. So far, the texturing ceramic has been demonstrated by hot forging, templated grain growth and magnetic field alignment for bulk materials [16,17]. Texturing of thin film also has been carried out using epitaxial growth or sol–gel coating of well-designed organic precursors [18,19]. In contrast, the preferred orientation of thick films prepared by tape casting method is not often observed.

In our work, the textured NBT–BT–KNN thick films have been prepared using tape casting method. The effects of the amount of KNN on the microstructure, ferroelectric, dielectric and piezoelectric properties are studied in detail.

* Corresponding author. Tel.: +86 21 65980544; fax: +86 21 65985179.
E-mail address: apzhai@tongji.edu.cn (J. Zhai).

1293-2558/$ – see front matter © 2011 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2011.02.014

2. Experiment

Bismuth oxides (analytical reagent), sodium carbonate (analytical reagent) and titanium oxides (analytical reagent) were used as starting materials. A conventional ceramic fabrication technique was used to prepare the matrix powders. The stoichiometric NBT powders were synthesized at 880 °C for 2 h by solid state reaction. The pre-calcined KNN powders were also prepared at 850 °C . Bismuth titanate synthesized from bismuth oxide and titanium oxides via salt molten method was applied as template. The XRD pattern and SEM image of these template particles are shown in Fig. 1(a) and (b). The template particles possessed a single Bismuth titanate phase with a plate-like morphology. The solution of toluene and dehydrated alcohol with the mass ratio of 2:1 was prepared as solvent. The matrix consisted with NBT, BT and KNN according to the stoichiometric ratio of $(1-x)(0.94\text{NBT}-0.06\text{BT})-x\text{KNN}$ ($x=0$, 0.01, 0.02 and 0.04). The 80 wt% matrix and 20 wt% bismuth titanate templates were added into the solvent and milled on roller mill for 15 h. The different composition between NBT–BT–KNN and bismuth titanate was compensated by the addition of sodium carbonate, titanium oxide, BT and KNN. The 20 wt% LS model bond (produced by Lingguang electric chemical materials Technology Corporation in Zhaoqing city, China) was added to the suspension and milled for anther 3 h to obtain the stable casting slurry. The device to perform tape casting is the conventional tape casting equipment. A gap of 100 μm under the blade is selected for the casting process. The green thick film was then cut and pressed on the platinum substrate by isostatic pressing under 200 MPa. The film is burned at 550 °C for removing the organic substance and then sintered at 1250 °C for 2 h.

The phase structures of the thick films were investigated with X-ray diffraction (XRD, Bruker D8 Advanced, German) with Cu Kα radiation. The degree of the grain orientation can be represented by Lotgering's factor which is calculated by the formula below [20]:

$$F = (P - P_0)/(1 - P_0) \tag{1}$$

Where P is the sum I (h00)/sum I (hkl), P_0 is the sum I_0 (h00)/sum I_0 (hkl). Sum I is the summation of the peak intensities of the XRD pattern of the sintered specimen. Sum I_0 is the summation of the XRD peak intensities of the equiaxed reference powder. Microstructures of the specimens were examined by scanning electron microscopy (SEM, JSM EMP-800). In order to determine the electric properties of the specimens, the gold electrode with a thickness of 80 nm and a diameter of 0.5 mm sputtered on the surfaces of the thick films. The temperature dependence of the dielectric constant and loss were measured from room temperature to 350 °C at frequencies of 100 kHz using a high-precision LCR meter (HP 4284A). The hysteresis loops and the longitudinal displacement field curves of the thick films were measured by ferroelectric test systems (Precision PremierII, made in USA) connected with a Miniature Plane-mirror Interferometer and the accessory Laser Interferometric Vibrometer (SP-S 120/500 Model, Made in German).

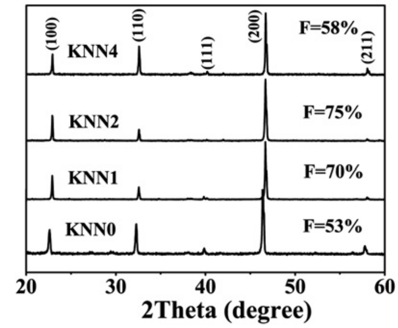

Fig. 2. XRD patterns of NBT–BT–KNN thick films.

3. Results and discussion

The XRD patterns of BNT–BT–KNN thick films are shown in Fig. 2. All the films mainly possess perovskite structure and trace second phases can be detected, which indicated that KNN diffuse into the NBT lattices to form a solid solution. It is noted that, the addition of KNN does not change the crystalline structure of thick films with the doping level studied. Meanwhile, as the KNN increasing, the diffraction peak shifts to large angles, which indicate the distortion of the crystal lattice of the thick films. The orientation degree value F was calculated from the Lotgering's method for BNT–BT–KNN thick film. With the addition of the KNN, the F value increased and reached to 75% with 2 mol% KNN modification.

The microstructure of grain oriented NBT–BT–KNN thick films sintered at 1250 °C for 2 h is shown in Fig. 3. It can be seen that the thick films give regular brick-like quadrangular grains and without the obvious presence of secondary phases. Distinct pores exist for all thick films and tend to decrease with the addition of the KNN. The existence of pores in the thick films can be mainly attributed to the large proportion of organic vehicle in the tape casting slurry and high volume percentage of bismuth titanate template particles. The organic vehicle was volatile and left pores in the green laminate during the binder burnout process. On the other hand, a fraction of bismuth titanate template particles with a plate-like morphology also made the thick films difficult to be densification. It is noticeable that the grain size changes slightly small with varying the KNN content. This may be attributed to the possibility that K^+ and Na^+ aggregates and forms secondary phases on a very small scale at the grain boundaries. This may restrict grain boundary movement and then the reduction in the mobility of the grain boundary weakens the mass transport. As a result, grain growth is slightly inhibited and smaller grains are formed. The images attached on the top right corner in Fig. 3(a) and (c) are the cross-section of the corresponding

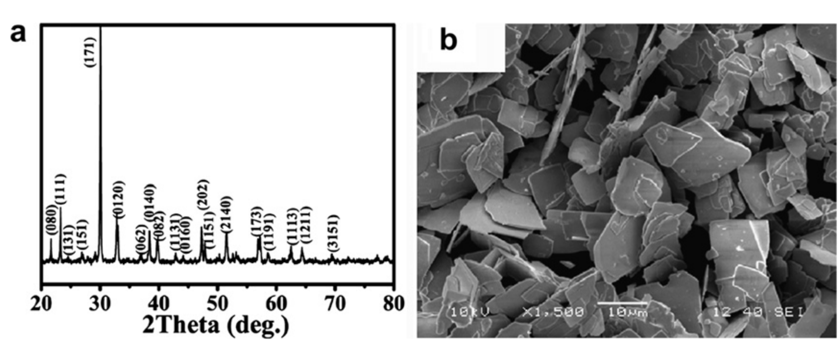

Fig. 1. XRD pattern and SEM image of $Bi_4Ti_3O_{12}$ templates.