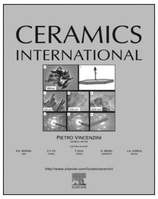
Ceramics International 42 (2016) 9577–9582

Contents lists available at ScienceDirect

Ceramics International

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



Structural and electrical properties of $Na_{0.5}Bi_{4.0}RE_{0.5}Ti_4O_{15}$ (RE=Tm, Yb and Lu) thin films

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ARTICLE INFO

Article history:
Received 23 December 2015
Received in revised form
5 March 2016
Accepted 5 March 2016
Available online 8 March 2016

Keywords:
A. Films
A. Sol–gel processes
C. Electrical properties
C. Ferroelectric properties

ABSTRACT

In the current study, a series of lanthanide ions, Tm, Yb and Lu, were used for doping at the Bi-site of the Aurivillius phase $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NaBTi) to investigate the structural, electrical and ferroelectric properties of the thin films. In this regard, $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ and the rare earth metal ion-doped $Na_{0.5}Bi_{4.0}RE_{0.5}i_4O_{15}$ (RE=Tm, Yb and Lu, denoted by NaBTmTi, NaBYbTi, and NaBLuTi, respectively) thin films were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by using a chemical solution deposition method. Formations of the Aurivillius phase orthorhombic structures for all the thin films were confirmed by X-ray diffraction and Raman spectroscopic studies. Based on the experimental results, the rare earth metal ion-doped $Na_{0.5}Bi_{4.0}RE_{0.5}Ti_4O_{15}$ thin films exhibited a low leakage current and the improved ferroelectric properties. Among the thin films, the NaBLuTi thin film exhibited a low leakage current density of 6.96×10^{-7} A/cm^2 at an applied electric field of 100 kV/cm and a large remnant polarization ($2P_r$) of 26.7 μC/cm^2 at an applied electric field of 475 kV/cm.

1. Introduction

Aurivillius phase $Na_{0.5}Bi_{4.5}Ti_4O_{15}$ (NaBTi), which belongs to the family of bismuth layer-structured ferroelectrics (BLSFs), has received considerable interests because of its unique piezoelectric, electromechanical and ferroelectric properties [1–3]. Specifically, good fatigue endurance, high piezoelectric coefficient, large electromechanical quality factor and high Curie temperature of NaBTi has made the compound an attractive candidate for a wide variety of potential applications, including sensor, actuator and ferroelectric nonvolatile random access memory devices [2,4–6]. The Curie transition temperature that was reported for the NaBTi thin film is higher than that of the $K_{0.5}Bi_{4.5}Ti_4O_{15}$ compound having the same crystal structure [4,7]. Moreover, NaBTi was proposed to be an excellent replacement for the toxic Pb(Zr,Ti)O_3, which is currently being extensively used in ferroelectric and piezoelectric devices [8]. The crystal structure of NaBTi consists of repeated layers of four pseudo-perovskite units $(Bi_{n-1}Ti_nO_{3n+1})^{2-}$ (n=4) alternating with bismuth oxide $(Bi_2O_2)^{2+}$intermediate layers directed toward the c-axis [9]. In the pseudo-perovskite units, some of the Bi atoms are replaced by Na atoms. At room temperature, the NaBTi has an orthorhombic structure with a=5.427 Å, b/a=1.006 and c=40.650 Å, and it undergoes a phase transition at 655 °C from ferroelectric phase ($A2_1am$) to para-electric phase ($I4/mmm$) [5,7].

Though NaBTi has several advantages, concurrently, it shows severe limitations, which are large conductivity and a high coercive electric field. Furthermore, the poling of this compound required relatively a high electric field due to two-dimensional orientation restriction in rotation of spontaneous polarization [5]. Many reports on experimental studies showed that cationic doping at the Bi- and/or the Ti-sites of BLSFs using rare earth (RE) and/or transition metal ions can significantly improve the electrical and the ferroelectric properties of the BLSF compounds [10–12]. Particularly, Bi-site modifications using RE metal ions have been reported to be more plausible to enhance the ferroelectric polarization of the BLSFs [4,12–14]. Moreover, doping with different RE metal ions has different influence on the electrical properties of the BLSFs. Therefore, it is necessary to optimize the most suitable RE metal ion to realize the best electrical and the ferroelectric properties in NaBTi.

In the current study, three lanthanide ions, viz. Tm^{3+}, Yb^{3+}, and Lu^{3+}were used for doping purpose at the Bi-site of NaBTi. The ionic radii of Tm^{3+}(1.22 Å), Yb^{3+}(1.22 Å), and Lu^{3+}(1.34 Å), which were calculated for the co-ordination number twelve, are smaller than that of the Bi^{3+}-ion (1.45 Å) [15]; hence, they can be readily substituted into the Bi-site of the NaBTi. Thin films of NaBTi and the RE metal ion-doped $Na_{0.5}Bi_{4.0}RE_{0.5}i_4O_{15}$ (RE=Tm, Yb and Lu, denoted by NaBTmTi, NaBYbTi, and NaBLuTi, respectively) were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by using chemical solution deposition (CSD) method. Systematic studies on the structural, electrical and ferroelectric properties were also carried out and the results are discussed here in detail.

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http://dx.doi.org/10.1016/j.ceramint.2016.03.040
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2. Experimental procedure

Thin films of NaBTi, NaBTmTi, NaBYbTi, and NaBLuTi were prepared on Pt(111)/Ti/SiO_2/Si(100) substrates by using a CSD method. The raw materials, sodium nitrate [$NaNO_3$], bismuth nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$], titanium isopropoxide [$Ti[OCH(CH_3)_2]_4$], thulium nitrate pentahydrate [$Tm(NO_3)_3 \cdot 5H_2O$], ytterbium nitrate pentahydrate [$Yb(NO_3)_3 \cdot 5H_2O$], and lutetium nitrate hydrate [$Lu(NO_3)_3 \cdot xH_2O$] were used for the preparation of the precursor solutions. 2-methoxy ethanol (2-MOE) [$CH_3OCH_2CH_2OH$] and acetic acid [CH_3COOH] were used as solvent and catalyst, respectively. For the preparation of the $Na_{0.5}Bi_{4.0}RE_{0.5}Ti_4O_{15}$ precursor solutions, a measured quantity of sodium nitrate was dissolved in 2-MOE at 40 °C and stirred for 30 min, after which acetic acid was added to the above solution and stirring was continued for another 30 min. To the above mixture, bismuth nitrate pentahydrate and *RE* metal nitrate, for doping purpose, were added and stirred for another 30 min. The Na–Bi–*RE* solution was continuously stirred for an additional 2 h to form a homogeneous solution. Separately, a homogeneous solution of 2-MOE and chelating agent acetyl acetone [$CH_3COCH_2COCH_3$] was prepared in a glove box under nitrogen atmosphere. Titanium isopropoxide was added to this solution and the mixture was stirred for 1.5 h. This homogenous Ti-solution was mixed with the Na–Bi–*RE* solution to form the $Na_{0.5}BiRE_{0.5}Ti_4O_{15}$ precursor solution. The final solution mixture was continuously stirred for 3 h to attain homogenization. Pure NaBTi precursor solution was also prepared for the purpose of comparison. Since, Na and Bi ions are highly volatile in nature, therefore, in these experiments 15% excess Na and Bi were used to maintain the stoichiometric composition. The overall concentrations of the solutions were adjusted to 0.1 M.

The precursor solutions of NaBTi, NaBTmTi, NaBYbTi, and NaBLuTi were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates by using spin coating method, which was optimized at an angular speed of 3000 rpm for 20 s. The spin-coated wet thin films were heated in two stages at 200 °C and 360 °C for 5 min on a hot plate to dry and eliminate any organic impurities, respectively. The coating and the baking processes were repeated 15 times to obtain the desired film thickness. Finally, the thin films were annealed at 500 °C for 3 min by rapid thermal annealing (RTA) under continuous flow of oxygen. Subsequently, the thin films were annealed at 700 °C for 3 min by RTA in an oxygen atmosphere for crystallization.

An X-ray diffractometer (Rigaku, MiniFlex II) and a Raman spectroscope (Jasco, NRS-3100) were used to study the structures of the $Na_{0.5}Bi_{4.0}RE_{0.5}Ti_4O_{15}$ thin films. A field emission scanning electron microscope (Tescan, MIRA II LMH) was used to examine the surface morphology. For electrical measurements, platinum electrodes with area 1.54×10^{-4} cm^2 were deposited on the top surfaces of the thin films by ion sputtering through a metal shadow mask. An electrometer (Keithley, 6517 A) and a low-frequency impedance analyzer (HP, 4192 A) were used to study the leakage current and the dielectric properties of the thin films, respectively. A standardized ferroelectric test system (Radiant Technologies Inc., Precision LC) was used to investigate the ferroelectric hysteresis loops of the thin films.

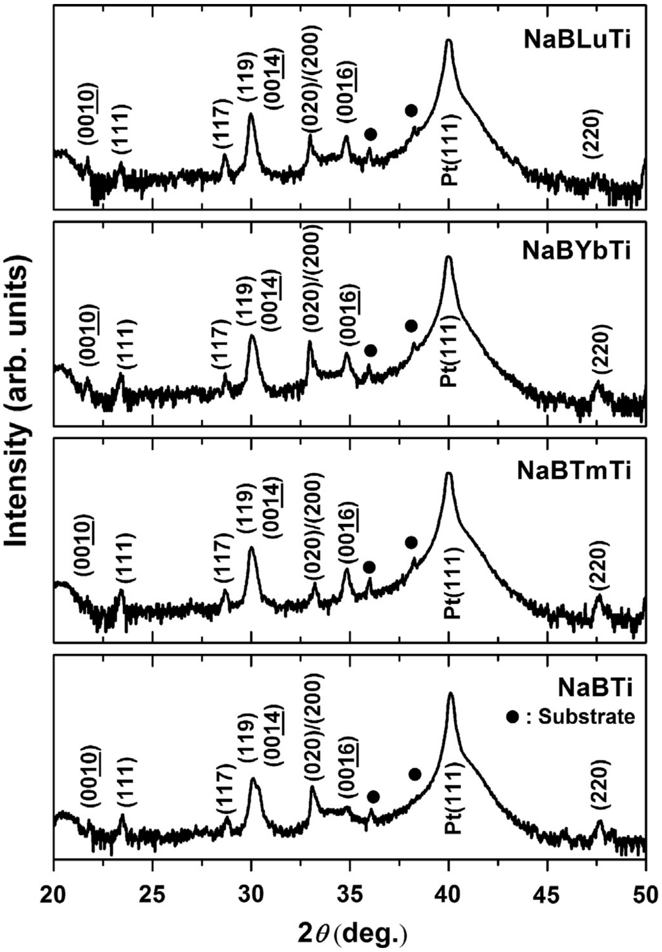

Fig. 1. XRD patterns of NaBTi, NaBTmTi, NaBYbTi and NaBLuTi thin films deposited on Pt(111)/Ti/SiO_2/Si(100) substrates.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the thin films deposited on Pt(111)/Ti/SiO_2/Si(100) substrates. The observed XRD patterns clearly revealed the formation of standard BLSF structure for all the thin films. The diffraction peaks of the thin films were indexed on the basis of Aurivillius phase having orthorhombic symmetry. None of the thin films showed any additional peaks corresponding to the secondary or impurity phases. These results implied that doping concentrations of the *RE* metal ions did not reach the solubility of the parent compound. However, slight changes were noticed in the major diffraction peaks corresponding to (119) and (00$\underline{14}$) planes of the *RE* metal ion-doped thin films. In the XRD pattern of the NaBTi thin film, the (119) and (00$\underline{14}$) peaks were clearly separated, while these peaks were overlapped and appeared as a broad peak in the *RE* metal ion-doped $Na_{0.5}Bi_{4.0}RE_{0.5}i_4O_{15}$ thin films. These results obviously signified a structural distortion in the $Na_{0.5}Bi_{4.0}RE_{0.5}i_4O_{15}$ thin films, which was due to the internal strain induced by the incorporation of *RE* metal ions into the Bi-site of the NaBTi.

Fig. 2 shows the Raman scattering spectra of the thin films measured at room temperature. The individual peaks were evaluated by fitting the measured spectra and decomposing them into their discrete Lorentz components, as depicted in Fig. 2. For the BLSFs, the characteristic Raman modes were observed in the range ~90–850 cm^{-1}. Here, the phonon modes in the low frequency region (~90–200 cm^{-1}) were related to the vibrations of *A*-site (Na and Bi) ions, and the phonon modes above 200 cm^{-1} were related to the stretching and bending vibrations of the TiO_6 octahedra in the pseudo-perovskite block [16,17]. The Raman scattering spectra obtained for the thin films were well correlated with those of the standard BLSF structures. The assignments of the individual phonon modes for all the thin films are given in Table 1. For the NaBTi thin film, the phonon mode observed at ~124 cm^{-1} can be related to the Bi–O bond in the pseudo-perovskite blocks