Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Structural phase transition, electrical and photoluminescent properties of Pr^{3+}-doped (1-x)$Na_{0.5}Bi_{0.5}TiO_3$-x$SrTiO_3$ lead-free ferroelectric thin films

Wenhua Huang, Shuai He, Aize Hao, Ni Qin, Muhammad Ismail, Jiang Wu, Dinghua Bao*

State Key Laboratory of Optoelectronic Materials and Technologies, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou 510275, China

ARTICLE INFO

Keywords:
Pr-NBT-xSTO thin films
Structural phase transition
Ferroelectric
Photoluminescence
Chemical solution deposition

ABSTRACT

Lead-free ferroelectric Pr^{3+}-doped (1-x)$Na_{0.5}Bi_{0.5}TiO_3$-x$SrTiO_3$ (x = 0–0.5) (hereafter abbreviated as Pr-NBT-xSTO) thin films were prepared on Pt/Ti/SiO_2/Si and fused silica substrates by a chemical solution deposition method combined with a rapid thermal annealing process at 700 °C, and their structural phase transition, dielectric, ferroelectric, and photoluminescent properties were investigated as a function of STO content. Raman analysis shows that with increasing STO content, the phase structures evolve from rhombohedral phase to coexistence of rhombohedral and tetragonal phases (i.e. morphotropic phase boundary), and then to tetragonal phase. The structural phase transition behavior has been well confirmed by temperature- and frequency- dependent dielectric measurements. Meanwhile, the variation in photoluminescence intensity of Pr^{3+} ions with different STO content in the NBT-xSTO thin films also indicates that there exists a clear structural phase transition when the film composition is close to the morphotropic phase boundary. Superior dielectric and ferroelectric properties are obtained in the Pr-NBT-0.24STO thin films due to the formation of morphotropic phase boundary. Our study suggests that Pr-NBT-xSTO thin films be promising multifunctional materials for optoelectronic device applications.

1. Introduction

Ferroelectric thin films have promising applications in microelectronics, optoelectronics, integrated optics, and micro-electromechanical systems such as capacitor, dynamic random access memory and ferroelectric random access memory, surface acoustic wave devices, micromotor, phase shifter, pyroelectric detector, optical waveguide modulator, optical frequency multiplier, due to their good properties including dielectric, piezoelectric, ferroelectric, pyroelectric, electro-optic, and nonlinear optic properties [1–4].

Among various studies of ferroelectric thin films, most efforts have been devoted to lead-containing ferroelectric thin films such as Pb(Zr,Ti)O_3, Pb($Mg_{1/3}Nb_{2/3}$)O_3-$PbTiO_3$ [5–7]. However, these lead-containing materials are harmful to environment and human bodies and are expected to be gradually replaced by lead-free materials. Sodium bismuth titanate, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), with strong ferroelectricity of P_r = 38 μC/cm^2 and high Curie temperature of T_c = 320 °C, is considered as one of the most promising candidates among the lead-free alternative materials [8–10]. But pure NBT has drawbacks of high coercive field (E_c = 73 kV/cm) and high conductivity that lead to difficulty in obtaining desirable electrical properties. It is known that electrical performance of ferroelectric materials can be improved through forming rhombohedral-tetragonal morphotropic phase boundary (MPB). For example, $Na_{0.5}Bi_{0.5}TiO_3$-$SrTiO_3$ (NBT-xSTO) ceramics exhibit good dielectric and electromechanical properties at the MPB composition where x is close to 0.25–0.28 [1011], and $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$-Bi($Mg_{0.5}Ti_{0.5}$)O_3 thin films prepared by chemical solution deposition, also present good ferroelectric properties near MPB [8]. In this study, we focus on the thin films of NBT-xSTO to investigate their phase transition and electrical properties. It is known that NBT itself is a relaxor, and it has several crystal structures including cubic, tetragonal, and rhombohedral phases, whereas STO has a cubic phase. Therefore, thin film solid solution of NBT and STO should exhibit interesting structural changes, and corresponding electrical properties are worth studying as well.

On the other hand, we noted that ferroelectric thin films can exhibit multifunctional properties by introducing rare earth ions such as Eu^{3+} and Pr^{3+} [12–14]. These rare earth ions can not only act as luminescent centers, but also can be used as structural probes since their luminescence properties are strongly sensitive to local environment [15–17]. It has been reported that Pr^{3+}-doped $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ thin films showed multifunctional properties including a strong red emission, and variation of photoluminescent (PL) intensity of Pr^{3+} ions can be used to probe the existence of MPB in $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$

* Corresponding author.
E-mail address: stsbdh@mail.sysu.edu.cn (D. Bao).

https://doi.org/10.1016/j.jeurceramsoc.2017.12.057
Received 17 October 2017; Received in revised form 25 December 2017; Accepted 26 December 2017

thin films [18]. Therefore, it is also interesting to check if PL of Pr ions can be used as a supplementary means to probe the phase transition of NBT-xSTO thin films, especially when normal X-ray diffraction cannot effectively differentiate phase structure change in some ferroelectric thin films.

Considering that doping concentration of Pr^{3+} ions in most inorganic PL materials is usually small [18–20], in this present work, we doped 0.2 mol% Pr^{3+} ions into NBT-xSTO thin films and systematically studied the structural phase transition, dielectric, ferroelectric, and photoluminescent properties of lead-free Pr^{3+}-doped NBT-xSTO (x = 0–0.5) thin films.

2. Experimental procedure

The 0.2 mol% Pr^{3+} doped NBT-xSTO (x = 0, 0.22, 0.24, 0.26, 0.28, 0.4, and 0.5) thin films were prepared via a chemical solution deposition method with spin-coating process. For synthesizing the precursor solutions, bismuth acetate $Bi(CH_3COO)_3$, sodium acetate $NaCH_3COO$, strontium acetate hemihydrate $Sr(CH_3COO)_2{\cdot}1/2H_2O$, praseodymium nitrate hexahydrate $Pr(NO_3)_3{\cdot}6H_2O$, and tetrabutyl titanate $Ti(OC_4H_9)_4$ were used as starting materials, and glacial acetic acid and 2-methoxyethanol with volume ratio of 2:1 as co-solvent, and acetylacetone as a complexing reagent to stabilize tetrabutyl titanate. Both Bi and Na compositions are 10% excessive in the precursor solutions for the purpose of compensating for the bismuth and sodium loss during subsequent thin film annealing process. The final precursor solutions, golden yellow-colored and transparent, were obtained with the concentration of 0.25 M. The thin films were prepared on $Pt/Ti/SiO_2/Si$ and fused silica substrates by spin-coating Pr-NBT-xSTO solutions at a speed of 3000 rpm for 20 s. After each spin-coating process, the thin film samples were annealed at 700 °C for 5 min in air via a rapid thermal annealing method. This procedure was repeated ten times to obtain the desired thickness of the films. Then Pt top electrodes were sputter deposited on the surface of the thin films on $Pt/Ti/SiO_2/Si$ substrates by using a shadow mask to form the metal-film-metal configuration for electrical measurements.

Crystal structure of Pr-NBT-xSTO thin films was analyzed by an X-ray diffractometer (XRD, D/MAX 2200 VPC, Rigaku, Tokyo, Japan) with Cu *Kα* radiation operated at a working current of 30 mA and a working voltage of 40 kV. A scanning electron microscope (SEM, JSM7000F, JEOL, Tokyo, Japan) was used to observe the surface and cross-sectional morphologies of the thin films. Raman spectra of Pr-NBT-xSTO thin films were recorded from 180 to 1000 cm^{-1} using Renishaw inVia + Plus Laser Micro-Raman Spectrometer (Derby-shire, U.K.) with an exciting light of 633 nm. The dielectric properties were measured using 4284A LCR meter (Agilent, Santa Clara, CA, USA) with the applied ac signal amplitude of 100 mV. The temperature dependence of the dielectric property of the thin films was evaluated using 4284A LCR meter connected with a Cryosystem (Quatro, Novocontrol, Hundsangen, Germany). The polarization-electric field (*P–E*) hysteresis loops were obtained at a frequency of 1 kHz using a ferroelectric analyzer (TF analyzer 2000, aixACCT, Germany). The PL spectra of the thin film samples were measured at room temperature by the Shimadzu RF-5310PC fluorescence spectrometer, and the excitation light source is a xenon lamp equipped with a grating monochromator.

3. Results and discussion

Fig. 1 shows XRD patterns of Pr^{3+}-doped NBT-xSTO (x = 0–0.5) thin films fabricated on $Pt/Ti/SiO_2/Si$ substrates via the rapid thermal annealing process at 700 °C. All of the films were crystallized to pure perovskite structure with a random orientation. Usually, the evolution of the (200)/(002) diffraction peaks as a function of STO concentration can be used to analyze the change in phase structure of NBT-based perovskite ceramic materials [21]. Obviously, it can be seen that the (200) diffraction peaks shift to lower angles with increasing STO

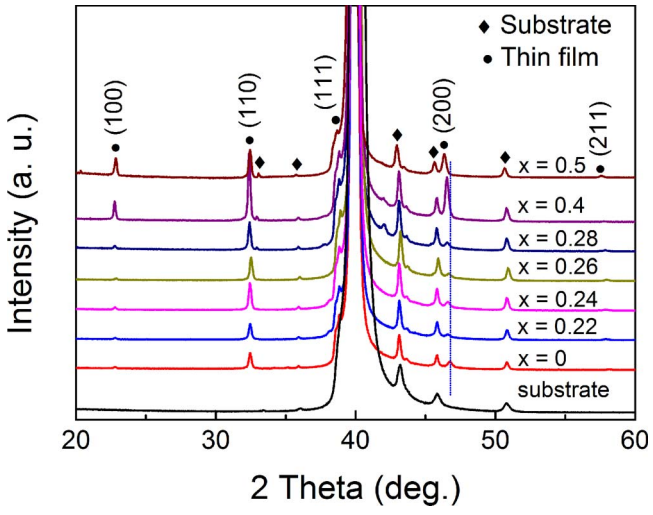

Fig. 1. X-ray diffraction patterns of the Pr^{3+}-doped NBT-xSTO (x = 0, 0.22, 0.24, 0.26, 0.28, 0.4, and 0.5) thin films.

content. This can be attributed to the lattice expansion by cause of the substitution of Sr^{2+} for Na^+ and Bi^{3+} as the ionic radius of Sr^{2+} ($r_{Sr}{}^{2+}$ = 1.18 Å) is larger than that of Na^+ and Bi^{3+} ($r_{Na}{}^{+}$ = 1.02 Å, $r_{Bi}{}^{3+}$ = 1.03 Å). This can be further proved by the variation of the lattice constant with STO content as shown in Fig. 2, assuming that the thin films are of pseudocubic phase. However, there is no clear splitting of (200)/(002) diffraction peaks at 2θ ~ 47° for the thin films as compared to NBT-xSTO ceramics. This indicates that phase structure changes (such as MPB) in Pr-NBT-xSTO thin films cannot be detected by normal XRD measurements [12]. Whereas in their ceramic counterpart, the splitting of (200)/(002) diffraction peaks at 2θ ~ 47° can be clearly observed. It has been reported that an MPB forms in NBT-xSTO ceramics when x = 0.25–0.28 [11].

NBT-xSTO thin films (x = 0.13, 0.15, 0.18, and 0.2) were also prepared on Si substrates by metal-organic solution deposition method [22]. However, some impurity phases such as γ-Na_2TiO_3 appeared in the thin films. Fu, et al. reported sol-gel preparation and dielectric tunable properties of NBT-xSTO thin films (x = 0, 0.2, 0.5, 0.8, and 1.0) with precursor solution of mixing NBT and ST solutions using ethanol as solvent of tetrabutyl titanate [23]. Also no splitting of (200)/(002) diffraction peaks at 2θ ~ 47° can be observed in the XRD patterns.

In order to clarify whether there is structural phase transition in the Pr-NBT-xSTO thin films, we use Raman scattering analysis to study the

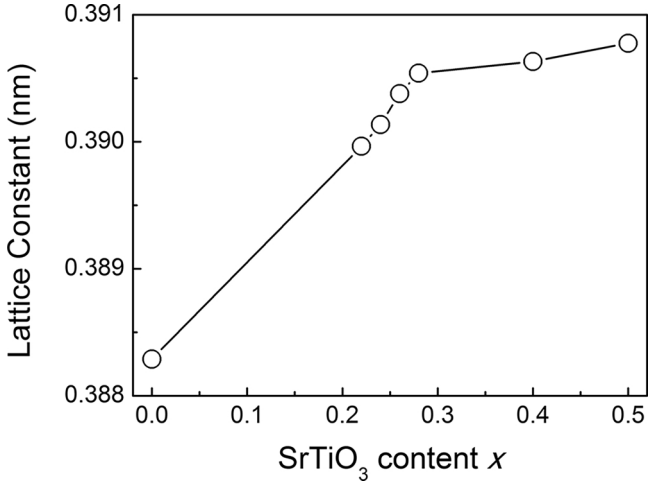

Fig. 2. The lattice constant of Pr^{3+}-doped NBT-xSTO thin films as a function of STO content.