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# Effects of Tb doping on structural and electrical properties of 47($Ba_{0.7}Ca_{0.3}$)$TiO_3$–0.53Ba($Zr_{0.2}Ti_{0.8}$)$O_3$ thin films at various annealing temperature by pulsed laser deposition

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## ABSTRACT

The ceramic thin films of 47($Ba_{0.7}Ca_{0.3}$)$TiO_3$–0.53Ba($Zr_{0.2}Ti_{0.8}$)$O_3$ (BCZT) + $x$ ($x$ = 0.2, 0.3, 0.4 and 0.5) mol% Tb were grown on Pt(111)/Si substrates with various annealing temperature by pulsed laser deposition. The XRD spectra confirm that Tb element can enhance the (l10) and (111) orientations in ceramic films. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images show that Tb-doping can increase particle size effectively. The surface of Tb-doped film annealed at 800 °C is uniform and crack-free, and the average particle size and mean square roughness (RMS) are about 280 nm and 4.4 nm, respectively. Comparing with pure BCZT, the residual polarization ($P_r$) of 0.4 mol% Tb-doped film annealed at 800 °C increase from 3.6 to 9.8 μC/cm$^2$. Moreover, the leakage current density value of Tb doped films are one order of magnitude ($5.33 \times 10^{-9} - 1.97 \times 10^{-8}$ A/cm$^2$ under 100 kV/cm) smaller than those of pure BCZT films ($1.02 \times 10^{-7}$ A/cm$^2$).

## 1. Introduction

Over the past two decades, the development of lead-free ceramics which can replace Pb(Zr,Ti)$O_3$ have become one of the most widely studied topics due to the increasing concerns on environment and human health associated with the electronic components that contain with toxic elements [1,2]. The barium titanate (BT) and the solid solution calcium barium zirconate titanate (BCZT) bulks have been widely investigated and become the research hotspot since reported by Ren et al. [3], which are considered as the most promising environment-friendly electrical ceramic materials because of their excellent piezoelectric and ferroelectric properties as compared to the other lead-based ceramics [4–8]. Moreover, the thin films of lead-free ceramic films have tremendous potential applications in dynamic random access memories, capacitors, and microelectronics sensor devices [9–14]. It is well known that pulsed laser deposition (PLD) method is considered as an important method for depositing polycrystalline as well as it has been used for many film fabrications, such as $PbTiO_3$, $SrBi_2Ta_2O_9$, ZnO, BT and ($Bi_{0.6}Tb_{0.3}La_{0.1}$)$FeO_3$ (BTLF) ceramic films [15–18]. The BCZT thin films were also widely prepared by PLD technique. Prabahar et al. prepared BCZT films by PLD with different deposition temperature, the $P_r$ of 4 μC/cm$^2$ and coercive field ($E_c$) of 32 kV/cm were obtained for BCZT film deposited at 700 °C [19]. Lin et al. investigated the effect of oxygen partial pressure on electrical properties for BCZT, and the films grown on $SrRuO_3$ with 200 mTorr possessed optimal ferroelectric properties, which the $P_r$ was 14.5 μC/cm$^2$ [20]. Piorra et al. prepared BCZT films with (111) orientation and relative permittivity ($\varepsilon_r$) and piezoelectric coefficients were 1010 and 80 pm/V [21]. Bhardwaj et al. fabricated multilayer (1-$x$)Ba($Zr_{0.2}Ti_{0.8}$)$O_3$–$x$($Ba_{0.7}Ca_{0.3}$)$TiO_3$ film, and 5 layers with $x$ = 0.7, 0.6, 0.5, 0.4 and 0.3 possessed optimal dielectrical properties ($\varepsilon_r$ = 701 and tanδ = 0.0061 at 1 MHz) [22]. Jiang et al. studied the effect of $CaRuO_3$ seed layer on dielectric properties of BCZT film, and found the $\varepsilon_r$ and tenability increased from 725% and 47–877% and 50.4% at 1 MHz, respectively [23].

For further improving the electrical properties of BCZT, many researchers manage to design the function of ceramics, which include stoichiometry, doping, buffer layer, and pulsed laser deposition variation [14,23–25]. For doping, as the rare earth element, Tb is a special case with mixed + 3 and + 4 valances and $Tb^{3+}$ could substitute at both A-site and B-site, whereas $Tb^{4+}$ would substitute at the B site in $ABO_3$ structure and it has been reported that Tb can improve residual polarization values of BCZT bulk counterpart [26–28]. Moreover, Tb can have stable properties in the deposition process because of the larger molar mass [29]. Therefore, Tb was deduced to have positive

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effects on electrical properties of BCZT ceramic film.

In our previous study, we found that the Tb can improve electrical performance of BCZT bulk counterpart effectively [26]. In this work, $x$ ($x$ = 0.2, 0.3, 0.4 and 0.5) mol% Tb-doped BCZT thin films grown on Pt (111)/Si substrates were prepared by PLD. The structure, surface topography, dielectric and ferroelectric properties of BCZT ceramic films with different Tb doping concentrations and annealing temperature have been reported.

## 2. Experimental

### 2.1. Materials

To prepare BCZT source powders, analytical-grade metal oxides and carbonate powders of $BaCO_3$ (99.80%), $TiO_2$ (98.00%), $CaCO_3$ (99.50%), and $ZrO_2$ (99.00%) were purchased from Sinopharm Chemical Reagent Co., Ltd. And $Tb_4O_7$ (99.99%) was purchased from Fuyu Co.,China.

### 2.2. Fabrication of BCZT

A series of ceramic targets of BCZT+ $x$ ($x$ = 0.2, 0.3, 0.4 and 0.5) mol% Tb were prepared by the conventional solid-state reaction technique. Raw materials of $BaCO_3$, $TiO_2$, $CaCO_3$, $ZrO_2$ and $Tb_4O_7$ were weighed according to the stoichiometric ratio and mixed by a ball grinder for 12 h, and then the mixed powders were calcined at 1200 °C for 2 h. The resulting mixtures were ball-milled again for 24 h and granulated with appropriate polyvinyl alcohol (PVA) as the binder. After that the resulting mixtures were pressed into disk-shaped pellets with about 20 mm diameter and 1 mm thickness under 10 MPa. The pressed pellets were sintered at 1410 °C for 6 h in the air atmosphere.

The BCZT thin films were grown on Pt/Si substrates kept at 650 °C by pulsed laser deposition (PLD) using a KrF eximer pulsed laser ($\lambda$ = 248 nm). The other process parameters such as oxygen partial pressure of 13.3 Pa, laser pulse repetition rate of 10 Hz, target-to-substrate distance of 40 mm, substrates temperature of 650 °C and laser energy of 300 mJ per pulse were used during the deposition. The as-deposited 0.4 mol% Tb-doped BCZT films were annealed at different temperature in air (700, 800 and 900 °C) for 3 h. And gold top electrodes of 0.2 mm diameter were sputtered deposited on the films. The platinum coating was used as a bottom electrode.

### 2.3. Characterization and electrical properties tests

The X-ray diffraction (XRD) data was collected by using X-ray diffractometer (X'Pert PRO, PANalytical, Netherlands) with Cu K$\alpha$ radiation of wavelength $\lambda$ = 0.154056 nm. And the scans 2θ angle ranges from the 20° to 60°. An atomic force microscopy (AFM, Digital Instruments, Veeco Metrology Group, Santa Barbara, CA) and scanning electron microscopy (SEM, Quanta 200, FEI Sieioa, and Netherlands) were employed to identify the microstructure and cross-sectional thickness of the materials. The dielectric properties of the composite films were obtained by a broadband dielectric spectrum analyzer (Alpha-A, Novocontrol, Germany) at room temperature and in frequency range from $10^2$ to $10^6$ Hz. The hysteresis measurements are directly sensitive to dipolar polarization versus applied electrical field. The measured electrical polarization ($P$) of the samples versus applied electrical field ($E$), referred to as the Polarization-Electrical field ($P$-$E$) curves. Thus, the ferroelectric properties of ceramic films at room temperature were obtained by ferroelectric tester (Radiant Multiferroic, USA).

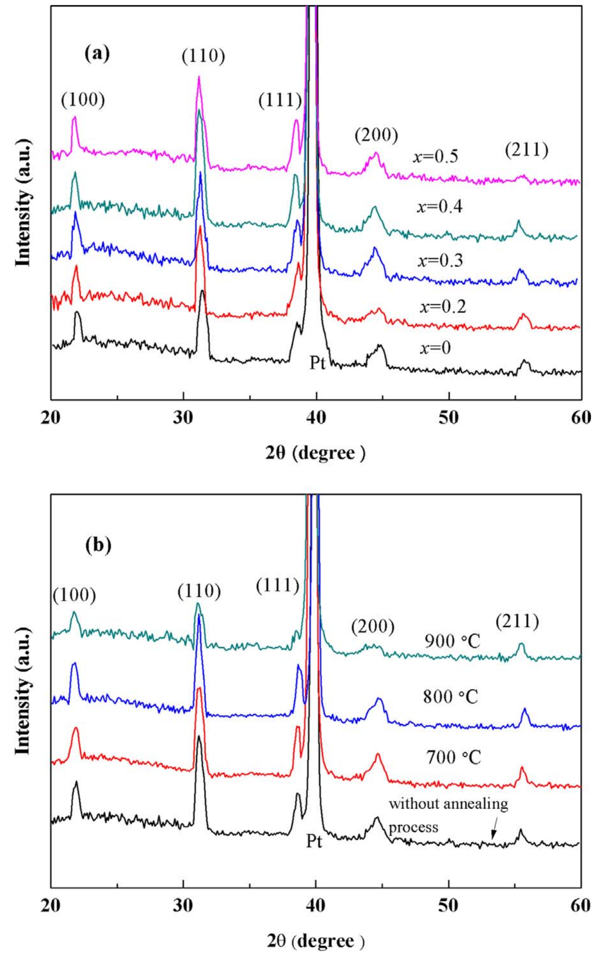


**Fig. 1.** XRD patterns of (a) $x$ mol%Tb doped-BCZT films and (b) 0.4 mol% Tb-doped BCZT films annealed at various temperature.

## 3. Results and discussion

### 3.1. XRD pattern

Fig. 1(a) (b) show the X-ray diffraction (XRD) pattern of the BCZT + $x$ ($x$ = 0.2, 0.3, 0.4 and 0.5) mol% Tb ceramics films and 0.4 mol% Tb-doped-BCZT films with various sintering temperature (700, 800 and 900 °C), respectively. The both XRD patterns show the films are polycrystalline with a perovskite structure and these peaks of (100), (110), (111), (200) and (211) are observed. No peaks from secondary phases or impurity phases can be observed, which indicates that Tb has diffused into BCZT lattice to form a solid solution with perovskite structure. From the Fig. 1, it can be seen that the peaks intensities of the ceramic films are influenced by Tb doped and annealing temperature obviously. The (110) and (111) peaks intensities of 0.4 mol% Tb-doped BCZT film with 800 °C are stronger than those of other films, suggesting that has preferred (110) and (111) orientations. For stable trivalent ions, the small ion (r < 0.87 Å) can occupy B-site, whereas large ion would occupy A-site (r > 0.94 Å), and intermediate ion could occupy both A-site and B-site [30,31]. The $Tb^{+3}$ with 0.92 Å ionic radius could substitute at both A-site and B-site according to a previous research [32]. In our previous study, Tb was found to occupy A-site in BCZT bulk [26]. It is known that the components of ceramic films are affected obviously by the molar mass of atom during PLD process. Therefore, in this case, Tb may occupy B-site due to the possible deficiency of Ti in ceramic films [29]. The appearance of B-site vacancies will lead to the collapse of part lattices in specimen. And these defects could be decreased by the addition of Tb in the films, which the Tb-doped films