Structural and electrical characterizations of Bi(Zn0.5,Ti0.5)O3 doped lead zirconate titanate ferroelectric films with enhanced ferroelectric properties

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Abstract

Bi(Zn0.5,Ti0.5)O3 (BZT) doped Pb(Zr0.4,Ti0.6)O3 (PZT) films were fabricated using a chemical solution deposition method and were characterized intensively in the present work. It was discovered that the room temperature remnant polarization and zero-field longitudinal piezoelectric constant of the BZT-doped PZT film were enhanced by 23% and 30%, respectively, as compared with those of the undoped PZT film prepared under the same experiment conditions. In order to explain the improved ferroelectric properties, the phase structures of the BZT–PZT and undoped PZT films were experimentally investigated in a broad temperature range (from 30 to 600 °C) by using the high temperature two-dimensional X-ray diffraction method. It was found that the improvement in ferroelectricity does not correspond to an elevated Curie temperature (Tc) or a substantially larger tetragonality (c/a). The difference on the change of Tc by doping of Bi-based perovskites in PZT solid solutions between this work and some previous investigations was explained on the basis of Zr/Ti ratio, and the necessity of an in-depth theoretical investigation was addressed.

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Keywords:
High temperature two-dimensional X-Ray diffraction
Phase transition
Bismuth zirconate titanate
Lead zirconate titanate
Ferroelectric films
Chemical solution deposition

1. Introduction

Perovskite compounds with an ABO3-type crystalline structure have been investigated for many years. Because of their desirable properties including large remnant polarization, small coercive field and low crystallization temperature, the Pb-based perovskite ceramics and films (e.g., Pb(Zr1−xTix)O3, i.e., PZT) have dominated the market of ferroelectrics and piezoelectrics for decades, being used in a variety of applications including actuators, sensors, and memory components [1–3]. However, environment concerns on the toxic lead in commercial products have pushed the scientific societies to seek for low Pb or Pb-free replacement materials [4–6]. Due to the similar “inert-pair” 6s2 electronic configuration of Bi3+ to that of the Pb2+ cation, Bi-based perovskites (Bi Bi3+ on the A-site) are considered to be promising alternatives to Pb-based ferroelectrics [7]. Among these materials, tetragonal Bi(Zn0.5,Ti0.5)O3 (BZT) has been reported to have a very high c/a ratio and a large calculated ferroelectric polarization, whereas it is not stable in its undoped form and can only be stabilized at high pressure [8–11]. Therefore, a ferroelectric solid solution consisting of a lead-based perovskite and BZT may provide a mutual opportunity for the application of both materials.

In recent years, PZT ceramics and films substituted with Bi-based perovskites have received intensive attentions from world-wide researchers. Grinberg et al. have shown that the nonmonotonic Curie temperature (Tc) trends in Bi75−xMg10−xZn2xTiO3 (B = Mg, Zn, Sr, Ti) solid solutions arise from the microscopic coupling between A-site and B-site displacements [12]. Cross et al. reported an increase of Tc from 350 to 380 °C in a 5% BiFeO3–95% PZT 40/60 film as compared with the undoped PZT film [13]. The most notable effect by the substitution of BiFeO3 took place in the Bi2Ti4O9 ferroelectric solid solution, where a tetragonal c/a ratio of ~1.11 (compared to 1.06 for PbTiO3) and Tc in excess of 700 °C were realized [14]. Through ab initio study, Grinberg et al. attributed the increase of Tc in BZT–PbTiO3 to the hybridization between the 4s and 4p orbit of O and the 2p orbit of Bi. This hybridization allows the formation of short, covalent Zn–O bonds, enabling favorable coupling between A-site and B-site displacements [15]. Wang et al. obtained a high remnant polarization (Pr = 33.2 μC/cm2) and a small tetragonal c/a ratio (c/a = 1.025) in the 15%BZT–85%PZT 52/48 solid solution [16], while Lee et al. reported a decreased ferroelectric Tc by about 45 °C in a PZT ceramic near its morphotropic phase boundary with 5 mol% BZT substitution [17], contrary to the trend of Tc increase in BZT substituted-PbTiO3. In our previous studies, X-ray photoelectron spectroscopy has been used to investigate the impact of BZT doping on the structure of PZT films, and we also investigated the frequency-dependent electrical properties of 3%BZT–97%PZT films [18,19]. Recently, M.T. Chentir et
al. have investigated the impact of intrinsic BZT content on the crystallographic and ferroelectric properties of PZT films and reported the decrease of the tetragonality \((c/a)\) ratio with increasing BZT content \[20\].

In order to better understand the phase transition process of BZT doped lead zirconate titanate, and to seek improved electrical properties, BZT doped PZT 40/60 films were characterized intensively in the present work. It was found that the 5% BZT–95% PZT 40/60 film has an enhanced room temperature remnant polarization \((2P_r \sim 80 \mu \text{C/cm}^2\) at 5 V applied voltage) as compared with that of the undoped PZT film \((2P_r \sim 65 \mu \text{C/cm}^2\) at 5 V applied voltage), but its phase transition process is almost the same as that of the undoped PZT film as is disclosed by the high temperature two-dimensional X-ray diffraction method \((\text{HT-XRD}^2)\) analysis.

2. Experimental details

The \((x)\text{Bi}(Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3-(1-x)\text{Pb}(Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3 \ (x = 0, 0.03, 0.05, 0.08, \text{and} 0.1)\) ferroelectric thin films were fabricated on Pt\((111)/\text{Ti/SiO}_2/\text{Si}(100)\) substrates by chemical solution deposition \((\text{CSD})\) using spin-coating. Commercially available metalorganic solutions \((\text{Toshiba Manufacturing Co. Ltd.) of Pb}(Zr_{0.5}\text{Ti}_{0.5})\text{O}_3 \ (\text{INS-PZT}, 110/40/60, 0.25 \text{mol L}^{-1}, 50 \text{ml})\) and Bi\((Zn_{0.5}\text{Ti}_{0.5})\text{O}_3 \ (\text{INS-BZT}, 110/50/50, 0.25 \text{mol L}^{-1}, 50 \text{ml}))\) were mixed together to obtain the stoichiometric \((x)\text{Bi}(Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3-(1-x)\text{Pb}(Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3\) solution. The carboxylate liquid precursors were spin coated at a rate of 500 rpm for 5 s first, and then at 3000 rpm for 20 s. The samples were then fully dried in a rapid thermal annealing \((\text{RTA})\) furnace at 330 °C for 4 min in order to remove residual organic compounds, followed by a cooling process for 5 min in air. These processes were repeated three times. The resultant films were annealed at 600 °C for 30 min in 1 L/min \(O_2\) by using a RTA furnace. The thicknesses of all the films were kept the same at ~205 nm. For measurements of the ferroelectric and electrical properties, dot-shaped Pt top electrodes \((200 \mu \text{m in diameter})\) were deposited on the film surface at room temperature by electron beam evaporation using a metal mask. After deposition of the Pt top electrodes, all of the films were annealed at 600 °C for 30 min in 1 L/min \(O_2\) by using a RTA furnace. For the purpose of measurement, the Pt bottom electrode layer was partially exposed by etching away the films using a mixed solution of HCl and HF acids.

The ferroelectric hysteresis curves \((P–E)\) were measured by using an RT66A standard ferroelectric test system \((\text{Radiant Technologies})\) at room-temperature. Leakage current density–voltage characteristics \((J–V)\) were measured by using an Agilent 4156C Precision Semiconductor Parameter Analyzer. Piezoelectric properties of the films were characterized by piezoresponse force microscopy using a SPA4000 and SPA300HV scanning probe microscope system \((\text{Seiko, Japan})\). The crystalline structures and lattice parameters of the films were investigated by temperature dependent XRD experiments, in which a Bruker D8 Discover diffractometer set in a D8S 1100 high temperature chamber \((\text{Anton Parr})\) was employed. The temperatures of the samples were increased from 30 °C to 600 °C and a 10 min waiting time was set for temperature stabilization at each temperature point. In the XRD \(θ–2θ\) measurements, the 20 range was set from 18° to 51°, with 1.2 kW power and Turbo X-ray source \((\text{Cu Ka})\).

3. Results and discussion

3.1. The electrical properties

\((x)\text{Bi}(Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3-(1-x)\text{Pb}(Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3 \ (x = 0, 0.03, 0.05, 0.08, \text{and} 0.1)\) films were deposited on Pt\((111)/\text{Ti/SiO}_2/\text{Si}(100)\) substrates by CSD method using spin-coating. Fig. 1 shows the ferroelectric hysteresis curves of the BZT doped PZT thin films with different \(x\) values measured at 10 kHz with an applied voltage of 10 V. The thicknesses of all films were kept the same and measured about 205 nm. The well saturated hysteresis curves can be observed for all of the samples with different BZT concentrations. At an applied voltage of 10 V, the \(2P_r\) values of all BZT doped PZT films are larger than that of the undoped PZT film \((-70 \mu \text{C/cm}^2\) ). For 5% BZT–95% PZT \((\text{BZT–PZT})\) film, the \(2P_r\) values are the largest at 90 \(\mu \text{C/cm}^2\). For all samples, the coercive fields \((E_c)\) are less than 95 V/cm. The 5% BZT–PZT film was chosen to be compared with undoped PZT film for the remaining experimental investigations.

The \(P–E\) characteristics of the BZT–PZT and undoped PZT films were measured under various applied voltages from 1 V to 5 V at 10 kHz. As shown in Fig. 2(a)–(b), the \(P–E\) hysteresis loops are well saturated. The \(2P_r\) value of the BZT–PZT film is about 80 \(\mu \text{C/cm}^2\), which is larger than that of the undoped PZT film \((-65 \mu \text{C/cm}^2\) ), and the \(E_c\) of both films is less than 70 V/cm. These results indicate that BZT–PZT film is a promising material candidate for applications in ferroelectric random access memories \((\text{FeRAM})\) since it satisfies the requirements of large remnant polarization and low operation voltage simultaneously. Fig. 2(c) shows the \(J–V\) characteristics of the two films. In the reverse bias condition \((0 \text{ to } 20 \text{ V})\), the leakage current density of the BZT–PZT film is less than that of the undoped PZT film. However, in the forward bias condition \((0 \text{ to } 20 \text{ V})\) the leakage current density of the BZT–PZT film is slightly larger than that of the undoped PZT film. This kind of leakage current behavior is in good agreement with the prediction based on the space-charge-limited conduction model \[21\]. When the absolute value of the external voltage is below 10 V, the leakage current densities of both films are below 10 \(-7\) A/cm\(^2\), which is good enough for applications in FeRAM \[22\]. Fig. 2(d) displays piezoelectric responses of the two films. As can be seen from the figure, typical well-shaped displacement-voltage “butterfly” curves were obtained for both films. The average zero-field \(d_{33}\) piezoelectric coefficient of the PZT film was found to be ~150 pm/V, which agrees fairly well with the theoretical value for a tetragonal PZT film near its morphotropic phase boundary with \((100)\) and \((110)\) preferred orientations \[23\]. On the other hand, the average zero-field \(d_{33}\) piezoelectric coefficient of the BZT–PZT film was found to be ~196 pm/V, ~30% enhancement over that of the pure PZT film. This improvement in zero-field \(d_{33}\) piezoelectric coefficient can be at least partially explained by the enhancement of remnant polarization \((-65 \mu \text{C/cm}^2\) in the pure PZT film to ~80 \(\mu \text{C/cm}^2\) in the BZT–PZT film, a 23% increase). Meanwhile, the maximum \(d_{33}\) piezoelectric coefficients of the BZT–PZT and undoped PZT films derived from the slopes of the curves were found to be 202 pm/V and 178 pm/V, respectively. This indicates that the extrinsic contribution to the \(d_{33}\) piezoelectric coefficient was small as compared with the intrinsic one.

Fig. 1. The polarization-electric field \((P–E)\) hysteresis loops of the prepared \((x)\text{Bi}(Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3-(1-x)\text{Pb}(Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3\) thin films with \(x = 0, 0.03, 0.05, 0.08, \text{and} 0.1\). The loops were measured at 10 kHz frequency with 10 V external voltage.
3.2. HT-XRD² method

In order to understand the phase transition process, it is necessary to obtain structural information of the films at elevated temperatures. In the present work, HT-XRD² micro-diffractometer (BRUKER-D8 DISCOVER with General Area Diffraction Detection System) equipped with a specially developed focusing microlens, a very powerful tool to investigate phase transition and crystalline structure, was used for this purpose. Fig. 3(a)–(b) shows the in-situ HT-XRD² patterns and corresponding XRD θ–2θ scan patterns of the two films at room-temperature, respectively. The ring-like diffraction spectra originate from polycrystalline films and they are called the “Debye rings”. The spot-like diffraction spectra originate from highly oriented films and single crystals. The correlations between the “Debye ring”, the spot-like diffraction pattern, and the diffraction peaks in the θ–2θ scan patterns, are indicated by the black arrows. A significant feature of HT-XRD² is that the crystallite size and texture can be directly estimated from the intensity distribution along the diffraction ring of each reflection.

3.3. The phase transition process

Fig. 4(a)–(b) shows the in-situ HT-XRD² patterns of the undoped PZT and 5% BZT–95%PZT films at temperatures from 30 to 600 °C. The high-temperature XRD θ–2θ scan patterns are obtained from the HT-XRD² patterns, and are shown in Fig. 4(c)–(d). It was found that both films show a pure perovskite structure without any other secondary phase. The almost identical features of the two XRD patterns suggest that 5% BZT doping does not affect the phase formation of the PZT perovskite structure. Taking advantage of the HT-XRD² approach which can provide deep insights into the structural phase evolutions, the present study have clearly demonstrated the particular temperature range corresponding to a localized phase transition from tetragonal to cubic structure, using a locally resolved HT-XRD² technique. When the temperature is below 275 °C, peak

Fig. 2. The P–E characteristics of (a) the undoped PZT film, and (b) the 5% BZT–95% PZT film measured under various voltages (from 1 V to 5 V) at 10 kHz. (c) The leakage current density–voltage (J–V) characteristics of the undoped PZT and 5% BZT–95% PZT films. (d) The displacement–voltage (D–V) curves of the undoped PZT and 5% BZT–95%PZT films.

Fig. 3. (a) Room-temperature HT-XRD² patterns of the undoped PZT and 5% BZT–95% PZT films and (b) the corresponding XRD θ–2θ scan patterns.
Fig. 4. HT-XRD$^2$ patterns of (a) the undoped PZT film, and (b) the 5% BZT–95% PZT film, and corresponding XRD $\theta$–$2\theta$ scan patterns of (c) the undoped PZT film, (d) the 5% BZT–95% PZT film at temperatures from 30 to 600 °C.

From the XRD $\theta$–$2\theta$ scan patterns, the lattice parameters ($a$ and $c$) of the two samples were calculated as a function of temperature, which are shown in Fig. 5(a). At room temperature, the $a$-axis lattice parameter of the undoped PZT film is 4.019 Å, while that of the 5% BZT doped PZT film is 4.016 Å. It can also be seen that, for both films, the $a$-axis lattice parameters increase and the $c$-axis lattice parameters decrease continuously with increasing temperature until they merge to the same value at the Curie temperature, indicating a tetragonal to cubic phase transition. These temperature-dependent evolutions of lattice parameters are similar to those of other lead titanate based ferroelectrics [14,16]. The tetragonal $c/a$ ratio as function of temperature are shown in Fig. 5(b). The $c/a$ ratio of 5% BZT–95% PZT film is slightly larger than that of the undoped PZT film in the low temperature region (below 275 °C), which indicates that the tetragonality is slightly enhanced by the doping of BZT. The tetragonal–cubic phase transition temperature was observed in the vicinity of 350 °C for both PZT and BZT–PZT films, as is indicated by the point where the $c/a$ ratio approaches 1.0. To further explain the temperature-dependent evolutions of the lattices, the change of unit cell volume ($a^2 \times c$) was plotted as a function of temperature in Fig. 5(b). In the ferroelectric phase, the unit cell volume increases with decreasing temperature due to the increase of tetragonal distortion ($c/a$) that resulted from the spontaneous polarization ($P_s$), which reflects the magnitude of ferroelectricity [24,25]. In the present work, the temperature dependences of the unit cell volume of both films are quite similar to that of PbTiO$_3$: the unit cell volumes in the tetragonal phase decrease linearly with increasing temperature and show a dramatic contraction in the vicinity of the Curie temperature [26]. On the other hand, the unit cell volume of BZT–PZT film is slightly smaller than that of the undoped PZT film, indicating an enhanced $P_s$ by the doping of BZT. This is consistent with the increase of the tetragonality.

The full width at half maximum (FWHM) of the (002) peaks in the XRD $\theta$–$2\theta$ scan patterns are shown in Fig. 5(c)–(d) as a function of temperature. Before the phase transition, the FWHM of the tetragonal (002) peaks ($\Delta \theta_{FWHM}$) of the two films decrease quickly with increasing temperature in an approximately linear fashion. When the temperature is higher than 350 °C, the FWHM decreases linearly with temperature with a much shallower slope. The two fitted line of the temperature dependence of FWHM connect at around 355 °C for both films, which is very close to their Curie temperature of 350 °C fitted from the XRD lattice parameters. From the above analysis, it is concluded that the lattice-temperature evolutions characterizing a ferroelectric phase transition can be interpreted from the HT-XRD$^2$ data in at least four different ways, i.e., the temperature dependent lattice parameters (as shown in Fig. 5(a)), the temperature dependent tetragonality (or ratio of lattice parameters) and unit cell volume (both are shown in Fig. 5(b)), and the temperature dependent crystallinity represented by the FWHM (as shown in Fig. 5(c)–(d)).
3.4. Discussions

In the present work on BZT doped PZT 40/60, the remnant polarization $P_r$ and the longitudinal piezoelectric property were enhanced by the doping of BZT while the Curie temperature $T_C$ remained the same. The tetragonality $c/a$ was found to be slightly larger in the doped PZT film, and its electrical insulating property was as good as that of the undoped film. These results are either new or different from those of the Bi$_2$BO$_3$–PZT ($B=$Mg, Zn, Zr, Ti) solid solutions [14–17]. This can be further discussed in the following two aspects:

1. The experiment data on the ferroelectric and piezoelectric properties of the Bi$_2$BO$_3$–PT solid solutions have been rarely reported due to the high electrical conductivity associated with these materials [14,16]. This is one of the driving forces of the present work. As has been shown in the present work and some recently published papers [16,17], once the leakage current has been reduced to a satisfactory level, BZT doped PZT solid solutions have great potentials for practical applications.

2. The differences on the change of $T_C$ by doping of Bi$_2$BO$_3$ in PZT solid solutions between the present experiment work and those recently published [14,16,17] can be empirically explained on the basis of Zr/Ti ratio. It seems that as the $Zr/Ti$ ratio is away from the Ti-rich side and approaches that of the morphotropic phase boundary (MPB-PZT, or PZT 52/48), the doping of BZT will decrease the Curie temperature of the PZT material [17] or lower its sintering temperature [16], and at the same time enhance its piezoelectric properties [16,17]. For PZT materials with a $Zr/Ti$ ratio between that of PT and MPB-PZT, a modest change or no change in the Curie temperature by doping of Bi$_2$BO$_3$ may be deduced as a first step by applying the “mixing rule”. This is consistent with our experiment results on BZT doped PZT 40/60 films. The explanation by Wang et al. [16] of the opposite effects on the local structure of tetragonal PZT–BZT solid solutions brought by PbZrO$_3$ and BZT, by using the concepts of tolerance factor and chemical pressure, is very important in helping understand the effects of $Zr/Ti$ ratio and dopant amount on the structure and properties of Bi$_2$BO$_3$ doped PZT solid solutions. To fully understand the experiment results, especially the substantially enhanced ferroelectricity, we are seeking help from theorists using a microscopic approach.

Considering that the Bi and Zn concentrations are on the order of several atomic percent in the doped PZT film, these dopants are likely to substitute independently or randomly, depending on the applied electric field and the corresponding free energy densities [27,28]. In order to better understand the impact of small amount of Bi and Zn dopants on the ferroelectric properties, first principle calculations of BZT–PZT 40/60 are needed, similar to what has already been done on Pb(Zr,Ti)O$_3$ and Bi(Zn,Ti)O$_3$ [29,30]. This kind of calculations will help determine which sites in the co-doped PZT lattice would give the lowest free energy.

4. Conclusions

In summary, a 5% BZT doped PZT 40/60 film showing an enhanced remnant polarization $P_r$ of about 80 μC/cm$^2$ (~23% improvement against that of the undoped PZT film) was fabricated using a chemical solution deposition method. The phase structures of the BZT–PZT and
undoped PZT films were experimentally investigated in a temperature range from 30 to 600 °C by using the HT-XRD2. It was found that this improvement in ferroelectricity does not correspond to an elevated Curie temperature or a substantially larger tetragonality (c/a). The zero-field and maximum $d_{33}$ piezoelectric coefficients of the BZT–PZT film were found to be 196 pm/V and 202 pm/V at room temperature, better than those of the undoped film (150 pm/V and 178 pm/V, respectively). The leakage current densities of the two films are comparable and meet the requirement for applications in FeRAM.

Acknowledgment

This work was financially supported by the Key Project of National Natural Science Foundation of China (NSFC) (Grant No. 11032010), the NSFC (Grant Nos. 51072171 and 61176093), the PCSIRT (IRT1080), the Hunan Provincial Innovation Foundation for Postgraduate (CX2011B248), the Doctoral Program of Higher Education of China (Grant No. 20104301110001). J. Ouyang and W. Zhang thank the financial support from the “Qi-Lu Young Scholar Fund” and the Independent Innovation Foundation of Shandong University, the NSFC of China (Grant Nos. 51002088 and 91122024), and the Shandong Province Outstanding Young Scientist Research Fund (Grant No. BS2010CL029).

References
