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Combined contributions of phase structure and preferred orientation on the piezoelectric properties of polycrystalline $(Pb_{0.94}La_{0.04})Zr_{0.6}Ti_{0.4}O_3$ thin films

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A B S T R A C T

Polycrystalline $(Pb_{0.94}La_{0.04})Zr_{0.6}Ti_{0.4}O_3$ thin films were fabricated by a sol–gel method on the Pt (111)/Ti/SiO_2/Si (100) substrates. Results from X-ray diffraction reveal that a strain-induced low-asymmetry monoclinic (M_B) phase exists in all the films as compared with its powder counterpart. Also, films exhibit a simple trend of pyrolysis-sensitive (100)-orient growth. Good piezoelectric longitudinal coefficient values are obtained in the films where a maximum around 130 pm/V is reached for the film pyrolyzing at 425 °C. These findings suggest that combined contributions of monoclinic phase and (100)-preferred orientation type as well as good surface quality will account for excellent piezoelectric properties for ferroelectric films.

1. Introduction

Ferroelectric thin films including lanthanum-doped $(Pb_{1-1.5y}La_y)(Zr_{0.60}Ti_{0.40})O_3$ (PLZT) have attracted much attention because of their potential applications in miniaturized piezoelectric devices for micro-electron-mechanical systems (MEMS) [1,2]. Earlier studies on PZT-like perovskite oxides believed that the origin of large piezoelectric properties near the morphotropic phase boundary (MPB, with a Zr/Ti ratio around 52/48) has been related widely to low symmetry monoclinic (M_A) phases sandwiched between rhombohedral (R) and tetragonal (T) phases [3–5]. Depending on the applied electric field direction and preferred orientation, different monoclinic (M_C,M_B) phases and orthorhombic phase have been experimentally with excellent piezoelectric properties [6,7]. These studies on PZT-like bulk ceramics emphasize the significance of crystal phases under external conditions such as composition, preferred orientation and the constraint effect in optimizing piezoelectric properties. For example, recent studies have revealed that superior piezoelectric d_{33} coefficient near the MPB can be obtained in niobium-doped PZT (PNZT) thin films [8]. Also, large remnant polarization changes can be induced by a thickness-independent mixture of (110) and (111) orientations for the $BiFeO_3$ thin films [9].

In this paper, we attempt to build a combined relation between the pyrolysis-sensitive microstructure and piezoelectric properties of sol–gel-derived $(Pb_{0.94}La_{0.04})Zr_{0.6}Ti_{0.4}O_3$ thin films. Within our knowledge, the property-associated phase structure of polycrystalline Zr-rich PLZT thin films has not been carefully examined. The La/Zr/Ti composition is chemically designed because its bulk counterpart is of pure R phase in the phase diagram [10].

2. Experimental

In terms of fabricating ferroelectric film, a sol–gel process has obtained particular interest because it offers both chemical homogeneity and reduced-temperature processing of uniform films [11]. The sol–gel method and spinning coating technique were used to fabricate the PLZT thin films, as described elsewhere [12]. Films' thickness (~200 nm) was measured by surface profile meter (Alpha-Step D-100, KLA-Tencor). The crystalline structure and a universal fiber texture were analyzed by XRD. Film leakage current density was measured using a ferroelectric test system (P-LC100, Radiant Technology). The piezoelectric hysteresis loops of the thin films were characterized by using SPM (SPI4000&-SPA300HV, Seiko) [13].

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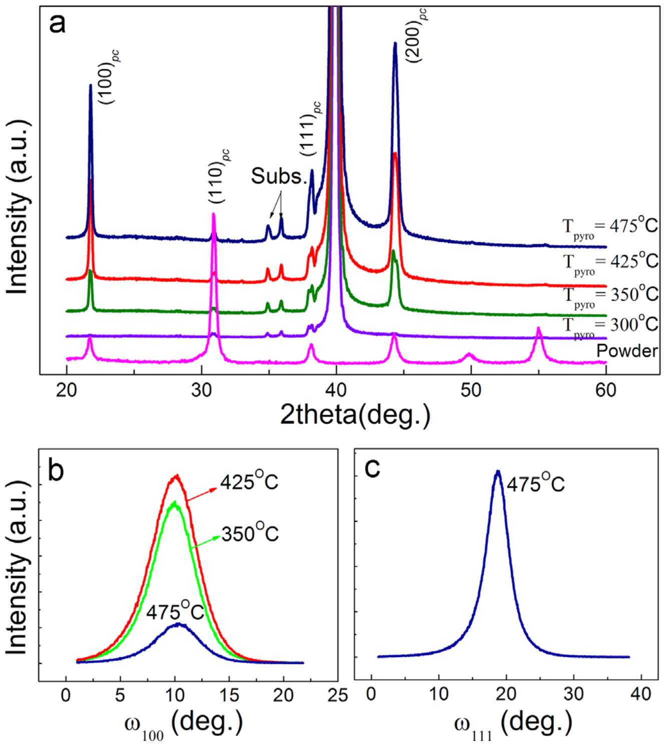

Fig. 1. (a) XRD patterns of the films with pyrolyzing temperatures from 300 °C to 475 °C. (b) ω-scan for the (100)-oriented films and (c) for the (111)-oriented film pyrolyzing at 475 °C.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the thin films with different pyrolysis temperatures. For the sol–gel process, pyrolysis is an indispensable step to obtain desired films with good surface quality whose major function is to remove organics in the precursor solution [14]. The films pyrolyzing at 350 °C and 425 °C exhibit an obvious (100)-oriented growth for its higher (100)/(111) intensity ratios. The appearance of strong (111) diffraction peak indicates a mixture of (111) and (100)-preferred orientation. We performed XRD ω-scan on the (100) and (111) diffraction for the thin films, as shown in Fig. 1(b)–(c). Using a symmetric Gauss peak-fitting procedure, the full width at half maximum (FWHM) value of the (100) diffraction curves is approximately of 4.9° suggesting highly (100)-preferred orientation of the films. Similarly, small FWHM value on (111) diffraction is calculated around 4.4° indicating a mixture of (100) and (111)-preferred orientation. Highly (100)-oriented growth mainly results from the presence of favorable (001)-oriented lead oxide buffer layer according to the literatures [15,16]. As the pyrolysis temperature is above 475 °C, those perovskite crystals directly nucleate from the (111) orientated substrate and suppress the precipitation of lead oxide. These results predict a pyrolysis-sensitive preferred orientation for the sol–gel-derived ferroelectric films.

The crystal phase of the polycrystalline thin films are characterized by three diffraction profiles shown in Fig. 2 including $(110)_{pc}$ at ψ=45°,$(111)_{pc}$ at ψ=54.7°and $(200)_{pc}$ at ψ=0° in a pseudo-cubic coordinate system. For the *R*-structured PZT bulk ceramic, it is known that $(110)_{pc}$ and $(111)_{pc}$ diffraction are both composed of double peaks with intensity ratios around 1:1 and

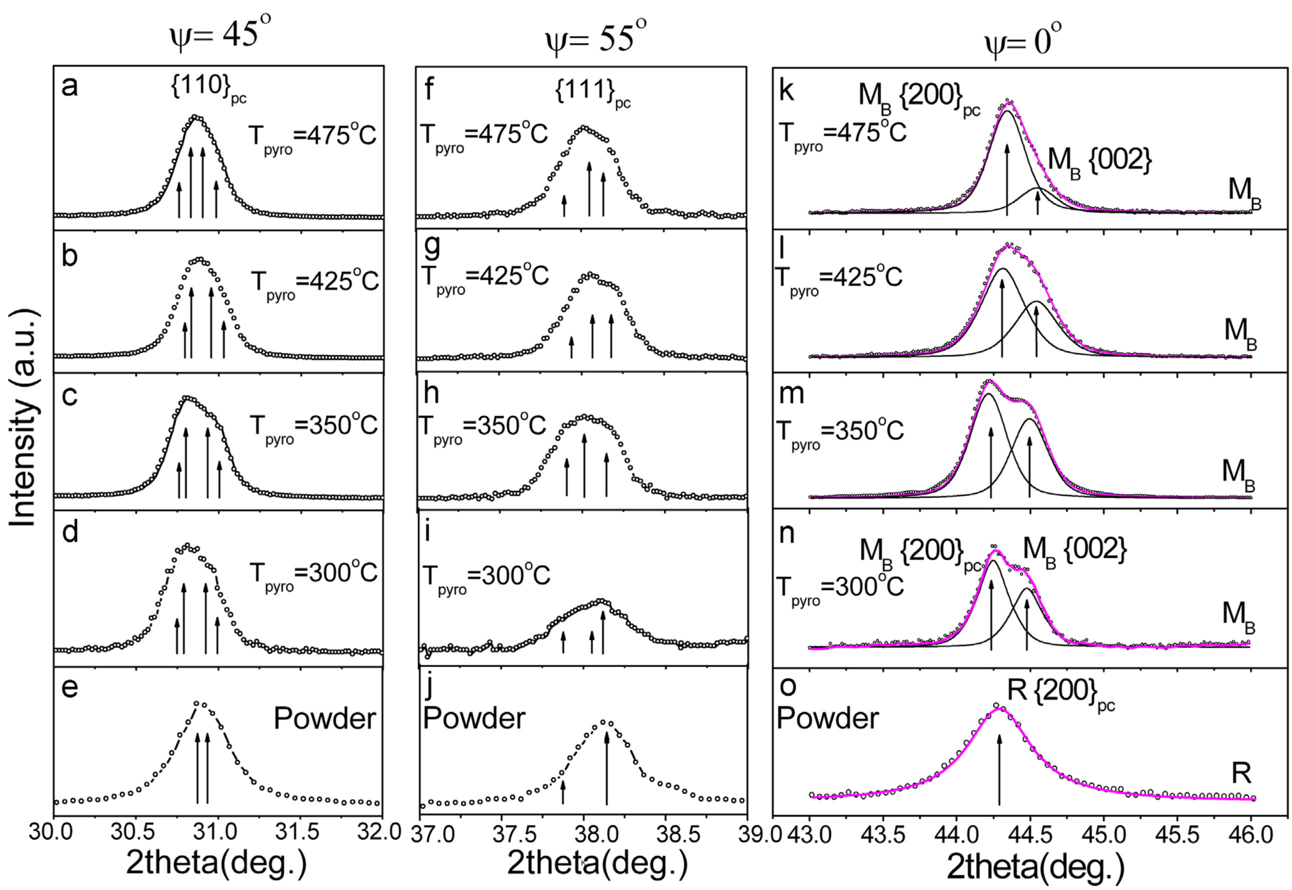

Fig. 2. XRD experimental results on three diffraction and the stress-free powder including the (110) diffraction peaks given by (a)–(e), (111) diffraction peaks given by (f)–(j) and the (200) diffraction peaks given by (k)–(o). The calculated $(200)_{pc}$ profile and peak locations corresponding to proposed crystal phases are also marked in pink line and black arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)