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Role of residual stress on phase transformations of $\text{Pb}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$ thin films obtained from chemical route

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ABSTRACT

The effects of heat treatment on the phase transformations of lead zirconate titanate $\text{Pb}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$ (PZT) thin films were studied. The pyrolysis temperature directly affected the densification, residual stresses, and suppression of the pyrochlore phase observed in the studied films. The evolution of the crystalline phases and the residual stress were characterized by different temperatures of pyrolysis in PZT thin films, using the X-ray diffraction technique. The phase transformations in the films are discussed in terms of theoretical and experimental calculations of residual stress.

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1. Introduction

Lead zirconate titanate, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT), is widely known for its technological importance in developing capacitors, sensors, actuators, and nonvolatile ferroelectric memory devices. For this reason, PZT in different forms (ceramics or thin films) has been one of the most studied ferroelectric materials in recent years. The PZT thin films have been intensively investigated for various applications, ranging from microelectronics [1] to capacitors [2].

Among several methods of preparing thin films, chemical methods have been intensively used due to their low cost and good stoichiometric control [3]. The method used to prepare thin films has a strong influence on their structural and electrical properties. Additionally, thermal stresses are often present in ferroelectric thin films prepared by chemical routes, and frequently, X-ray diffraction (XRD) [4] and Raman spectroscopy [5,6] techniques have been used to evaluate the stresses on these films. In this work, we studied the effect of pyrolysis on the structure and residual stress in PZT thin films prepared by a polymeric chemical method. The XRD and Rietveld refinements were the main tools used to evaluate the structural properties and residual stresses of the PZT films as a function of the pyrolysis temperature. The main contribution of this work is to investigate the possible mechanisms responsible for the origin of the residual stress during the growth of crystalline phases in the PZT films. In particular, the compositional shift in the PZT phase due to the pyrochlore phase growth is considered. The nature of the residual stress on the films is discussed in accordance with the theoretical prediction.

2. Experimental method

The PZT thin films were prepared to study the effect of pyrolysis on the crystallization of the perovskite phase. Films with $\text{Pb}(\text{Zr}_{0.50}\text{Ti}_{0.50})\text{O}_3$ nominal composition, including a PbO excess of 10 mol%, were deposited on the $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}(100)$ substrate by using a chemical route based on the modified Pechini method, as described elsewhere [7]. A polymeric resin with metallic ions randomly distributed along the polymeric chain had been used to prepare the films by spin coating them at 5,000 rpm for 30 seconds. In this step, six samples had been prepared at different temperatures of pyrolysis. The pyrolysis procedure was carried out in the air, putting each film directly in an electric furnace preheated at temperatures of 150°C, 300°C, 350°C, 400°C, and 450°C, respectively, for 30 minutes. After this step, the procedure was repeated with the deposition of a new layer of polymeric resin up to six times and repetition of the same procedure to remove the organics. Upon obtaining the desired film thickness, a final heat annealing was performed for all films in a conventional electric furnace at 700°C for 1 hour to promote the final film crystallization. Typically, after a full pyrolysis, crack-free films with a thickness of 500 nm on average were obtained.

The XRD measurements were performed by using a Rigaku Ultima IV diffractometer with $\text{CuK}\alpha$ (1.5406 Å) radiation at room temperature in a step-scan mode, using the grazing incidence configuration at a fixed $\theta = 5^\circ$ angle and scanning the $2\theta^\circ$ angle from 20° to 60° . For the Rietveld [8] refinements, XRD data were employed as input parameters for the general structure analysis system (GSAS) [9] refinement code under the EXPGUI interface [10]. To simulate the presence of the pyrochlore phase with the perovskite phase, the following models were considered: a pure tetragonal phase (T) for pyrochlore-free PZT thin films, and coexistence of the tetragonal (T) and cubic phases (C) for the films with the perovskite phase and the presence of the pyrochlore phase. The tetragonal phase with $P4mm$ space group was considered, where the Pb^{2+} ion occupies sites at (0, 0, 0), $\text{Zr}^{4+}/\text{Ti}^{4+}$, O_I^{2-} at $(1/2, 1/2, z)$, and O_{II}^{2-} at $(1/2, 0, z)$. Moreover, the pyrochlore phase was simulated with the cubic phase with $Fd3m$ space group, where the Pb^{2+} ion occupies sites at (0, 0, 0), $\text{Zr}^{4+}/\text{Ti}^{4+}$ at $(1/2, 1/2, 1/2)$, O_I^{2-} at $(x, 1/8, 1/8)$, and O_{II}^{2-} at $(1/8, 1/8, 1/8)$. In refinements with the coexistence of phases (T+C), the occupation factor was refined.

3. Results and discussion

Figure 1(a) depicts the selected (100), (110), (111), and (200) profiles of PZT thin films with different pyrolysis temperatures. The indexed (hkl) peaks in this figure refer to the tetragonal phase of the PZT. The shoulder observed at around $2\theta \approx 29^\circ$ for films pyrolyzed at 350°C and 450°C is associated with the pyrochlore phase [11]. For these films, Rietveld refinements of the XRD patterns were performed considering the coexistence of the perovskite and pyrochlore phases. The profiles of the PZT thin films for a pure tetragonal phase (T) and the coexistence of tetragonal and cubic phases (T+C) are shown in Figure 1(a). The obtained cell parameters for these refinements are summarized in Table 1. The splitting of (200) reflections occurring for PZT films pyrolyzed at 400°C and 450°C in Figure 1(a) clearly indicates a compositional shift to Ti-rich compositions, toward the tetragonal side in the composition-temperature phase diagram of the PZT system. The presence of the secondary pyrochlore phase at higher pyrolysis temperature causes this compositional change in the

Figure 1. (a) The experimental data (ball), calculated fit (red lines) and difference (bottom lines) of various reflections for PZT thin films with different pyrolysis temperature, using structural models: Tetragonal (T) and coexistence of Tetragonal + Cubic (T+C) phases. Bars represent calculated positions of the Bragg reflections of the tetragonal (bar) and cubic (cross). (b) Tetragonality factor (c/a), calculated with lattice parameters obtained from refinements, behavior of difference $\Delta\theta = 2\theta_{200} - 2\theta_{002}$ in 2θ peak positions refined for both (002) and (200) for tetragonal reflections and phase fractions of PZT thin films as a function of pyrolysis temperature. Lines are drawn as a guide to the eye in Fig. (b).

perovskite phase. Then, for refinements we consider the pyrochlore phase of the $\text{Pb}_2(\text{Zr}_{1-x}\text{Ti}_x)_2\text{O}_6$ structure [11,12]. According to the refinements, the obtained Zr/Ti occupancy factors for both perovskite and pyrochlore phases were summarized in Table 1. It is observed that for the PZT perovskite phase the Zr/Ti ratio changes from 50/50, for the films pyrolyzed at 150°C and 300°C, to 46/54, 40/60, and 45/55 for the films pyrolyzed at 350°C, 400°C, and 450°C, respectively.

Table 1. Refined structural parameters of PZT thin films with different pyrolysis temperature for the tetragonal and cubic coexistence (T+C); and pure tetragonal phase (T) models.

Pyrolysis	Tetragonal (P4mm)			Cubic (Fd3m)		R-factors χ^2 R_{wp}	
	Cell parameters		Occupancy Zr / Ti	Cell parameters			
	a (Å)	c (Å)		a (Å)			
450°C	4.018	4.109	45/55	10.180	55/45	2.8	14.4
400°C	3.979	4.104	40/60	10.092	60/40	2.4	14.6
350°C	4.057	4.122	46/54	10.246	54/46	2.5	13.8
300°C	4.064	4.122	50/50			2.8	15.0
150°C	4.067	4.107	50/50			2.5	14.4

From the refined parameters, Figure 1(b) plots the phase fractions for perovskite and pyrochlore phases (bottom), the difference $\Delta\theta = 2\theta_{200} - 2\theta_{002}$ in 2θ peak positions (center) and the tetragonality factor (c/a) of PZT thin films (top) as a function of pyrolysis temperature. The phase fractions determined with these refinements indicate a maximum amount $\sim 12\%$ of the pyrochlore phase and a minimum amount $\sim 88\%$ of the perovskite phase for the film pyrolyzed at 450°C . The maximum $\Delta\theta = 1.46$ observed for the film pyrolyzed at 400°C indicates a more Ti-rich composition for this film. This observation corroborates the obtained results for the Zr/Ti ratio shown in Table 1, where we observe that that PZT films pyrolyzed at 400°C is more Ti-rich than the film pyrolyzed at 450°C . These results suggest that the pyrolysis at 400°C is energetically favorable to grow Zr-rich pyrochlore compositions in the PZT films. The shifts in the 2θ peak position for (100), (110), and (111) reflections (not shown here) confirm the Ti-rich composition at higher pyrolysis temperatures and Ti-stoichiometric for lower pyrolysis temperatures. The pyrolysis temperature dependence of the tetragonality factor (c/a) shows essentially the same shape such as observed for the $\Delta\theta$ in Figure 1(b). This is a clear evidence of the relationship between the tetragonality factor and the Ti amount in the PZT composition. This result agree with reported by other authors, the tetragonality factor in bulk PZT ceramics changes from 1.01 to 1.06 for Ti-rich compositions, from Zr/Ti = 50/50 to PbTiO₃ compositions [13].

Residual stress is difficult to avoid in ferroelectric films obtained from high temperatures to low temperatures during the synthesis process. A method to quantify the residual stress in ferroelectric thin films from XRD data has recently been proposed [14]. In this model, the contribution of piezoelectric coupling on the residual stress is taken into account, as reported by other authors [4], where the surface residual stress is calculated as:

$$\sigma_{res} = K\varepsilon_{33}, \quad (1)$$

where $K = -1.012 \times 10^{11} \text{ N/m}^2$ is the piezoelectric coupling factor [4], by using the elastic stiffness coefficients, and the piezoelectric and dielectric coefficients of PZT ceramics, as used by other researchers [15]. To calculate the out-of-plane strain (ε_{33}), information about Bragg peak intensities and positions of the strain-free PZT powder was extracted from the Inorganic Crystal Structure Database (ICSD); in this case, we admitted a compositional error of 2 mol% Ti for the compositions listed in Table 1 for the tetragonal phase. The PZT compositions used as reference for these calculations were Pb(Zr_{0.50}Ti_{0.50})O₃ (ICSD: 90475), Pb(Zr_{0.45}Ti_{0.55})O₃ (ICSD: 55700) and Pb(Zr_{0.40}Ti_{0.60})O₃ (ICSD: 90474). Then the obtained values for ε_{33} were 2.45×10^{-3} , 3.87×10^{-3} , 4.92×10^{-3} , -8.13×10^{-3} , and -2.60×10^{-3} for the films prepared at 150°C , 200°C , 300°C , 350°C , 400°C , and 450°C pyrolysis temperatures, respectively. Next, the residual stress (σ_{res}) in Equation (1) could be calculated at different pyrolysis temperatures.

Considering the crystallographic data from PZT powder and refined data from PZT films, the residual stress was evaluated. Figure 2(a) shows the residual stress of PZT thin films as a function of the pyrolysis temperature. Negative values observed in the residual stress indicate compression behavior, while positive values show tensile residual stress. To understand the pyrolysis temperature dependence of the residual stress, the theoretical residual stress (σ_{res}) can be written as [4,16]:

$$\sigma_{res} = \sigma_{ep} + \sigma_{in} + \sigma_{th} + \sigma_{tr}, \quad (2)$$

Figure 2. Calculated values for: (a) Residual stress, (b) thermal stress and (c) phase transition stress as a function of pyrolysis temperature of PZT thin films. Lines are drawn as a guide to the eye.

where σ_{ep} is epitaxial stress, σ_{in} means intrinsic stress, σ_{th} refers to thermal stress, and σ_{tr} signifies the phase transition stress. Since the structural relaxation relieves this stress from epitaxial strain with the growth temperature, epitaxial stress does not contribute to residual stress [4]. Intrinsic stress is generally due to the incomplete structural order that appears during the deposition process. To calculate intrinsic stress, the difference of the c-axis lattice parameters before and after the pyrolysis needs to be known, which in our case is difficult to obtain.

Thermal stress is induced by the difference of thermal expansion coefficients between the thin film and the substrate during cooling after crystallization, and it can be written as:

$$\sigma_{th} = \frac{E_f}{1 - \nu_f} \left\{ \left[\alpha(c)_f - \alpha_{s1} \right] (T_{gr} - T_{tr}) + \left[\alpha(t)_f - \alpha_{s2} \right] (T_{tr} - T_0) \right\}, \quad (3)$$

where E_f and ν_f are the elastic modulus and Poisson's ratio, respectively, and they are reported as 130 GPa and 0.3 for $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin films prepared by pulsed laser deposition [4]. The $\alpha(c)_f$ and $\alpha(t)_f$ parameters are the thermal expansion coefficients of PZT thin films in the basal plane for the cubic ($9.0 \times 10^{-6} \text{ K}^{-1}$) and tetragonal phases at room temperature. According to the results provided with Rietveld refinements, a compositional

shift to Ti-rich composition would be expected from our samples. Then the thermal expansion coefficients of PZT at room temperature as a function of composition were calculated by using the following formula: $\alpha = (11.51 - 17.36x + 17.71x^2) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, where x is the Ti mole fraction [17]. Table 2 summarizes the calculated thermal expansion coefficients. The coefficients $\alpha_{S1} = 4.2 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{S2} = 2.6 \times 10^{-6} \text{ K}^{-1}$ are the thermal expansion coefficients of the substrate above and below the phase transition temperature (T_{tr}) [17]. The transition temperatures (T_{tr}), due to the cubic to tetragonal phase transition occurring upon the cooling of the growth temperature T_{gr} (700°C) [17,18], are also summarized in Table 2. Then the thermal stresses were calculated from Equation (3). The results are plotted in Figure 2(b) as a function of the pyrolysis temperature. The thermal stresses are positive, and they increase as the pyrolysis temperature rises. The observed behavior for the thermal stress is a consequence of the compositional shift observed for the PZT films, since both the phase transition temperature and thermal expansion coefficient of the films increase with the increase in the pyrolysis temperature.

The phase transition stress is a result of the changes in the lattice parameters of the PZT film upon the cooling of the growth temperature. In the present study, the compositional shift leads to a change in the phase transition temperature of these films, such as Ti-rich compositions having a higher transition temperature, as shown in Table 2. The in-plane phase transition stress σ_{tr} on the film surface can be written as follows [14]:

$$\sigma_{tr} = -\frac{E_f}{2\nu_f}(\varepsilon_{tr}). \quad (4)$$

Based on the elasticity theory, the out-of-plane strain (ε_{tr}) along the x_3 -axis can be evaluated by $\varepsilon_{tr} = \sum_{x=1}^m \varepsilon_{tr}^{h_x k_x l_x} \nu^{h_x k_x l_x}$, where the normal strain on an oblique plane ($\varepsilon_{tr}^{h_x k_x l_x}$) was previously defined [14]. In any case, it is possible to estimate the values for ε_{tr} by obtaining the parameter $\nu^{h_x k_x l_x}$ that correlates the peak intensities for the bulk and the film, as well as considering the lattice parameters at different compositions at room temperature (summarized in Table 1) and the lattice parameters at high temperature, $a_0(T_{700})$ at the cubic phase, extracted from the literature and summarized in Table 2 [19,20]. The calculated values for the out-of-plane phase transition strain (ε_{tr}) are 7.12×10^{-3} , 7.35×10^{-3} , 8.43×10^{-3} , -2.13×10^{-3} , and 5.83×10^{-4} for the films obtained at 150°C , 300°C , 350°C , 400°C , and 450°C pyrolysis temperatures, respectively.

The phase transition stresses (σ_{tr}) were calculated and are shown in Figure 2(c) as a function of the pyrolysis temperature. The phase transition stress is negative for all films, except

Table 2. Summary of pyrolysis temperature, refined PZT (Zr/Ti) composition, thermal expansion coefficient at room temperature for tetragonal phase of PZT thin films, phase transition temperature and lattice parameter at high temperature for bulk ceramics of PZT.

Pyrolysis	PZT (Zr/Ti)	$\alpha(t_f)(^\circ\text{C}^{-1})$	$T_{tr}(^\circ\text{C})$	$a_0(T_{700}) \text{ \AA}$
450°C	45/55	7.32×10^{-6}	407.0	4.067
400°C	40/60	7.47×10^{-6}	418.4	4.054
350°C	46/54	7.30×10^{-6}	400.0	4.067
300°C	50/50	7.26×10^{-6}	392.6	4.075
150°C	50/50	7.26×10^{-6}	392.6	4.075

for the film produced with the pyrolysis temperature at 400°C, where there is a tensile contribution to the residual stress. Otherwise, it would be expected that the sum of different contributions of stress could result in total residual stress. However, in this work, we could not quantify intrinsic stress. Nonetheless, other authors report that intrinsic stress is always negative, independent of the thickness or the annealing temperature [4,14]. However, the origin of the tensile stress observed at 400°C, in our films is not yet completely clear. However, our results suggest a strong relationship between thermal (σ_{th}) and transition (σ_{tr}) stresses with Ti composition increasing in the PZT films. It is reasonable, since Ti-rich compositions in PZT leads to higher phase transition temperatures (T_{tr}) and to higher expansion coefficients (α), as summarized in Table 2. Then, we believe that the compositional shift is the most important contribution for the observed residual stress in our PZT films. Anyway, further experiments are in progress to clarify the nature of the residual stress in the PZT thin films studied in this work.

4. Conclusions

In summary, the pyrolysis temperature effects on the phase transformations and residual stress were investigated for PZT thin films. We observed a coexistence between the pyrochlore and perovskite phases for PZT thin films pyrolyzed at temperatures higher than 350°C, while films prepared under lower pyrolysis temperatures shows only the perovskite phase. The presence of the pyrochlore phase leads to a higher compositional shift in the PZT perovskite phase to Ti-rich compositions at pyrolysis temperature of 400°C. The evaluated thermal, transition and residual stresses reach its maximum values at this pyrolysis temperature. The accordance of these maxima with higher compositional shift and higher tetragonality factor observed for PZT films, suggest that compositional shift to Ti-rich is the most important contribution for the observed residual stress in our PZT films.

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