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# Structural, Dielectric and Ferroelectric Properties of Mixed Texture $PbZr_{0.20}Ti_{0.80}O_3$ Thin Films Prepared by a Chemical Method

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*Titanium-rich lead zirconate titanate compositions are very attractive for pyroelectric applications. Crystalline texture can result in significant thin film properties optimization. In contrast, preparation of textured films requires specific processing parameters. In this work,* $PbZr_{0.20}Ti_{0.80}O_3$*-PZT20/80 thin films with a mixed (001)(100)/(111) texture on Pt(111)/Ti/*$SiO_2$*/Si substrates were obtained through a chemical method by optimizing thermal treatment conditions. Pole figure exhibited a 6.5% texture for the (100) crystalline plane. Dielectric constant and dissipation values for textured PZT films at 100 kHz were 159 and 0.04, respectively. Remanent polarization and coercive field were 13* $\mu C/cm^2$ *and 119 kV/cm, respectively.*

**Keywords** PZT; thin film; texture; dielectric; ferroelectric

## Introduction

Ferroelectric lead zirconate titanate [$Pb(ZrTi)O_3$-PZT] solid solution is one of the most investigated materials system in thin film form because of its potential for important applications such as memories, micro-actuators, optical waveguide devices, spatial light modulators and sensors [1]. These applications are due to the excellent piezoelectric,

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*Corresponding author. E-mail: prgm@iris.ufscar.br pyroelectric, ferroelectric and dielectric PZT properties [2–4]. For pyroelectric applications [5], compositions located close to either $PbZrO_3$ or $PbTiO_3$ have received great interest [6]. Comparatively to the most studied morphotropic phase $PbZr_{0.53}Ti_{0.47}O_3$ (PZT53/47) composition, zirconium-rich and titanium-rich compositions exhibit lower dielectric constant values and can then exhibit higher pyroelectric coefficients. On the other hand, PZT thin films properties depend on many factors including deposition substrate, crystalline orientation, film thickness and microstructure. Crystalline orientation is one of the most important factor that can result in significant properties optimization [7]. In turn, the control of thin films crystalline orientation is very difficult and strongly influenced by the deposition method, deposition substrate and thermal treatments.

The growth of PZT thin films is nucleation controlled [8], and is mainly affected by the substrate and interface properties. Numerous studies for the control of the PZT orientation on various substrates [9, 10] and using seed buffer layers [11] have been reported. For the $Pt/Ti/SiO_2/Si$ substrate (most common thin film substrate), previous studies showed that the PZT(111) texture is found to be nucleated by a $Pt_xPb(111)$ interface layer and PZT(100) texture is found to be nucleated by a PbO(001) interface layer [12–14]. The formation of one or another transient nucleation phase is very sensitive to thermal treatment conditions (heating rate, organic compounds pyrolysis and annealing temperatures) that are specific for each thin film deposition method.

Many different physical and chemical methods like RF-Sputtering, pulsed laser deposition (PLD), sol-gel, metalorganic chemical vapor deposition (MOCVD) and others have been used to prepare textured or preferred orientation PZT thin films [9, 15–17]. The solution-based methods offer advantages including compatibility to photolithography, low processing temperature, excellent compositional control, uniform homogeneity, easy fabrication over large areas and low cost.

Among the solution-based methods, sol-gel and metallo-organic decomposition (MOD) processes are detached manly to the lower processing annealing temperatures. The disadvantages of these methods are the expensive cost of the starting precursors and the necessity of controlled atmospheres in the handling of precursors and prepared solutions. The obtaining of oriented PZT thin films by sol-gel and MOD processes has been the purpose of a number of studies.

An alternative to the sol-gel and MOD processes is the polymeric solution method proposed by Araújo and collaborators [18], that consists in preparing stable deposition polymeric solutions based in the Pechini method [19, 20] and using oxide precursors as starting materials. The main advantage of this method, comparing to the sol-gel and MOD processes, is that it uses less expensive starting precursors. A few works [21, 22] investigated the preparation of PZT thin films through the polymeric solution method. Until now none of these papers report straight studies on orientation degree and correlations to the physical properties in PZT thin films produced through the polymeric solution method.

In this paper, structural and physical properties characterizations were carried out in $PbZr_{0.20}Ti_{0.80}O_3$-PZT20/80 thin films prepared by the polymeric solution method. Different crystallization procedures were applied and the conditions which result in textured PZT thin films were detached. In the textured thin films pole figures were obtained and the orientation degree could be determined. Dielectric and ferroelectric properties were investigated and the results related to the orientation degree were compared with random oriented films.

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**Table 1**
Thin films thermal treatments routes

| Thermal treatment route | Organic compounds pyrolysis | | Crystallization | |
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| | Pre-treatment | Post-treatment | Furnace | Conditions |
| 1 | 350°C/30 minutes | 400°C/3 hours | RTA | 700°C/10 min/air |
| 2 | 350°C/30 minutes | 700°C/1 minute | RTA | 700°C/10 min/air |

## Experimental Procedure

PZT thin films were prepared by a previous reported [18] chemical solution method based in the preparation and deposition of a polymeric resin in which the PZT formation ions were homogeneously incorporated in a polymeric matrix. The resin was obtained by the dissolution of calcined PZT, prepared by conventional mixed oxides route, in an acid ($HNO_3$/distilled water) solution. The solution was then stabilized by the addition of a chelating agent (citric acid) and etilenoglycol. Increasing the solution temperature to around 80°C, metallic ions form chelates with the citric acid and after, at temperatures around 100°C, a polymerization reaction takes place forming the final stable polymeric resin with the metallic PZT ions incorporated in the polymer network.

PZT resin was deposited on $Pt/Ti/SiO_2/Si$ substrates by spin-coating at 3500 rpm for 30 s. Deposited films were then pre-heat-treated on a hot plate at 350°C for 30 minutes to promote the solvents evaporation and organic compounds pyrolysis. After this step, films were prepared using two different thermal treatment routes (listed in Table 1).

As an additional organic pyrolysis treatment, in the first route, film was thermal treated in a conventional furnace (heating rate of 5°C/minute) at 400°C for 3 hours and, in the second route, film was treated at 700°C for 1 minute using a rapid thermal annealing (RTA) process, that consisted in reaching instantaneously (heating rate $\approx$80°C/s) the final treatment temperature. Seven successive resin layers depositions and thermal treatments were performed for each film to reach a final thickness of around 500 nm. The final crystallization process, which consists in the formation of a crystalline PZT phase, was carried out in a RTA furnace at 700°C for 10 minutes in air atmosphere for the two routes.

In the crystallized thin films, structural characterizations were conducted by X-ray diffraction (XRD) using $CuK_\alpha$ radiation in a Rigaku rotaflex RU200B equipment. The texture degree was measured from reflection x-ray pole figures obtained in a Rigaku texture diffractometer configured in the Schultz geometry attached to the Rigaku rotaflex equipment. The times random approach $TR = \frac{\int Ph(y)dy}{\int dy}$, where $\int Ph(y)dy$ is the summation intensity of the pole figure and $\int dy$ is the total area of the pole figure, was used to quantify the texture in the thin films [23].

Dielectric measurements were performed in an Agilent 4284A Precision LCR Meter in the 1 kHz to 1 MHz frequency range. Ferroelectric properties were extracted from the obtained hysteresis loops using a Sawyer-Tower circuit and a digital oscilloscope at room temperature and 1 kHz.

## Results and Discussions

Figure 1 shows X-ray diffraction patterns for PZT20/80 thin films obtained from the two different crystallization thermal treatment routes. A single crystalline PZT phase formation

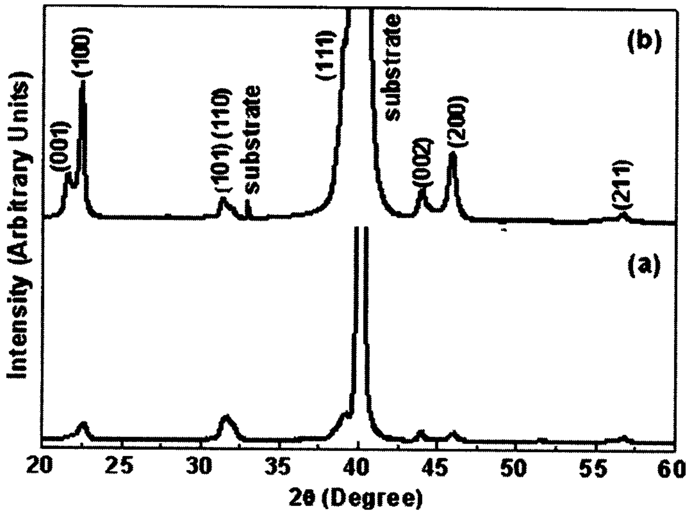

**Figure 1.** X-ray diffraction patterns of PZT20/80 thin films obtained from different thermal treatments routes. (a) route 1 and (b) route 2. See Table 1.

can be observed and, for the thin film prepared under the first route (Fig. 1(a)), no significant difference can be observed in the relative peak intensities. The thermal treatment at 400°C for 3 hours in the first route seems to promote the formation of random oriented seeds or a random oriented interfacial layer between the film and substrate that, even though using the RTA process for crystallization, preferred crystalline orientation was not obtained in the thin films. Figure 1(b) shows the X-ray diffraction pattern for the film prepared under the second route. For this crystallization procedure, thin film revels a better crystalline phase formation and a clear increase of the (001), (100), (111), (002) and (200) peak intensities comparatively to the (101) and (110) peak which are the most intense peaks in the diffraction pattern of random oriented PZT's. The organic pyrolysis thermal treatment at 700°C for 1 minute via rapid thermal annealing (heating rate ≈80°C/s) preferentially promotes the formation of a PbO (001) buffer layer which matches the lattice parameters with the PZT (001)/(100) and plays a role of seed to the next deposited layers. The (111) peak is also intense and shows that a $Pt_XPb(111)$ is also formed using this pyrolysis process. During the final crystallization thermal treatment (700°C for 10 minutes via RTA process), the oriented grains grow to form the final microstructure and the (001)(100)/(111) mixed texture.

Figure 2 shows the pole figure on the (100) plane for the PZT20/80 thin film that has a mixed texture. The TR value of 6.5% in the pole figure center is the orientation degree of the (100) PZT plane parallel to the substrate surface (substrate perpendicular is parallel to the PZT unit cell perpendicular). We can see also a distortion of the (100) PZT plane with respect to the substrate surface plane (lines around the pole figure center) indicating that some of the (100) PZT planes are not really parallel to the substrate surface.

Dielectric measurements (Fig. 3) show that textured films (Fig. 3(b)) exhibit dielectric constant values 2.2 times higher than those of non-oriented films. Dielectric constant values at 100 kHz frequency for textured and random oriented films were 159 and 71, respectively. Dissipation factor (tan$\delta$) for non-oriented films exhibits higher values than textured films. For non-oriented and textured thin films at 100 kHz frequency tan $\delta$ is 0.08 and 0.04, respectively. Dielectric constant and dissipation factor obtained here are in well agreement hermal treat-

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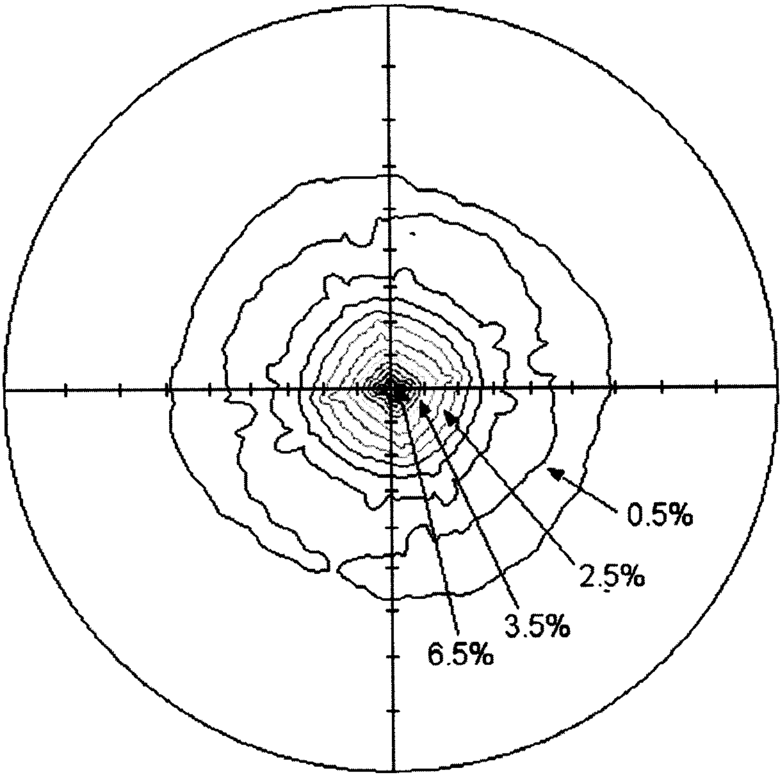

**Figure 2.** Pole figure on the (100) plane for textured PZT20/80 thin film.

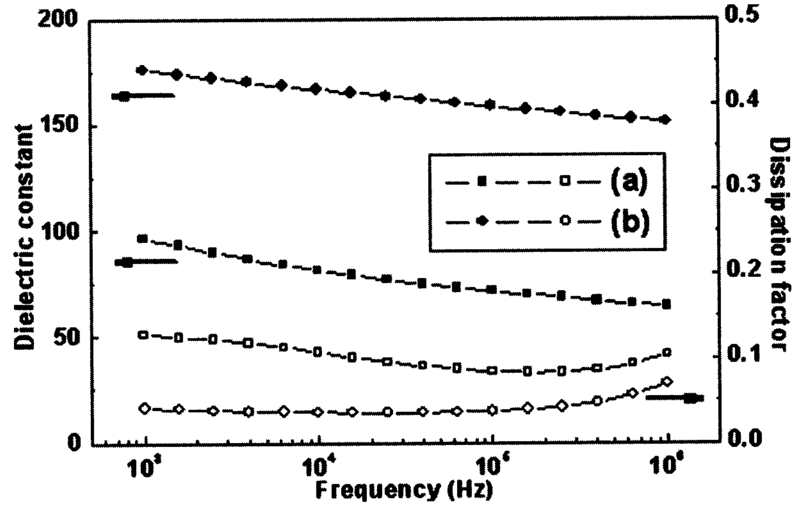

**Figure 3.** Dielectric constant and dissipation factor as a function of frequency for PZT20/80 thin films prepared under the routes 1 (a) and route 2 (b). See Table 1.

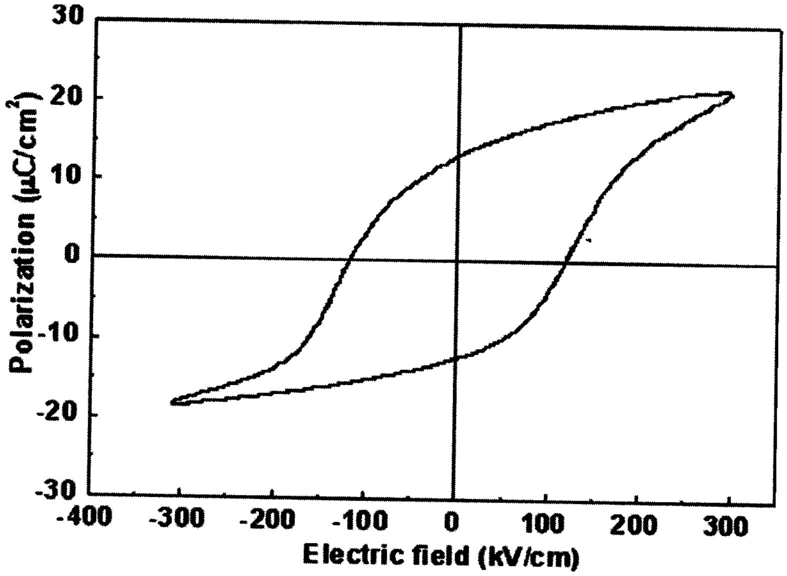

**Figure 4.** Hysteresis loop, measured at 1 kHz, of PZT20/80 thin films prepared under the routes 2. See Table 1.

with values from thin films prepared by others authors [24] using different methods and make possible application of these thin films in pyroelectric detectors [2].

Typical ferroelectric hysteresis loop collected at room temperature and 1 kHz is shown in Fig. 4. Remanent polarization ($P_r$) and Coercive field ($E_c$) for textured films were around 13 and 119 kV/cm, respectively. The distortion (asymmetry) observed in the hysteresis loop can be associated to the presence of dissimilarity between the two electrode/film interfaces. While the upper electrode/film interface does not pass by any thermal treatment, the lower electrode/film interface passes by all the seven deposited layers thermal treatments. As a result, crystalline interface defects will be different in the two interfaces, resulting in anomalies like that observed in hysteresis loops [17].

## Conclusions

PZT thin films with the composition $PbZr_{0.20}Ti_{0.80}O_3$ were prepared by a chemical polymeric method. Thin films crystalline orientation showed to be greatly influenced by the preparation thermal treatments. Thin films with (001)(100)/(111) mixed textures were successful obtained using a layer by layer rapid thermal annealing process. Pole figure on the (100) plane shows an orientation degree of 6.5% for this plane parallel to the substrate surface. Dielectric and ferroelectric measurements showed that (001)(100)/(111) textured PZT films exhibit dielectric constant values (159 at 100 kHz) 2.2 times higher than non-oriented films and remanent polarization and coercive field of 13 $\mu C/cm^2$ and 119 kV/cm, respectively. Dielectric and ferroelectric properties are in well agreement with those obtained by other authors in thin films prepared through different methods and these values make possible the application of such materials in pyroelectric sensors.

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