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Sol-gel reaction stability studied: Influence in the formation temperature and properties of ferroelectric thin films

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ABSTRACT

Lead zirconium titanate (PZT) sol-gel solutions were prepared based on distilled lead acetate precursor solutions. A detailed analysis of the distillation effect on the lead precursor and the final PZT solution were carried out by Infrared and Raman techniques. It was found that the increase in the number of distillation steps experienced by the lead precursor solutions removes the constitutional water and increases the lead acetate-2-methoxyethanol interconnectivity; thus improving stability and avoiding the aging effect of the resulting PZT solutions. The thermal decomposition process of the PZT solutions was analyzed based on the thermogravimetric (TG) and differential thermogravimetric analysis (DTA) measurements. It was found that as the number of distillation steps in the lead precursor solutions increases, the decomposition rate increases and the formation temperature of pure perovskite PZT films decreases. X-ray diffraction (XRD) technique was used to study the film phase formation. A pure perovskite phase at 500 °C was found by the XRD analysis after the second distillation step. Scanning electron microscope technique was used to carry out the microstructural analysis. Dense microstructure was found in all analyzed films and an incipient columnar grain growth was revealed in PZT films prepared based on lead precursor solution with more than three distillation steps. The dependence of the dielectric, ferroelectric and piezoelectric properties on the number of distillation steps was revealed and a correlation between the distillation process, film microstructure properties and electrical performance was established.

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1. Introduction

Ferroelectric thin films have been extensively investigated for a variety of applications ranging from non-volatile memories (NV-FeRAM) to micro-electro-mechanical systems (MEMS) [1,2]. However, most of these ferroelectric thin films applications require processing compatibility with the major fabrication procedures used in semiconductor industry [3–5]. One of the main ferroelectric thin films incompatibilities is their relatively high crystallization temperature, typically over 600 °C; this temperature combined with an oxygen atmosphere often causes metal oxidation (specifically of the titanium interlayer commonly used for adhesion purposes [6]). High processing temperatures of ferroelectric films require special precautions such as: development of barrier layers or introducing unnecessary steps into a

batch fabrication procedure [6,7]. This is particularly important for micromechanical applications, where the introduction of additional interlayers and mechanical stress produced by the high temperature annealing are detrimental in the actuation and sensing capabilities of many microdevices. It is also believed that for ferroelectric thin film processing at temperatures lower than 500 °C, silicon wafers can be replaced by inexpensive glass and even plastic substrates allowing the formation of novel devices (e.g., thin film MEMS) [8].

Among all the ferroelectric materials, lead zirconium titanate (PZT) thin films show the highest application potentials due to the exceptional ferroelectric, pyroelectric and piezoelectric properties; mainly for the compositions close to morphotropic phase boundary ($PbZr_{0.52}Ti_{0.48}O_3$), where the multiple polarization states may contribute to enhance their dielectric and piezoelectric properties [9,10]. Ferroelectric PZT thin films have been prepared by several chemical and physical methods, such as: sol-gel process, metallo-organic decomposition (MOD), radio frequency sputtering (RFS), and pulse laser deposition (PLD) [9,11–13].

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Among them, sol-gel method provides higher composition ratio control. Unfortunately, this method shows two important disadvantages: the *chemical instability* of the precursor solutions and the relatively *high processing temperature* to obtain monophasic films [14]. For those reasons, the preparation and analysis of stable precursor solutions, which lead to the formation of high-quality ferroelectric PZT films at low sintering temperatures, is extremely important.

In this paper we analyzed the influence of the multiple distillations in the lead precursor solution and its effect on the solution stability, the decomposition process and the sintering temperature. Dielectric, ferroelectric and piezoelectric properties of the PZT films will be presented and analyzed, taking into account the structural changes caused by the distillation process.

2. Experimental procedure

High purity reagents were selected for the preparation of the PZT solutions: extra pure lead acetate trihydrate (99.99%) ($\text{Pb}-(\text{OOC}-\text{CH}_3)_2 \times 3\text{H}_2\text{O}$), tetra-*n*-propyl-orthozirconate (70%) in *n*-propanol and tetra-isopropyl-orthotitanate (99.99%) were used as reagents. Meanwhile, 2-methoxyethanol (99.99%) was used as a stable matrix solvent. The preparation of the PZT solutions with a zirconium titanium rate of 52/48 was based on the Budd et al. method [15,16] and a precursor solution modification. Firstly, solvent is warmed up to 78 °C, in order to dissolve the lead precursor as reported by Budd et al. [15,16]. This standard procedure is followed by a modification in the preparation method, which consists in multiple distillation steps of the lead acetate–2-methoxyethanol precursor solutions. The temperature of the solution is increased up to 125 °C, remaining at this temperature for 30 min. This procedure is carried out with the intention of eliminating low molecular weight compounds (water and free acetic acid). Solvent loss is recovered by the addition of approximately 20% of pure 2-methoxyethanol. This addition is carried out *in situ*, except in the last distillation step where the system is cooling down to room temperature before the addition of 2-methoxyethanol. The above-mentioned is carried out in order to preserve the desired molar concentration. The distillation process could be repeated several times; however, after five distillations the process is not useful because the properties of the PZT films remain unchangeable.

Viscosity measurements were performed using a Carry-Met CSL Digital Rheometer and recorded at one day, one month, six months and twelve months after preparation. Infrared measurements were carried out using a Mattson (Madison, WI, USA) 7000 FTIR spectrometer. The infrared (IR) patterns were recorded between 400 and 4000 cm^{-1} , using 128 scans at a 2 cm^{-1} resolution. Raman spectra of the lead acetate precursor material, the distilled lead precursor solutions and the resulting PZT solutions were collected using a standard Bruker RFS 100/S Raman spectrometer. The measurements were carried out at room temperature in the range of 400 and 3600 cm^{-1} using 128 scans at a 2 cm^{-1} resolution.

A complementary Raman study was carried out at frequencies below 800 cm^{-1} , focusing on the dependence of the lattice dynamics on the number of distillation steps. These measurements were performed by a T64000 Jobin Iyon spectrometer equipped with a CCD detector and a Spectra Physics laser working at 541 nm. The spectra resolution was $\sim 1 \text{ cm}^{-1}$.

Thermogravimetric (TG) and differential thermogravimetric analysis (DTA) measurements of 2 ml of PZT solutions gelated at 80 °C during 24 h were performed using a Seteram Labsys TG-DTA/DSC analyzer.

All the films were spin-coated onto Pt/TiO₂/SiO₂/Si substrates using a Karl Suss RC5 spin coater. Each individual layer, spinning at

3000 rpm@30 s, was dried at 200 °C during 1 min and pre-sintering at 500 °C during 10 min. After 15 coating layers, the pre-annealed films were crystallized (annealed) at 500 °C during 1 h. Films X-ray diffraction (XRD) patterns were recorded using a Rigaku D-max diffractometer with copper $\text{k}\alpha$ radiation. The measurements were performed in a step mode (0.01°/10 s), from 20° to 80° in two theta. Scanning electron microscopy images were archived using a field emission scanning electron microscope (Hitachi S4100 at 25 kV@11 mA).

In order to carry out the electric characterization 120 nm thick gold electrodes were deposited on the top of the PZT films by radio frequency magnetron sputtering technique. The dielectric measurements were performed at room temperature using a Hewlett-Packard precision LCR 4284A meter with a driving voltage of 100 mV@1 kHz. The hysteresis loop measurements were carried out using the ferroelectric analyzer TF Analyzer 2000, equipped with ferroelectric module. A double-beam laser interferometer, with an active stabilization of the working point and a lock-in amplifier PerkinElmer 7265 collector system, was used to measure the piezoelectric coefficient of the films [17].

3. Results and discussion

3.1. Solution analysis and decomposition process

Fig. 1 shows the viscosity curves of the PZT solutions prepared based on lead acetate–methoxyethanolic precursor solutions with 1–5 distillation steps (D), as a function of the elapsed time after the preparation process. During the first six months (4320 h), no aging effects were observed in all the prepared solutions; however, above this period PZT solutions prepared based on lead precursor solution with one (1D) and two (2D) distillation steps show an increase in their viscosity, which is a clear indicator that an aging process is taking place. On the other hand, the viscosity of the PZT solutions prepared based on lead precursor solution with three (3D) or more distillation steps did not increase, thus confirming that these solutions are stable during all the analyzed period.

It is expected that the increase in the number of distillation steps done on the lead acetate–methoxyethanolic precursor solutions eliminates the constituent water and the free acetic acid presented in the lead acetate trihydrated precursor, stimulating the interaction of the lead acetate with the 2-methoxyethanol. The increase in the lead acetate–2-methoxyethanol interaction could be the responsible of the formation of more stable lead precursor solutions with a higher endurance to aging effects. Two

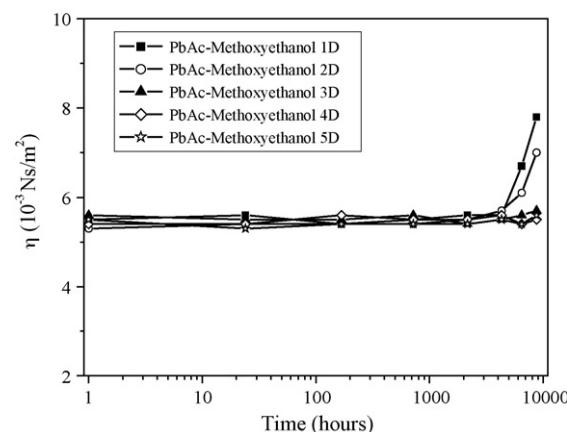


Fig. 1. Viscosity behaviour of the different PZT solutions prepared based on lead acetate–methoxyethanolic precursor solutions with 1–5 distillation steps, as a function of the time elapsed after the preparation process.

different processes can contribute to the increase in the stability and aging endurance of the PZT solutions, as the number of distillation steps in lead acetate-methoxyethanolic solutions increases: (1) the elimination of the hydrolyzing groups, and (2) the cation chelating by an organic layer, which both are a direct consequence of the water elimination from the reaction environment.

Fig. 2 shows the infrared spectra of the lead acetate-methoxyethanolic precursor solutions, with one and five distillation steps. The increase in the number of distillation steps eliminates the free acetic acid ($C=O$, 1710 cm^{-1}) and decreases the intensity of various peaks. The main changes in the IR patterns were found in the intensity of the peaks of the CH , CH_2 , CH_3 ($2500\text{--}3000\text{ cm}^{-1}$ bands), OH (3500 cm^{-1} band) and $Pb-(OOC-CH_3)_2$ ($1200\text{--}1600\text{ cm}^{-1}$ bands), which decreases with the increasing the number of distillations.

Some authors [18] have reported that by refluxing the lead acetate precursor in 2-methoxyethanol, one of the acetate groups is replaced, resulting in the formation of the soluble lead precursor, $Pb(OOCCH_3)(OCH_2CH_2-O-CH_3) \times 0.5H_2O$. However, it is not exactly correct. The decrease in the intensity of the some infrared peaks resulting from a progressive solution distillation or refluxing (Fig. 2) cannot be correlated with a replacement of the acetate group, because any replacement of the acetate group results in a variation of the infrared peaks position and not in their intensity. This fact is also supported by organic chemical rule that states that the alkoxy groups do not replace the carboxyl groups, due to the higher stability of the last one [19]. Therefore, the decrease in the intensity of the bands with number of distillation steps increase could be associated with the substitution of the constituent water by a nucleophilic specie, such as the 2-methoxyethanol and/or the elimination of this constituent water during the distillation process.

As aforesaid, the substitution of the constituent water ($O-H$ band) by an electronegative methoxyethanol $O-H$ or $C-O-C$ bands chelate the Pb^{2+} cation, increasing the reactivity of the lead acetate-methoxyethanolic solutions towards the zirconium and titanium species when these species are added to the solutions. It is well known that the 2-methoxyethanol $C-O-H$ dentate ligands substitute partially or totally the propoxyl ($CH_3CH_2CH_2O^-$ or RO^-) groups [19] when metallic propoxides ($M-OR$) are added to the solution. The substitution of the propoxyl groups results in a lead-zirconium-titanium ions network, increasing the stability of the PZT solutions. Generally, residual *n*- and iso-propoxides are eliminated during the mixing process at $80\text{ }^\circ\text{C}$ (24 h), but could also remain in the solution as a viscosity controller.

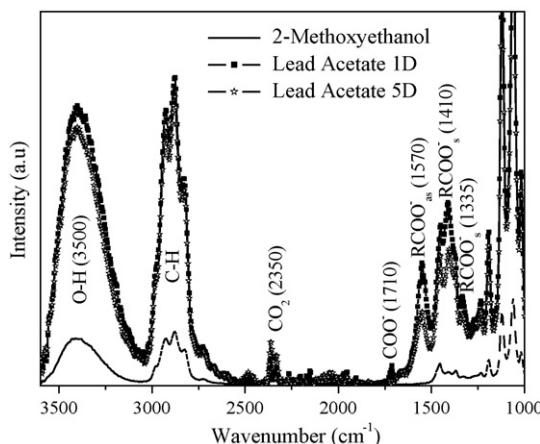


Fig. 2. Infrared spectra of the lead acetate-methoxyethanolic precursor solutions with one and five distillation steps.

Fig. 3 shows the $400\text{--}4000\text{ cm}^{-1}$ Raman patterns of the 2-methoxyethanol solvent and the lead acetate-methoxyethanolic precursor solutions with one and five distillation steps. The increase in the number of distillation steps does not induce notable shifts or changes in the Raman frequency position for certain modes. Moreover, the acetate group reference bands do not appear in the Raman patterns, which is a consequence of the molecular symmetry. The inset plot of Fig. 3 shows the lead-oxygen-carbon band ($Pb-O=C$), which changes with the increase of the number of distillation steps. The small change in the position of the $Pb-O$ bands in the Raman spectra suggests a modification in the surrounding of the lead acetate resulting from the possible constituent water elimination and subsequent lead acetate-methoxyethanol interaction.

A complementary Raman study was carried out in order to find out possible changes in the low frequency modes of the lead acetate-methoxyethanolic precursor solutions as the number of distillation steps increase, as shown in Fig. 4. Significant low frequency modes changes were observed in the $100\text{--}700\text{ cm}^{-1}$ range, where various modes become clearly visible just after the first distillation step. A model of independent damped harmonic oscillators was used to fit the experimental data in order to determine the frequency, width, and intensity of those modes, as a function of the number of distillation steps (see Fig. 4a–c). As it is observed in Fig. 4a, two additional modes with frequencies located at ~ 120 and 650 cm^{-1} , associated with 2-methoxyethyl modes ($Pb-O_{-R}-O-C_2H_5$, $R = 2\text{-methoxyethyl}$), become active only after the second distillation step. Their intensities do not decrease, instead keep constant or even increase. The *unchange* character of these bands is an indication of a complex lead saturation. It seems that the band appearing at lower wavenumber is an indication of the lead and alcoxylic oxygen interaction, whereas the low energy band is due to the interaction of the lead atom with the low-charge and sterically constrained ether oxygen ($C-O-C$). The width of these modes increases slightly, revealing the existence of some degree of disorder, which could be associated with various molecular rearrangements in the precursor solution, resulting from the distillation procedure.

Infrared and Raman results evidence an increasing interaction between the 2-methoxyethanol and the lead acetate ($Pb-O$) groups as the number of distillation steps experimented by the lead acetate-methoxyethanolic precursor solution increase. In fact, this result indicates that the acetate groups are not replaced by the methoxyethanol and that the low molecular weight compounds like the constituent water and the free acetic acid

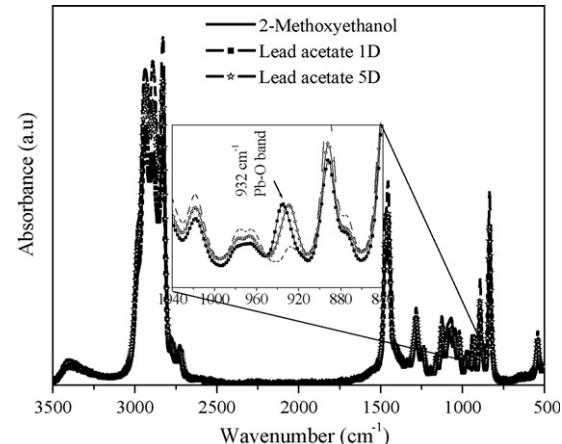


Fig. 3. Raman patterns of the 2-methoxyethanol solvent and the lead acetate-methoxyethanolic precursor solutions with one and five distillation steps.

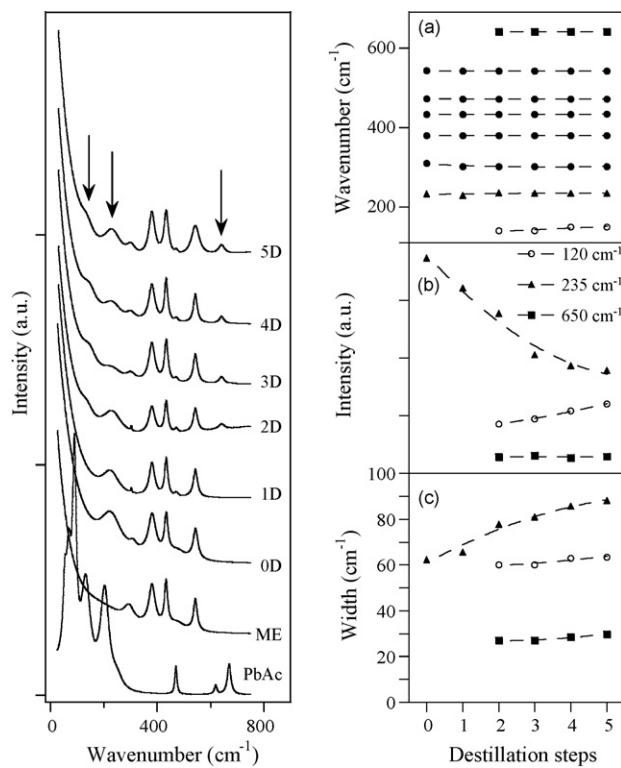


Fig. 4. Raman patterns of lead acetate trihydrate, 2-methoxyethanol and distilled lead acetate-methoxyethanolic solutions in the range of 25–800 cm^{-1} . (a–c) shows the wavenumber, intensity and width of the lead acetate-methoxyethanolic solutions low frequency modes versus the number of distillation steps.

have been eliminated from the solution. The above-mentioned results confirm that the higher stability and the aging endurance of the PZT solution does not result of the substitution of the acetate groups, as shown by Schwartz [18] and in fact, it is a result of the elimination of the constitutional water and the increase of the lead acetate–2-methoxyethanol interaction in the lead precursor solutions.

It could be expected that the distillation process carried out on the lead acetate–methoxyethanolic solutions is unnecessary, since the stability of the lead solution might be also archived by a drying process of the lead acetate trihydrated precursor. However, it is not precisely true. Fig. 5 and Table 1 show the lead acetate trihydrate decomposition process up to 500 °C. Thermogravimetric and differential thermal analysis (DTA) curves show an early evaporation of environmental water followed by evaporation of the lead acetate free acetic acid and the constituent water up to 150 °C. Those processes are followed by a dimerization or/and polymerisation of the lead acetated trihydrated (140–240 °C), which is embedded in the final step of the constituent water evaporation process. Forward increases in the drying temperature of the lead acetated trihydrated result in lead carbonate and lead oxide

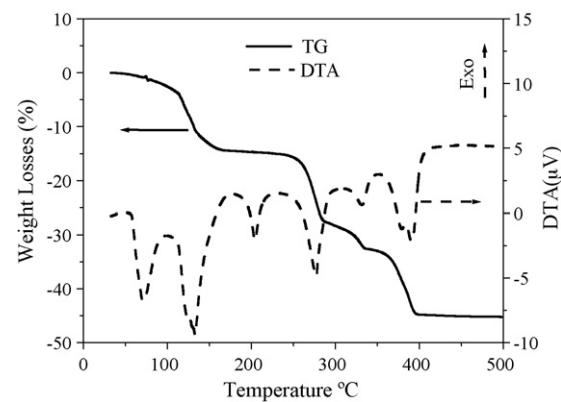


Fig. 5. Thermogravimetric analysis and differential thermal analysis of the lead acetate trihydrate precursor.

formations. As shown in Fig. 5 and Table 1, the elimination of the constituent water using a drying process result in di- or/and polymerisation of the lead acetate, which reduce the reactivity of this dry lead precursor toward the 2-methoxyethanol and avoid the formation of a stable lead precursor solution.

Fig. 6 shows the infrared patterns of the PZT solutions prepared based on lead acetate–methoxyethanolic precursor solutions with several number of distillation steps. A small shift is experimented by the IR bands located at 1720, 1410 and 1335 cm^{-1} as the number of the distillation steps in the lead acetate–methoxyethanolic solutions increase. This behaviour could be associated to the increases in the strength of M–O bond, resulting from the formation of R–O–M–O–R structures (M = Pb, Ti, Zr) instead of R–O–M–O–H structures, as the number of distillation steps experimented by the lead acetate–methoxyethanolic solutions increase.

Fig. 7 shows the Raman patterns of the PZT solutions prepared using precursor based on lead acetate–methoxyethanolic precursor solutions with one, two and three distillation steps. There are small shifts in the bands located at 1356, 1155 and 1100 cm^{-1} ; however, the main change is observed at 604 cm^{-1} , where a new band appear after three distillation steps. This band is also visible on the PZT solutions prepared based on two distilled lead precursor solutions, but at 612 cm^{-1} and with a lower intensity. This means that the increases in the interaction between the lead acetated and 2-methoxyethyl solvent as the number of distillation steps increases (Fig. 4), somehow affects the interaction of the zirconium and titanium precursors with the lead acetated–2-methoxyethyl precursor solution.

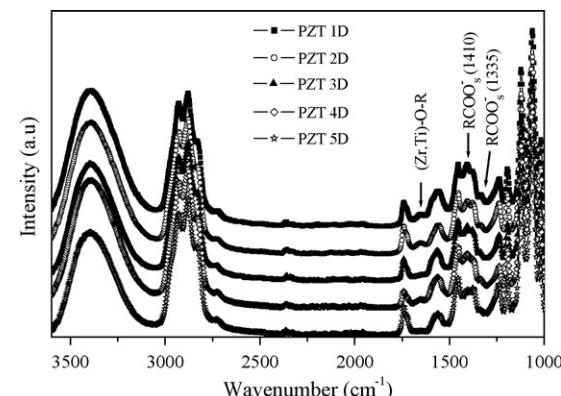


Fig. 6. Infrared spectra of the PZT solutions prepared based on lead acetate–methoxyethanolic precursor solutions with different distillation steps.

Table 1

Weight losses occurred during the decomposition process of $\text{Pb}(\text{Ac})_2 \times 3\text{H}_2\text{O}$

Temperature (°C)	Parameters		
	Detected compounds	Theoretic weight losses (%)	Experimental weight losses (%)
25	$\text{Pb}(\text{Ac})_2 \times 3\text{H}_2\text{O}$	0	0
150	$\text{Pb}(\text{Ac})_2$	14.3	15.2
300	PbCO_3	29.5	29.6
395	PbO	41.2	44.5

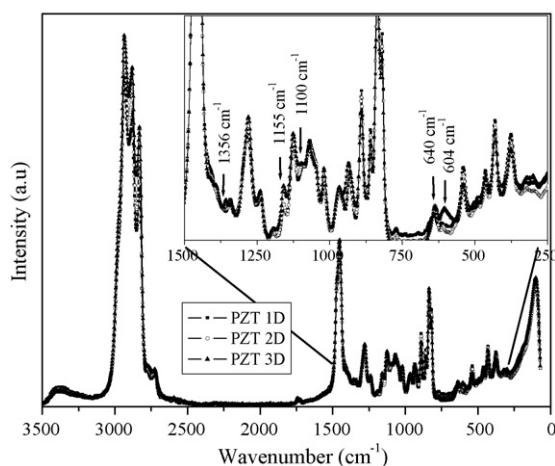


Fig. 7. Raman patterns of the PZT solutions prepared based on lead acetate-methoxyethanolic precursor solutions with one, two and three distillation steps.

Fig. 8 shows the comparison of TG curves of dried PZT solutions prepared based on lead acetate-methoxyethanolic solutions with one and five distillation steps. There are four major steps during the heat-treatment process: solvent elimination, organic decomposition, oxide formation and material phase formation. The weight losses experienced by the system as the temperature increase up to 120 °C are obviously related with the elimination of the solvent [20,21]; meanwhile, the range over the 120 °C and below the 300 °C is associated with the decomposition of most of the organic species and their subsequent carbonate formation. It is clear that the organic decomposition is faster and the weight losses is higher as the distillation step number increase; apparently due to the higher cation-methoxyethanol interaction and the progressive elimination of the low molecular weight compounds. The oxide formation starts above 350 °C, showing accentuate differences among the 1D, 3D and 5D curves. The broad shoulder at ~350–450 °C in the TG analysis of the 1D solution is completely correlated with the decomposition of titanium and zirconium hydro-alkoxides and subsequent oxide formation, which take place at ~365 and the 440 °C, respectively. The stabilization of the weight losses at ~470 °C for 3D and 5D solution and ~500 °C for the 1D solution suggests the formation of a stable perovskite PZT phase.

Fig. 9 shows the DTA curves of PZT sol-gels prepared based on lead acetate-methoxyethanolic precursor solutions with one, three and five distillation steps.

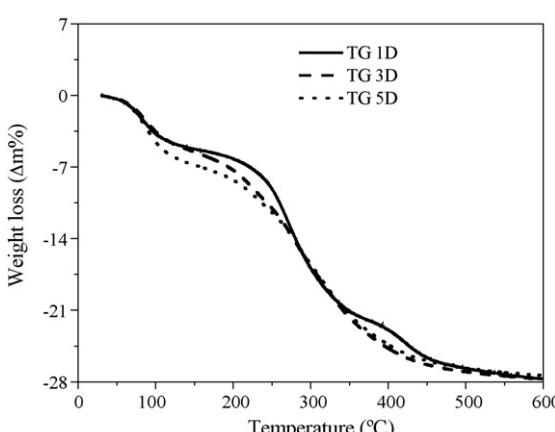


Fig. 8. Thermogravimetric analysis of dried PZT solutions prepared based on lead acetate-methoxyethanolic solutions with one, three and five distillation steps.

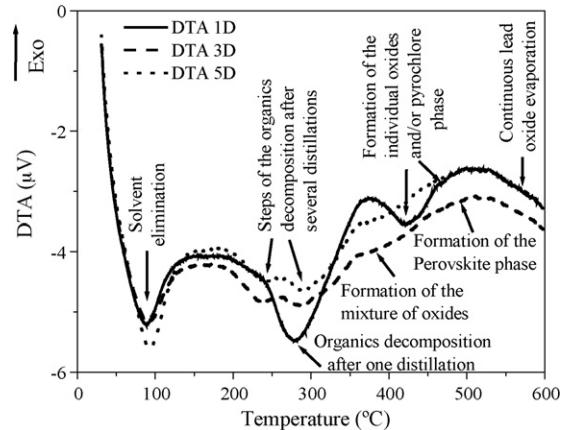


Fig. 9. DTA curves of dried PZT solutions prepared based on lead acetate-methoxyethanolic solutions with one, three and five distillation steps.

three and five distillation steps. The differential thermal analysis of the 1D, 3D and 5D samples is quite different, mainly in two intervals (those around 200–300 and 350–450 °C), indicating different decomposition and reaction rates. The decomposition (reaction) of the PZT precursor solution based on 1D lead acetate solutions shows a broad single carbonate formation peak around 280 °C, certainly associated with the water content in the precursor solution and a clear oxide formation around 430 °C. The oxide formation process is thought to be followed by a metastable pyrochlore formation determined by the small second peak around the 450 °C. Finally, the desire perovskite PZT phase formation becomes visible around 480 °C.

Meanwhile, the decomposition of the PZT solution based on 3D and 5D lead acetate precursor solutions shows a double DTA peaks at 240 and 280 °C, which are associated with the organic decomposition and the partial formation of carbonates. This process is followed by a continuous band, which starts near 350 °C. The shape of the peak suggests that the oxide formation occurs with simultaneous interaction of the cations (Pb, Zr and Ti) and oxygen specie, leading the early perovskite phase formation. This means that an independent oxide formation (i.e., PbO, ZrO₂ or TiO₂) is not taken place. The above-mentioned complex oxide formation is the responsible for the elimination of the metastable pyrochlore phase and the early apparition of the PZT perovskite phase near the 460 °C. In other words, the increase of the distillation process (≥ 3 D) results in low PZT perovskite phase formation.

3.2. Formation and microstructure analysis of PZT films

Some modifications, based on TG and DTA measurements, were brought into the standard PZT heat-treatment process [15]. Drying process was carried out at 200 °C during 2 min and the pre-annealing process performed at 500 °C during 10 min, with the purpose to obtain a rapid decomposition of organics and a semi-crystallization of the coating layer. This semi-crystallized layer acts as a seed layer for the next coating, leading an early formation of the PZT perovskite phase in this coating layer [22,23]. The multiple coating was followed by an annealing process at 500 °C during 1 h, in order to obtain a perovskite PZT film.

Fig. 10 shows the X-ray diffraction patterns of the PZT films prepared based on lead acetate-methoxyethanolic precursor solutions with one, three and five distillation steps. All films show the PZT perovskite phase peaks; however, films coming from lead precursor solutions with single and double distillation steps show

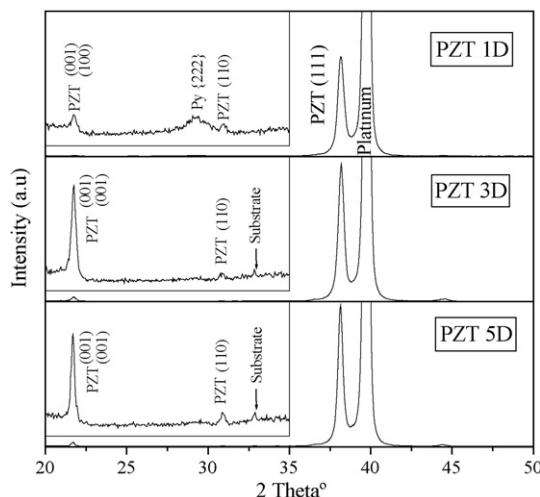


Fig. 10. X-rays patterns of PZT films prepared based on lead acetate-methoxyethanolic solutions with different number of distillation steps and annealed at 500 °C during 1 h. Inset plots show an enlargement of the X-ray patterns in the 20–35° range.

also residual pyrochlore phase. The formation of the pyrochlore phase might be enhanced by the separated formation of the ions oxides and the high amount of the lead precursor. Generally, this unreacted lead excess is diffused to grain boundary and the film's surface [24]. In the film with multiple ($D \geq 3$) distillation steps of the lead precursor solution, the pyrochlore peak is suppressed indicating that all lead excess is consumed by firing at 500 °C during 1 h. All the films show a high degree of (1 1 1) texture with an appreciable intensity of the (1 0 0)/(0 0 1) peaks in films prepared with more than two distillation steps of the lead precursor. The results show that with the increase of the number of distillation steps in the lead precursor solution, the traces of

pyrochlore or other lead oxide (secondary) phases are eliminated and a pure perovskite PZT phase is remained.

Surface microstructure images of the PZT films prepared based on lead acetate solution with one and five distillation steps are shown in Fig. 11. An unclear microstructure with few rosette-type features is observed in the SEM top-view image of the film prepared with one distillation step of the lead precursor solution, in agreement with the X-ray pattern of this film. Rosette structures are frequently observed when residual pyrochlore is present on the surface [25,26]. On the other hand, clear grains of the size of ~50 nm are visible on the plan-view image of the film prepared with five distillation steps of the lead precursor, with no evidence of rosette (pyrochlore) structure. Films processed based on lead acetate-methoxyethanolic precursor solutions with multiple distillation steps ($D \geq 3$), show pyrochlore peak suppression, which indicates that the lead excess in the film surface is burned out during the firing process.

Fig. 12 shows the SEM cross-section microstructure images of the PZT films prepared based on lead acetate-methoxyethanolic solutions with one and five distillation steps. Dense microstructure is archived in all the films. Moreover, an incipient columnar grain growth is observable in the film prepared using several ($D \geq 3$) number of distillation steps in the lead precursor, showing that an accelerated crystallization process is taking place in these samples.

Microstructure images and TG-DTA and X-rays measurements show that the increase of the number of distillation steps on the lead precursor solution favours the formation of pure PZT perovskite phase at lower annealing temperature, which is entirely consistent with the results achieved in the chemical solution analysis.

3.3. Electrical properties of the PZT films

Table 2 shows the electrical properties of the PZT films prepared based on modified PZT solutions. Dielectric, ferro-

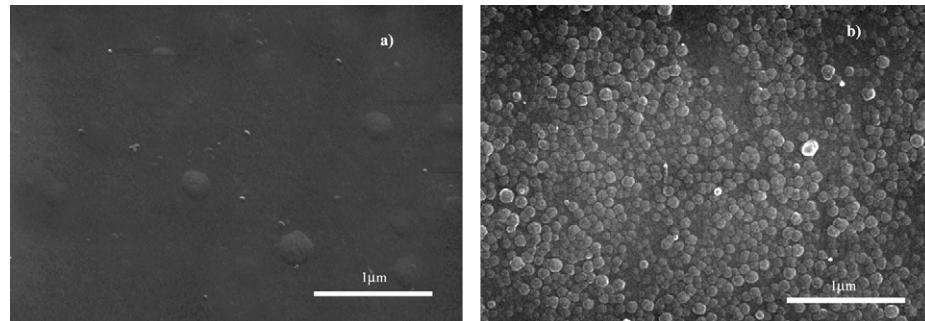


Fig. 11. SEM plan-view microstructure images of the PZT films prepared based on lead acetate-methoxyethanolic solutions with (a) one and (b) five numbers of distillation steps.

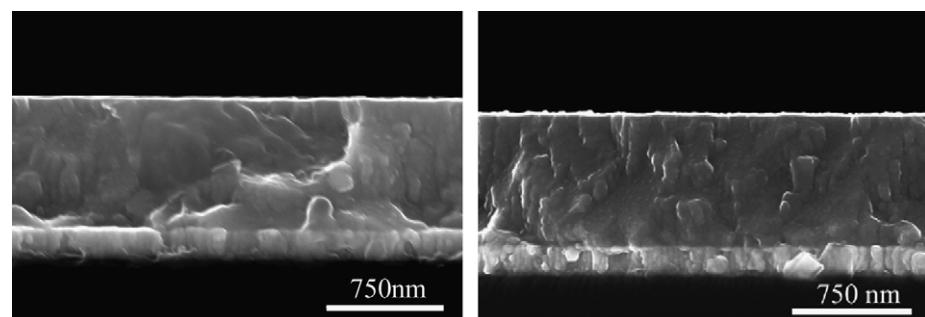


Fig. 12. SEM cross-section microstructure images of the PZT films prepared based on lead acetate-methoxyethanolic solutions with one (left) and five (right) numbers of distillation steps.

Table 2

Dielectric, ferroelectric and piezoelectric properties of the PZT films prepared based on modified PZT solutions

Films	Properties					
	Dielectric constant	Dielectric loss (%)	Remanent polarization, Pr ($\mu\text{C}/\text{cm}^2$)	Applied field, E (kV/cm)	Coercive field, Ec (kV/cm)	Piezoelectric coefficient, d ₃₃ (pm/V)
PZT1D	1174	4.8	33.4	250	63.5	31.2
PZT2D	1548	4.8	36.8	250	60.8	44.0
PZT3D	1795	5.0	38.0	250	60.4	56.9
PZT4D	1836	4.2	39.0	250	61.0	61.4
PZT5D	1850	3.8	38.9	250	60.8	63.8

electric and piezoelectric properties of the PZT films increase progressively up to three distillation steps of the lead precursor solution and remain *practically* constant for the higher distillation steps ($D \geq 3$). Meanwhile, the dielectric losses show a different behaviour, remaining *practically* constant up to three distillation steps in the lead precursor solution and decreasing progressively for higher number of distillation steps ($D \geq 3$). These results are consistent with both, infrared and Raman studies of the lead precursor solutions, which show that after three distillation steps, the constitutional water is removed and a higher lead acetate–2-methoxyethanol interaction occurs; and also with the microstructure analysis of the PZT film, which show that over the three distillation steps carried out in the lead precursor, the residual second phase is prevented and an incipient columnar grain growth takes place.

4. Conclusions

It could be concluded based on the infrared and Raman analysis that the increase in the number of distillations steps carried out during the preparation of the lead acetate-methoxyethanolic precursor solutions, removes the constitutional water and increases the lead acetate–2-methoxyethanol interaction. The higher interconnectivity in the lead acetate-methoxyethanolic precursor solution and the water environment resulting from the distillation process, prevent the titanium and zirconium hydroxide formation, improve the stability of the PZT solutions, reduce the aging effect and accelerated the temperature decomposition process. The acceleration of the PZT solution temperature decomposition process leads to a continuous formation of a complex oxide matrix and an early formation of a pure PZT perovskite. Dielectric, ferroelectric and piezoelectric properties of the PZT films increase as the number of distillation steps increases, which is a clear consequence of the structural change induced by the modifications on the lead precursor solutions.

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