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ORIGINAL PAPER: SOL-GEL AND HYBRID MATERIALS FOR DIELECTRIC, ELECTRONIC, MAGNETIC AND FERROELECTRIC APPLICATIONS

Chelate route for the synthesis of $PbZr_xTi_{1-x}O_3$ thin films

L. Imhoff[1] · S. Barolin[1] · N. Pellegri[1] · M. G. Stachiotti[1]

Abstract A chemical solution deposition route using the chelate approach was developed for the synthesis of $PbZr_xTi_{1-x}O_3$ thin films. The route avoids the highly toxic 2-methoxyethanol used in previous formulations and offers the advantage of a simple and rapid solution synthesis without the need of distillation and refluxing strategies. The use of acetoin as chelating agent allows a transition between amorphous and final perovskite phases with no segregation of secondary phases during film growth. The obtained $PbZr_xTi_{1-x}O_3$ films presented a thickness of ~150 nm and exhibited good dielectric and ferroelectric properties. It was found that rapid thermal annealing facilitates the perovskite formation process and produces films with better ferroelectric properties than those sintered in conventional furnaces.

Graphical Abstract
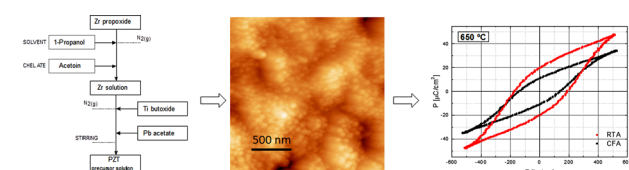
1 Introduction

The dominant ferroelectric material for practical applications is lead-zirconate-titanate (PZT, $PbZr_xTi_{1-x}O_3$) because of its large piezoelectric constant, large remnant polarization, and large dielectric constant. In particular, deposition of PZT thin films is a subject of interest in the area of microelectronic devices, such as nonvolatile ferroelectric random access memories and micro-electro-mechanical systems. A variety of fabrication techniques have been applied to the preparation of PZT thin films [1]. Among them, chemical solution deposition (CSD) processes such as sol–gel are versatile methods that allow the fabrication of films within a wide range of compositions, with precise stoichiometry control and low cost [2]. In CSD techniques, solution preparation is a crucial step. It generally involves the use of metal-organic compounds that are dissolved in a common solvent. Chemical solution processes based on the use of 2-methoxyethanol are the most widely used, primarily due to its ability to solubilize a variety of starting reagents. In fact, most of the previous works involving the synthesis of PZT thin films are based on a 2-methoxyethanol route [3–5]. We note, however, that 2-methoxyethanol is a highly toxic compound.

The chelate route constitutes an alternative solution synthesis approach, which also utilizes alkoxide compounds as starting reagents [6]. Unlike true sol–gel routes, the chelate method does not involve distillation and refluxing strategies, making the solution preparation process simpler. This route relies on the molecular modification of the alkoxide compounds through reactions with other reagents, namely, chelating agents that provide stability to the precursor solutions. Acetic acid, acetylacetone, or amine compounds are the chelating agents most commonly used. For instance, a chelate route using diethanolamine (DEA) as

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complexing agent was developed for the fabrication of PZT thin films [7]. This route showed the crystallization of perovskite PZT phase at a relatively low temperature (500 °C). However, the DEA compound used as chelating agent produces the segregation of metallic lead during film growth. A similar problem was found in the fabrication of $SrBi_2Ta_2O_9$ thin films using alkanolamines as chelating agents, where the segregation of transient metallic bismuth was detected [8]. The amine group is a powerful Lewis base, which reduces cations during the evaporation of solvent and formation of the film, and the presence of metallic ions during film growth can produce undesirable effects in the electrical properties of the films. α-hydroxyketones have emerged as good chelating agents due to their stabilization effects on metal alkoxides solutions [9, 10]. In this work we have developed an optimized chelate route for the fabrication of PZT thin films using acetoin (3-hydroxy-2-butanone) as chelating agent. The route offers the advantage of a simple and rapid solution synthesis without the segregation problem produced by the alkanolamines. The process was optimized by determining the lead excess necessary to compensate the volatilization loss that takes place during the heat treatment. Two different thermal treatments were compared to investigate the effect of heating rate on electrical properties: conventional furnace annealing (CFA) and rapid thermal annealing (RTA).

2 Experimental procedure

We synthesized PZT thin films with zirconium concentration $x = 0.52$ in the region of the morphotropic phase boundary of PZT. Lead acetate, zirconium propoxide, and titanium butoxide were used as metal precursors; acetoin and 1-propanol were used as chelating agent and solvent, respectively. First, zirconium propoxide (Zr $(OCH_2CHCH_3)_4$, 70% Aldrich) was dissolved in 1-propanol. Acetoin (3-hydroxy-2butanone, $CH_3COCH(OH)$ CH_3, Aldrich) was added in the diluted alkoxide with a molar ratio [Zr/acetoin] = 1/4. Afterwards, titanium butoxide (Ti($OCH_2CH_2CH_2CH_3$)$_4$, 99% Aldrich) and lead(II) acetate trihydrate (Pb(CH_3CO_2)$_2$·3H$_2$O, 99+% Aldrich) were added to the stabilized zirconium solution with continuous stirring, and the final mix was agitated in ultrasonic bath for 20 min. The alkoxides were manipulated and incorporated to the solution under nitrogen atmosphere. To investigate the effects of volatilization loss on film properties, different amounts of the lead precursor were added to the solutions. We concluded that a 20% excess of lead acetate is necessary to compensate the volatilization loss during heat treatment. The final concentration of the precursor solution was 0.2 M. A flow chart for the chemical solution processing of PZT precursors is presented in Fig. 1.
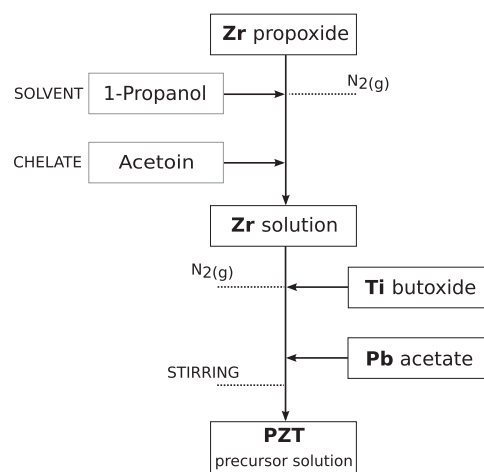
Fig. 1 Flow chart for the preparation of PZT precursor solution

To prepare the films, the precursor solutions were spin-coated on Pt/TiO$_x$/SiO$_2$/Si substrates at 4000 rpm for 15 s. The wet films were dried at 250 °C for 5 min in a hot plate. Two different thermal treatments were performed at temperatures between 450 and 700 °C: CFA and RTA. For the multi-layer process the coating/heat-treatment cycle was repeated four times. In the CFA process, each layer was heat-treated by placing it into a preheated furnace at the desired temperature for 3 min, and then quenched in air. The multi-layer coating was finally annealed for 15 min. In the RTA, each layer was quickly heated-up to the desired temperature (heating rate 50 °C/s), kept 1 min at that temperature, and then quenched in air.

Dynamic viscosity of the precursor solution was measured with an A&D Company SV-10 vibro viscometer. Absorption infrared spectra were recorded in the 4000–400 cm^{-1} range using a Spectrum One Perkin Elmer FTIR spectrophotometer. Several drops of PZT sols were deposited in KBr pellets and then dried at 100 °C. Also, PZT sol was deposited in a double-side-polished silicon substrate and then sintered in conventional furnace at 700 °C for 15 min. KBr disks and clean silicon substrates were used as reference. Thermal analyses (DTA-TGA) of gel powders were performed using a Shimatzu DTG 60 H equipment with a heating rate of 10 °C/min from room temperature up to 700 °C in normal atmosphere. Crystal structure was analyzed by X-ray diffraction (XRD) using a Philips X'Pert Pro X-ray diffractometer with Cu K$_\alpha$ radiation of wavelength 1.5406 Å at a scan rate of 0.02^0/s. For the films, the measurements were made with grazing incident X-ray diffraction using a parallel beam optics for diffraction. Surface morphology was observed by scanning electron microscopy (FEG-SEM Quanta 200) and atomic force microscopy (AFM NanoTec ELECTRONICA) in tapping mode using a silicon probe with 80 kHz resonance frequency and a constant force of 2.7 N/m. For electrical studies, 0.6-mm
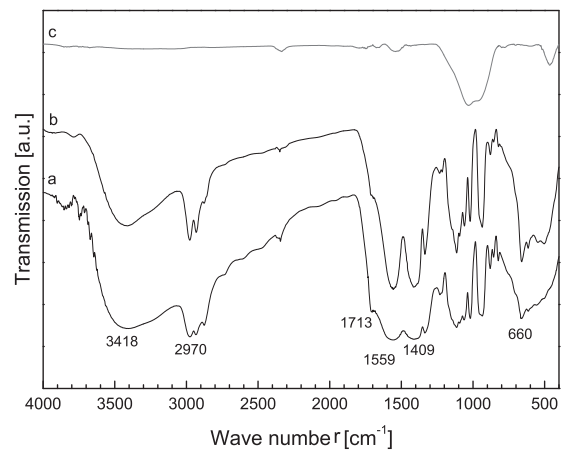
diameter Pt top electrodes were deposited by DC sputtering on the films and then annealed at 350 °C for 10 min. The Pt layer of the substrates was used as bottom electrode. Dielectric properties were measured using an LCR meter (QuadTech 7600 plus). Ferroelectric properties were evaluated using a ferroelectric test system (a conventional Sawyer-Tower circuit) applying AC signals at 50 Hz at room temperature.

The film thickness was estimated from SEM images of samples annealed at 600 and 700 °C in CFA and RTA. The thickness values for the four-layer films oscillates between 170 and 140 nm for films annealed at 600 and 700 °C, respectively, and no significant differences were observed for CFA and RTA. The thickness of the film treated at 550 °C by RTA was assumed to be 170 nm as a possible value to construct the graphic.
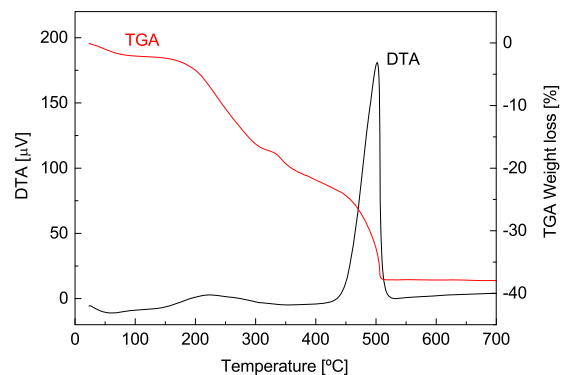

Fig. 2 FTIR spectra of PZT dried sols with 2 days of ageing (**a**) and 36 days of ageing (**b**). FTIR spectra of a PZT film annealed at 700 °C (**c**)

3 Results and discussion

A clear yellow PZT precursor solution was obtained from the chelate route depicted in Fig. 1. The addition of acetoin provided stability to the PZT solution by retarding the hydrolysis and condensation rates. The stability was tested by measuring the viscosity as a function of time at room temperature (23 ± 1) °C. We found that the solution can be stored for at least 5 weeks at 8 °C without any appreciable change in viscosity measurement, (2.6 ± 0.3) cp.

FTIR spectra of PZT dried sols with 2 and 36 days of ageing are shown in Fig. 2a and b. No differences were observed in the position of absorption bands, nor any shifting that we could attribute to modifications in chemical bonds. Also, no new absorptions bands appeared in the aged sol. The analysis of the absorption bands present in the FTIR spectra is presented below. At high frequencies, 3500–3000 cm^{-1}, the broad band, corresponding to O–H

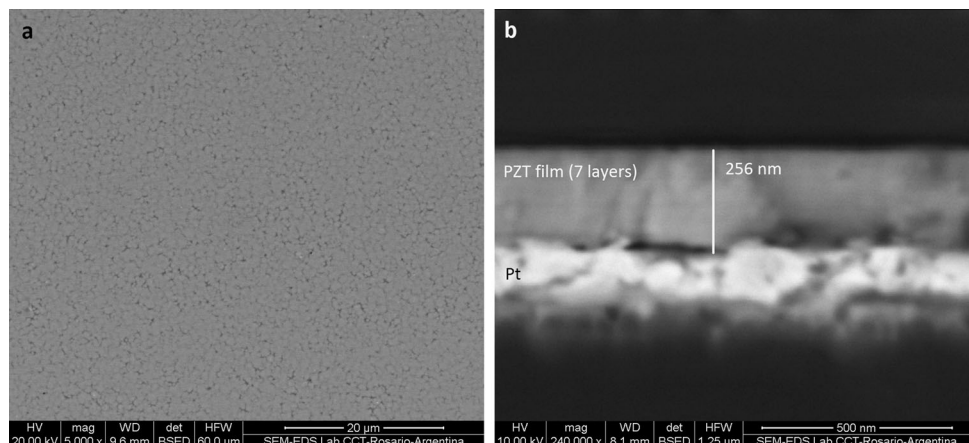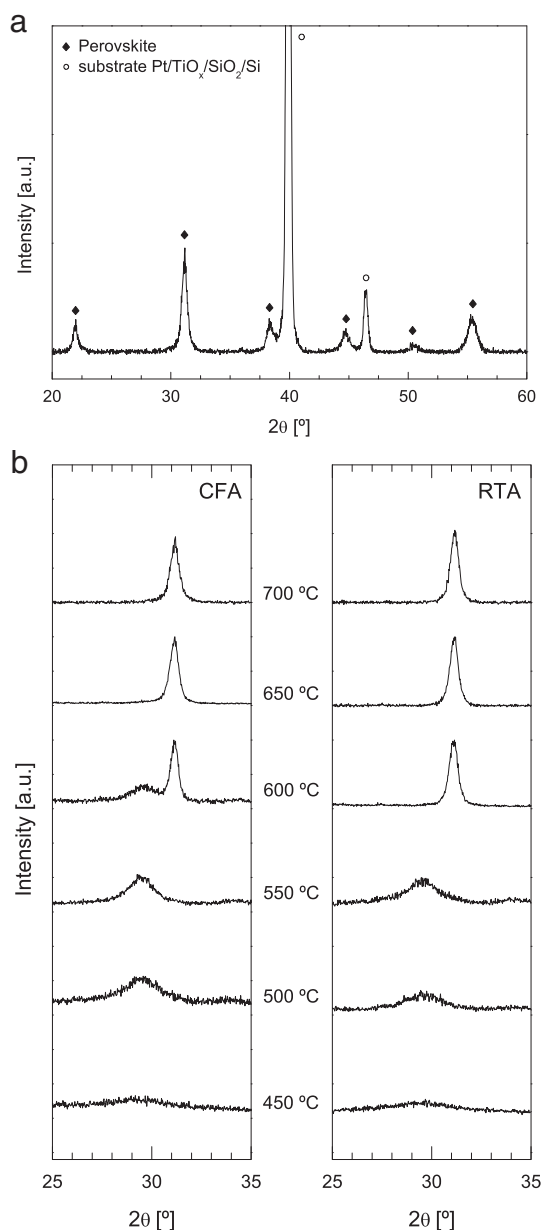**Fig. 3** DTA-TGA curves of gel powders prepared from the PZT precursor solution

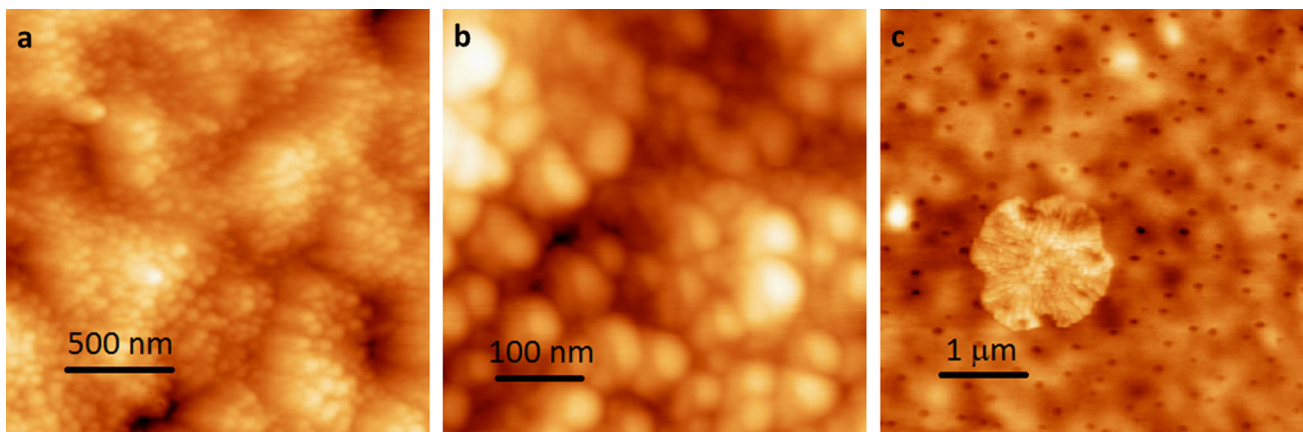**Fig. 4** Top surface (**a**) and cross-sectional (**b**) SEM images of a PZT thin film annealed by CFA at 700 °C

Fig. 5 a XRD patterns of PZT thin film annealed at 700 °C by CFA. **b** XRD patterns of PZT films annealed at different temperatures by CFA (*left panel*) and RTA (*right panel*). Only the data for angles between 25° and 35° is shown
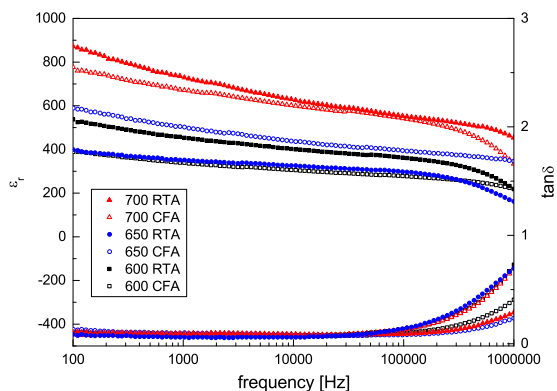
158 cm^{-1}, which indicates a bridging configuration for the acetate group [11]. The increase of acetate bands with sol ageing can be explained by a substitution in bond coordination between acetates and metals with advanced alkoxide stabilization reactions [12]. Between 1000 and 1250 cm^{-1}, C–O stretching bands are observed. At 800–990 cm^{-1}, the C–H bending modes appear [13–15]. The absorptions between 400 and 700 cm^{-1} could be assigned to M–O (M=Ti, Zr, Pb). We can particularly associate the peak at 660 cm^{-1} with Ti–O–Ti bond [12, 16]. These bands increase in the aged sol, which is expectable according to progress in hydrolysis and condensation reactions. In conclusion, the analysis made for FTIR spectra has a good correlation with the rheologic behavior of sols with different days of ageing: no advanced cross-linking is observed, so no increase in viscosity values is measured. Also, the small amounts of water used in the sol–gel process are responsible for the small progress of hydrolysis and condensation reactions. It is worth mentioning the recurrence of the obtained results in films prepared with solutions aged up to 1 month.

Gel powders were prepared from the precursor solution by solvent evaporation in air atmosphere at 90 °C for 24 h. Figure 3 shows DTA-TGA curves for the obtained powder. The TGA curve shows a constant weight loss due to the decomposition and burning of the residual organic groups. The sample loses 37% mass upon heating to 550 °C. No weight loss is observed above that temperature. The thermal effects recorded by DTA include a broad weak endothermic effect at 70 °C, and a succession of exothermic peaks between 180 and 570 °C. The strongest peak in the range 425–570 °C is attributed to the elimination of the last organic residues, such as hydroxyls, with a simultaneous onset of the crystallization process.

The resulting films fabricated by CFA and RTA were found to be dense, free of cracks, and well adhered to the substrates. To illustrate that point, we present in Fig. 4 top surface (a) and cross-sectional (b) SEM images of a 7-layer PZT film treated at 700 °C by CFA. Similar features were observed for films treated at lower temperatures (for both, CFA and RTA) and with a small number of layers. From here onwards the presented results correspond to 4-layer films. Figure 5a shows the XRD pattern of a PZT film treated at 700 °C by CFA. A similar pattern is obtained for RTA. So, films annealed at 700 °C present a perovskite phase with randomly oriented polycrystalline structure and no other intermediate phases, such as pyrochlore, were observed. The formation process of the perovskite phase was investigated by XRD analysis of films annealed at different temperatures. Figure 5b shows the patterns for films treated by CFA (*left panel*) and RTA (*right panel*) at temperatures between 450 and 700 °C. For the sake of simplicity only the data for angles between 25° and 35° are presented. Upon heating to 450 °C the sample remains

stretching is present, which could be caused due to residual solvent and a contribution of metal hydroxides M–OH (M=Zr, Ti) formed after hydrolysis of the alkoxides groups. Also, both spectra exhibit absorption at 2980–2876 cm^{-1}, corresponding to C–H stretching. Stretching vibration of C=O group present in the chelate (acetoin) and acetates causes an absorption in 1713 cm^{-1}. The symmetric and asymmetric stretches of the COO^{-} group present in acetates are represented by absorption bands at 1410 and 1568 cm^{-1}. The difference in frequency between the two was

Fig. 6 Topographic AFM images of PZT thin films annealed by RTA at 600 °C (**a, b**) and 550 °C (**c**)

Fig. 7 Dielectric constant (ε_r) and loss factor (tan δ) as a function of frequency for PZT films annealed at different temperatures using RTA and CFA
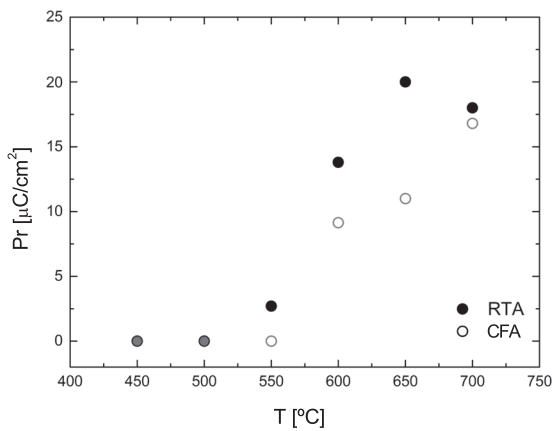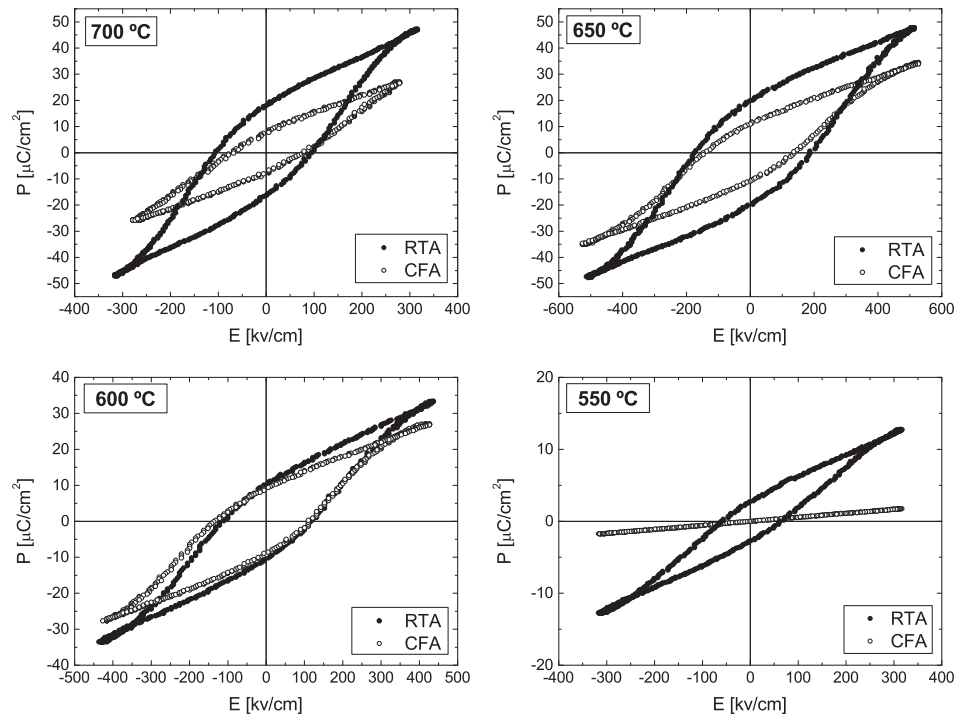
amorphous, while at 500 °C the reflections of the pyrochlore-type phase ($2\theta = 28.7°$) becomes discernible. The pyrochlore phase remains stable up to 550 °C, where the transformation to perovskite PZT phase starts, evidenced by the peak (110) at $2\theta = 31.1°$. After heating up to 600 °C the perovskite reflections are more pronounced and the peaks corresponding to the pyrochlore-type phase are diminished. While a single perovskite phase is obtained in the film treated by RTA at 600 °C, the corresponding film treated by CFA displays the coexistence of the two phases. In this way the RTA process favors the formation of the perovskite phase. It is worth to note that no other crystalline phases than the ones corresponding to the intermediate pyrochlore and the final perovskite structures appear during the overall thermal evolution of the samples. This indicates that this acetoin-based chelate route avoids the segregation of metallic lead or lead oxide during the sinterization process of the film, as occurs in the case of using DEA as chelating agent [7]. In the FTIR spectra of the sintered film showed in Fig. 2c, it is observed that many of the organic

bands were eliminated, and an important absorption appears at low frequencies, associated to metal–oxygen bonds corresponding to perovskite structure, according to the XRD results previously shown.

The topography of the films was investigated by AFM. Figure 6a and b shows images for the film annealed at 600 °C by RTA. The film treated by CFA displays similar microstructure and grain size. The microstructure examination showed fine-grained microstructure with average grain size about 45 nm (SD: 14 nm). Similar microstructures and grain sizes were observed for films annealed at 650 and 700 °C. Figure 6c shows that the surface of the film treated at 550 °C by RTA exhibits rosette-type structures, similar to that reported extensively in the literature for sol–gel-derived PZT films [17], separated by a fine-grained matrix. The rosette structure was known to be a perovskite phase, whereas the matrix is attributed to the pyrochlore phase. The rosettes are scattered randomly in the film and the poorly crystallized pyrochlore phase is located between the structures. The approximate diameter of each rosette is about 2 μm. The film treated at 550 °C by CFA displays only tiny grains of the untransformed pyrochlore phase without the presence of rosettes.

Finally, the electrical quality of the films was tested. The dielectric properties were investigated in terms of the dielectric constant (ε_r) and loss factor (tan δ), which were measured as a function of frequency in the range 100 Hz–1 MHz. Figure 7 shows the room-temperature properties of films for different annealing temperatures. The permittivity shows low dispersion with frequency. The loss factor also displays a flat behavior up to 100 kHz, but it increases to higher values in the high-frequency region. This behavior is due to the resonance effect in the test circuit [18]. The films annealed at 700 °C exhibit the higher dielectric constants (~800 at 1 KHz), and this may be due to the better perovskite crystallinity and grain growth. Figure 8 shows the ferroelectric hysteresis loops of the PZT films annealed at

Fig. 8 Polarization vs. applied field characteristics of PZT thin films annealed at different temperatures using RTA and CFA

Fig. 9 Variation of the remnant polarization as a function of sintering temperature

which indicates that RTA improves the ferroelectric properties of the films. Even more, while the film treated by RTA at 550 °C exhibits a tiny hysteresis loop, the CFA film displays dielectric behavior. This supports that RTA favors the formation of the perovskite phase at lower temperature, in agreement to that was observed in XRD and AFM studies.

It is interesting to compare the electrical properties of the films with existing results found in the literature. We chose the paper of Xiao et al. [20] that uses 2-methoxyethanol to fabricate PZT films of ~100 nm thickness using a CFA similar to the CFA used in this work (i.e., the specimens were directly put into the furnace that had reached the set temperature without the rising period of temperature). We found that the electrical properties of the films fabricated at 600 °C by CFA are better than the ones reported in ref. [20] (we have compared them with randomly preferential orientation films annealed at 600 °C for 1 h). The films prepared with 2-methoxyethanol showed good dielectric and ferroelectric properties with $\varepsilon_r = 348$, $\tan \delta = 0.137$ (both measured at 1 kHz) and $P_r = 5.39 \, \mu C/cm^2$, while with chelate route ε_r, $\tan \delta$, and P_r are 339, 0.078, and 9.14 $\mu C/cm^2$, respectively.

4 Conclusions

We developed a chelate route for the fabrication of PZT thin films using acetoin as chelating agent. This offers the advantage of a simple and rapid solution synthesis, without the need of distillation or refluxing strategies. The high stability of these solutions allowed their utilization for

different temperatures. The loops exhibit the typical shape observed for ferroelectric thin films [19]; it is well known that the remnant polarization in thin films is lower than in the bulk because the substrate interface limits the poling ability of the ferroelectric materials. Figure 9 shows the variation of the remnant polarization (P_r) as a function of sintering temperature. The trend of the remnant polarization is also readily related to the variation in grain size and perovskite crystallinity with sintering temperature. We observe, however, a noticeable difference between the two thermal treatments. The remnant polarization values of the films treated by RTA are higher than those annealed by CFA,

several weeks. Also, the route replaces the highly toxic 2-methoxyethanol used in previous formulations. Unlike alkanolamines, the use of acetoin as chelating agent avoids the segregation of metallic lead during film growth. Consequently, films of ~150 nm thickness fabricated with this route exhibited good dielectric and ferroelectric properties. Although the route is compatible with the two thermal treatments generally applied for the fabrication of thin films (CFA and RTA), PZT films treated by RTA exhibit better ferroelectric properties. We thus hope that the present chelate approach will be useful for other researchers as a rapid, simple, and non-toxic one-pot reaction method for the fabrication of PZT-based thin films.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

1. Izyumskaya N, Alivov Y-I, Cho S-J, Morko H, Lee H, Kang Y-S (2007) Processing, structure, properties and applications of PZT thin films. Crit Rev Solid State Mater Sci 32:111–202
2. Schwartz RS, Schneller T, Waser R (2004) Chemical solution deposition of electronic oxide films. C R Chim 7:433–461
3. Pandey SK, James AR, Raman R, Chatterjee SN, Goyal A, Prakash C, Goel TC (2005) Structural, ferroelectric and optical properties of PZT thin films. Physica B 369:135–142
4. Guo H, Bao D, Zhang Y (2008) Characterization of PZT ferroelectric thin films prepared by a modified sol-gel method. IEEE International Ultrasonics Symposium Proceedings 2130–2133.
5. Mirzaei A, Bonyani M, Torkian S (2016) Synthesis and characterization of nanocrystalline PZT powders: from sol to dense ceramics. Process Appl Ceram 10(1):9–16
6. Schwartz RW (1997) Chemical solution deposition of perovskite thin films. Chem Mater 9:2325–2340
7. Bel Hadj Tahar R, Bel Hadj Tahar N, Ben Salah A (2007) Preparation and characterization of PZT solid solutions via sol–gel process. J Cryst Growth 307:40–43
8. Machado R, Santiago ML, Stachiotti MG, Frattini A, Pellegri N, Bolmaro R, de Sanctis O (2008) Effects of acetoin as chelating agent on the preparation of $SrBi_2Ta_2O_9$ thin films from non-hydrolyzing precursors. J Sol-Gel Sci Techn 48:294–302
9. Ohya T, Kabata M, Ban T, Ohya Y, Takahashi Y (2002) Effect of α-hydroxyketones as chelate ligands on dip-coating of zirconia thin films. J Sol-Gel Sci Techn 25:43–50
10. Takahashi Y, Ohsugi A, Arafuka T, Ohya T, Ban T, Ohya Y (2000) Development of new modifiers for titanium alkoxide-based sol-gel process. J Sol-Gel Sci Techn 17:227–238
11. Doeuff S, Henry M, Sanchez C, Livage J (1987) Hydrolysis of titanium alkoxides: modification of the molecular precursor by acetic acid. J Non-Crys Solids 89:206–216
12. Shakeri A, Abdizadeh H, Golobostanfard MR (2014) Synthesis and characterization of thik PZT films via sol-gel dip coating method. Appl Surf Sci 314:711–719
13. Coffman PR, Barlingay CK, Gupta A, Dey SK (1996) Structure evolution in the PbO-ZrO2-TiO2 sol-gel system: part II-pyrolysis of acid and base-catalyzed bulk and thin film gels. J Sol-Gel Sci Techn 6:83–106
14. De-Qing Z, Shao-Jun W, Hong-Shan S, Xiu-Li W, Mao-Sheng C (2007) Synthesis and mechanism research of an ethylene glycol-based sol-gel method for preparing PZT nanopowders. J Sol-Gel Sci Techn 41:157–161
15. Fè JL, Norga G, Wouters DJ, Nouwen R, Van Poucke LC (2000) Absorption-reflection infrared spectroscopy studies of sol-gel prepared ferroelectric Pb(Zr,Ti)O3 thin films on Pt electrodes. J Sol-Gel Sci Techn 19:149–152
16. Méndez-Vivar J, Mendoza-Serna R, Gómez-Lara J, Gaviño R (1997) Spectroscopic study of SiO2-TiO2 sols prepared using stabilizing agents. J Sol-Gel Sci Techn 8:235–241
17. Chapin L, Myers SA (1990) Microstructural characterization of ferroelectric thin films for non-volatile memory applications. Mater Res Soc Symp Proc Fall 200:231–235
18. Thomas R, Varadan VK, Komerneni S, Dube DC (2001) Diffuse phase transition, electrical conduction, and low temperature dielectric properties of sol-gel derived ferroelectric barium titanate thin films. J Appl Phys 90:1480–1488
19. Li J, Wang C, Liu M, Ma J (2013) Effect of annealing process on properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films prepared by sol-gel method. Ferroelectrics 445:32–38
20. Xiao M, Li S, Lei Z (2015) Study of (111)-oriented PZT thin films prepared by a modified sol-gel method. J Mater Sci Mater Electron 26:4031–4037