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Preparation and characterization of PLT thick-films produced by a chemical route

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Abstract

Thick-films of lanthanum modified lead titanate ceramic $(Pb_{1-x}La_x)TiO_3$ with $x=0.10$, 0.15 and 0.20 were prepared by a co-precipitation chemical process where oxide powders were used as precursors. The co-precipitated particles were dispersed in an organic vehicle in order to prepare the material for deposition. The films were deposited by dip coating on corning 7059 glass and chrome/nickel alloy substrates. The initially deposited films were amorphous and a heat treatment was necessary to crystallize them. Initially, the heat treatment was for volatilizing the organic material present in the films and in a second stage to crystallize them at higher temperatures. The crystallization of the films was monitored through X-ray diffraction analysis. The dielectric constant was measured at 1 kHz and the observed values were compared with those of bulk ceramic. The phase transition temperature of the films with $x=0.20$ was measured and the value observed agreed with those of bulk ceramic.

Keywords: $(Pb,La)TiO_3$; PLT; Films; Dielectric properties; Ferroelectric thick films

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1. Introduction

Ferroelectric ceramic films arouse scientific and technological interests[1] because of its high dielectric constant, piezoelectricity and pyroelectricity. Applications include micro actuators, nonvolatile memories, optical waveguide, thin-film capacitors, infrared detectors and surface acoustic wave devices.[2,3]

The materials based on lead oxide as titanates, zirconates and niobates reveal the best-appropriated characteristics for applications as ferroelectric ceramic films. The reason is the high lead oxide volatilization at high temperature that facilitates stoichiometric accommodation and accelerates the crystallization.[4] For multicomponent oxide films the major difficulties are to have precise composition control, well-defined structure and to reproduce characteristics as verified in bulk ceramic.[3]

Physical and chemical methods are used to produce ceramic thin films. For multicomponent oxides ceramic films the chemical sol-gel process is one of the best to prepare films because it permits easy stoichiometric control and large areas of depositions.[3,5] However, in this process expensive organometalic precursors are commonly used. Sputtering and chemical vapour deposition (CVD) are physical methods compatible with semiconductor technology, but show difficulties in controlling homogeneity and stoichiometry.[3,6] Otherwise, crack-free thick-films are very difficult to produce by sol-gel and physical techniques.[3,6] By sol-gel many coatings are necessary in order to achieve thick-films and this may provoke cracks during the film's heat treatment.[5,6] By sputtering many hours are necessary for deposition to produce a thick-film and this procedure may increase the inhomogeneity and cause a deviation in the stoichiometry.[6,7] In all methods used to prepare thin films, atoms are deposited on the substrate and a heat treatment with a temperature around 600 °C is sufficient to crystallize and sinter the coating.[1–7]

For electronic applications where sensitive elements have large area extensions, thick-films may be necessary in order to prevent electrical shorts and to reduce the probability of an electrical breakdown, once the commercial available ceramic substrates have a roughness of

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more than 1 μm.[8] Many sensors have characteristics based on dimensions of the sensitive elements and it is just because thick-films are important.

The usual technology employed to prepare ceramic thick-films for applications as sensors start from a paste prepared with calcinated ceramic powders and an organic vehicle.[7–11] This paste is printed on a substrate and fired at high temperatures in order to sinter and densificate the ceramic coating. For PZT thick-films the temperature of firing is around 1200 °C.[7–11]

New methods were used to produce thick-films. Daniel Chen et al.[12] employed a modified sol-gel process and by making many coatings they made PZT thick-films deposited on silicon wafers. Barrow et al.[13] used a mixture of PZT powders and a sol-gel matrix as ceramic/ceramic composite to produce thick-films and also by making many coatings deposited on platinized silicon substrates. In both cases, as stated by the authors the films are crack free and show some differences in the values of the relative dielectrics constants.

In this work, (Pb,La)TiO_3 PLT thick-films of ferroelectric ceramic were prepared by an alternative chemical route based on a co-precipitation process where the oxide powders are used as precursors. After a chemical dispersion treatment applied to the co-precipitated particles, the films were deposited by dip coating on conductive corning 7059 glass and chrome/nickel alloy substrates. These films were submitted to different thermal treatments in order to eliminate organic additives and crystallize the ceramic coating once the deposited materials were amorphous. An X-ray diffraction investigation of the film crystallization as a function of thermal treatment temperature and time is described. Thick-film properties reported include dielectric constant and phase transition temperature.

2. Experimental procedure

The chemical route used in this work was based on the co-precipitation method developed by Menegazzo and Eiras.[14] The method consists of a mixture of titanium, leads and lanthanum oxides powder, calcined at a temperature of 850 °C for 3 h, in order to promote a solid state reaction and to form a new oxide powders structure. The calcined powders were dissolved in hot nitric acid (≈78 °C) by 2 h under strong agitation, once some of the oxide's precursors do not react with nitric acid. By adding ammonia hydroxide to the agitated solution, until pH is about 9∼10, the hydroxides cation's co-precipitate. In order to eliminate salts remain in the precipitated material it was washed with distilled and deionized water by successive decantation.

The amount of each oxide used in the composition was calculated by nominal formula $(Pb_{1-x},La_x)TiO_3$. By this procedure is assumed that each lanthanum atom replaces one lead atom. In this case, to maintain the eletroneutrality for each two La^{+3} incorporated in the composition one Pb^{+2} vacancy must be formed. According the calculation by nominal formula there is a lead oxide excess of x/2 presents in each composition. So, the increase of La contents increases the concentration of PbO excess. The excess of PbO helps to avoid a deficit of lead oxide in the composition after the heat treatment for film's crystallization at high temperatures, which can occur due to PbO volatilization.

To prepare films with this material is necessary to disperse and stabilize it. The PLT dispersion was done adding deflocculant (ammonium polyacrilate) until the medium viscosity is a minimum. The deflocculant serves to disperse the particles in the medium acting to avoid the agglomerate formation. Adding plus two wt.% of binders (polyvinyl acetate), in order to give some mechanical resistance to the dry coating before final firing. Finally the dispersion treatment is completed with an addition of 0.2 ml/gram of ethylene glycol and controlling viscosity of the resulting material with water and alcohol (isopropanol). The ethylene glycol was used as an additive in order to prevent cracking and to improve the film's surface smoothness. Samples of the dispersed materials were submitted to differential thermal analyses and thermogravimetric analyses (DTA/TG) to determine the better firing temperature for volatilizing the organic additives and the mass loss during heat treatment.

Parallel, powders from the precipitated materials were prepared to serve as structural pattern for the films.

The film's quality and morphology depend of the dispersion treatment applied to the precipitated material and on the thermal treatment applied to the films. All the organic additions done during the dispersion treatment serve to improve the film's homogeneity and morphology. Low concentrations of plastificants (water and ethylene glycol) increase the viscosity, thicker and crack the films during the first stage of heat treatment, while excessive concentration of plastificants reduces the viscosity and provokes morphological inhomogeneties in the coating.

Thick ceramic films of lanthanum modified lead titanate, with molar lanthanum concentration of 10, 15 and 20%, were deposited by dip coating on conductive corning 7059 glass and chromium/nickel alloy substrate. The glass substrates were cleaned with acetone and sulfuric ether while chromium/nickel alloys were cleaned with a solution of sulfuric and nitric acid and finally both kinds of substrates were washed with distilled and deionized water and dried at 80 °C.

Films were deposited by dip coating with different velocities of deposition (from 1 to 2 mm/s) and with different medium viscosity (from 600 to 2000 centipoises). Each film received up to five coatings. The film's thickness shows dependence with the medium viscosity, and deposition velocity. The thickness was measured with a Mitutoyo micrometer checker and the measurements were made in different positions on the film surfaces and in different films of the same composition.

The deposited films were heat treated in two stages: the first stage at 350 °C by 1.5 h with heating rates less than 2 °C/min in order to eliminate organic components present in the coating material. In the second stage, at higher and different temperatures to crystallize and to study the evolution of the film's crystallization once the material deposited was initially amorphous.

The temperatures used to crystallize the films were 500, 550, 600, 650 and 700 °C by 1.5 h with heating rates around 5 °C/min. Furthermore, the films were submitted to temperatures of 600 and 700 °C by an elapse of time of 0.5, 3.0 and 6.0 h, in order to study their structure stability with firing time. Between each coating, the films were dried at ~ 85 °C and fired at 350 °C to volatilize the water, alcohol and the polymerized organic components.

The phases and lattice parameters of these films were determined through X-ray diffraction measurements made at room temperatures with CuK_α radiation. The degree of film's crystallization fired at different temperatures was monitored through these measurements.

Finally, the top electrode of silver was printed on the films and fired at 590 °C. The film's dielectric constants were determined through capacitance measurements made with an impedance analyser HP-4194A in films deposited on chromium/nickel alloy substrates. The chromium/nickel blades serve as a substrate and bottom electrodes once its conductivity stayed unaltered after the heat treatment. Furthermore, the temperature of phase transition of PLT20 films was determined through the measurement of capacitance as a function of temperature. This measurement was done only in PLT20 films due to temperature limitations in the disposable equipment.

Samples of the precipitated material (hydroxides) and films were prepared in order to be observed with a scanning electron microscope (SEM). This observation permits verification of the film's surface quality and determination of the average particle diameter. The average particle diameter of the hydroxides determined through SEM pictures was 0.3 μm.

3. Results and discussion

The thermal gravimetric and differential thermal analysis (DTA/TG) (Fig. 1) show an endothermic peak around 110 °C corresponding to a volatilization of adsorbed water and two exothermic peaks at 310 and 410 °C, respectively, related to the temperature of organic additives' combustion and the temperature of hydroxides' decomposition. As can be observed at the temperature of 410 °C the film's crystallization starts. The water mass loss was about 50% and the polymerized organic substances were about 30%.

During the first stage of heat treatment a careful choice of the temperature, time and heating rate was necessary to minimize the risk of the cracking that can occur due to organic additive volatilization that takes place at this stage. This can produce large pores in the final ceramic coating. The temperature of 350 °C for the first stage of heat treatment was chosen after various tests to avoid crack. These tests were performed at different temperatures between 280 and 400 °C and at each temperature the film's surfaces were observed with an optical microscope.

The lanthanum modified lead titanate compositions have a tetragonal unit cell of the perovskite type in a ferroelectric phase and cubic unit cell in a paraelectric phase. The analysis of the X-ray diffraction data of the films with $x = 0.10$ (PLT10) (Fig. 2), shows that the film's crystallization was partial at the temperatures of heat treatment of 500 and 550 °C. At 500 °C the peak around $2\theta = 44.3°$ related to the crystallographic plane (002) of a PLT composition does not appear. At 550 °C there is an intermediary phase represented by the peak around $2\theta = 30.0°$, which is not related to the PLT composition. The heat treatment at the temperature of 600 °C completely crystallizes the firms, while heat treatments at 650 and 700 °C generates a pyroclore and a TiO_2 phases, as can be observed in X-ray diffraction patterns the two peaks around $2\Theta = 27.5°$ and 26.2° are characteristics of these phases.[15]

For films with $x = 0.15$ (PLT15) the X-ray diffraction data show (Fig. 3) that for heat treatment at the temperatures of 500 and 550 °C there is a co-existence of red-lead oxide phases with PLT phases. The heat treatment at the temperature of 600 °C completely

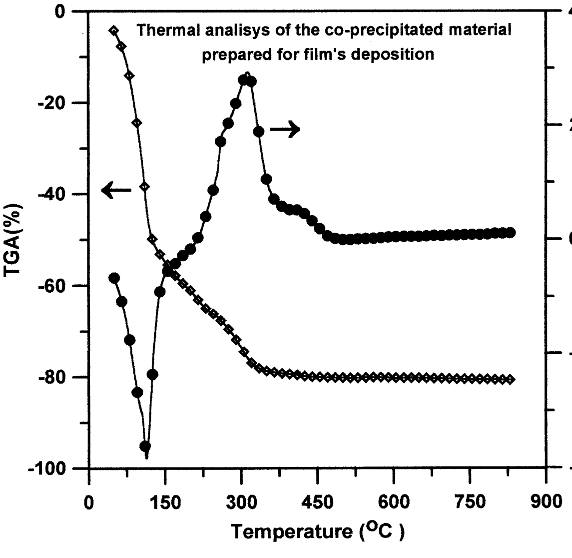

Fig. 1. Thermal analysis of the dispersed co-precipitated material.

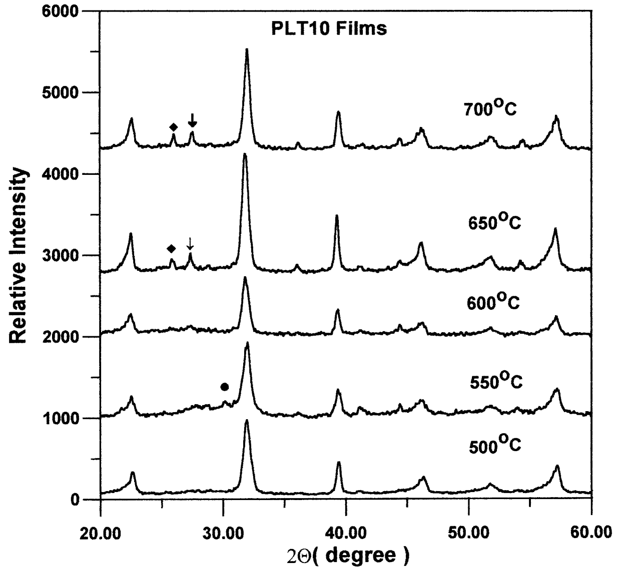

Fig. 2. X-ray diffraction patterns of PLT10 films fired at different temperatures, where the symbol (↓) represents the pyroclore and (◆) represents the TiO_2 phase and (●) shows red-lead oxide phases.

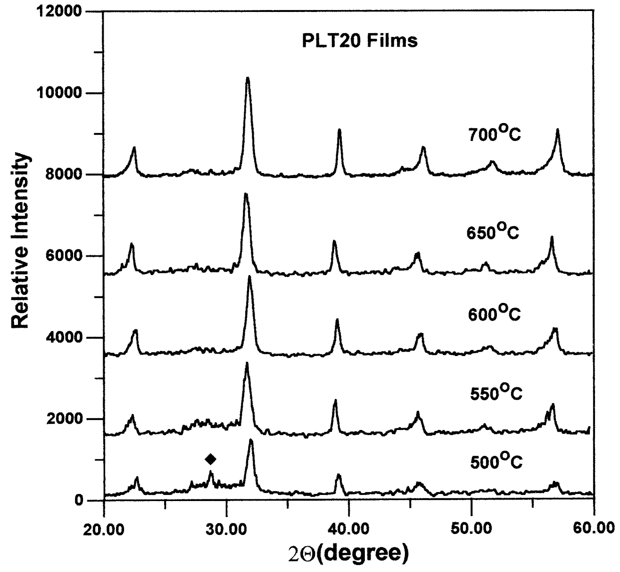

Fig. 4. X-ray diffraction patterns of PLT20 films fired at different temperatures, where (◆) shows red-lead oxide phases.

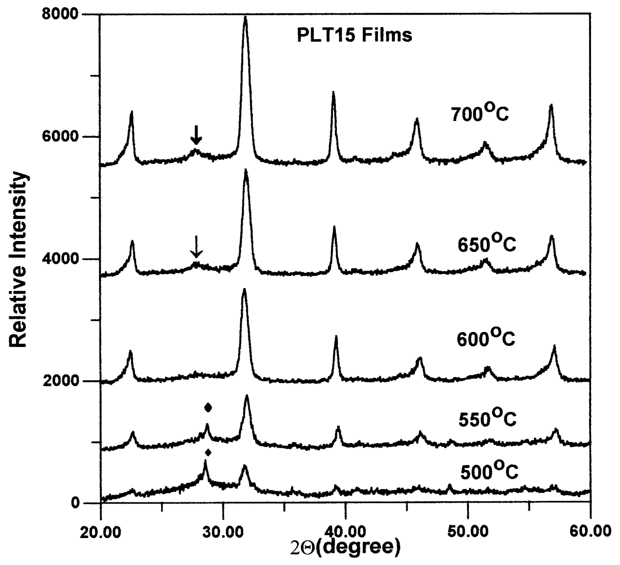

Fig. 3. X-ray diffraction patterns of PLT15 films fired at different temperatures, where the symbol (↓) represents the pyroclore and (◆) shows red-lead oxide phases.

crystallizes the films. Otherwise, the pyroclore phase clearly appears only at the temperatures of heat treatment of 650 and 700 °C.

The films with $x = 0.20$ (PLT20) the X-ray diffraction data (Fig. 4) show that at the temperature of 500 °C red-lead oxide phases co-existent with PLT phases. The heat treatment at the temperature of 600 °C completely crystallizes the films. Otherwise, the pyroclore phase does not appear clearly at the other two higher temperatures used for heat treatment.

Vasant and Kumar[15] observed the presence of pyroclore phases in PZT films and it was attributed to an excess or a deficit of lead oxide content in perovskite compositions. Normally, the excess of lead oxide is added to the ceramic compositions based in PbO in order to compensate the volatilization of this oxide at high temperatures. Takayama et al.[16] observed the same behaviour in PLT films deposited by sputtering.

The quantity of lead oxide excess present in the PLT films composition affects its crystallization kinetics. Low lead oxide excess reduces the temperature at which the pyroclore phase appear, case of PLT10, while high lead oxide excess increases the temperature at which the pyroclore phase appears, case of PLT20.

The increases of lanthanum concentration in the compositions reduce the tetragonality factor (ratio c/a of unit tetragonal cells) as can be observed in Fig. 5. The parameter c is reduced and the parameter a increased while the unit cell's volume stays unchanged. The lattice parameter's comparisons were made between films heat treated at 600 °C because all films of all compositions used here, were totally crystallized at this temperature. This behaviour agrees with the results obtained in PLT films by Takayama et al.[16] The same tendencies and values were observed in PLT bulk ceramic with identical La concentration.[17] This guarantees that the stoichiometry of the films was preserved during all stages of films processing.

The measured film's thickness varies from 5 to 20 μm. Films with three coatings prepared from medium with viscosity of 900cP (centipoise) and deposition speed of 1.6 mm/s show thicknesses of 9 μm. Films with two coatings prepared with the same material and same conditions show a thickness of 5 μm. The better quality films were produced under these conditions of viscosity and deposition velocity.

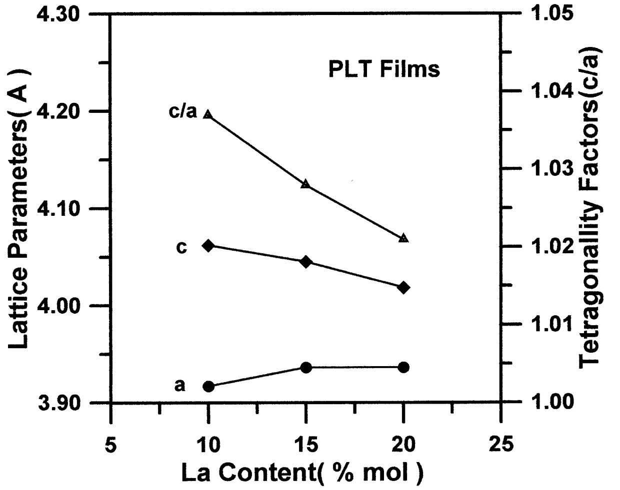

Fig. 5. Lattice parameters and tetragonality factors of the PLT films showing the influence in unit cells of lanthanum concentration.

Table 1
Relative dielectric constant values of films and bulk measured at 1 kHz

	PLT10	PLT15	PLT20
ε' (films)	476	564	1.523
ε' (bulk)	460	542	820

The analysis of X-ray diffraction data of films heat treated at 600 °C for different times (0.5, 3.0 and 6.0 h), showed a stable unit cell volume and, consequently, structural stability. Otherwise, those films fired at 700 °C for the same times (0.5, 3.0 and 6.0 h), showed that the lattice parameters change continuously with the time of heat treatment, that means, there is a structural instability with time. This is supposed to be associated with lead oxide volatilization.

Table 1 shows the dielectric constant values of the films and bulks measured at 1 kHz. The values for PLT10 and PLT15 films are compatible with those observed in bulk ceramics with the same compositions measured at the same frequency. Otherwise, PLT20 films show a dielectric constant value nearly twice the value observed in the bulk ceramic of the same composition. This is most probably associated with a presence of space charge polarization because the relative dielectric constant falls to a value less than half of the measured ones when submitted to a measurement under temperature. It can be verified in the initial values of the relative dielectric constant in Fig. 6. The bulk dielectric constant values measured in this work agree with those of the literatures.[17]

The dielectric loss factor values were high for all films, and the *tgδ* was around 0.8. This fact indicates that for an insulator material the electric conduction was high.

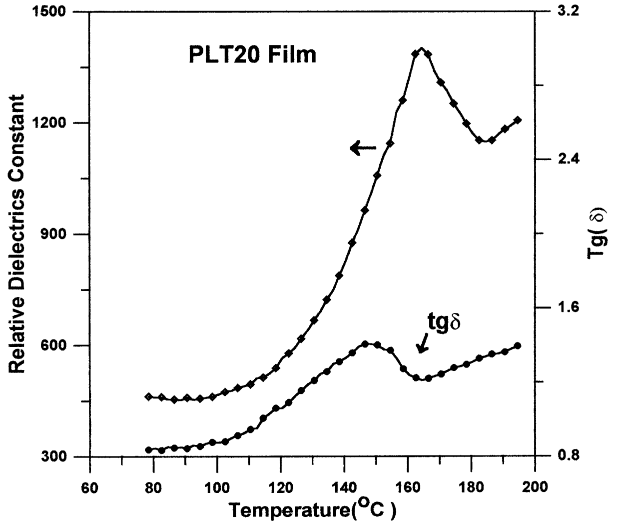

Fig. 6. Measurement of the PLT20 films relative dielectric constant and loss factors at 1 kHz as a function of temperature.

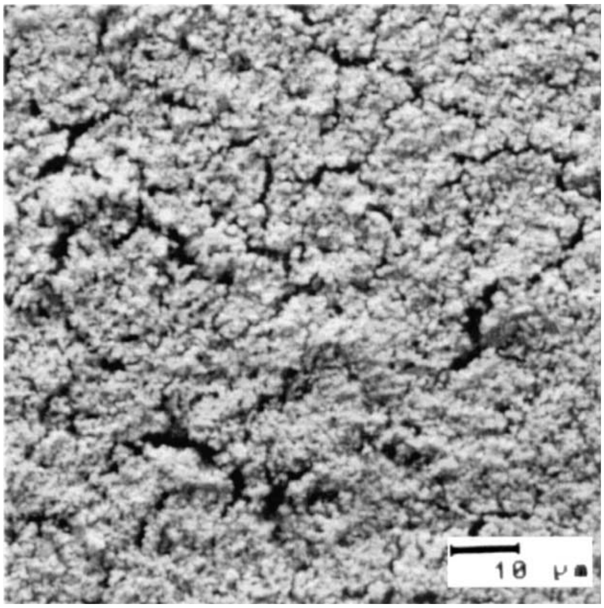

Fig. 7. Surface SEM micrographs of the PLT20 film (600 °C, 1.5 h), magnified by 1000.

The observations of the films surface with SEM reveals the presence of microcracks (Fig. 7). This can explain the high dielectric loss factor and the conductivity observed in these films. When the top electrode was applied to the surface's film the silver penetrates in these microcracks and it redistributes the electric field causing an increase in the conductivity and in the dielectric loss factor.

These microcracks may be caused by differences in the thermal expansion between the films materials and substrates and/or by a non ideal heat treatment applied to the films.

Finally, the temperature of phase transition determined in PLT20 films (Fig. 6) was 165 °C, while this temperature observed in PLT20 bulk ceramic was 163 °C.[17] This again confirms that stoichiometry does not change during the film's preparation. According to Iijima et al.[18] the difference of 1 mol% of La concentration in PLT compositions changes the phase transition temperature in 18 °C. Same highs the dielectric loss factor shows a maximum value at a temperature that is lower than the phase transition temperature (Fig. 6). Shwartz et al.[19] observed this same behaviour and temperature values in PLT20 films prepared by sol-gel.

4. Conclusion

An alternative chemical route was used to prepare ceramic thick-films where co-precipitated amorphous particles were deposited instead of calcinated particles as commonly used in thick-film technology. This procedure reduces the final temperature of heating treatment (600 °C) by half of the used in the conventional technology for thick-films (≈1200 °C). Consequently, this reduces the problems of a choice of the substrates and bottom electrodes for the films.

The microcracks present in the films are a clear indication of some fail in the film's processing. As a consequence, further experiments are needed to optimize this thick-film fabrication process.

The measured film's dielectric constant and phase transition temperature show values compatible with those of bulk ceramics. The properties and characteristics of the films prepared in this work reveals that stoichiometry is preserved during all stages of film's preparation and expose the great potential of the used process.

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