Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1615–1619

www.elsevier.com/locate/jeurceramsoc

# Compositional and structural study of ferroelectric multilayer $(Pb,La)TiO_3/(Pb,Ca)TiO_3$ sol–gel thin films

R. Poyato[a,*], M.L. Calzada[a], L. Pardo[a], J. García López[b], M.A. Respaldiza[b,c]

[a]*Inst. Ciencia de Materiales de Madrid (CSIC). Cantoblanco. 28049 Madrid, Spain*
[b]*Dept. de Física Atómica, Nuclear y Molecular. Univ. Sevilla, PO Box 1065, 41080 Seville, Spain*
[c]*Centro Nacional de Aceleradores (CNA). Parque Tecnológico Cartuja 93. 41092 Seville, Spain*

**Abstract**

Multilayer ferroelectric thin films were prepared in this work by multiple deposition and crystallization onto $TiO_2/Pt/TiO_2/Ti/(100)Si$ substrates, of $(Pb_{0.76}Ca_{0.24})TiO_3$ (PTC) and $(Pb_{0.88}La_{0.08})TiO_3$ (PTL) air stable solutions prepared by the diol sol-gel route. Two types of heterostructures were prepared: PTC/PTL/PTC and PTL/PTC/PTL. These films were studied by Rutherford Backscatering Spectroscopy. X-ray diffraction (XRD) analysis of the samples was also carried out, to determine the structural and textural characteristics of the films. RBS studies have shown that the compositions of the PTL and PTC layers in the multilayer heterostructures are close to the nominal ones. Moreover, no interdifussion has been found between the PTL and PTC layers. The RBS analysis has also shown that the $TiO_2$ layer onto the substrate is fully incorporated in the perovskite structure during crystallization, and is related to the $<111>$ orientation present in the PTC/PTL/PTC heterostructure. Ferroelectric hysteresis cycles have been obtained and remanent polarizations of $P_r \sim 38$ and 27 $\mu C/cm^2$ have been found in PTL/PTC/PTL and PTC/PTL/PTC heterostructures, respectively.


*Keywords:* Sol-gel processes; Spectroscopy; X-ray methods; Ferroelectric properties; Perovskites

## 1. Introduction

During recent years, there has been great interest in the ferroelectric heterostructures with concentration gradient, and those built with successive layers with different compositions, due to their unique properties.

It has been shown that compositionally graded $Pb(Zr,Ti)O_3$,[1] $(Pb,Ca)TiO_3$[2] and $(Pb,La)TiO_3$[3] thin films have unconventional ferroelectric properties, such as large polarization offsets in hysteresis loops. Multilayer $Pb(Zr,Ti)O_3/PbTiO_3$[4] and $Pb(Zr,Ti)O_3/(Pb,La)(Zr,Ti)O_3$[5] thin films have outstanding dielectric ferroelectric and pyroelectric properties. A pyroelectric coefficient of $\gamma \sim 3.8 \times 10^{-8}$ $Ccm^{-2}K^{-1}$ has been found for multilayer $Pb(Zr,Ti)O_3/PbTiO_3$, which in addition to its low permittivity, $\varepsilon_r = 389$, gives place to a high figure of merit, $F_D \sim 20.3 \times 10^{-6}$ $Pa^{-1/2}$.

The occurrence and extent of interdiffusion of the compounds between layers and its effect on the properties of the films has scarcely been studied.

Among the perovskite-type thin films, $(Pb,Ca)TiO_3$ and $(Pb,La)TiO_3$ are attractive materials because of their good properties and have been widely studied.[6] However, studies on multilayer $(Pb,Ca)TiO_3/(Pb,La)TiO_3$ films have not been reported up to date.

In this work, we present an structural and compositional study by means of X Ray Diffraction and Rutherford Backscattering Spectroscopy of multilayer $(Pb,Ca)TiO_3/(Pb,La)TiO_3$ heterostructures, and show their ferroelectricity.

## 2. Experimental procedure

Calcium-modified lead titanate and lanthanum-modified lead titanate precursors solutions were synthesized by diol-based sol-gel processes described elsewhere.[7,8] Nominal compositions of the solutions were $Pb_{0.76}Ca_{0.24}TiO_3$ (PTC) and $Pb_{0.88}La_{0.08}TiO_3$ (PTL).

* Corresponding author. Tel.: +34-91-334-9000; fax: +34-91-372-06-23.
*E-mail address:* rpoyato@icmm.csic.es (R. Poyato).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00452-7

Multilayer heterostructures were prepared by alternate deposition and crystallization of the PTC and PTL solutions onto $TiO_2/Pt/TiO_2/Ti/SiO_2/(100)Si$ substrates. Two different heterostructures were prepared: PTC/PTL/PTC and PTL/PTC/PTL.

The Si-based substrates were prepared by an evaporation–oxidation process, where Ti layers were deposited by evaporation and subjected to oxidation at 500 °C, and the Pt electrode was annealed at 800 °C for 30 min.

Amorphous films were deposited by spin-coating at a velocity of 2000 rpm for 45 s, in a class 100 clean room. Pyrolisis of these films was carried out on a hot plate at 350 °C for 60 s. Each deposited and pyrolised layer was crystallized in air by rapid thermal processing (RTP) at 650 °C for 50 s, at an average heating rate of 30 °C/s. Deposition, pyrolisis and crystallization process was repeated three times.

Orientations of the heterostructures were analyzed by X-ray diffraction (XRD) with Bragg–Brentano geometry, using a Siemens D500 powder diffractometer with a Cu anode. The 111 peaks of the film and of the Pt electrode appeared overlapped in the XRD patterns. To avoid this, θ and 2θ were misaligned by an angle of ~3°. In this way, it was possible to use pseudovoigt functions for the decoupling of the two peaks.

Profile composition of the films as well as interdifussion between the different layers of the heterostructures were analyzed by Rutherford Backscattering Spectroscopy (RBS). For this study, a 3 MV Tandem accelerator, using a 5.9 MeV $^4He^{++}$ beam with the surface barrier detector set at 165°, was used. The spectra were taken at a tilt angle of −8°. High energy RBS was used to get a good resolution and the separation of the signals of the heavy elements.[9] The RBS experimental data were analyzed using the RUMP simulation code.[10]

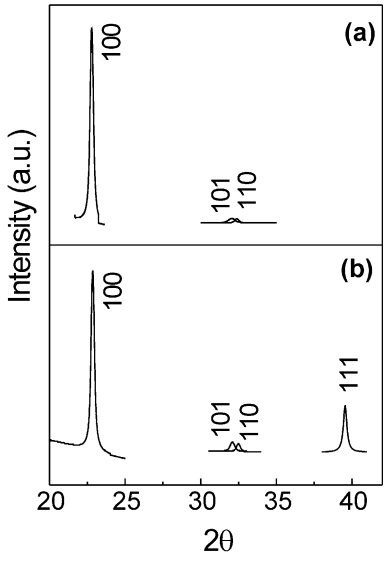


Fig. 1. XRD peaks profiles of the heterostructures, (a) PTL/PTC/PTL and (b) PTC/PTL/PTC.

Error in the calculation of the composition was ~10%. A bulk density of the PTL layers of ~7.7 g/cm$^3$, of the PTC layers of ~7.1 g/cm$^3$ and of the Pt of ~21.4 g/cm$^3$ were considered for the calculation of thickness. A roughness of ~100 Å at the PTL/PTC surfaces was considered in the simulation to get the best fit.

J–E ferroelectric hysteresis loops were measured with a modified Sawyer–Tower circuit using sinusoidal waves of 1 kHz after 0.15 mm diameter Pt electrodes were deposited on the films surfaces by sputtering.

## 3. Results

The XRD peaks profiles of the films, obtained from the XRD patterns, are shown in Fig. 1. The heterostructures are not randomly oriented, but show preferential orientations. The texture has <001>/<100> main components. A <111> contribution is also found in the PTC/PTL/PTC heterostructure.

Fig. 2 shows the RBS experimental spectra and the simulations of the two multilayers, PTL/PTC/PTL and PTC/PTL/PTC. Heterostructures of the films deduced from the simulations are depicted in the insets. The

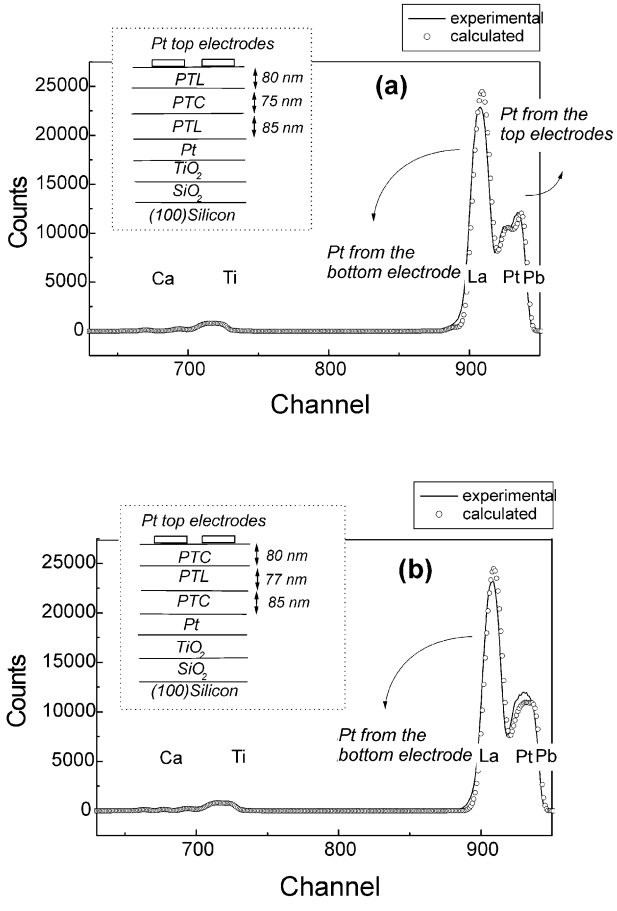


Fig. 2. RBS experimental spectra and simulations of the heterostructures, (a) PTL/PTC/PTL and (b) PTC/PTL/PTC.

Table 1
Ratios Pb/Ti, La/Ti and Ca/Ti, deduced from the simulations of the experimental RBS spectra

| Film | PTL layers | | PTC layers | |
|---|---|---|---|---|
| | Pb/Ti | La/Ti | Pb/Ti | Ca/Ti |
| PTL/PTC/PTL | 0.98±0.10 | 0.09±0.01 | 0.84±0.08 | 0.22±0.02 |
| PTC/PTL/PTC | 0.98±0.10 | 0.09±0.01 | 0.84±0.08 | 0.22±0.02 |
| Theoric ratios | 0.88 | 0.08 | 0.76 | 0.24 |

ratios Pb/Ti, La/Ti and Ca/Ti of the PTL and PTC layers deduced for each heterostructure from the simulations of the experimental RBS spectra are shown in Table 1. These ratios are close to those of the nominal compositions, $Pb_{0.88}La_{0.08}TiO_3$ and $Pb_{0.76}Ca_{0.24}TiO_3$, taking into account the error of the measurement, ~10%. Substantial interdifussion has not been found between the PTL and PTC layers.

The details of the experimental spectra where the Ti and Ca signals appear are shown in Fig. 3. It has to be noted that the $TiO_2$ layer on top of the substrate is not distinguished in the experimental spectra of both films. The signal of this layer is close to the Ti signal from the film, however, if a thin layer of $TiO_2$ were present on top of the substrate, a peak would appear close to the signal from the film.

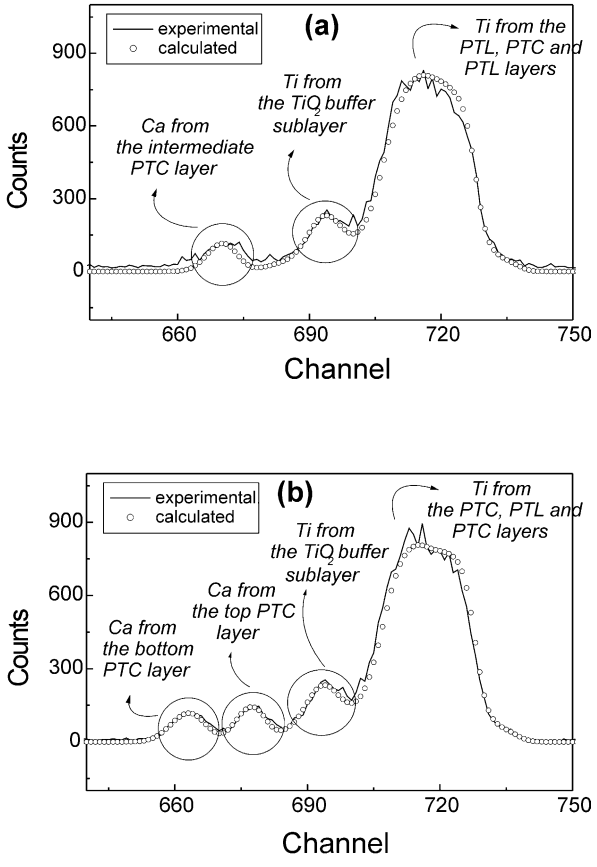


Fig. 3. Details of the experimental spectra and simulations for the interval in which the Ti and Ca signals appear, (a) PTL/PTC/PTL and (b) PTC/PTL/PTC.

Well defined J–E ferroelectric hysteresis loops, with similar values of coercive fields, $E_c \sim 100$ kV/cm, have been found (Fig. 4). High values of remanent polarization have been obtained in the two heterostructures, with $P_r \sim 38$ and 27 μC/cm$^2$ in PTL/PTC/PTL and PTC/PTL/PTC, respectively.

## 4. Discussion

The preferential orientations of the films reveal the existence of heterogeneous nucleation at the film-substrate interface and at the interfaces between layers. This is related to the used RTP crystallization, which diminishes the amount of pores homogeneously distributed in the film that could act as nucleation sites, giving place to randomly oriented films.[11] The multiple deposition and RTP crystallization favours that the texture partly extends to the layers deposited on the top, because each layer nucleates and grows on the previously crystallized layer.

The <001>/<100> orientations are the main components of texture in both heterostructures. Above the transition temperature, when the crystallization takes place, the (100) crystals provide the minimum surface energy,[12] which promotes their preferential growth. On cooling down to the tetragonal phase, the <001> and <100> directions are not equivalent anymore, giving place to the mixed orientation. It can be concluded that this mixed orientation is the natural one of the tetragonal perovskites, and it can take place both at the film-substrate interface and at the interfaces between layers.

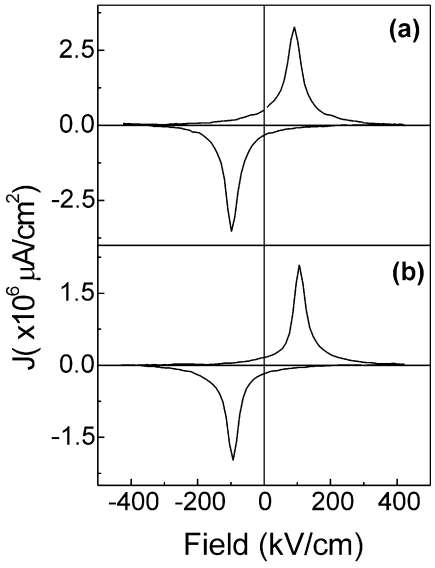


Fig. 4. J–E ferroelectric loops of the heterostructures, (a) PTL/PTC/PTL and (b) PTC/PTL/PTC.

The existence of a very thin Ti or $TiO_2$ layer onto the Pt has been shown to be related to the appearance of a <111> preferential orientation in PTL and PTC films.[13,14]

From the RBS analysis it is concluded that the $TiO_2$ layer is fully incorporated in the perovskite structure during crystallization of the phase, a result that has been obtained previously for PTL films onto annealed Ti/Pt/Ti/(100)Si substrates.[14] It is clear that the incorporation of the $TiO_2$ layer to the first layers of the film is directly related to the <111> orientation present in the PTC/PTL/PTC heterostructure. However, this component is not the preferential one in this heterostructure, and even though the same processing has been used to obtain both films, no <111> orientation has been found in the PTL/PTC/PTL heterostructure.

The <111> orientation only nucleates on the Ti rich film-substrate interface, so the sole mechanism available to extend it to the top layers is the nucleation of the new crystals onto the <111> oriented grains. A decrease of the <111> contribution with the increase of deposited layers has been previously found for PTL fims.[15,16] This is due to the existence of certain porosity between the layers, which stops the nucleation onto the <111> grains of the already crystallyzed layer.[16]

In the heterostructures, the lack of sensible interdifussion between PTC and PTL layers reveals that there exist discontinuities at the layer-to-layer interfaces. These discontinuities could be due to the existence of porosity at the interfaces, which make difficult the nucleation of the new crystals onto the underlying <111> oriented grains, and thus, interrupting the transmission of the <111> orientation to the top layers. Also, the different compositions of the layers, with slight different lattice characteristics, favour these discontinuities at the interfaces.

## 5. Conclusions

Multilayer heterostructures with alternated layers of PTC and PTL have been prepared onto $TiO_2$/Pt/$TiO_2$/Ti/$SiO_2$/(100)Si substrates. A diol-based sol–gel route, and multiple deposition and RTP crystallization have been used.

RBS studies have shown that the compositions of the PTL and PTC layers in the multilayer heterostructures are close to the nominal ones. Moreover, no interdifussion has been found between the PTL and PTC layers. The RBS analyses have also shown that the $TiO_2$ layer onto the substrate is fully incorporated in the perovskite structure during crystallization, and is related to the <111> orientation present in the PTC/PTL/PTC heterostructure.

The inhomogeneities between the PTC and PTL layers, most probably due to the existence of porosity between them and to the slight differences in their lattice parameters, interrupt the transmission of the <111> orientation to the top layers resulting in a small <111> contribution in the films. Thus, the natural <001>/<100> orientations are the preferential ones in the heterostructures.

J–E ferroelectric hysteresis cycles have been obtained and remanent polarizations of $P_r \sim 38$ and 27 $\mu C/cm^2$ have been found in PTL/PTC/PTL and PTC/PTL/PTC heterostructures, respectively.

## Acknowledgements

This work was supported by project MAT99-1269-CE of Spanish MCyT and COST528 EC Action.

## References

1. Brazier, M., McElfresh, M. and Mansour, S., Unconventional hysteresis behavior in compositionally graded $Pb(Zr,Ti)O_3$ thin films. *Appl. Phys. Lett*., 1998, **72**(9), 1121–1123.
2. Bao, D., Yao, X. and Zhang, L., Dielectric enhancement and ferroelectric anomaly of compositionally graded $(Pb,Ca)TiO_3$ thin films derived by a modified sol–gel technique. *Appl. Phys. Lett*., 2000, **76**(19), 2779–2781.
3. Bao, D., Mizutani, N., Yao, X. and Zhang, L., Dielectric and ferroelectric properties of compositionally graded $(Pb,La)TiO_3$ thin films on Pt/Ti/$SiO_2$/Si substrates. *Appl. Phys. Lett*., 2000, **77**(8), 1203–1205.
4. Liu, W., Ko, J. S. and Zhu, W., Preparation and properties of multilayer $Pb(Zr,Ti)O_3/PbTiO_3$ thin films for pyroelectric application. *Thin Solid Films*, 2000, **371**, 254–258.
5. Liu, W., Jiang, B. and Zhu, W., Self-biased dielectric bolometer from epitaxially grown $Pb(Zr,Ti)O_3$ and lanthanum-doped $Pb(Zr,Ti)O_3$ multilayered thin films. *Appl. Phys. Lett*., 2000, **77**(7), 1047–1049.
6. Algueró, M., Kholkin, A., Calzada, M. L. and Pardo, L., Dependence of functional properties on processing in sol–gel $(Pb,La)TiO_3$ thin films. *Appl. Phys. A*, 2000, **71**, 195–202.
7. Sirera, R. and Calzada, M. L., Multicomponents solutions for the deposition of modified lead titanate films. *Mat. Res. Bull*., 1995, **30**(1), 11–18.
8. Pardo, L., Poyato, R., González, A., Calzada, M. L., Lynch, E., O'Brien, S., Kelly, P. V., Stolichnov, I. and Guillon, H., Ca and La-modified lead titanate sol–gel thin films by UV-assisted processing for piezoelectric sensors. *Ferroelectrics*, 2002, **367**, 335–340.
9. Tesmer, J. R. and Nastasi, M., *Handbook of Modern Ion Beam Techniques*. 13, 1998, 837-841.
10. Doolittle, L. R., Algorithms for the rapid simulation of Rutherford backscattering spectra. *Nucl. Instr. and Meth*., 1985, **B9**, 344–351.
11. Algueró, M., Calzada, M. L., Quintana, C. and Pardo, L., Ferroelectricity of lanthanum-modified lead titanate thin films obtained by a diol-based sol–gel method. *App. Phys. A*., 1999, **68**, 583–592.
12. Liu, Y. and Phulé, P. P., Nucletion- or growth-controlled orientation development in chemically derived ferroelectric lead zirconate titanate $(Pb(Zr_xTi_{1-x})O_3$, $x = 0.4)$ thin films. *J. Am. Ceram. Soc*., 1996, **79**(2), 495–498.
13. Poyato, R., Gonzalez, A., Calzada, M. L. and Pardo, L., High pyroelectric coefficients of Ca-modified lead titanate sol–gel thin

films obtained by multiple deposition and crystallization. *Ferroelectrics*, 2002, **271**, 385–390.

14. Calzada, M. L., Poyato, R., García López, J., Respaldiza, M. A., Ricote, J. and Pardo, L., Effect of the substrate heterostructure on the texture of lanthanum modified lead titanate thin films. *J. Eur. Ceram. Soc.*, 2001, **21**(10–11), 1529–1533.
15. Poyato, R., Calzada, M. L., Ricote, J., Pardo, L. and Willing, B., Spontaneous pyro and piezoelectricity of sol–gel La-modified lead titanate thin films. *Int. Ferroelectrics*, 2001, **35**, 77–86.
16. Ricote, J., Poyato, R., Algueró, M., Pardo, L., Calzada, M. L. and Chateigner, D., Texture development in modified lead titanate thin films obtained by chemical solution deposition on Si-based substrates. Submitted to *J. Am. Ceram. Soc.* (in press).