Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of the European Ceramic Society 25 (2005) 2325–2329
www.elsevier.com/locate/jeurceramsoc

Crystallisation of $Pb_{1-x}Ca_xTiO_3$ ferroelectric thin films as a function of the Ca^{2+} content

I. Bretos*, J. Ricote, R. Jiménez, J. Mendiola, R.J. Jiménez Riobóo, M.L. Calzada

Inst. Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

Abstract

Lead calcium titanate ($Pb_{1-x}Ca_xTiO_3$) thin films with x from 0 to 0.50 were prepared by chemical solution deposition. Crystallinity of the films was studied as a function of calcium content and processing temperature. These studies were carried out on films deposited onto oxidised (1 0 0) Si substrates by means of X-ray diffraction. The analysis seems to indicate that the grain size of the films decreases as Ca^{2+} content increases, which was confirmed from the scanning force microscopy images of the films. X-ray data reveal that kinetics of grain growth in films with Ca^{2+} contents over 40 at% is very slow. Increase of calcium also produces a decrease in tetragonality of the perovskite films. Besides, it was observed that reflections of the perovskite appear at higher temperature in the films with larger Ca^{2+} contents. Brillouin spectroscopy was used to follow the evolution of the elastic properties of the films with temperature. This study shows an elastic instability at temperatures between 475 °C and 500 °C that can be associated to complete film crystallisation. Dielectric and ferroelectric properties were measured on films deposited onto platinised silicon substrates and crystallised at 650 °C. The films with 50 at% of Ca^{2+} still have ferroelectric properties, showing diffuse ferro-paraelectric transitions and slim ferroelectric hysteresis loops.

Keywords: Films; Sol–gel processes; X-ray methods; Perovskites; Calcium lead titanate

1. Introduction

Lead titanate, $PbTiO_3$, is a ferroelectric material with a perovskite structure that is tetragonal at room temperature with a tetragonality of $c/a = 1.064$. The inherent anisotropy of lead titanate along the c-axis causes an elevated spontaneous polarisation ($P_s > 50\,\mu C/cm^2$), which makes it appropriate for ferro, pyro and piezoelectric applications. Substitution of Pb^{2+} by Ca^{2+} leads to calcium modified lead titanate, $(Pb_{1-x}Ca_x)TiO_3$ (PCT) that has lower c/a values as Ca^{2+} doping increases. Ferroelectric properties of PCT bulk ceramics as a function of Ca^{2+} content were first reported by Yamamoto et al.[1] Further studies[2–7] corroborated that the amount of Ca^{2+} in these ceramics played a critical role on their structural and electrical properties.

During the last three decades, the development of the microelectronic industry has led to the conformation of ferroelectrics in thin film form. Chemical Solution Deposition (CSD) is one of the techniques used for fabrication of films. PCT films with low Ca^{2+} contents ($Ca^{2+} \sim 24\%$) have been extensively studied due to their excellent ferro, piezo and pyroelectric properties.[8–12] However, literature for films with large Ca^{2+} contents is not as extensive as in PCT bulk ceramics. CSD fabrication of PCT films with a maximum Ca^{2+} content of 40 at% has been recently reported.[9,13,14] Also, authors of this work have shown preliminary results on PCT films prepared by CSD with Ca^{2+} contents up to 50 at%.[15–17] Here, we want to show the effect of calcium content on the crystallisation of $(Pb_{1-x}Ca_x)TiO_3$ films with x from 0 to 0.5.

2. Experimental

Solutions of calcium-modified lead titanate ($Pb_{1-x}Ca_x TiO_3$) (PCT) with different calcium contents were synthesised following a method described elsewhere.[16,18] Precipitate-free solutions with a 10 mol% excess of PbO were prepared, containing the equivalent of ~1 mol of $Pb_{1-x}Ca_xTiO_3$ per litre of solution and with $x = 0$, 0.24, 0.30,

---

* Corresponding author. Tel.: +34 91 3349000; fax: +34 91 3720623.
E-mail address: ibretos@icmm.csic.es (I. Bretos).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.051

0.40 and 0.50. These solutions and films derived from them will be denoted hereinafter as PCT0, PCT24, PCT30, PCT40 and PCT50.

For the study of the films crystallisation, a single coating of the former solutions was deposited by spin-coating at 2000 rpm for 45 s onto oxidised (1 0 0) silicon substrates. The deposited wet layers were dried on a hot plate at 350 °C for 60 s. Crystallisation of the films was carried out by rapid thermal processing (RTP) in air at temperatures between 400 °C and 650 °C for 50 s and with a heating rate of 30 °C/s.

Evolution of crystallinity of the films was monitored by X-ray diffraction analysis with the Bragg-Brentano geometry (XRD) and with a grazing incidence of $\alpha = 1^\circ$ (GIXRD). The 1 1 1 PCT perovskite peaks of the films recorded by XRD were fit to pseudo-Voight curves. The width at half maximum (FWHM) value of the peaks was calculated from these curves.

Brillouin Spectroscopy (BS) was performed at room temperature on the PCT50 films treated at different temperatures.

PCT films were also prepared by RTP at 650 °C onto Pt/TiO$_2$/SiO$_2$/(1 0 0)Si substrates to study their dielectric and ferroelectric properties.[16] Surfaces of these films were observed by scanning force microscopy (SFM).

3. Results and discussion

Fig. 1a–e depict the variation with temperature of the width at half maximum (FWHM) values of the 1 1 1 diffraction peak measured by XRD in the PCT perovskite films on silicon, for different Ca^{2+} contents. An exponential decay with increasing temperature is observed for films with low Ca^{2+} doping. However, films with Ca^{2+} contents over 40 at% show almost constant values of FWHM. The broadening of the 1 1 1 peak is due to grain size and micro-strain. The decrease with temperature of the FWHM values of the PCT films with low calcium content (Fig. 1a–c) can be associated to an increase in grain size and also to changes in micro-strain with temperature, to which contribute the paraelectric–ferroelectric transition that these films suffer during cooling after crystallisation. However, PCT films with large Ca^{2+} contents (Fig. 1d and e) crystallise into the paraelectric phase that here is also the stable phase at room temperature. Then, not too much change in micro-strain should be expected. The steady FWHM values with temperature indicate that both micro-strain and grain size maintain almost constant with temperature in the PCT films with a Ca^{2+} content over 40 at%. A decrease of grain size of the films with the Ca^{2+} content is confirmed here in the SFM images of Fig. 2. At 650 °C, PCT24 films have an average grain size of ∼100 nm (Fig. 2a), whereas PCT50 films have grains of ∼50 nm (Fig. 2b).

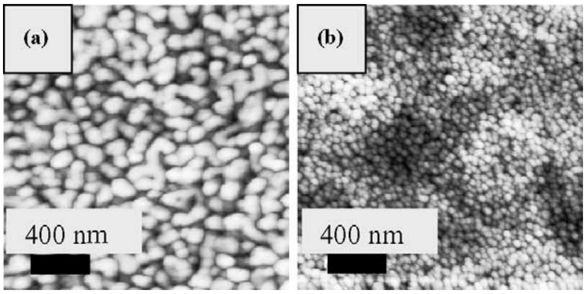

Fig. 2. SFM images of (a) PCT24 and (b) PCT50 films, treated at 650 °C.

Differences in crystallisation of the films with the Ca^{2+} content can be deduced from Fig. 3. At 400 °C none of the films show by GIXRD peaks indicative of crystalline phases,

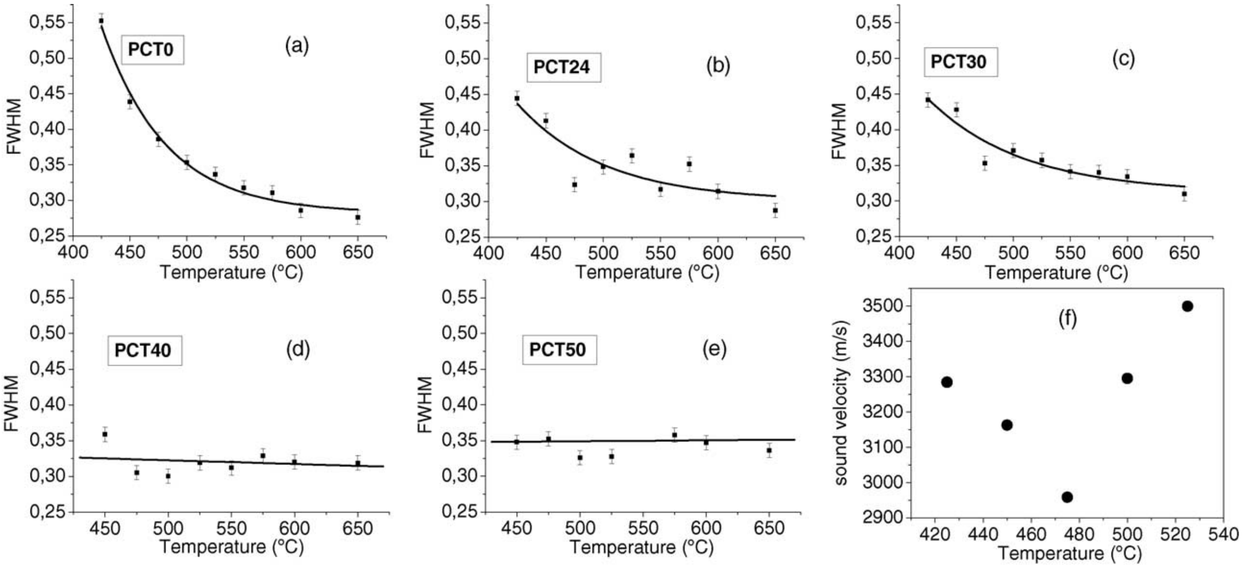

Fig. 1. Variation with temperature of FWHM values of the 1 1 1 perovskite peak measured by XRD with the Bragg-Brentano geometry, for the films (a) PCT0, (b) PCT24, (c) PCT30, (d) PCT40 and (e) PCT50. (f) Brillouin spectroscopy (BS) data that show the variation of the sound velocity at increasing temperatures for the films PCT50.

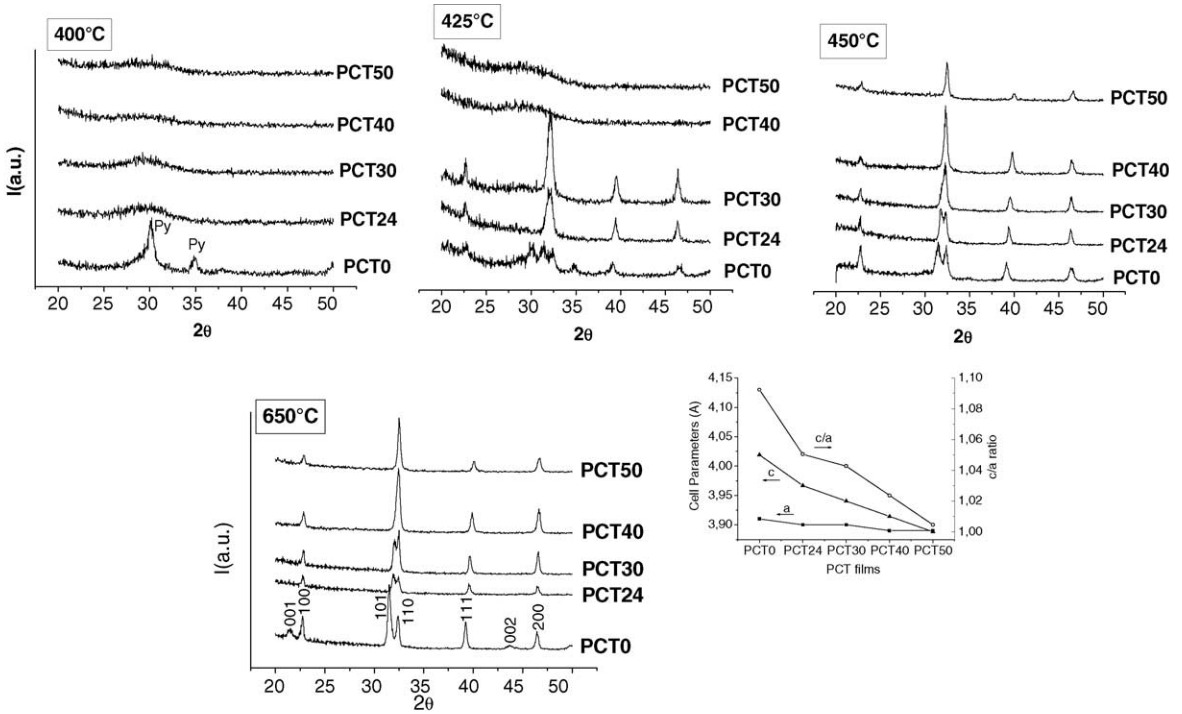

Fig. 3. GIXRD patterns of PCT films treated at different temperatures and with different Ca^{2+} contents. Py is a pyrochlore-type phase. Indexed peaks correspond to the perovskite. Inset shows the variation of the perovskite cell parameters (*a* and *c*) and of the tetragonality (*c*/*a*), as a function of the Ca^{2+} content.

with the exception of the PCT0 film, which shows reflections corresponding to pyrochlore phase. After treating the films at 425 °C, PCT40 and PCT50 films remain amorphous, while films with low calcium concentrations show reflections corresponding to the perovskite together with a large background characteristic of amorphous or low-crystalline phases. Coexistence of perovskite and pyrochlore is detected in the pattern of the PCT0 film. At 450 °C and higher temperatures, the X-ray patterns show the formation of a perovskite phase for all the films, although it is still possible to detect a relatively large background in the patterns of the films PCT40 and PCT50 treated at 450 °C. As presented in Fig. 3, the films treated at 650 °C show by GIXRD the formation of a single perovskite. Pure lead titanate (PCT0) films have a tegragonal structure with a tetragonality of $c/a \sim 1.09$. Substitution of Pb^{2+} by Ca^{2+} produces a decrease in *c*/*a*, obtaining a pseudo-cubic structure for PCT50 film (inset of Fig. 3).

Results of Figs. 1 and 3 indicate that crystallisation temperature increases and growth kinetics is slow for PCT films with Ca^{2+} contents over 40 at%. Films with Ca^{2+} contents below 40 at% show an exponential decay for the FWHM of the 1 1 1 perovskite peak that can be associated mainly to grain growth, whereas this kind of behaviour does not appear for the other films. Once the perovskite peaks are detected by GIXRD in the films PCT40 and PCT50 at 450 °C (Fig. 3), grain growth seems not to occur. This would suggest that crystallinity does not evolve with temperature so quickly in these films as in PCT films with low calcium. However, BS results obtained in PCT50 films show an elastic instability for the dependence of the room temperature sound velocity at increasing temperatures (Fig. 1f). Note how the sound velocity decreases with temperature up to ∼475 °C. Then, it starts to increase. The initial decrease is indicative of the formation of nano-crystals inside of an amorphous matrix. This structural change is accompanied by a softening of the sound velocity. In the temperature range between 475 °C and 500 °C, the elastic instability appears, indicating the formation of coarse-grained films and thus, the complete crystallisation of the films. The elastic properties of the films completely change and an abrupt increase in the sound velocity is produced, which is related with the expected hardening of the sample. This behaviour has previously been reported for PCT24 films, where the elastic instability was observed at similar temperatures.[19,20] Therefore, BS results indicate that complete crystallisation of the PCT50 films occurs at temperatures of ∼500 °C, like in films with low calcium. Reflections detected by X-ray diffraction in films treated at lower temperatures correspond to perovskite (Fig. 3), but this crystal phase is coexisting here with amorphous phases up to ∼500 °C, where the BS results (Fig. 1f) show the total conversion of the film into crystalline perovskite. However, grain growth with temperature seems to be hindered in PCT films with large amounts of calcium where crystalline films are formed by sub-100 nm grains (Figs. 1e and 2b).

In spite of the nanometric grain size of the films PCT50 crystallised at 650 °C and of the proximity of the perovskite structure to the paraelectric phase at room temperature, these films exhibit a low ferroelectric activity (Fig. 4a). Very diffuse

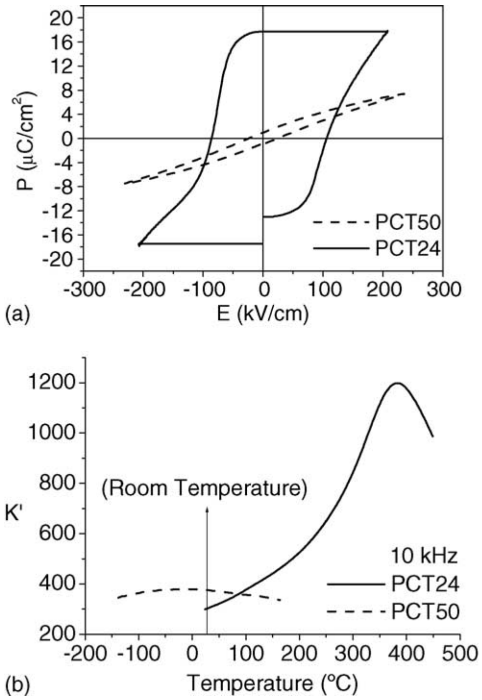

Fig. 4. Comparison of ferroelectric and dielectric properties between the PCT24 and the PCT50 films: (a) compensated ferroelectric hysteresis loops and (b) permittivity values with temperature.

ferro-paraelectric transitions are measured in the films with permittivity values at room temperature larger than those of films with low calcium (Fig. 4b). As an example of application, properties of PCT films with large Ca^{2+} contents could be exploited in dynamic random access memories, whereas applicability of the dielectric and ferroelectric properties of films with low calcium has been widely reported.[9–12]

4. Conclusions

Lead calcium titanate ($Pb_{1-x}Ca_xTiO_3$) films prepared by chemical solution deposition and with x from 0 to 0.50 are completely crystallised into the perovskite phase at temperatures of ∼500 °C. At lower temperatures, the films show the coexistence of perovskite and amorphous phases, whereas over 500 °C the films are full-converted into perovskite. In spite of the no dependence of the crystalline conversion of the films with the Ca^{2+} content, the films with low Ca^{2+} amounts develop a larger grain size than that of films with high Ca^{2+} contents. The films with Ca^{2+} contents of 50 at% are formed by sub-100 nm grains and show ferroelectric activity and diffuse ferro-paraelectric transitions with permittivity values at room temperature larger than those of films with low calcium content.

Acknowledgments

This work has been funded by Spanish projects CICyT MAT2001-1564 and CM-07/0084/2002. I. Bretos is grateful to the Spanish MCyT for his FPI PhD grant. J. Ricote and R. Jiménez acknowledge the support of the Ramón&Cajal Spanish MCyT program.

References

1. Yamamoto, T., Saho, M., Okazaki, K. and Goo, E., Electrical properties and microestructure of Ca modified $PbTiO_3$ ceramics. *Jpn. J. Appl. Phys.*, 1987, **26**, 57–60.
2. Mendiola, J., Jiménez, B., Alemany, C., Pardo, L. and del Olmo, L., Influence of calcium on the ferroelectricity of modified lead titanate ceramics. *Ferroelectrics*, 1989, **94**, 183–188.
3. King, G. and Goo, E., Effect of the *c*/*a* ratio on the domain structure in $(Pb_{1-x},Ca_x)TiO_3$. *J. Am. Ceram. Soc.*, 1990, **73**, 1534–1539.
4. Eremkin, V. V., Smotrakov, V. G., Shevtsova, S. I. and Kozakov, A. T., *x*, *T* phase diagram of $Pb_{1-x}Ca_xTiO_3$ crystals ($0 \leq x \leq 0.62$). *Phys. Solid State*, 1994, **36**, 191–192.
5. Ganesh, R. and Goo, E., Dielectric and ordering behaviour in $Pb_xCa_{1-x}TiO_3$. *J. Am. Ceram. Soc.*, 1997, **80**, 653–662.
6. Ranjan, R., Singh, N., Pandey, D., Siruguri, V., Krishna, P. S. R., Paranjpe, S. K. *et al.*, Room temperature crystal structure and relaxor ferroelectric behaviour of $Pb_{0.5}Ca_{0.5}TiO_3$. *Appl. Phys. Lett.*, 1997, **70**(24), 3221–3223.
7. Chandra, A. and Pandey, D., Evolution of crystallographic phases in the system $(Pb_{1-x}Ca_x)TiO_3$: a Rietveld study. *J. Mater. Res.*, 2003, **18**(2), 407–414.
8. Yamaka, E., Watanabe, H., Kimura, H., Kanaya, H. and Ohkuma, H., Structural, ferroelectric and pyroelectric properties of highly *c*-axis oriented $Pb_{1-x}Ca_xTiO_3$ thin film grown by radio-frequency magnetron sputtering. *J. Vac. Sci. Technol A*, 1988, **6**(5), 2921–2928.
9. Kholkin, A. L. and Calzada, M. L., Calcium modified lead titanate thin films for electromechanical applications. *J. Phys. IV France*, 1998, **8**(P9), 195–198.
10. Sirera, R., Calzada, M. L., Carmona, F. and Jiménez, B., Ferroelectric thin films of calcium modified lead titanate by sol–gel processing. *J. Mater. Sci. Lett.*, 1994, **13**, 1804–1805.
11. Calzada, M. L., Jiménez, R., Ramos, P., Martín, M. J. and Mendiola, J., Ferroelectric improvements of (Pb, Ca)TiO_3 thin films. *J. Phys. IV France*, 1998, **8**(PR9), 53–56.
12. Jiménez, R., Calzada, M. L. and Mendiola, J., *c*-Axis oriented sol–gel (Pb, Ca)TiO_3 ferroelectric thin films on Pt/MgO. *Thin Solid Films*, 1999, **348**, 253–260.
13. Li, H., Tang, X., Li, Q., Liu, Y., Tang, Z., Zhang, Y. *et al.*, Optical functions of Ca-modified $PbTiO_3$ thin films determined by spectroscopic ellipsometry. *Solid State Commun.*, 2000, **114**, 347–350.
14. Pontes, F. M., Pontes, D. S. L., Leite, E. R., Longo, E., Santos, E. M. S., Mergulhao, S. *et al.*, Influence of Ca concentration on the electric, morphological and structural properties of (Pb, Ca)TiO_3 thin films. *J. Appl. Phys.*, 2002, **91**(10), 6650–6655.
15. Calzada, M. L., Bretos, I., Jiménez, R., Ricote, J. and Mendiola, J., X-ray characterisation of chemical solution deposited $PbTiO_3$ films with high Ca doping. *Thin Solid Films*, 2004, **450**, 211–215.
16. Bretos, I., Ricote, J., Jiménez, R., Mendiola, J. and Calzada, M. L., Processing of chemical solution deposited Ca-modified $PbTiO_3$ films for high frequency components and dynamic random access memories. *Integr. Ferroelectr.*, 2004, **61**, 105–110.
17. Jiménez, R., Alemany, C., Calzada, M. L. and Mendiola, J., Relaxor-like behavior of $Pb_{.5}Ca_{.5}TiO_3$ thin films. *Ferroelectrics*, 2004, **302**, 461–466.

18. Sirera, R. and Calzada, M. L., Multicomponent solutions for the deposition of modified lead titanate films. *Mater. Res. Bull.*, 1995, **30**(1), 11–18.
19. Krüger, J. K., Ziebert, C., Schmitt, H., Jiménez, B. and Bruch, C., Evidence of an elastic instability between the amorphous and the microcrystalline state of Ca-modified lead titanate as revealed by Brillouin spectroscopy. *Phys. Rev. Lett.*, 1997, **78**(11), 2240–2243.
20. Jiménez-Riobóo, R. J., Calzada, M. L., Krüger, J. K. and Alnot, P., Elastic properties by Brillouin spectroscopy of sol–gel (Pb, Ca)TiO_3 films. *J. Appl. Phys.*, 1999, **85**(10), 7349–7354.