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Size effects on $Pb_{0.5}Ca_{0.5}TiO_3$ thin films

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Abstract

$Pb_{0.5}Ca_{0.5}TiO_3$ thin films with thickness between 80 and 700 nm have been prepared by deposition of sol–gel precursor solutions onto $Pt/TiO_2/SiO_2/(1\,0\,0)Si$ substrates and crystallized by rapid thermal processing (RTP). Dielectric measurements with temperature and frequency, and atomic force microscopy (AFM) micrographs have been performed. Two maxima are detected in the curve of variation of permittivity with temperature (K'–T). The AFM images of the films surfaces show a non-dependence of the mean grain size (~50 nm) with the film thickness. However, relaxor-like properties of the films are dependent on the films thickness. Experimental results and dielectric anomalies observed are discussed in terms of the possible existence of a morphotropic phase boundary (MPB) and the formation of a dead-layer in the films during their processing.

Keywords: Perovskites; Thin film; Sol-Gel processes; Dielectric properties

1. Introduction

The interest on the properties of $Pb_xCa_{1-x}TiO_3$ solid solution has increased during the last years. Coming from the lead side ($PbTiO_3$) the increase in the Ca content produces a lowering in the tetragonality *c*/*a* ratio of the structure producing shifting to lower temperature of the ferroelectric-to-paraelectric transition, reducing the remnant polarization and increasing the room temperature dielectric constant.[1] On the other side, the $CaTiO_3$ behaves as an incipient ferroelectric up to $x = 0.28$ and has a ferroelectric relaxor behaviour when $x = 0.35$.[2] The $x = 0.5$ compound presents relaxor-like characteristics and orthorhombic *Pbnm* structure like that of the $CaTiO_3$.[3] Besides, it has been observed in ceramic powders the existence of a morphotropic phase boundary for $0.6 \leq x \leq 0.4$ where tetragonal (*P4mm*) and orthorhombic (*Pbnm*) phases coexist.[4] Relaxor properties of films with these compositions can be of interest in applications that requires high frequencies or high charge storage. But it is well known in the thin film technology the difficulty to obtain thin films with the same properties than those of the counterpart bulk ceramics. This is because of the relative small grain size of thin films, chemical reaction with substrate, contact potentials between ferroelectric and electrode, and biaxial strain can produce a dead-layer during processing.[5] The above indicated applications need films with different thickness. The storage of large charge in dynamic random access memories (DRAM) is improved as film thickness is decreased (≤100 nm). On the other hand for tunable and high freque ncy applications films with thickness ≥200 nm are useful. Thin films of $Pb_{0.5}Ca_{0.5}TiO_3$ composition belong to the morphotropic phase boundary and present relaxor like properties attractive from both the basic and applied point of view.[6] In this work the effect of the thickness on the microstructure and dielectric properties of sol–gel prepared $Pb_{0.5}Ca_{0.5}TiO_3$ thin films is studied and discussed.

2. Experimental procedure

2.1. Thin film preparation

Solutions containing the equivalent of 0.1 and 0.3 mol of $Pb_{0.5}Ca_{0.5}TiO_3$ per litre of solution were prepared by a sol–gel method reported elsewhere.[7] Films with different thickness were fabricated by the successive deposition, drying and rapid thermal crystallisation at 923 K of layers of the

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former solutions. Film thickness was measured by profilometry. The solution with concentration of 0.1 mol/l was used for the preparation of films with thickness lower than 100 nm, whereas films with thickness of 295, 520 and 675 nm were derived from the solution with concentration of 0.3 mol/l.

Crystalline structure of the films was monitored by grazing incidence X-ray diffraction (GIXRD), using a grazing angle of $\alpha = 1^\circ$.

The microstructural characterization of the surfaces of the prepared films has been preformed using an atomic force microscopy (AFM).

2.2. Electrical characterization

Pt 20 nm/Au 150 nm dot electrodes of 2×10^{-3} cm^2 were deposited on the films surface using a shadow mask, to perform electrical characterization. Postannealing at 500 K in O_2 atmosphere of capacitors above prepared was performed.

A LCR-meter HP 4284A was used to measure dielectric permittivity as a function of temperature (2 K min^{-1}) and at several frequencies using a home made cryostat, between 120 and 450 K in the heating and cooling runs.

3. Results and discussion

The GIXRD diagrams of the films with different thickness of Fig. 1, show a pseudocubic structure without appreciable second phases. The intensities of the perovskite peaks point to a preferred orientation along the 1 0 0 direction in all the films. This orientation has been semi-quantified by the calculation of the ratio I_{100}/I_{110} of the films and comparing them with the random ceramic value of 0.13. The results that are depicted in Fig. 1 showed a clear 1 0 0 preferred orientation for all the films.

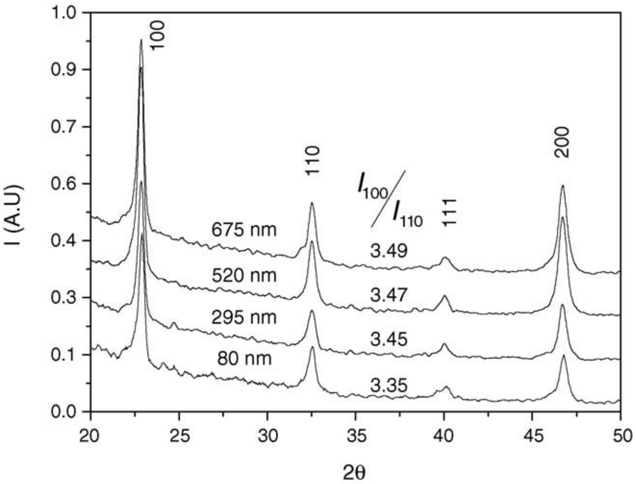

Fig. 1. GIXRD patterns of sol–gel prepared $Pt_{0.5}Ca_{0.5}TiO_3$ thin films of different thickness. The corresponding film thickness is depicted on the diffraction pattern. The patterns are displaced in the vertical axis for clarity. The ratio I_{100}/I_{110} is depicted in the plot for each diffraction pattern.

The AFM images of the surfaces of the thicker and thinner prepared films are included in Fig. 2. An average grain size of around 50 nm was obtained in both films. These results indicate that the thickness of the film do not have a clear effect on grain size.

The dielectric variation at 10 kHz as a function of temperature for the films (Fig. 3) showed a similar shape of the curve, but a markedly decrease of the dielectric constant as the film thickness decreases. In the heating run (Fig. 3a), two maxima in the dielectric constant are detected. However, in the cooling run a single maximum is observed that shifts to higher temperature as the film thickness decreases (Fig. 3b) (the temperatures at maximum for the different films are depicted in the plot).

The dielectric constant dispersion data for the 675 nm film during the heating run is displayed in Fig. 4a.The maximum that appears at lower temperature shifts to higher temperatures when frequency increases. On the other hand, the position of the maximum detected at higher temperatures is almost independent of the frequency. Dispersion results during the cooling run (Fig. 4b), shows the shift to higher temperatures of the single maximum. The shift of the maximum of dielectric constant with the frequency temperature is found

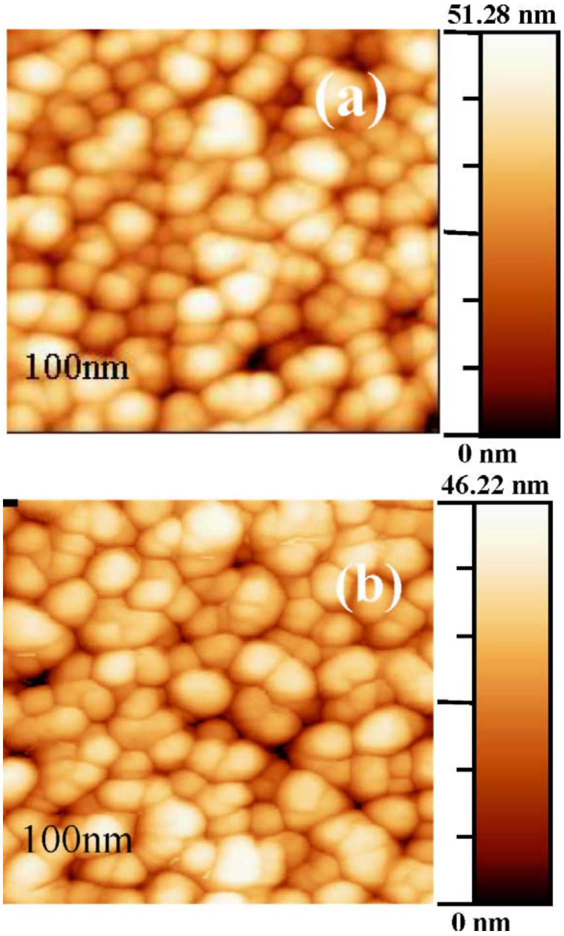

Fig. 2. AFM surface images of the films with thickness thickest film (a) and the thinnest one (b).

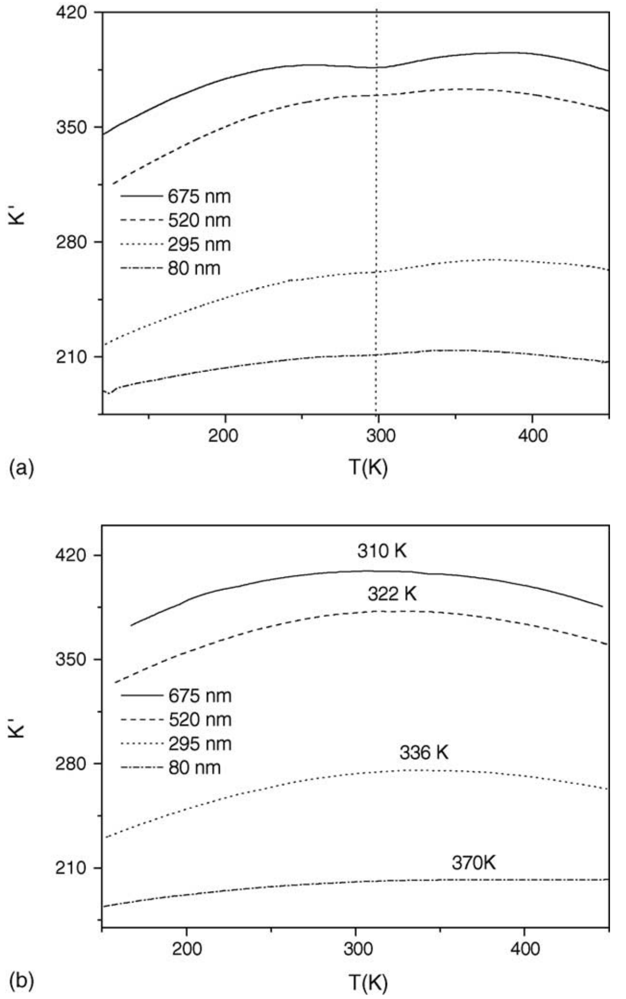

Fig. 3. Dielectric constant variation with temperature at 10 kHz: (a) heating run, the dashed line indicates the room temperature at the laboratory and (b) cooling run. The temperatures at maximum of dielectric constant are depicted in the plot for each film thickness.

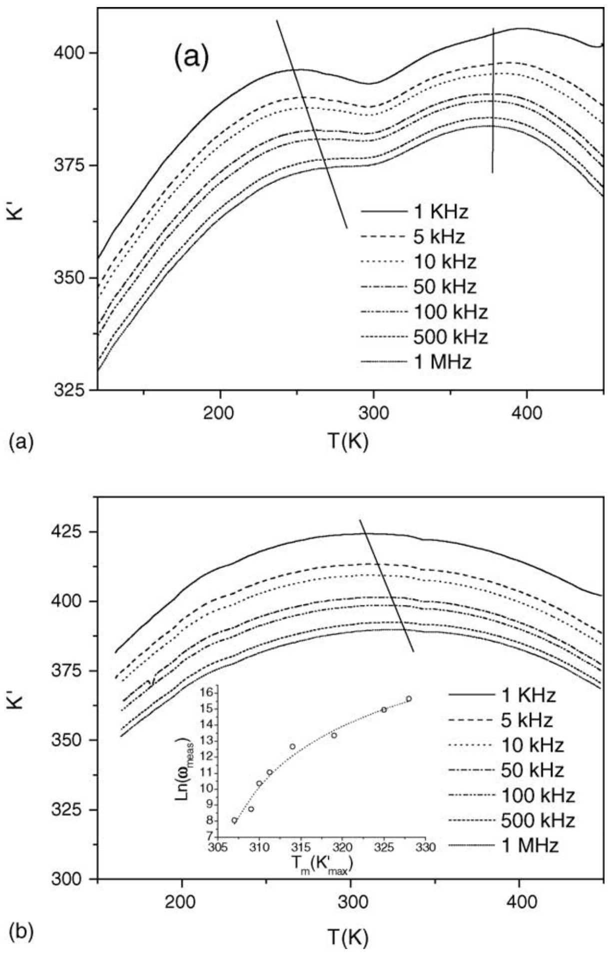

Fig. 4. Dielectric constant variation with temperature at different frequencies for the 675 nm thickness film: (a) cooling run and (b) heating run. In the inset the fit of the Volge–Fulcher–Taman relation to the temperature at maximum of the dielectric constant during the cooling run is included. In both plot the continuous lines are a guide to the eye for the temperature at maximum shift.

to follow the phenomenological Volger–Fulcher–Taman relation:

$$\omega = \omega_0 \exp\left(\frac{-E_\mathrm{a}}{T_\mathrm{max} - T_\mathrm{f}}\right) \tag{1}$$

Inset in Fig. 4b, where ω_0 is the attempt frequency; E_a is the activation energy and T_f is the freezing temperature. The obtained values are: $\omega_0 = 5.\ 10^7$, $E_\mathrm{a} = 0.014$ eV, $T_\mathrm{f} = 293$ K.

Chandra et al.[4] have detected in ceramic powders of $\mathrm{Pb_{0.5}Ca_{0.5}TiO_3}$ composition the coexistence of orthorhombic *Pbnm* and tetragonal *P*4*mm* phases. The appearance of two maxima in dielectric dispersion during the heating run, one with relaxational character at lower temperature and the other one without temperature shift, could be due to the coexistence of phases in a composition close to the morphotropic phase boundary. It should be pointed out that both maxima are also evident in the dielectric loss dispersion, with the shift of the maximum of lower temperature to higher temperatures as frequency increases (not shown). During the cooling a single maximum is observed that is placed at an intermediate temperature between those of the two maxima during the heating run (Fig. 4a and b). It can be also observed that the dielectric constant maximum follows a clear trend in decreasing the film thickness in the cooling run meanwhile in the heating run there is not trend of the maxima (Fig. 3a and b). On the other hand, if we look at the relative minima between maxima during the heating run we can conclude that its temperature position is independent of the film thickness and close to the room temperature, see the dashed line in Fig. 3a. This experimental evidence supports the possibility that the observed effect is rather due to an ageing effect than to a coexistence of phases, although it could be also possible. Ageing of relaxor ferroelectrics is a well-known effect due to stabilization of nanosized polar clusters by charge defects present in the sample.[8] The effect of the ageing at a temperature where the polar nanoclusters exist is to decrease the dielectric constant at the ageing temperature producing two maxima where the lower temperature one keeps the relaxation behaviour meanwhile the other one behaves as corresponding to a normal diffuse ferroelectric transition. When temperature increases well above the last maximum one the polar nanoclusters tends to disappear and there is a re-organization of charge. Thus, during cooling a normal relaxor-like behaviour is obtained produced by the polar nanoclusters dynamics.

If we keep our attention on the cooling results it is evident that the film thickness rules the change in the dielectric constant values and temperature at maximum shifts of the dielectric constant. Here we can avoid the effect of grain size as long as the surface microstructure observed in the AFM is representative of the bulk of the film.

Fig. 5 shows the variation of the dielectric constant measured at 10 kHz and 300 K as a function of the film thickness. The continuous line is the fit of the experimental data to the approximate equation of two capacitors in series model:

$$\frac{t_m}{K'_m} = \frac{t_m - t_i}{K'_b} + \frac{t_i}{K'_i} \qquad (2)$$

where K'_m is the measured dielectric constant, K'_b is the bulk dielectric constant, K'_i is the interfacial layer dielectric constant, t_m is the total film thickness, t_i is the interface layer thickness. The obtained results are $K'_b = 480$; $K'_I = 60$; $t_i = 197$ Å. The thickness of the interfacial layer (dead-layer) is close to the value for the depletion layer thickness estimated for Pt/$SrTiO_3$/Pt capacitors (∼200 Å).[9] It should be noted that consider the same K'_b value for all the thickness is a rough approximation because the temperature at maximum is increasing in decreasing the film thickness (Fig. 3b). The obtained result from the series model is just a guide to the existence of a lowering of the dielectric constant in approaching the film/electrode interface.

The appearance of dead-layers in ferroelectric thin films is inherent to their heterostructure. Reaction layers between the interface and the film can produce this. The contact potential between the ferroelectric and electrode can give rise to a dead-layer.[9] The total residual stress produced during the thin film preparation produce a lowering in the dielectric constant as well.[10]

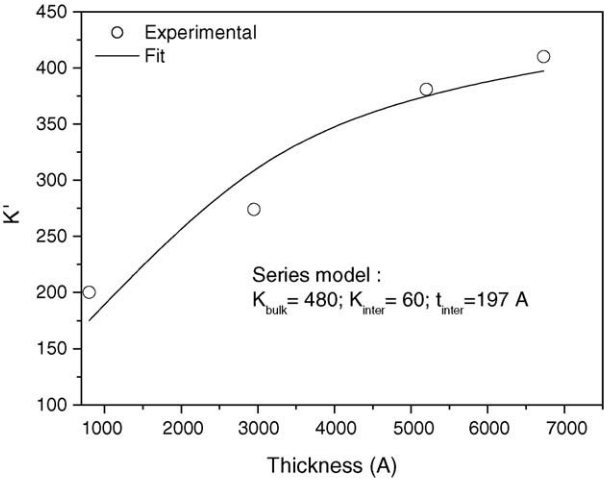

Fig. 5. Variation of the dielectric constant a s a function of the film thickness measured at 10 kHz and 300 K. The continuous line is the fit to the two capacitors in series model. The results of the fit are depicted in the plot.

In the sol–gel film formation the sol-drying stresses are very large due to the strong mass loss produced. The layer-by-layer deposition and crystallization tends to reduce the effect but it should be still the larger one. In ferroelectric thin films the shift to larger temperatures of the dielectric constant maximum due to tensile stresses has been reported several times.[11] In relaxor-like thin films the influence of the sign of the stresses on the temperature shift of the dielectric constant maximum is not still resolved for non-epitaxial films. Also a dc bias field can produce the same effects in ferroelectric materials and bias fields can be also be produced at the film/electrode interface.[9] Nevertheless, the shift of the dielectric constant maxima as well as the reduction in value should be related to the presence of dead-layer of lower dielectric constant produced among other factors by the relaxation of the stress induced during the sol–gel preparation. The possibility of existence of a chemical modified layer can be avoided as a result of the performed RBS analysis in films prepared in the same way and with the same composition.[12] Our preliminary results on the cell strain change as a function of the film thickness do not indicate a clear trend as well as the microstrains deduced from the diffraction peaks integral width the variance method. Further work is running in order to clarify the origin of the dead-layer in these films.

4. Conclusions

The film thickness has a strong influence on the dielectric constant value and temperature at maximum position. The appearance of two maxima in the dielectric constant variation with temperature can rather be related to an ageing effect than to a coexistence of orthorhombic and tetragonal phases in a composition close to a morphotropic phase boundary. The film microstructure is not responsible of the observed changes in the dielectric behaviour with the film thickness. A dead-layer probably related with the relaxation of the stresses developed during the film preparation can be the responsible of the observed effects.

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