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Quantitative Analysis of Preferential Orientation Components of Ferroelectric Thin Films

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A quantitative study of the preferred orientation of lanthanum and calcium modified lead titanate thin films, including the measurement of pole figures and calculation of orientation distribution function (OD), is presented. The main preferential orientation components are identified as <001> and <100> perpendicular to the film surface. Variations of the texture strength and the contribution of these components to the final texture are observed with changes in the film thickness or the substrate used. These variations are correlated to the ferroelectric properties of these films. This information can be used to optimise the preparation process to obtain improved thin films for pyroelectric and piezoelectric applications.

Keywords: Texture; Orientation Distribution Function; Ferroelectric; Thin Films; Modified Lead Titanate

INTRODUCTION

It is well known that the presence of any preferred crystallographic orientation, or texture, is a determinant factor of the behaviour of ferroelectric thin films. Despite the growing interest in producing highly oriented thin films for applications, complete quantitative texture analysis works are not found in the literature of ferroelectrics until recently [1]. Pole figures, i.e., the angular distribution of a chosen crystallographic direction with respect to the sample coordinates, are measured and from them an orientation distribution (OD) is calculated. This provides information about all the components contributing to the crystallographic orientation of the material, and quantifies the degree of orientation by the so-called texture index.

Among the ferroelectric compositions, modified lead titanates have been widely studied because of their interesting piezo and pyroelectric properties, which make them suitable for infrared sensors and electromechanical applications [2-4]. In this work we study La modified lead titanate (PTL) thin films with different thickness and Ca modified (PTC) deposited on different substrates. The aim is to establish the influence of these modifications on the resulting texture, and to show its correlation with properties, such as the remanent polarisation or pyroelectric factors, which determine their suitability for applications.

MATERIALS AND EXPERIMENTAL PROCEDURE

Thin films of lead titanate modified with La, $Pb_{0.88}La_{0.08}TiO_3$ (PTL), and Ca, $Pb_{0.76}Ca_{0.24}TiO_3$ (PTC), were obtained by spin-coating deposition of sol-gel processed solutions [5,6]. PTL films were obtained by multiple coating deposition on a substrate of $Pt/TiO_2/Si(100)$ and crystallised by direct insertion in a preheated furnace at 650°C for 12 min. Different number of layers has been used: 1, 3 and 5 layers for PTL-1, PTL-3 and PTL-5, respectively. For PTC films we use two different substrates Pt/MgO(100) (PTC-Mg) and $Pt/SrTiO_3(100)$ (PTC-Sr). Two coatings were deposited and each one was crystallised by rapid thermal processing (heating rate 30°C/s) at 700°C for 50 s. The thickness of the films was measured by profilometry.

Measurement of experimental pole figures was carried out with a Huber four-circle goniometer mounted on an INEL X-ray generator (Cu $K\bar{\alpha}$ wavelength) using 5°x5° steps to cover the whole pole figure. A curved position sensitive detector (INEL CPS-120) was used to acquire a complete diffraction pattern at each position of the sample, decreasing considerably data acquisition times. The integrated intensities are treated and corrected for absorption, volume variations and delocalisation effects using INEL software programs. Pole figures are normalised into distribution densities, which are expressed as multiples of a random distribution (m.r.d.). A sample without any preferred orientation has pole figures with constant values of 1 m.r.d. From several of these pole figures we refined the orientation distribution (OD), f(g), following the Williams-Imhof-Matthies-Vinel iterative method (WIMV) [7]. This function describes the amount of crystallites with an orientation between **g** and **g**+d**g** (**g** = αβγ, Euler angles). The quality of the refinement is assessed by the reliability factors (RP0 and RP1, for global and values above 1 m.r.d. respectively). From the OD we can calculate interesting pole figures which are not available experimentally, analyse the different orientation components present, and calculate parameters indicative of the texture strength, like the texture index: $F^2 = \frac{1}{8\pi^2}\sum_i [f(g_i)]^2 \Delta g_i$. The calculations to obtain and manipulate the OD have been carried out with the Berkeley Texture Package (BEARTEX) [8].

Ferroelectric hysteresis loops were measured with a modified Sawyer-Tower circuit and an oscilloscope, at a frequency of 50 Hz. Pyroelectric coefficients, γ, were calculated from the pyroelectric currents obtained after applying a triangular thermal wave of amplitude 3°C and a frequency of 2 10^{-3} Hz, leading to an effective temperature gradient of 2.6 °C/min.

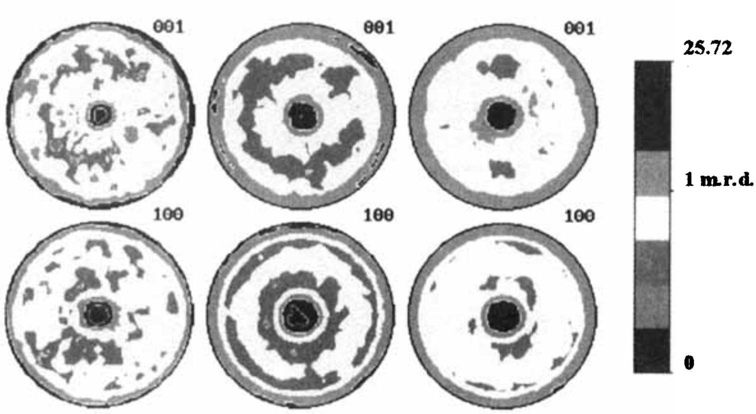
RESULTS AND DISCUSSION

Lanthanum modified lead titanate thin films

Results of the quantitative texture analysis are summarised in Table 1. The low values of the reliability factors RP0 and RP1 show the good quality of the OD refinement. We identify a mixed <001>,<100> preferred orientation perpendicular to the film surface, with a very weak component along <221>. Figure 1 shows the calculated pole figures corresponding to {001} and {100} planes. The highest distribution densities are found in the centre of the figure. This reflects the fact that there is a large fraction of crystals with <001> or <100> directions perpendicular to the sample surface. In order to compare the contributions of these two orientation components we compare the values of those density maxima (Figure 1). It can be observed that they are very similar in the three films analysed, with a tendency to be slightly higher for {100} planes in PTL-1 and PTL-3, e.g., 909 and 1077 m.r.d. for {001} and {100}, respectively. We can conclude that the two main preferential orientation components are approximately equally important.

TABLE 1 Texture parameters of PTL thin films, together with their remanent polarisation, P_R.

Sample	Components of texture	Texture index (m.r.d.^{2})	RP0 (%)	RP1 (%)	P_R (μC cm^{-2})
PTL-1	<001>,<100>	10.5	36	16	--
PTL-3	<001>,<100>	6.2	22	16	27
PTL-5	<001>,<100>	3.9	19	15	11



PTL-1 **PTL-3** **PTL-5**

FIGURE 1 {001} and {100} recalculated pole figures of PTL thin films. Equal area projection and logarithmic density scale. **See Color Plate I at the back of this issue.**

As the number of layers increases, the thickness goes from 130 nm (PTL-1) to 560 nm (PTL-5), and the texture index decreases (Table 1). This effect can also be seen in Figure 1, with a decrease of the distribution density maxima from PTL-1 to PTL-5. This progressive loss of the degree of orientation, which is not possible to observe by grazing incidence X-ray diffraction [9], gives a new insight into the evolution of the properties of the film with thickness. Apart from the very thin PTL-1, from which it was not possible to obtain hysteresis loops, the remanent polarisation [9] decreases as the texture strength of the film decreases (Table 1).

The net polarisation of a polycrystalline material is the sum of the contributions of the individual crystals. For tetragonal perovskites the polar axis corresponds to the <001> direction. The projection of the polar vector on the direction of the applied electric field (perpendicular to the film) will give the contribution of that crystal to the net polarisation. Therefore, the highest contributions will come from the crystals whose polar axes, <001>, are perpendicular to the film surface. An increase of the texture index involves in this case a higher fraction of crystals oriented along this direction, thus resulting in an increase of the net polarisation. This scenario seems to correspond to the variations observed in PTL thin films with different thickness and degrees of orientation. An increase of the number of deposited layers in this case eliminates the high leakage currents present in the single coated films and allows the measurement of hysteresis loops, but decreases the polarisation values due to a gradual loss of the preferred orientation.

TABLE 2 Texture parameters of PTC thin films, together with their spontaneous pyroelectric coefficient, γ_s, and after a poling process, γ_p, with an electric field of 8 V.

Sample	Components of texture	Texture index (m.r.d.^{2})	RP0 (%)	RP1 (%)	γ_s (10^{-8} C cm^{-2} K^{-1})	γ_p
PTC-Mg	<001>,<100> weak <111>	5.2	22	10	1.5	3.2
PTC-Sr	<001>,<100>	32.1	26	24	1.1	2.0

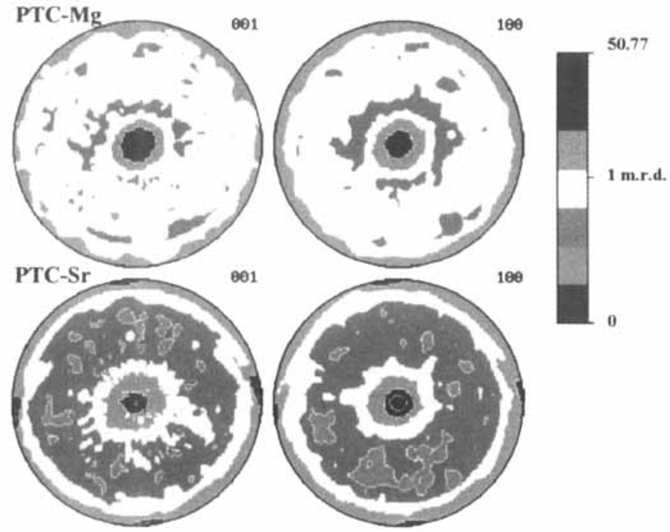


FIGURE 2 {001} and {100} recalculated pole figures of PTC thin films. Equal area projection and logarithmic density scale. **See Color Plate II at the back of this issue.**

Calcium modified lead titanate thin films

Table 2 contains the results of the texture studies of two PTC films of the same thickness deposited on different substrates. We obtain again a mixture of <001> and <100> preferential orientation components perpendicular to the film surface, with a weak contribution along <111> for the film deposited on Pt/MgO (PTC-Mg). This film also exhibits a low value of the texture index (5.2 m.r.d.^{2}) when compared to the highly textured PTC-Sr, deposited on Pt/$SrTiO_3$ (32.1 m.r.d.^{2}).

We compare the values of the density maxima in the centre of the {001} and {100} pole figures in Figure 2 to study their contribution to the final texture. For the PTC-Mg film the contribution is slightly higher for {001} than for {100} planes perpendicular to the film surface (8.23 and 5.82 m.r.d., respectively), while for the PTC-Sr the largest contribution comes from the {100} planes (17.68 and 50.77 m.r.d. for {001} and {100}, respectively). Therefore, we can summarise saying that PTC films deposited on different substrates present mainly a mixed preferred orientation that changes with the substrate chosen. The use of Pt/MgO results in films with a higher density of crystals oriented along <001> than along <100> perpendicular to the film surface. The Pt/$SrTiO_3$ substrate produces highly oriented films, but in this case there is a strong contribution from crystals oriented along <100>.

The pyroelectric coefficients, measured before and after poling the film [10], are shown in Table 2. Their values are higher for PTC-Mg, which presents the lowest <100> contribution of the two films, despite the strong texture of PTC-Sr. It has been shown that the pyroelectric coefficients obtained after poling decrease with time until they reach the initial, spontaneous values [10] . This fact emphasises the interest of the control of the development of the texture, which seems to be a determinant factor of the spontaneous pyroelectric coefficient of the film.

To explain the influence of the presence of preferred orientations on the pyroelectric coefficient of these films, we have to take into account the contributions to the net polarisation of the film, directly related to it. As we have explained before, an increase of the fraction of crystals oriented along <001> perpendicularly to the film surface leads to an increase of the net polarisation, and consequently of the pyroelectricity. However, in this case, the film with the highest pyroelectric coefficients, PTC-Mg, presents the lowest contribution from crystals oriented along <001> of the two PTC films studied. Thus, it is necessary to consider the contribution of crystals with the <001> direction parallel to the sample surface (<100> perpendicular to the surface). These crystals will give, if any, the weakest contribution to the net polarisation. If a high fraction of them are present in the thin film, the contributions to the net polarisation will diminish. This is the case for PTC-Sr, where the contribution to the texture of crystals oriented along <100> is so important that the pyroelectric coefficients decrease as a result.

CONCLUSIONS

From the quantitative analysis of the mixed <001>, <100> preferred orientation of ferroelectric modified lead titanate thin films we have obtained the following results, which demonstrate the importance of texture as a determinant factor of the final properties of the films:

1. The increase of the film thickness by increasing the number of deposited layers leads to a decrease of the texture strength that results in a reduction of the remanent polarisation.
2. The use of a Pt/$SrTiO_3$ substrate, compared to Pt/MgO, produces highly textured films, but with a strong contribution from crystals whose polar axis is in the plane of the film, which reduces the spontaneous pyroelectric coefficients of the films.

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