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Combined X-ray Texture-Structure-Microstructure Analysis Applied to Ferroelectric Ultrastructures: A Case Study on $Pb_{0.76}Ca_{0.24}TiO_3$

L. CONT[ab], D. CHATEIGNER[ad], L. LUTTEROTTI[b], J. RICOTE[c], M.L. CALZADA[c], J. MENDIOLA[c],

[a] *LPEC, Univ. du Maine, BP 535, 72085 Le Mans, FRANCE;* [b] *DIM, Univ. Di Trento, 38050 Trento, ITALY;* [c] *Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, SPAIN;* [d] *CRISMAT-ISMRA, 14050 Caen, FRANCE*

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A new methodology for a quantitative description of texture, structure and other microstructural parameters of thin layers using X-ray diffraction is presented and applied to the case of a ferroelectric thin film of $Pb_{0.76}Ca_{0.24}TiO_3$ on a $Pt/TiO_2/SiO_2/Si$ substrate. The approach allows the quantitative texture analysis of the ferroelectric thin film and the Pt electrode, refining simultaneously their structure, layers thickness, mean crystallite size and microstrain state. The powerfulness of this methodology is discussed and compared with other approaches.

Keywords Texture; Structure; X-Ray diffraction combined approach; Ferroelectric thin films; Modified lead titanates;

INTRODUCTION

The microstructure of ferroelectric thin films is a determinant factor of their final properties, which are used in a wide range of technological applications [1,2]. Different techniques are used for this characterisation, and among them, X-ray diffraction has been routinely used as a non-destructive characterisation of texture, strain state, particle size, crystallographic structures, ... However, when applied to anisotropic polycrystalline samples, the classical diffraction approaches generally fail. For instance, a usual Bragg-Brentano diffraction diagram may not

reveal all diffracted lines of a compound when it is strongly textured, making its structural determination impossible, and at the same time preventing any quantitative texture analysis. This is usually the case of ferroelectric thin films.

In this work, we have chosen a relatively recently developed approach [3], which is able to determine all the parameters accessible by X-ray diffraction through the combination of adequate refinement procedures, which allow the study of layered multiphase compounds. As an example, we apply it to a $Pb_{0.76}Ca_{0.24}TiO_3/Pt/TiO_2/SiO_2/Si(100)$ ultrastructure.

MATERIALS AND EXPERIMENTAL PROCEDURE

A thin film of Ca-modified lead titanate of the nominal composition $Pb_{0.76}Ca_{0.24}TiO_3$ (PTC), was obtained by spin-coating deposition of a sol-gel processed solution [4] on a $Pt/TiO_2/SiO_2/Si(100)$ substrate previously treated at 650°C during 30 min. The 4 layers deposited were crystallised layer-by-layer by rapid thermal processing (heating rate ~30°C/s) at 650°C for 50 s. Once the film is crystallised, a further thermal treatment at 650°C during 1 hour is performed (heating rate 10°C/min). The expected thickness of the PTC and Pt layers were approximately 400 nm and 50 nm respectively.

X-ray measurements were carried out with a Huber four-circle goniometer mounted on an X-ray generator equipped with a curved position sensitive detector (INEL CPS-120), as explained elsewhere [5]. Spin-coated films usually exhibit fibre textures [5,6], which means that intensities are varying only with χ. Therefore, we summed all diagrams in φ for identical χ angles (11 resulting diagrams), in order to first refine background, 2θ offset and defocusing effects. The nominal composition was used in the refinement, starting with bulk-like cell parameters. A first cycle applied to all the diagrams extracted the integrated intensities using the Le Bail algorithm [7]. These intensities are used for a first refinement of the orientation distribution (OD) by the WIMV [8] or the entropy modified WIMV (E-WIMV) [9] iterative methods. The OD obtained is then introduced in the cyclic Rietveld refinement of the diagrams. The new refined parameters are used for a new WIMV cycle to obtain a new OD, and so on. In this way, the OD refinement takes progressively account of the microstructural and structural reality, while the Rietveld analysis is corrected for texture in

a physically sound manner. All the necessary calculations were carried out in the MAUD package [10] in which the layered model for ultrastructures measurements using a curved detector was implemented [11]. The refinement quality is assessed by the comparison of the experimental and recalculated diagrams and by the reliability factors: RP for OD refinement, Rw and R_{Bragg} for Rietveld refinement.

RESULTS AND DISCUSSION

The experimental diagrams show a strong Pt preferred orientation with {111} parallel to the film plane (Fig. 1). The PTC film texture is difficult to analyse from θ-2θ spectra, because of the overlap between peaks of the ferroelectric film and the underlying substrate. Up to now, the direct integration method used [5,6] extracts the texture information of the thin film only from those peaks not influenced by the underlying layers of the substrate, reducing considerably the input data used in the OD refinement. In this case, the structural data used for the OD calculations correspond to ceramic materials of equivalent compositions, with crystals not growing with substrate-imposed restrictions. Therefore, the correct quantitative texture analysis (QTA) of both phases can only be calculated using the combination of the Rietveld and WIMV-like algorithms. Figure 1 shows two refinement results for the diagrams measured at $\chi = 0°$ using the WIMV and E-WIMV algorithms. One can directly see the better refinement obtained using the E-WIMV approach, particularly for the very sharp peaks of Pt, which already denotes a strong texture, and of the ones corresponding to the Si single crystal. Note that we are able with this procedure to perform a reliable analysis of the Pt layer, which is covered by the ferroelectric thin film, thanks to the layer model implemented in the calculations. Figure 2 shows a selected series of diagrams measured at increasing tilt angles, with their corresponding refinements using the E-WIMV approach. All the diagrams are nicely reproduced, with reliability factors R_{Bragg} as low as 4.7 % (Tab. 1). The small observed discrepancies are due to strong substrate peak feet. From the refined orientation distribution we can recalculate the pole figures (Fig. 3), for the PTC and Pt layers.

The refinement was made on the 19 and 4 first available pole figures for PTC and Pt, respectively, but we present only the low-indices ones. In agreement with the diffraction diagrams, all the

reliability factors indicated a better refinement using the E-WIMV approach (Tab. 1), which also indicated a stronger texture (higher texture indexes) both for PTC and Pt layers. This is due to the better ability of the E-WIMV algorithm to represent strong textures.

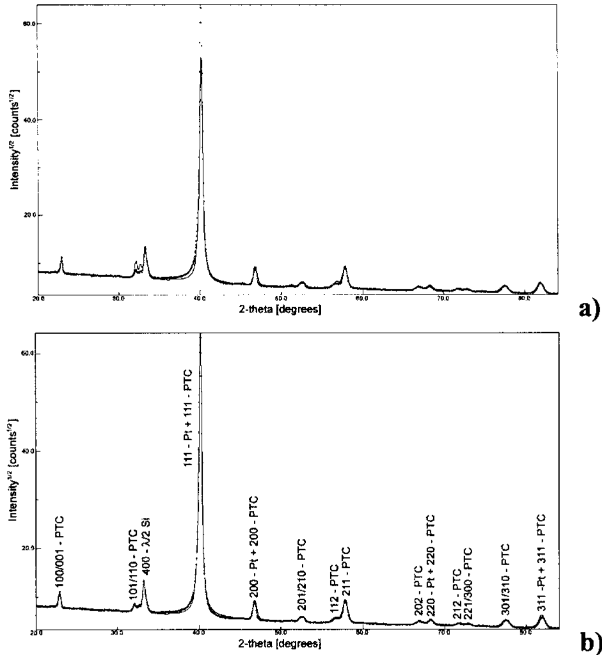

FIGURE 1 Experimental (dotted line) and refined (solid line) diagrams for $\chi = 0°$, using the WIMV **(a)** and E-WIMV **(b)** approaches.

Texture indexes are 2 mrd^2 for PTC and 41 mrd^2 for Pt (mrd-multiples of a random distribution [5,6]). While the Pt layer only shows preferential orientation along <111>, the ferroelectric PTC film has also a small component along <100> perpendicular to the film. Interestingly, no significant component along <001> is observed (Fig. 3). The results of the microstructural parameters (Tab. 2) reveal the presence of larger microstrains in the PTC films than in the Pt layer, which presents the largest mean crystallite size. This is consistent with the fact that crystallites of the PTC film have sizes not larger than one tenth of the total layer thickness, while the Pt layer exhibits a mean crystallite size which extends to the full thickness of the layer. The values obtained for the Pt and PTC layers thickness are very close to the expected ones.

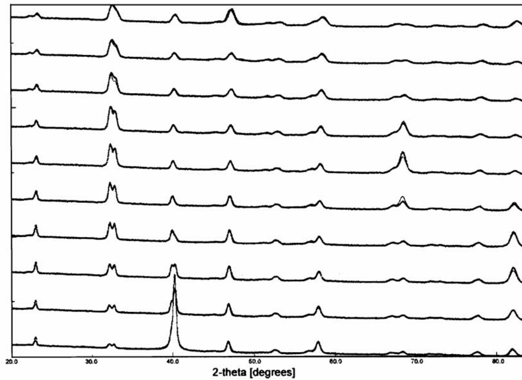

FIGURE 2 Experimental (dotted line) and refined (solid line) diagrams from $\chi = 5°$ (bottom) to $\chi = 45°$ (top) step 5°, using E-WIMV combined with Rietveld analysis.

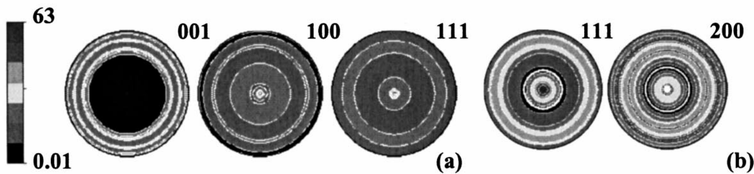

FIGURE 3 Pole figures recalculated by E-WIMV for **(a)** PTC film (linear density scale) max. value=3.8 mrd, min. value=0.1 mrd) and **(b)** Pt layer (logarithmic density scale). Equal area projections.

	Pt Texture Index (m.r.d.^{2})	PTC Texture Index (m.r.d.^{2})	Pt RP_0 (%)	PTC RP_0 (%)	Rw (%)	R_{Bragg} (%)
WIMV	48.1	1.3	18.4	11.4	12.4	7.7
EWIMV	40.8	2	13.7	11.2	7	4.7

TABLE 1 Texture indexes and Reliability factors for the refinement of the PTC ultrastructure

Compared to previous studies [5,6], the approach appears to be much more powerful in extracting structural, microstructural and textural parameters in complex samples. Parameters divergence reveals to be astonishingly low, provided strongly dependent parameters were not released at the same time. This stability is very probably due to the high number of experimental pole figures taken into account in the

refinements, allowing a decrease of the defocusing effect (large at high χ-ranges) and a reduction of the number of OD solutions.

	Cell parameters (Å)	Cryst. Size (Å)	μstrain param.	Layer thickness (Å)
Pt	3.955(1)	462(4)	0.0032(1)	458(3)
PTC	a=3.945(1) c=4.080(1)	390(7)	0.0067(1)	4080(1)

TABLE 2 Refined parameters for the PTC and Pt layers

In summary, we present in this paper a new methodology for the analysis of X-ray diffraction data. Up to now, it has not been possible to obtain simultaneously reliable results of texture, structure and other microstructural parameters. This method also allows the study of other layers like the Pt bottom electrode. Applied to a ferroelectric thin ultrastructure, we extract important information for the optimisation of the material in view of its application in devices, which will be the focus of further work.

Acknowledgements

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