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Improvements in the X-ray characterisation of electroceramic thin films by the application of a novel combined analysis procedure

J. Ricote ICMM-CSIC. (Spain)

D. Chateigner CRISMAT-ENSICAEN (France)

L. Lutterotti Università di Trento (Italy)

Dr. J. Ricote

ICMM

Ferroelectric Materials Department

Materials Science Institute of Madrid *Spanish Council of Scientific Research*

CSIC

OUTLINE

Introduction

Ferroelectric thin films and texture

Combined method of X-ray diffraction analysis

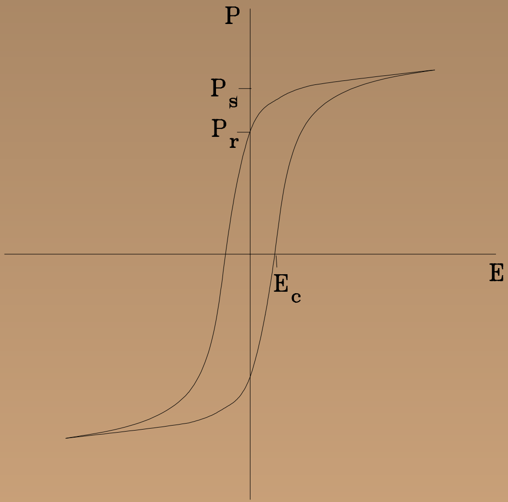
Results of the analysis of ferroelectric thin films with the combined method

Separation of the contribution of different texture components.

Simultaneous texture and structure determination of substrate and film.

Conclusions

Improvement of performance by texture control in ferroelectric thin films



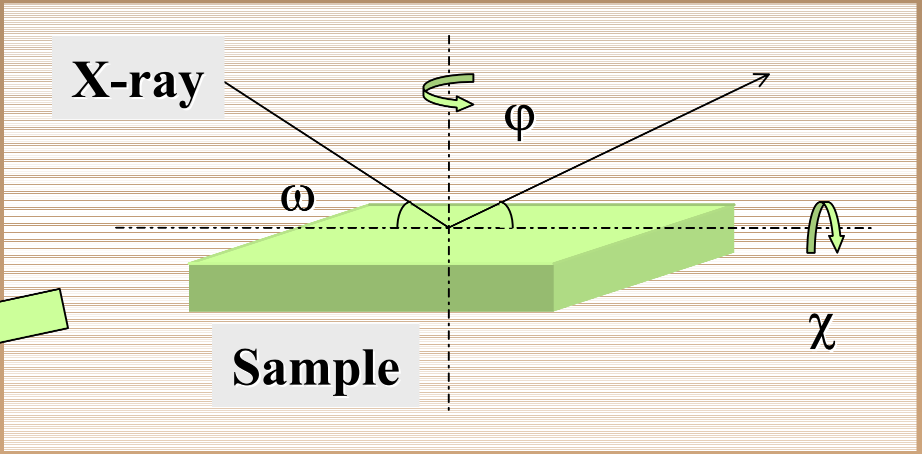
Ferroelectrics *are polar dielectrics in which the direction of polarization can be re-oriented by application of an electric field.*

◆ *The figures of merit that determine the **efficiency** of ferroelectric materials in technological applications (i.e. piezoelectric coefficient in MEMS) strongly **depends on the net polarization** of the material*

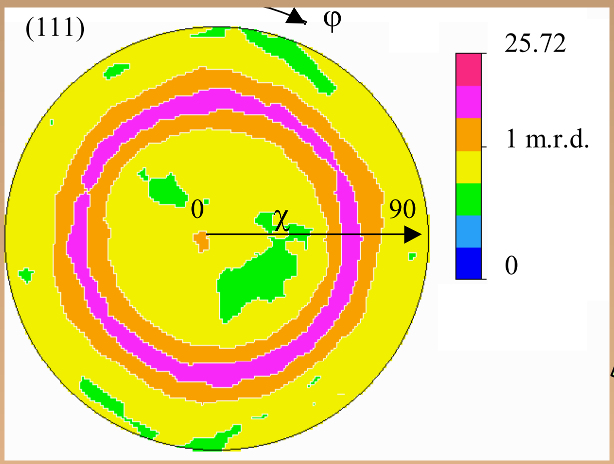
*The **polarization value depends on several factors,** among them: **TEXTURE. Preferential orientation along the polar axis produces an improved ferroelectric behaviour***

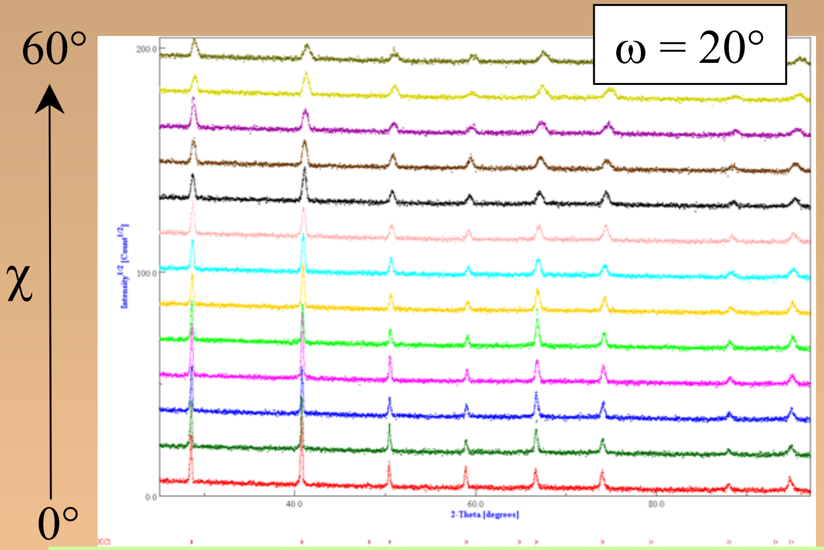
◆ *In general, the **polycrystalline** ferroelectric materials need a **Poling process** with an intense electric field, in order to obtain any spontaneous polarization. **This is not needed in highly textured thin films along the polar axis***

Generation of a pole figure



Pole figure



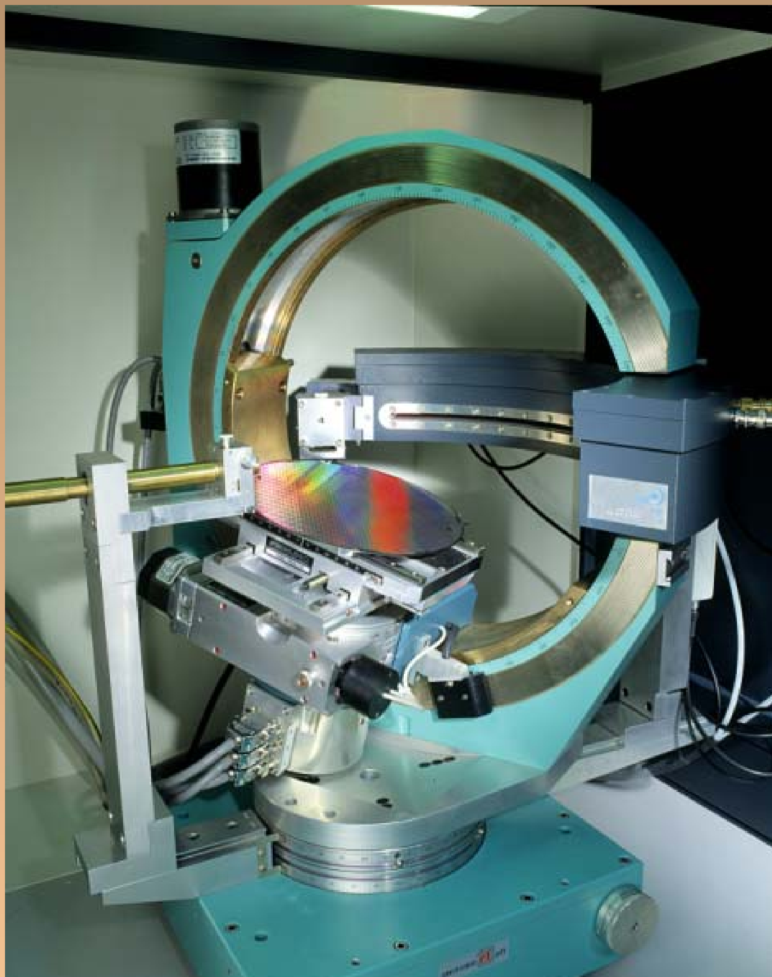


Refinement of individual spectra

m.r.d. = multiple of a random distribution

(a sample without any preferred orientation shows pole figures with constant values of 1 m.r.d.)

Equipment used for pole figure measurements



DIFFRACTOMETER EQUIPED WITH:

- Four-circle goniometer
- Curve position sensitive detector (PSD)

(MDM-Italy; developed in the ESQUI project)

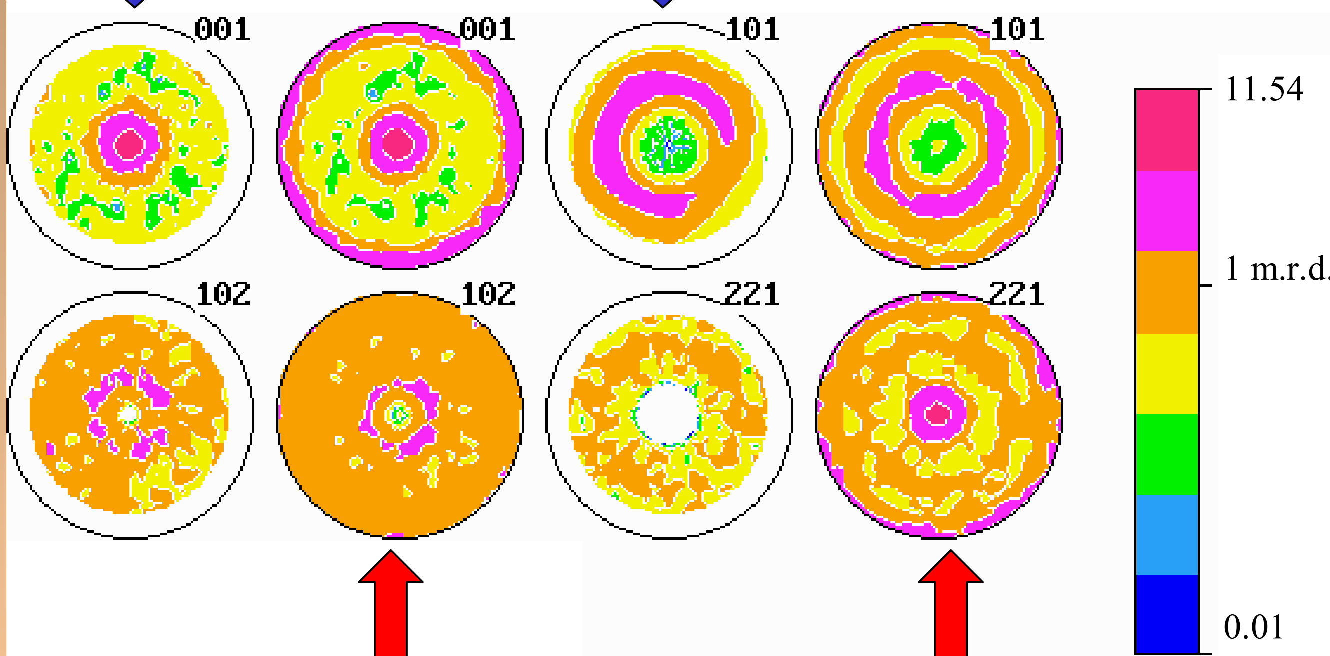
European-GROWTH project "x-ray Expert System for electronic films QUality Improvement-ESQUI"

Advanced texture determination: Quantitative Texture Analysis

From the experimental pole figures we obtain by an iterative process an ***ORIENTATION DISTRIBUTION FUNCTION (ODF)***

Experimental pole figures (incomplete)

$f(g); g = \alpha,\beta,\gamma$



Recalculated pole figures from ODF

Quantitative Texture Analysis

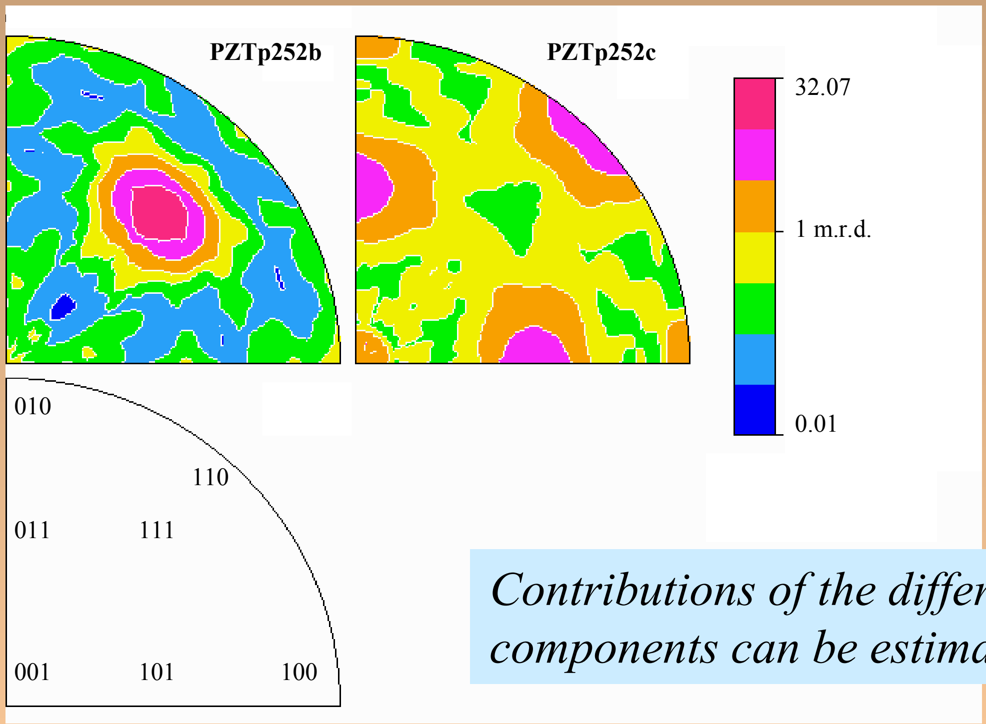
Orientation Distribution Function (ODF)

⇙ ⇘

Texture Index (F^2)
(degree of orientation)

$$F^2 = \frac{1}{8\pi^2} \sum_i \left[f(g_i) \right]^2 \Delta g_i$$

Inverse pole figures
(texture components)



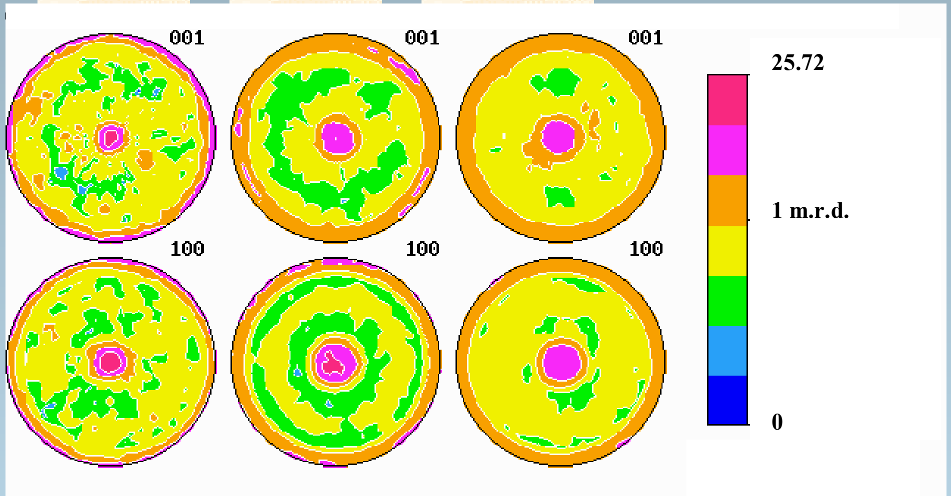
Contributions of the different components can be estimated

Inverse pole figure:
It describes the densities for crystal directions falling into the fixed sample direction y.

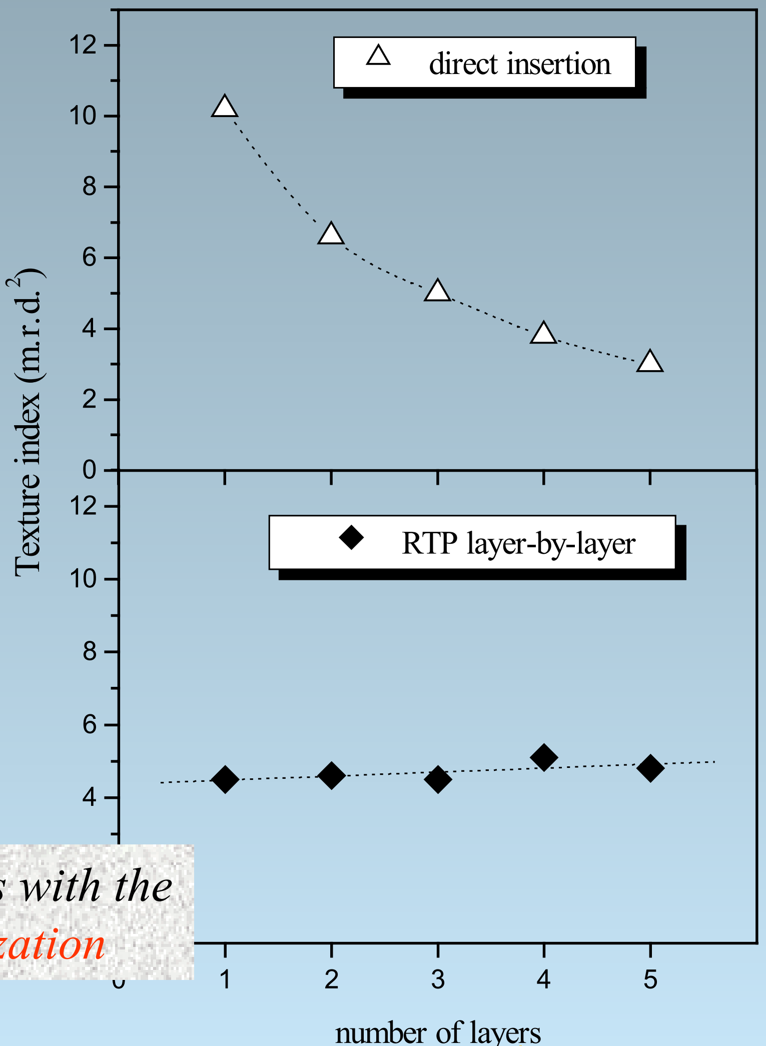
Quantitative Texture Analysis of polycrystalline ferroelectric thin films

Thickness dependence of texture

110 nm | 250 nm | 370 nm



Similar contribution of the texture components (mixed <001> and <100> orientation)



Thickness effect disappears with the layer-by-layer crystallization

PTL on Pt/TiO_2/(100)Si

*PTL: Lanthanum modified lead titanate

J. Ricote et al. J. Am. Ceram. Soc., 86 [9], 1571-77 (2003)

Deduction of effective physical properties

$$S^c = \begin{pmatrix} 6.5 & -0.35 & -7.1 & 0 & 0 & 0 \\ -0.35 & 6.5 & -7.1 & 0 & 0 & 0 \\ -7.1 & -7.1 & 33.3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 14.5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 14.5 & 0 \\ 0 & 0 & 0 & 0 & 0 & 9.6 \end{pmatrix} x10^{-3}/GPa$$

Elastic properties of tetragonal $PbTiO_3$ single crystal

Kalinichev et al. J. Mater. Res. 12, 2623 (1997)

Geometric mean

$$S = \begin{pmatrix} 10.1 & -3.2 & -3.4 & 0 & 0 & 0 \\ -3.2 & 10.1 & -3.4 & 0 & 0 & 0 \\ -3.4 & -3.4 & 10.3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 12.9 & 0 & 0 \\ 0 & 0 & 0 & 0 & 12.9 & 0 \\ 0 & 0 & 0 & 0 & 0 & 13.3 \end{pmatrix} x10^{-3}/GPa$$

$$\begin{pmatrix} 9.9 & -3.2 & -3.2 & 0 & 0 & 0 \\ -3.2 & 9.9 & -3.2 & 0 & 0 & 0 \\ -3.2 & -3.2 & 9.9 & 0 & 0 & 0 \\ 0 & 0 & 0 & 13.3 & 0 & 0 \\ 0 & 0 & 0 & 0 & 13.2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 13.2 \end{pmatrix} x10^{-3}/GPa$$

PTL on Pt/TiO_2/(100)Si
Mixed <001>,<100> orientation

PTL on Ti/Pt/Ti/(100)Si
Mixed <111> and <001>,<100> orientation

*PTL: Lanthanum modified lead titanate

J. Ricote et al. Mat. Sci. Forum 426-432, 3433-38 (2003)

Further advances in X-ray characterisation: Combined analysis

INTEGRATED INTENSITIES

Iterative process WIMV

Orientation Distribution Function

Rietveld refinement

LATTICE PARAMETERS

Stress analysis

RESIDUAL STRESS
Stress distribution function

Generally, labs perform a partial determination of these parameters

It allows a simultaneous and more precise determination of parameters

Software used is **MAUD**

General purpose program for diffraction spectra fitting developed by L.Lutterotti.
http://www.ing.unitn.it/~luttero/maud/

RESULTS OF THE APPLICATION OF THE COMBINED METHOD

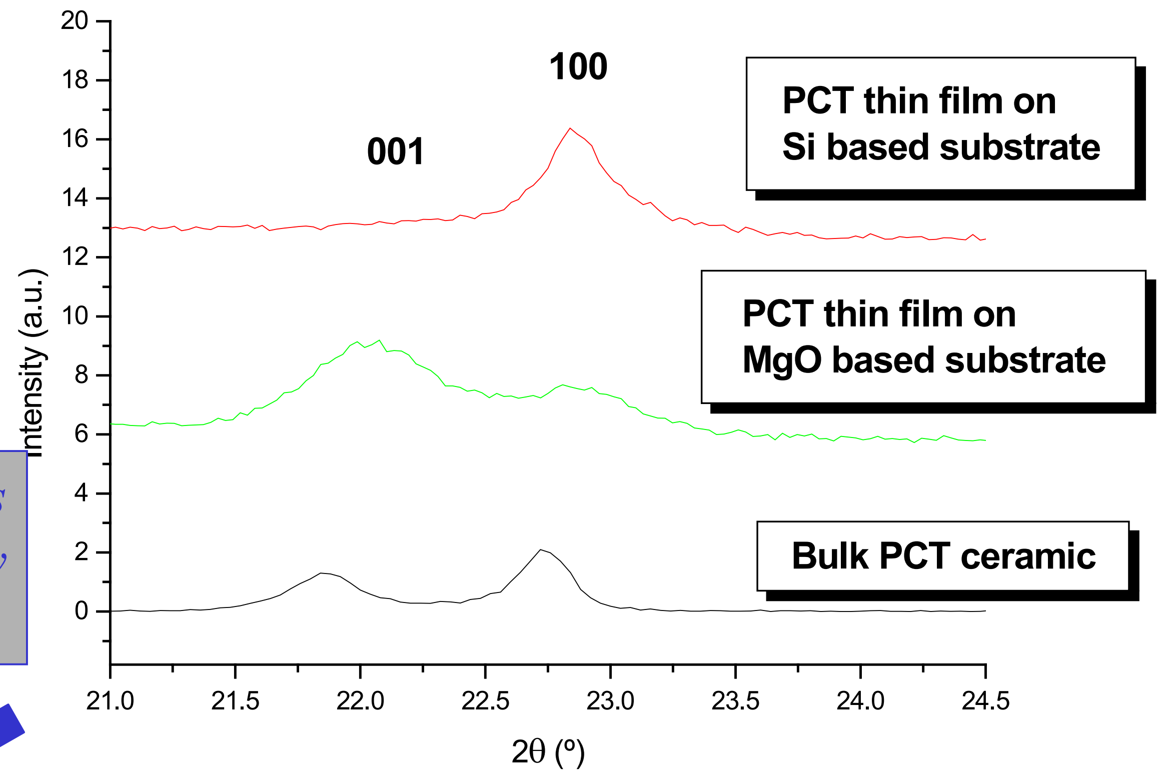
Limitations of the simple Quantitative Texture Analysis (I)

We need to know the lattice parameters prior to the texture analysis

Ca modified lead titanates (PCT):

a = 3.8939 Å
c = 4.0496 Å
(bulk ceramic values JCPDS 39-1336)

Lattice parameters are affected by STRESS in thin films



PCT thin films on $Pt/TiO_2/(100)Si$:

a = ? Å
c = ? Å

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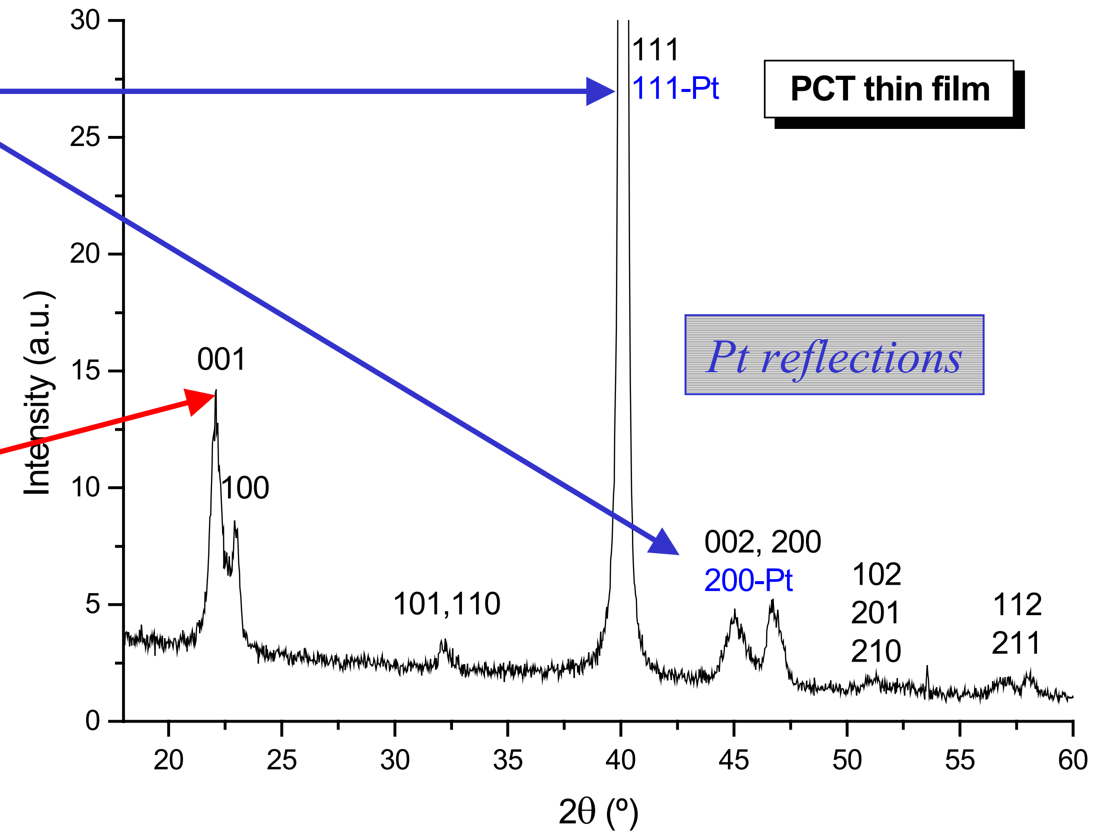
Limitations of the simple Quantitative Texture Analysis (II)

Structural parameters are difficult to obtain due to:

Substrate influence:
overlapping of reflections from the film and the substrate

TEXTURE effects:
peaks that do not appear at low χ angles

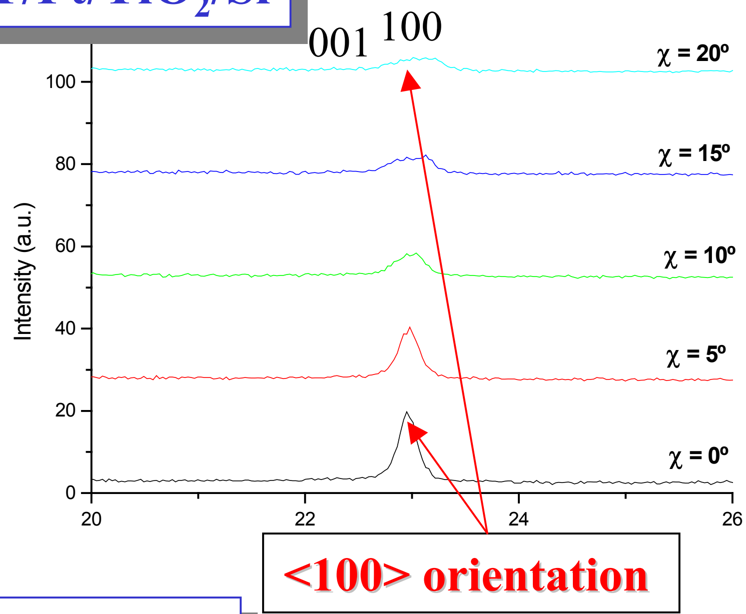


We need a simultaneous analysis of texture and structure of both film and substrate to solve completely the texture of the films

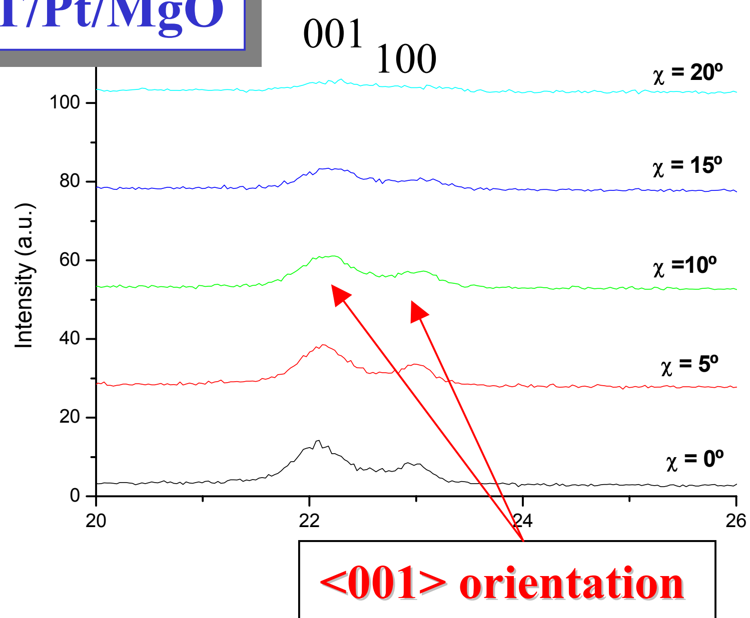
Separation of the contribution of texture contributions

(simple Quantitative Texture Analysis)

PCT/Pt/TiO_2/Si



PCT/Pt/MgO



PCT film under tensile stress:

σ = +1182 Mpa

QTA results:

Estimated contribution texture components.

<001>	<100>
62%!!	**38%!!**

PCT film under compressive stress:

σ = -700 Mpa

QTA results:

Estimated contribution texture components

<001>	<100>
55%!!	**45%!!**

Separation of the contribution of texture contributions
(Combined Method)

Instead of the integration of the overlapped peak (“**integral approach**”), and separating both contributions during the WIMV process, the combined method allows to deconvolute the peaks first, before the ODF calculation starts. As a result a more correct estimation of the contributions of <001> and <100> contributions is possible.

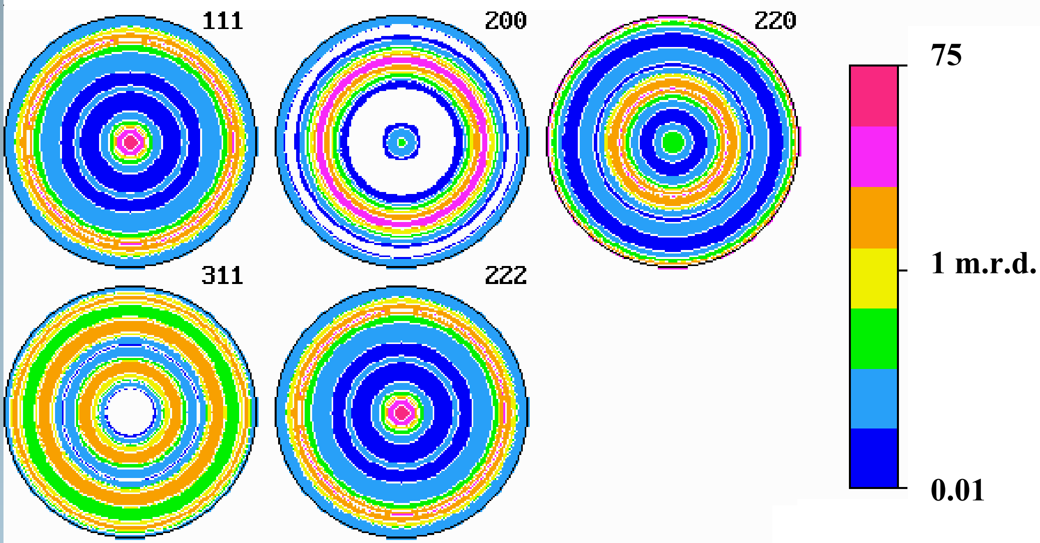
QTA results:

Sample	Stress	Lattice parameters	Estimated contrib. <001>	Estimated contrib. <100>	Pyroelectric Coefficient (10^{-8} C cm^{-2} K^{-1})
PCT/Pt/TiO_2/Si	σ = +1182 MPa	c = 3.877 Å a = 3.977 Å	7%	93%	0.3
PCT/Pt/MgO	σ = -700 MPa	c = 3.883 Å a = 4.020 Å	68%	32%	1.5

Simultaneously, we observe the effect of the applied stress on the lattice parameters

Simultaneous texture determination of substrate and film

(Combined Method)



Pt layer
<111> fibre orientation

New information on the Pt layer provided by the combined method

	Texture index F^2 (mrd^2)	R factors (%)
non-treated substrate		
Pt	129	R_W=13, R_B=12
annealed substrate		
Pt	199	R_W=8, R_B=14
Pt (Recryst. 1h)	199	R_W=9, R_B=20
Pt (Recryst. 2h)	195	R_W=9, R_B=14
Pt (Recryst. 3h)	222	R_W=27, R_B=12

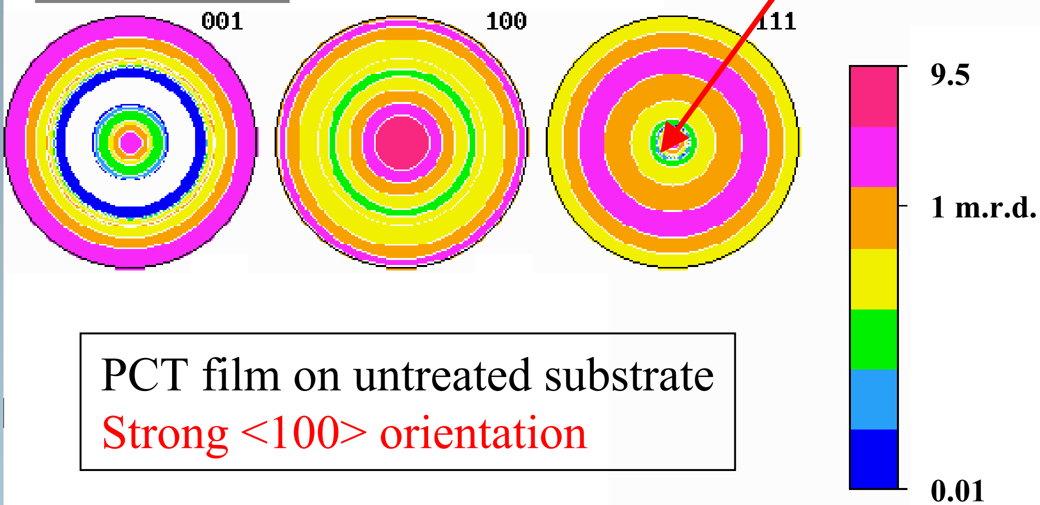
Annealing of the substrate, which involves crystal growth, results in an increase of the degree of orientation of the Pt layer.

Texture determination of film

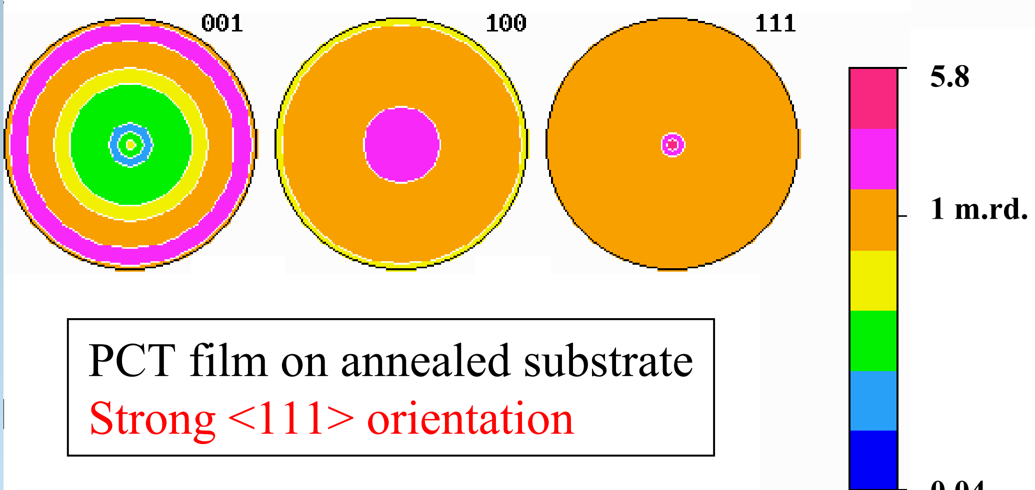
(Combined Method)

PCT film

Small <111> texture contribution not observed by conventional QTA



PCT film on untreated substrate
Strong <100> orientation



PCT film on annealed substrate
Strong <111> orientation

Effect of the annealing of the substrate in the type of texture developed

	Texture index F^2 (mrd^2)
non-treated substrate	
PTC	5.2
annealed substrate	
PTC	2.1
PTC (Recryst. 1h)	2.1
PTC (Recryst. 2h)	2.5
PTC (Recryst. 3h)	2.5

Effect on the degree of orientation of the PCT film

New information on contribution of texture components provided by the combined method

CONCLUSIONS

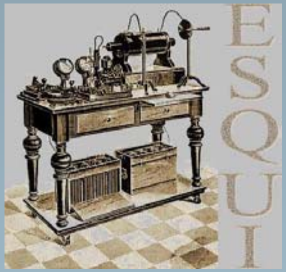
The application of the combined method to ferroelectric calcium modified lead titanate thin films has proved to produce more accurate and reliable results than more traditional X-ray diffraction analysis approaches. It also provides **simultaneously information on the structure, microstructure and texture of both the deposited film and the substrate**, revealing important characteristics of the Pt layer used in this study as bottom electrode.

An important aspect covered is the **better resolution of the texture and, specifically of the contribution of the different texture components**, obtained by the combined method. We have shown two examples:

Separation of <001>,<100> components
Reveal of small <111> texture component

see also:
J. Ricote and D. Chateigner J. Appl. Cryst. 37, 91-95 (2004)
J. Ricote et al. Thin Solid Films 450, 128-133 (2004)

Acknowledgements



European-GROWTH project (G6TD-CT99-00169)
"x-ray Expert System for electronic films QUality Improvement-ESQUI"

CSIC-CNRS collaboration projects

CSIC

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COST

COST Action 528
Chemical Solution Deposition of Thin Films