

Texture-Structure-Microstructure: a  
combined analysis by x-ray diffraction  
of  $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$  / Pt /  $\text{TiO}_2$  /  $\text{SiO}_2$  /  
Si-(001)

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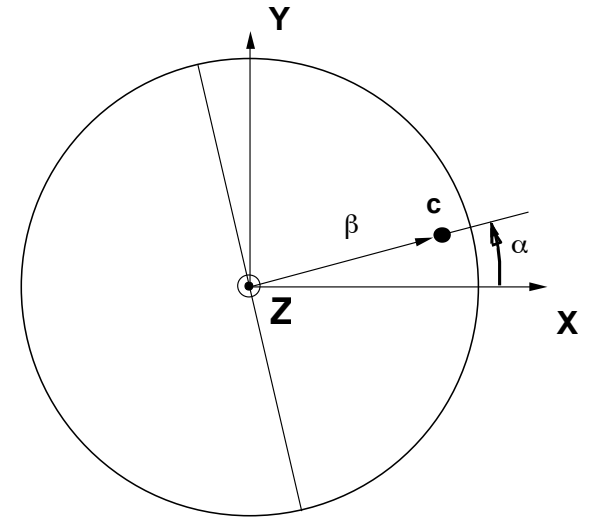
# Summary

- Usual up-to-date approaches for polycrystals
  - Texture
  - Structure-Microstructure
  - Problems on ultrastructures
- Combined approach
  - Experimental needs
  - Methodology-Algorithm
  - Ultrastructure implementation
  - Case study on  $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$
- Future trends

# Usual Texture Analysis

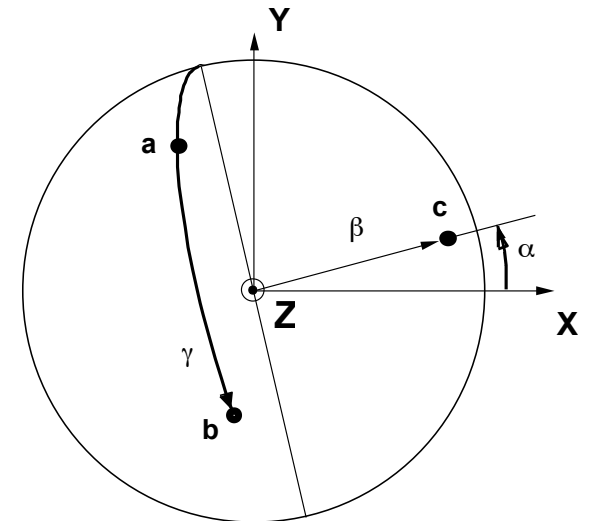
{hkl} pole figure measurement + corrections:

$$\frac{dV(\chi\phi)}{V} = \frac{1}{4\pi} P(\chi\phi) \sin\chi \, d\chi \, d\phi \quad \longrightarrow$$



We want  $f(g)$  (ODF): with  $g = (\alpha, \beta, \gamma)$

$$\frac{dV(g)}{V} = \frac{1}{8\pi^2} f(g) \, dg \quad \longrightarrow$$



We have to invert (Fundamental equation of Texture Analysis):

$$P_{hkl}(\bar{y}) = \frac{1}{2\pi} \int_{\langle hkl \rangle // \bar{y}} f(g) d\tilde{\varphi}$$



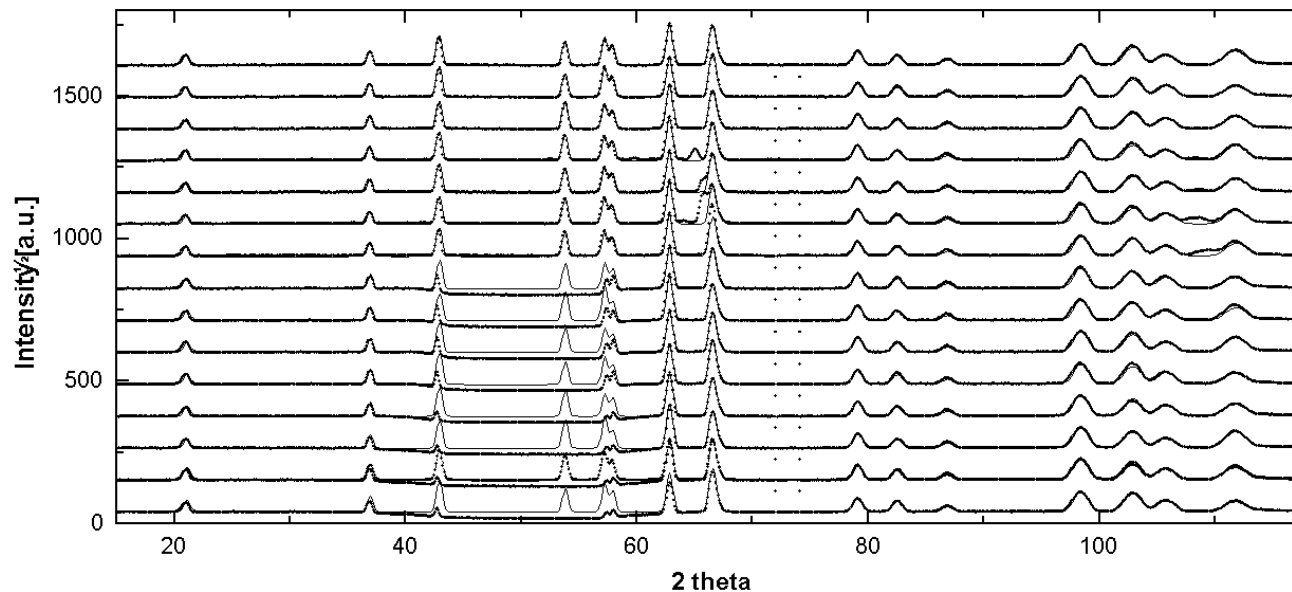
WIMV refinement method:  
Williams-Imhof-Matthies-Vinel

$$f^{n+1}(g) = N \left[ \frac{f^n(g) f^0(g)}{\prod_{hkl} \left( P_{hkl}^n(\bar{y}) \right)^{\frac{1}{l}}} \right]$$

# Usual Structure-Microstructure Analysis

## (Full pattern fitting, Rietveld Analysis)

$\text{Si}_3\text{N}_4$  matrix with SiC whiskers:



Random powder: 
$$I(2\theta) = \sum_{hkl, \text{ phases}} I_{hkl, \text{ phases}}(2\theta) S_{hkl, \text{ phases}}(2\theta) + \text{bkg}(2\theta)$$

$$I_{hkl}(2\theta) = S |F_{hkl}|^2 m_{hkl} \frac{L_P}{V_c^2}$$

S: scale factor (**phase abundance**)

$F_{hkl}$ : **structure** factor (includes Debye-Waller term)

$V_c$ : **unit-cell** volume

$$S_{hkl}(2\theta) = S_{hkl}^I(2\theta) * S_{hkl}^S(2\theta)$$

$S^I$ : instrumental broadening

$S^S$ : Sample aberrations

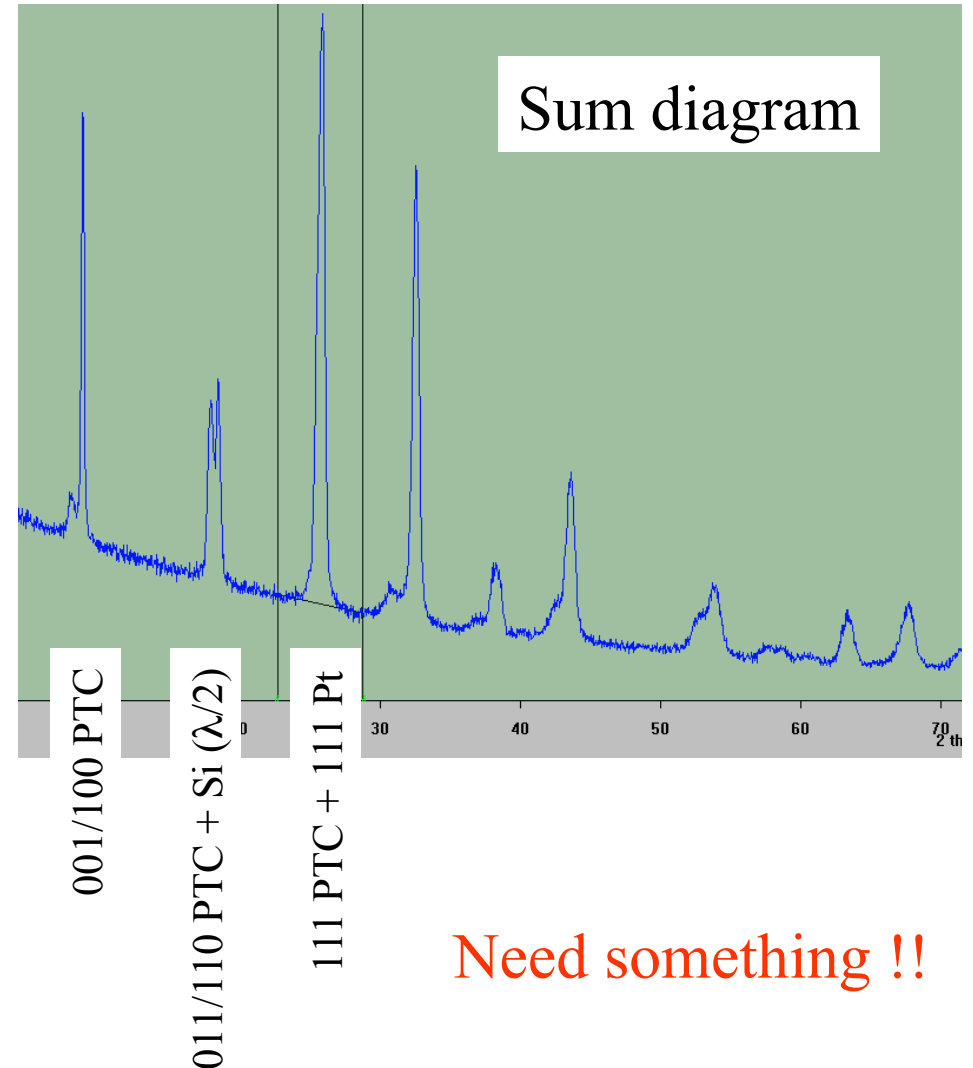
**crystallite sizes (iso. or anisotropic)**

**rms microstrains  $\epsilon$**

# Problems on ultrastructures

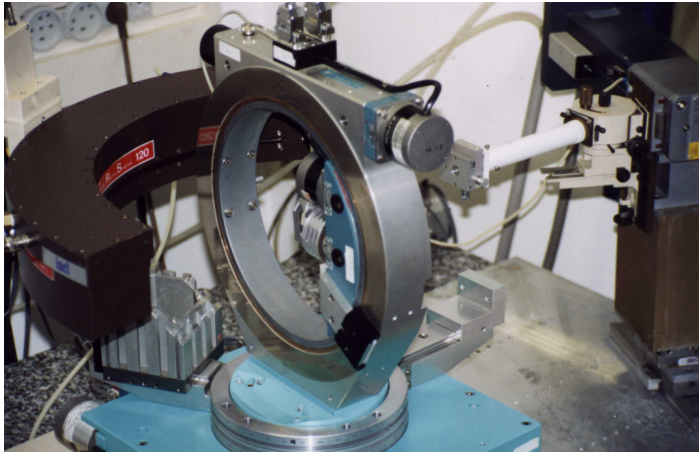
Ferroelectric film (PTC)
Electrode (Pt)
Antidiffusion barrier ( $\text{TiO}_2$ )
Oxide (native, thermally grown)
SC Substrate (Si)

- Strong intra- and inter-phase overlaps
- Mixture of very strong and lower textures
- texture effect not fully removable: ~~structure~~
- structure unknown: ~~texture~~



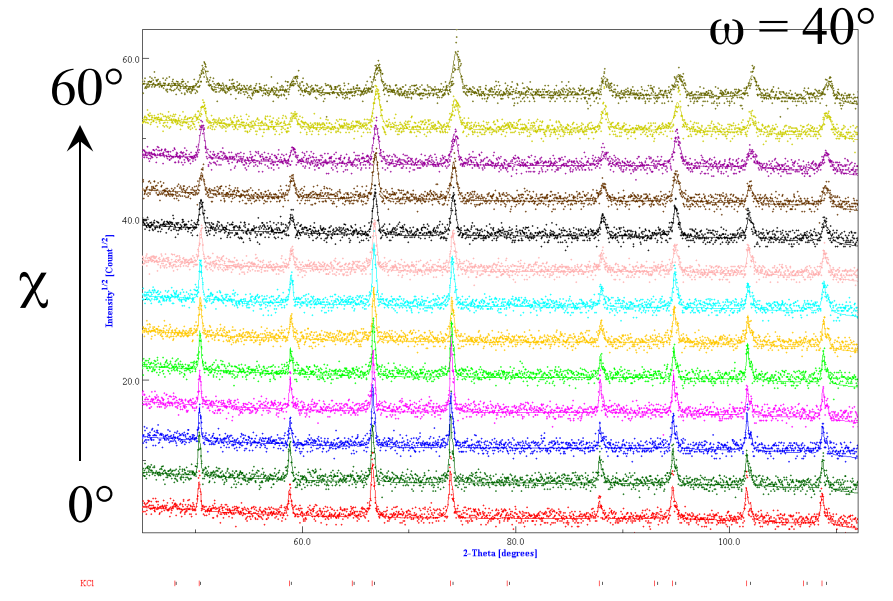
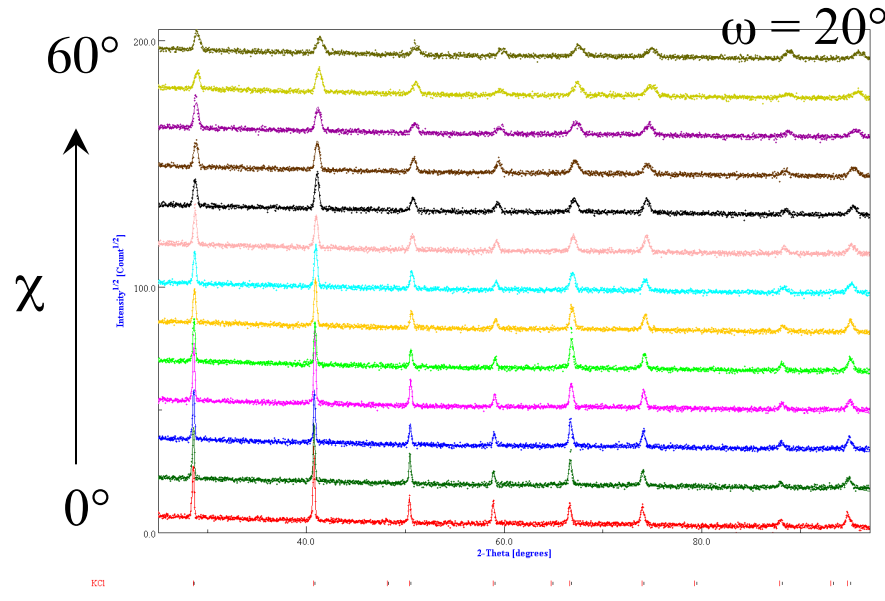
# Combined approach

## Experimental needs



Mapping Spectrometer space for correction of:

- instrumental resolution
- instrumental misalignments

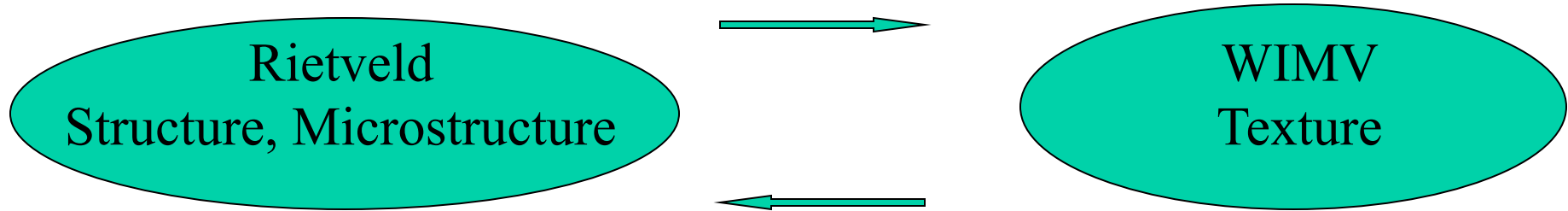




## Methodology-Algorithm

Correction of intensities for  
texture:

$$I_{hkl}(2\theta, \chi, \varphi) = I_{hkl}(2\theta) P_{hkl}(\chi, \varphi)$$



Pole figure extraction (Le  
Bail method):  $P_{hkl}(\chi, \varphi)$

Rietveld and WIMV algorithm are alternatively used to correct for each others contributions: Marquardt non-linear least squares fit is used for the Rietveld.

## Ultrastructure implementation

Corrections are needed for volumic/absorption changes when the samples are rotated. With a CPS detector, these correction factors are:

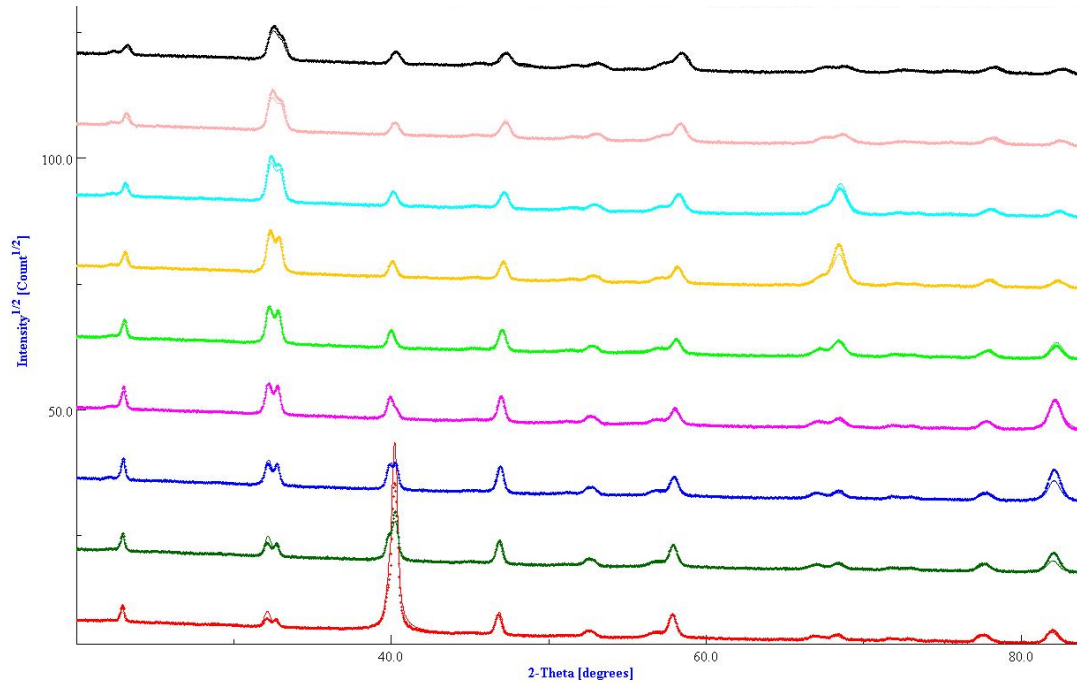
$$C_{\chi}^{\text{top film}} = g_1 (1 - \exp(-\mu T g_2 / \cos \chi)) / (1 - \exp(-2\mu T / \sin \omega \cos \chi))$$

$$C_{\chi}^{\text{cov. layer}} = C_{\chi}^{\text{top film}} \left( \exp(-g_2 \sum \mu'_i T'_i / \cos \chi) \right) / \left( \exp(-2 \sum \mu'_i T'_i / \sin \omega \cos \chi) \right)$$

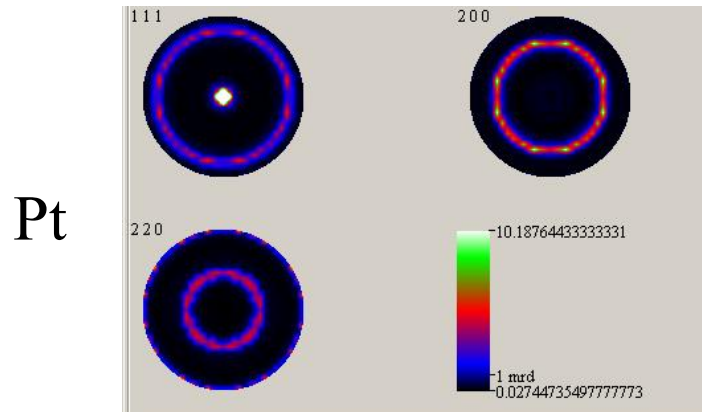
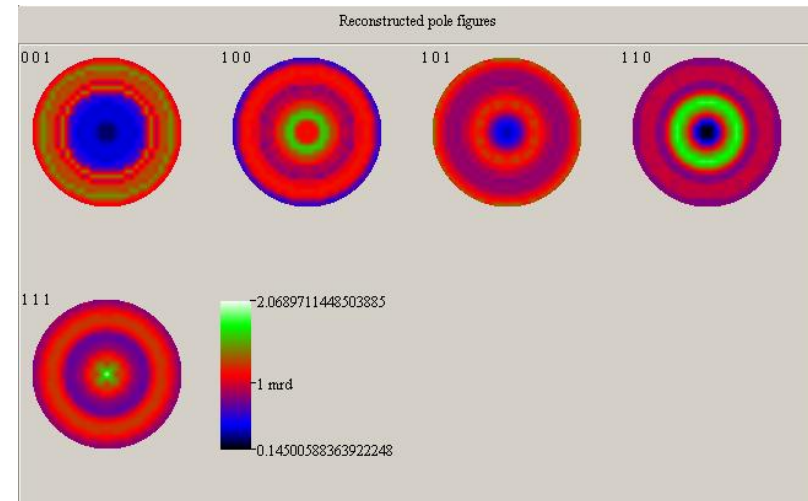


Gives access to **individual Thicknesses**  
in the refinement

# Case study on $\text{Pb}_{0.76}\text{Ca}_{0.24}\text{TiO}_3$



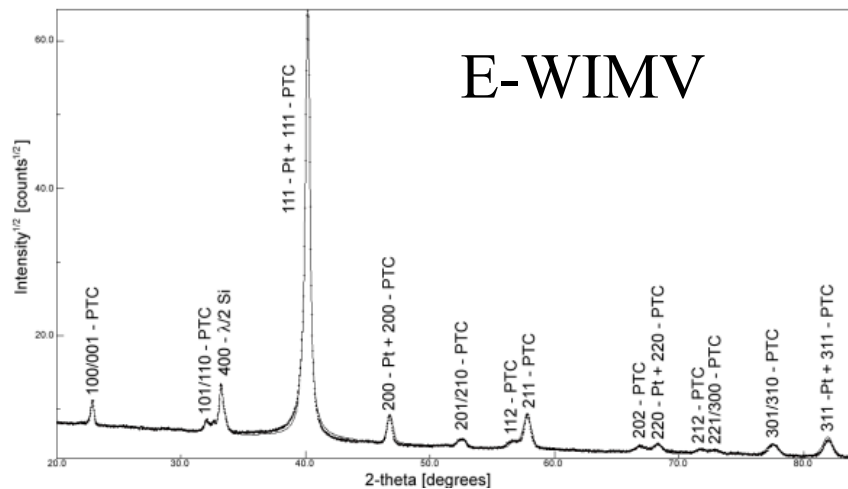
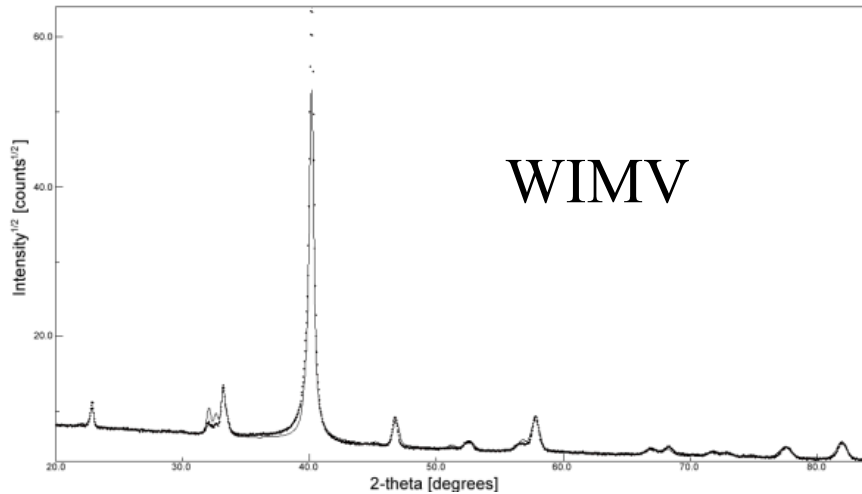
PTC



$$\begin{aligned}
 a &= 3.955(1) \text{ \AA} \\
 T' &= 462(4) \text{ \AA} \\
 t'_{\text{iso}} &= 458(3) \text{ \AA} \\
 \varepsilon' &= 0.0032(1)
 \end{aligned}$$

$$\begin{aligned}
 a &= 3.945(1) \text{ \AA} \\
 c &= 4.080(1) \text{ \AA} \\
 T &= 4080(10) \text{ \AA} \\
 t_{\text{iso}} &= 390(7) \text{ \AA} \\
 \varepsilon &= 0.0067(1)
 \end{aligned}$$

# WIMV vs Entropy modified WIMV approach



Better refinement with E-WIMV:

- lower reliability factors (structure and texture)

- better high density level reproduction

Texture	Pt Texture Index (m.r.d. <sup>2</sup> )	PTC Texture Index (m.r.d. <sup>2</sup> )	Pt RP <sub>0</sub> (%)	PTC RP <sub>0</sub> (%)	R <sub>w</sub> (%)	R <sub>Bragg</sub> (%)
WIMV	48.1	1.3	18.4	11.4	12.4	7.7
EWIMV	40.8	2	13.7	11.2	7	4.7

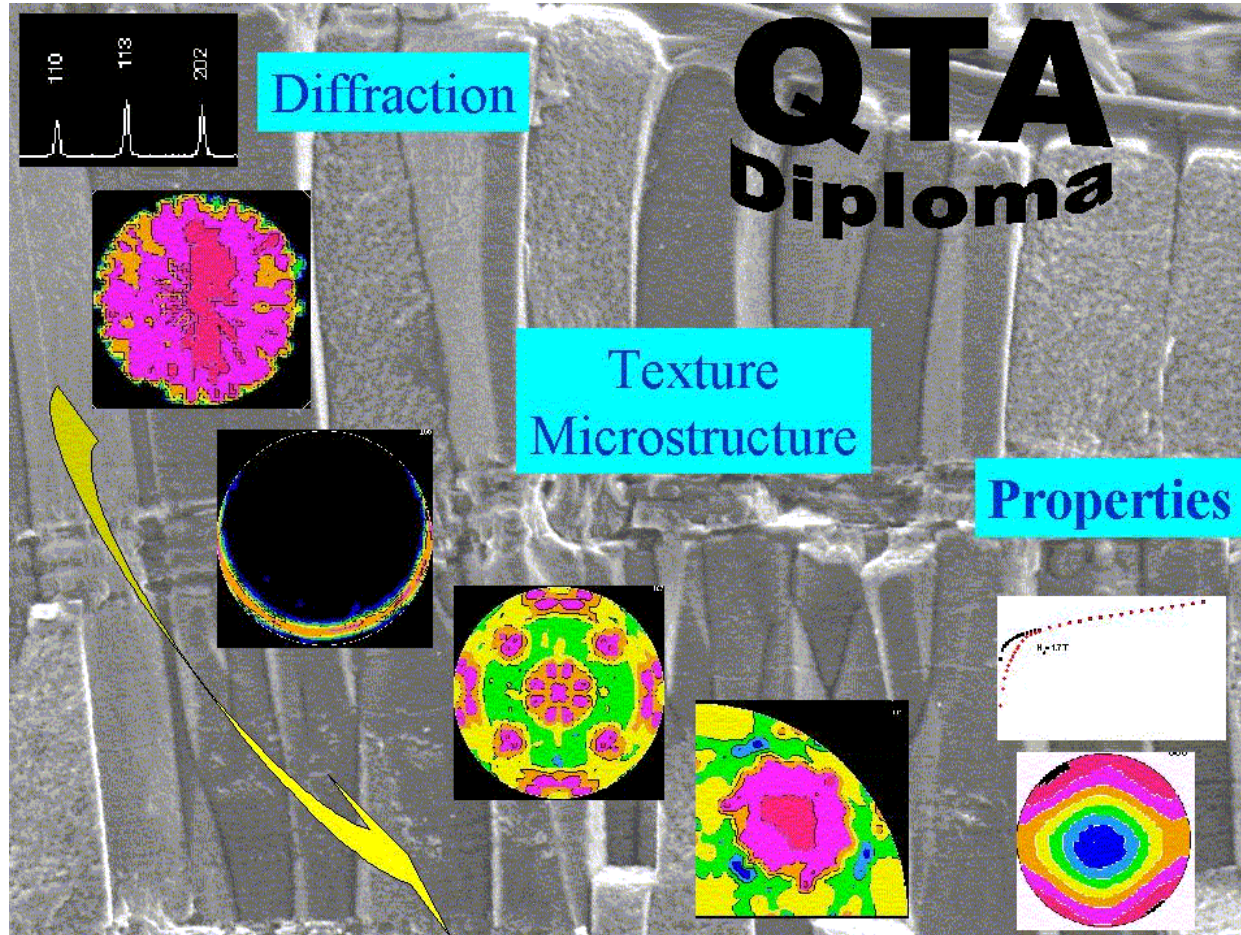
## Future trends

- Combining with reflectivity measurements: independently measured and refined thicknesses, electron densities and roughnesses
- Adding residual stress determinations
- **Multiple Analysis Using Diffraction**, a web-based tutorial for the combined approach: search MAUD (Luca Lutterotti)
- **Quantitative Texture Analysis** Internet Course: <http://lpec.univ-lemans.fr/qta> (Daniel Chateigner)

## Acknowledgements

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# Quantitative Texture Analysis Internet Course



<http://lpec.univ-lemans.fr/qta>