Combined Analysis of thin structures: structure, microstructure, texture, stresses, phase, nanocrystals …

at once in a single approach !

Daniel Chateigner, L. Lutterotti, M. Morales, Ph. Boullay

IUT-UCBN, CRISMAT-CIMAP

Univ. Trento

Geo-Bio Center 14th June 2012, Munchen

Structure determination on real (textured) samples
Problem 1

Structure and QTA: correlations ?

f(g) and $|F_{\mathbf{h}}|^2$ are different !

f(g):

-Angularly constrained: $[h_1k_1l_1]^*$ and $[h_2k_2l_2]^*$ make a given angle: more determined if F^2 high

- lot of data (spectra) needed

$|F_{\mathbf{h}}|^2$:

-Position, f_i, and Debye-Waller constrained

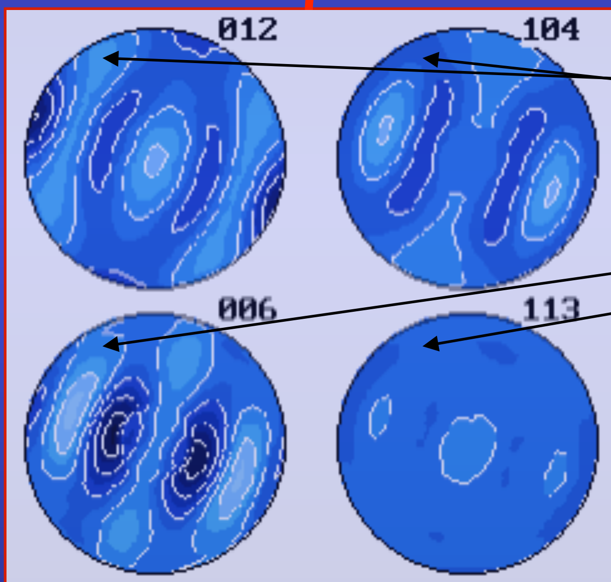
- work on the sum of all diagrams on average

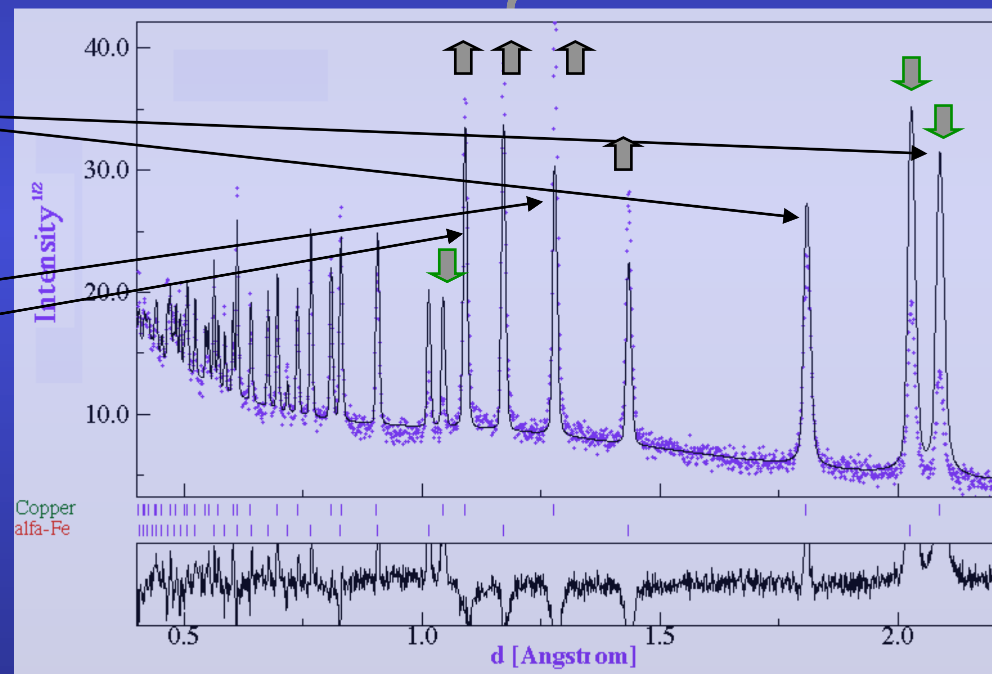
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra





Le Bail extraction + ODF: WMV, E-WIMV, Generalized spherical harmonics, components, ADC, entropy maximisation …

Why not benefit of texture in Structure determination ?

Perfect powders:
- overlaps (intra- and inter-p
- no angular constrain
- anisotropy difficult to resc

Single pattern

Single crystals:
- reduced overlaps
- max angular constrains
- Perfect texture: max anisotropy

Many individual diffracted peaks

Textured powders:
- reduced overlaps
- angular constrain = f(texture strength)
- Intermediate anisotropy

Many patterns to measure and analyse

Rietveld-Structure

$$y_c(\mathbf{y_S},\theta,\eta) = y_b(\mathbf{y_S},\theta,\eta) + I_0 \sum_{i=1}^{N_L} \sum_{\Phi=1}^{N_\Phi} \frac{\nu_{i\Phi}}{V_{c\Phi}^2} \sum_h Lp(\theta) j_{\Phi h} \left|F_{\Phi h}\right|^2 \Omega_{\Phi h}(\mathbf{y_S},\theta,\eta) P_{\Phi h}(\mathbf{y_S},\theta,\eta) A_{i\Phi}(\mathbf{y_S},\theta,\eta)$$

Texture

$$P_k(\chi,\phi) = \int_\varphi f(g,\varphi)\, d\varphi$$

- Generalized Spherical Harmonics (Bunge):

$$P_k(\chi,\phi) = \sum_{l=0}^{\infty} \frac{1}{2l+1} \sum_{n=-l}^{l} k_l^n(\chi,\phi) \sum_{m=-l}^{l} C_l^{mn} k_n^{*m}(\Theta_k \phi_k)$$

$$f(g) = \sum_{l=0}^{\infty} \sum_{m,n=-l}^{l} C_l^{mn} T_l^{mn}(g)$$

- Components (Helming):

$$f(g) = F + \sum_c I^c f^c(g)$$

- WIMV (William, Imhof, Matthies, Vinel) iterative process:

$$f^{n+1}(g) = N_n \frac{f^n(g) f^0(g)}{\left(\prod_{\mathbf{h}=1}^{I} \prod_{m=1}^{M_h} P_{\mathbf{h}}^{n}(\mathbf{y}) \right)^{\frac{1}{IM_h}}}$$

$$f^0(g) = N_0 \left(\prod_{\mathbf{h}=1}^{I} \prod_{m=1}^{M_h} P_{\mathbf{h}}^{exp}(\mathbf{y}) \right)^{\frac{1}{IM_h}}$$

E-WIMV (Rietveld only):

$$f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left(\frac{P_{\mathbf{h}}(\mathbf{y})}{P_{\mathbf{h}}^{n}(\mathbf{y})} \right)^{r_n \frac{w_h}{M_h}}$$

with $0 < r_n < 1$, relaxation parameter,
M_h number of division points of the integral around k,
w_h reflection weight

- Entropy maximisation (Schaeben):

$$f^{n+1}(g) = f^n(g) \prod_{m=1}^{M_h} \left(\frac{P_{\mathbf{h}}(\mathbf{y})}{P_{\mathbf{h}}^{n}(\mathbf{y})} \right)^{\frac{r_n}{M_h}}$$

- arbitrarily defined cells (ADC, Pawlik): Very similar to E-WIMV, with integrals along path tubes

Residual Stresses shift peaks with y

Problem 2

Stress and QTA: correlations ? f(g) and <C_{ijkl}>

f(g):

- Moves the $\sin^2\Psi$ law away from linear relationship
- Needs the integrated peak (full spectra)

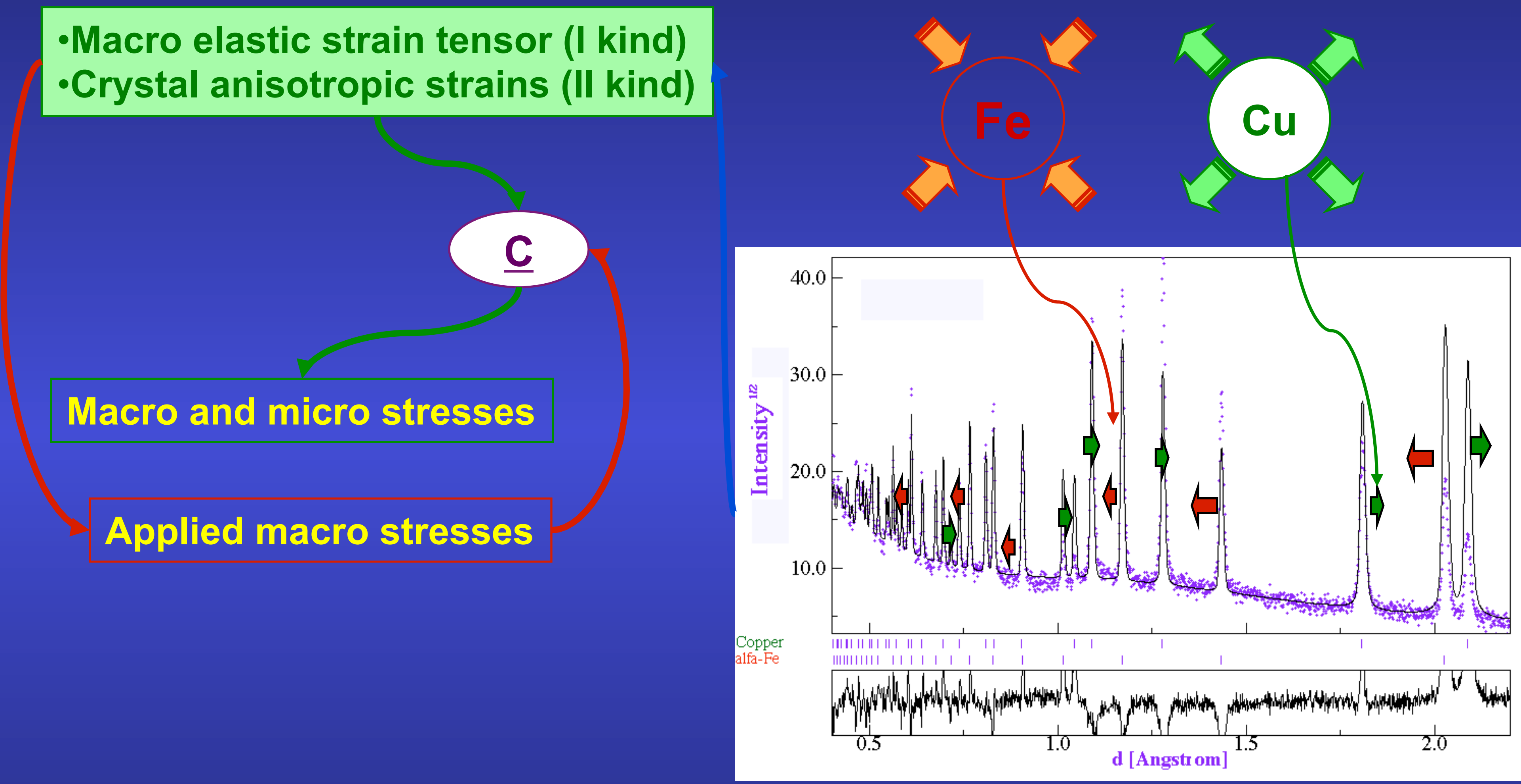
strains:

- Measured with pole figures
- needs the mean peak position

Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches

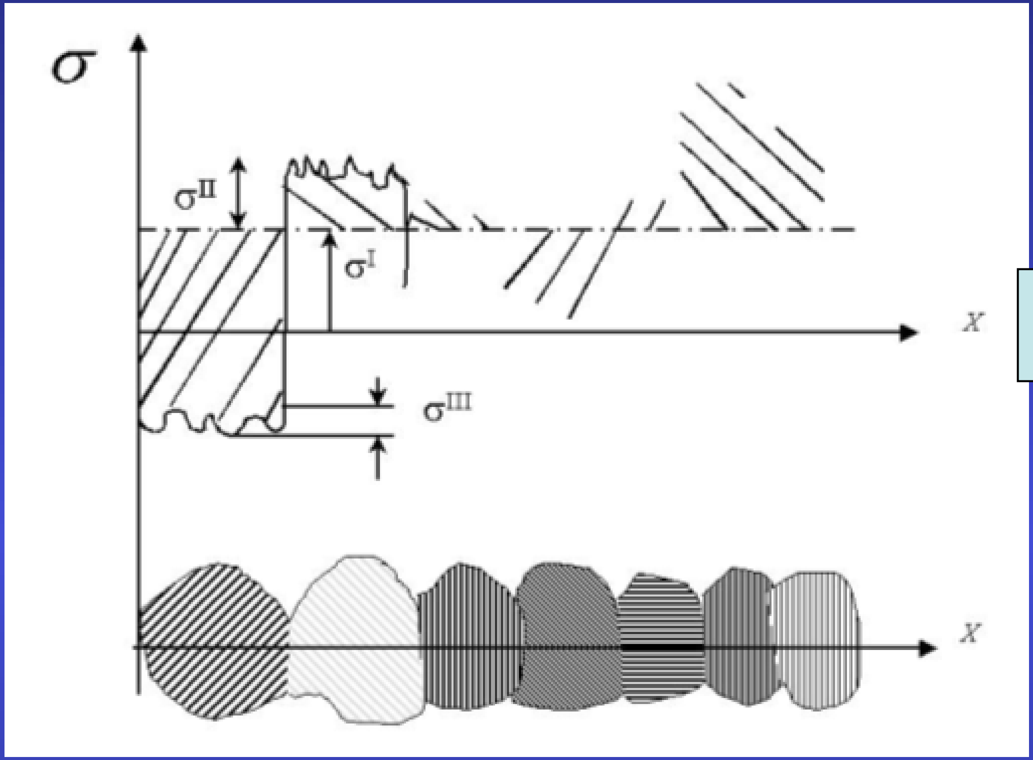
Residual Stresses and Rietveld



Isotropic samples: triaxial, biaxial, uniaxial stress states

Textured samples: Reuss, Voigt, Hill, Bulk geometric mean approaches

Strain-Stress



$$\boldsymbol{\varepsilon}(\mathbf{X}) = \boldsymbol{\varepsilon}^{\mathrm{I}} + \boldsymbol{\varepsilon}^{\mathrm{II}}(\mathbf{X}) + \boldsymbol{\varepsilon}^{\mathrm{III}}(\mathbf{X})$$

$$\langle S \rangle_{geo}^{-1} = \exp\left[-\sum_{m=1}^{N} \nu_m \ln S_m \right] = \exp\left[\sum_{m=1}^{N} \nu_m \ln S_m^{-1} \right] = \left\langle S^{-1} \right\rangle_{geo} = \langle C \rangle_{geo}$$

or

$$\langle S \rangle_{geo}^{-1} = \left[\prod_{m=1}^{N} S_m^{\nu_m} \right]^{-1} = \prod_{m=1}^{N} S_m^{-\nu_m} = \prod_{m=1}^{N} \left(S_m^{-1} \right)^{\nu_m} = \left\langle S^{-1} \right\rangle_{geo} = \langle C \rangle_{geo}$$

Layered systems

Problem 3

Layer, Rietveld and QTA: correlations: f(g), thicknesses and structure

f(g):

- Pole figures need corrections for abs-vol
- Rietveld also to correct intensities

layers:

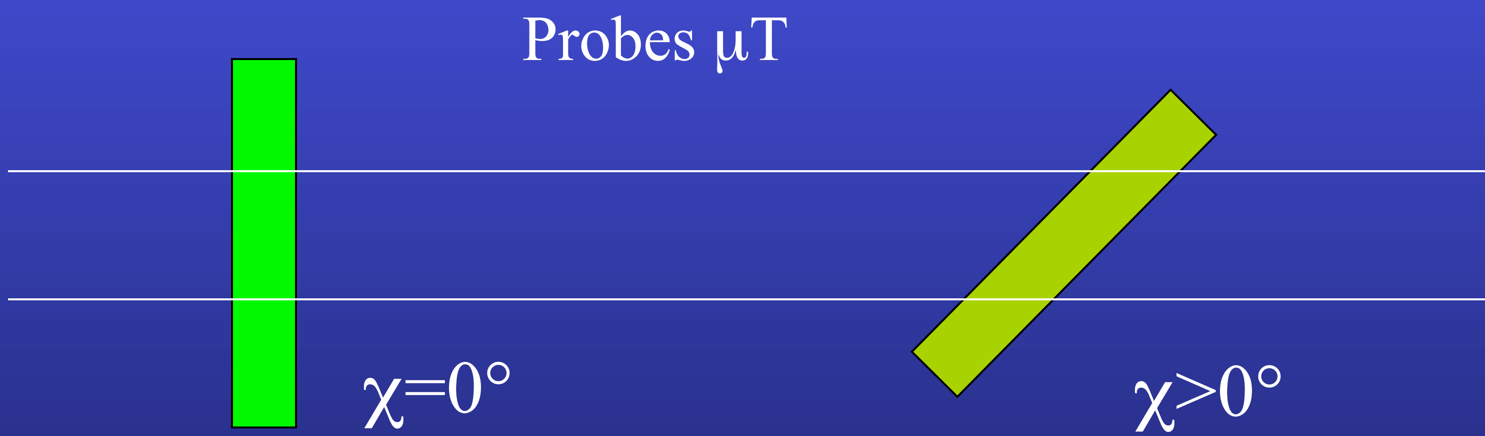
- unknown sample true absorption coefficient μ
- unknown effective thickness (porosity)

Layering

Asymmetric Bragg-Brentano

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

$$C_{\chi}^{\text{cov. layer}} = C_{\chi}^{\text{top film}}\left(\exp\left(-g_2 \sum \mu_i' T_i' / \cos\chi\right)\right) / \left(\exp\left(-2 \sum \mu_i' T_i' / \sin\omega\cos\chi\right)\right)$$



Phase and Texture

Problem 4

Phase and QTA: correlations: f(g), S_Φ

f(g):

- angular relationships
- plays on individual spectra
- essential to operate on textured sample

S_Φ:

- plays on overall scale factor (sum diagram)

Phase analysis

- Volume fraction

$$V_{\Phi} = \frac{S_{\Phi} V_{uc\Phi}^{2}}{\sum_{\Phi} \left(S_{\Phi} V_{uc\Phi}^{2} \right)_{\Phi}}$$

- Weight fraction

$$m_{\Phi} = \frac{S_{\Phi} Z_{\Phi} M_{\Phi} V_{uc\Phi}^{2}}{\sum_{\Phi} \left(S_{\Phi} Z_{\Phi} M_{\Phi} V_{uc\Phi}^{2} \right)_{\Phi}}$$

Z = number of formula units

M = mass of the formula unit

V = cell volume

How it works

Le Bail extraction

$$T_{hkl}^{k} = T_{hkl}^{k-1} \frac{\sum_i I_i^{exp} S_{hkl}^{i}}{\sum_i I_i^{calc} S_{hkl}^{i}}$$

- Starts with nominal intensities (T_{hkl})
- Computes the full pattern (I^{calc})
- Uses the formula to compute next T_{hkl}
- Cycle the last two steps until convergence

- In Maud, options:
  - Only few cycles for texture (3-5) necessary
  - The range for the weighting of the profile can be reduced
  - Background subtracted or not

Structure and Residual Stresses (shift peaks with **y**)

Problem 5

Stress and cell parameters: correlations: peak positions and C_{ijkl}

Cell parameters:
- Measured at high angles
- Bragg law evolution

strains:
- Measured precisely at high angles
- stiffness-based variation, also with Ψ

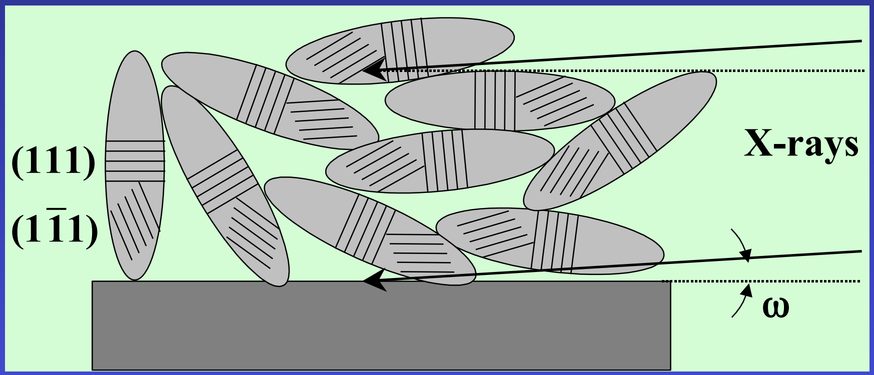
Shapes, microstrains, defaults, distributions
Problem 6

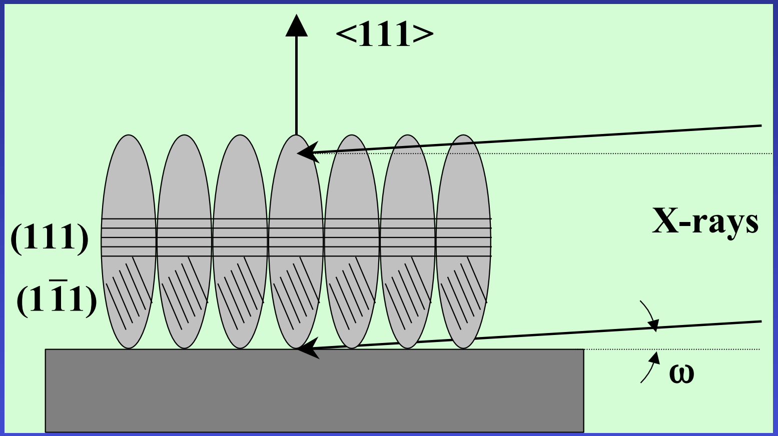
Shapes …. and stress-texture-structure: correlations ?

Shapes …:
- line broadening problem
- average positions modified
- if anisotropic: modification changes with **y**

Stress-texture-structure:
- need "true" peak positions and intensities
- need deconvoluted signals

Anisotropic sizes and microstrains



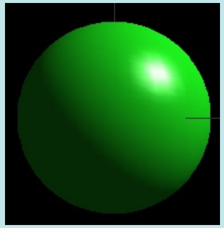


- Texture helps the "real" mean shape determination
- Determination by peak deconvolution + Popa formalism

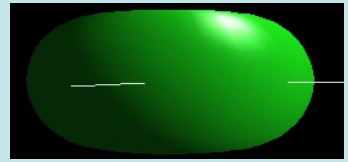
$$\langle R_{\mathbf{h}} \rangle = R_0 + R_1 P_2^0(x) + R_2 P_2^1(x)\cos\varphi + R_3 P_2^1(x)\sin\varphi + R_4 P_2^2(x)\cos 2\varphi + R_5 P_2^2(x)\sin 2\varphi + \ldots$$

$$\langle \varepsilon_{\mathbf{h}}^2 \rangle E_{\mathbf{h}}^4 = E_1 h^4 + E_2 k^4 + E_3 \ell^4 + 2E_4 h^2 k^2 + 2E_5 \ell^2 k^2 + 2E_6 h^2 \ell^2 + 4E_7 h^3 k + 4E_8 h^3 \ell + 4E_9 k^3 h + 4E_{10} k^3 \ell + 4E_{11} \ell^3 h + 4E_{12} \ell^3 k + 4E_{13} h^2 k \ell + 4E_{14} k^2 h \ell + 4E_{15} \ell^2 k h$$

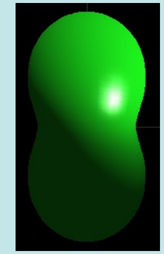
$\bar{1}$



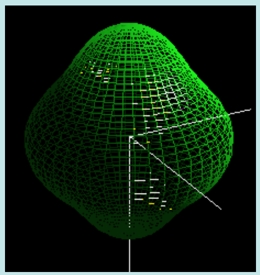
R_0



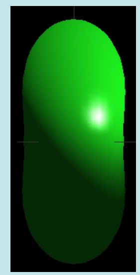
R_0, $R_1 < 0$



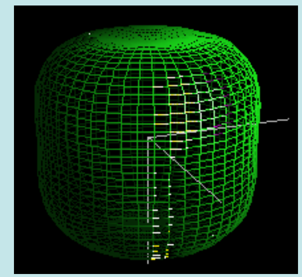
R_0, $R_1 > 0$



R_0, $R_6 > 0$

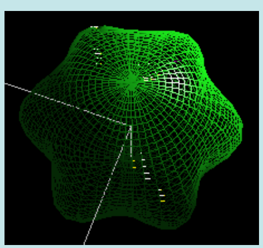


R_0,
R_2 and $R_6 > 0$

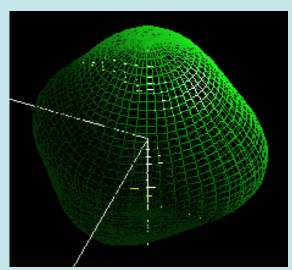


R_0, $R_6 < 0$

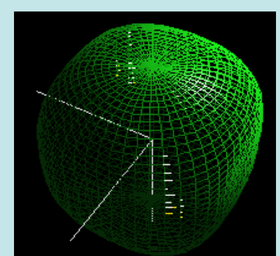
6/m



R_0, $R_4 > 0$



R_0, $R_1 > 0$

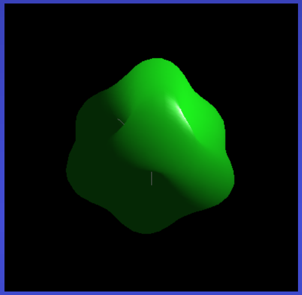


R_0, $R_1 < 0$

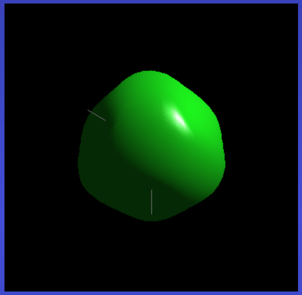
m3m

Gold thin films

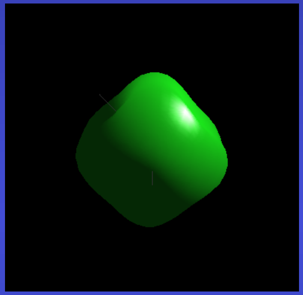
Crystallite size (Å) along	Film thickness					
	10nm	15nm	20nm	25nm	35nm	40nm
[111]	176	153	725	254	343	379
[200]	64	103	457	173	321	386
[202]	148	140	658	234	337	381



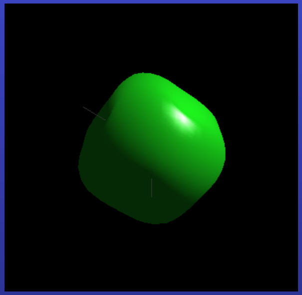
10 nm



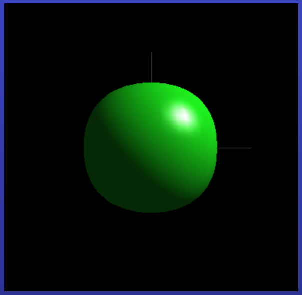
15 nm



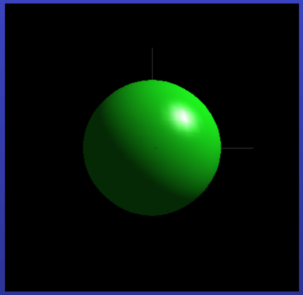
20 nm



25 nm

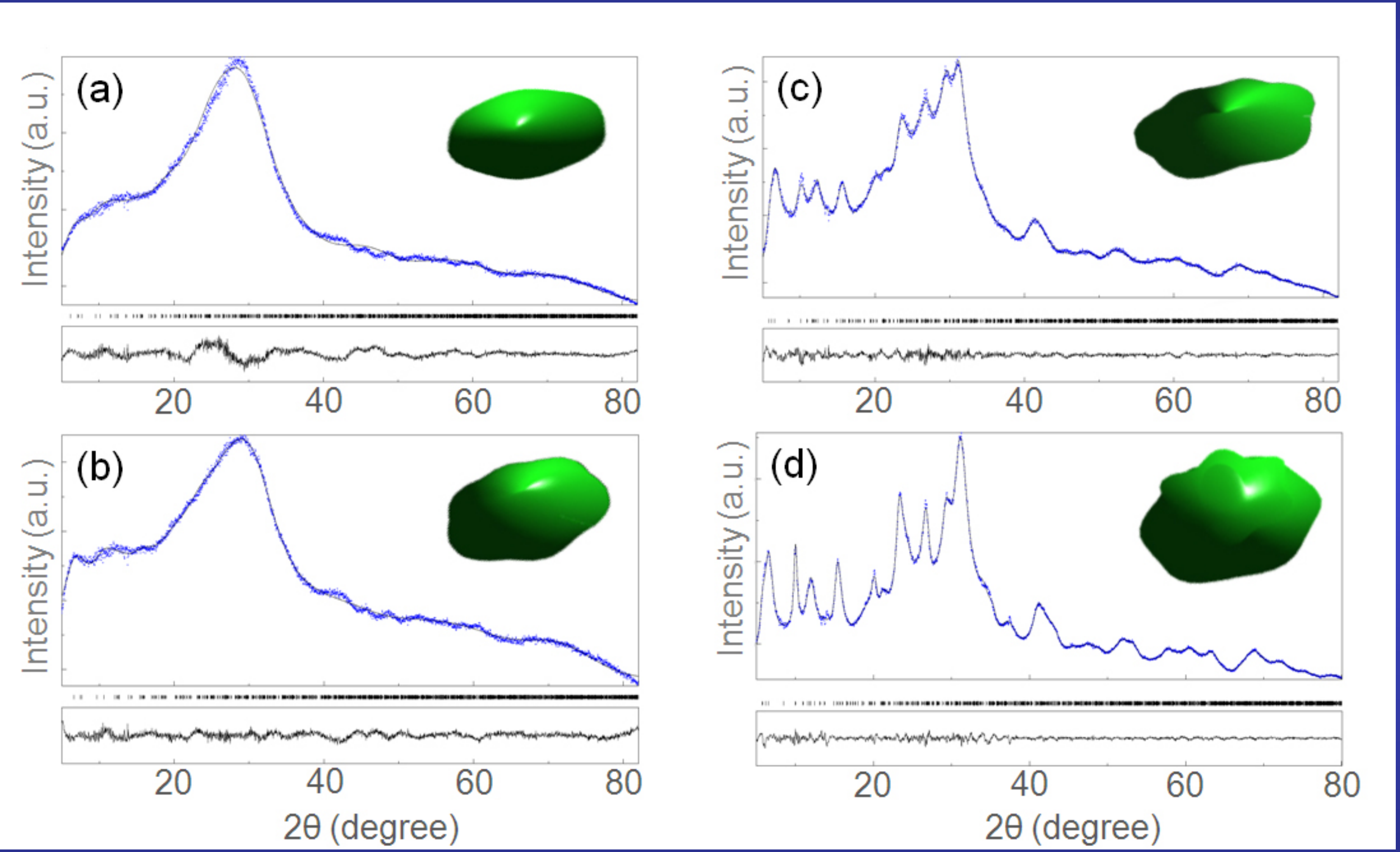


35 nm



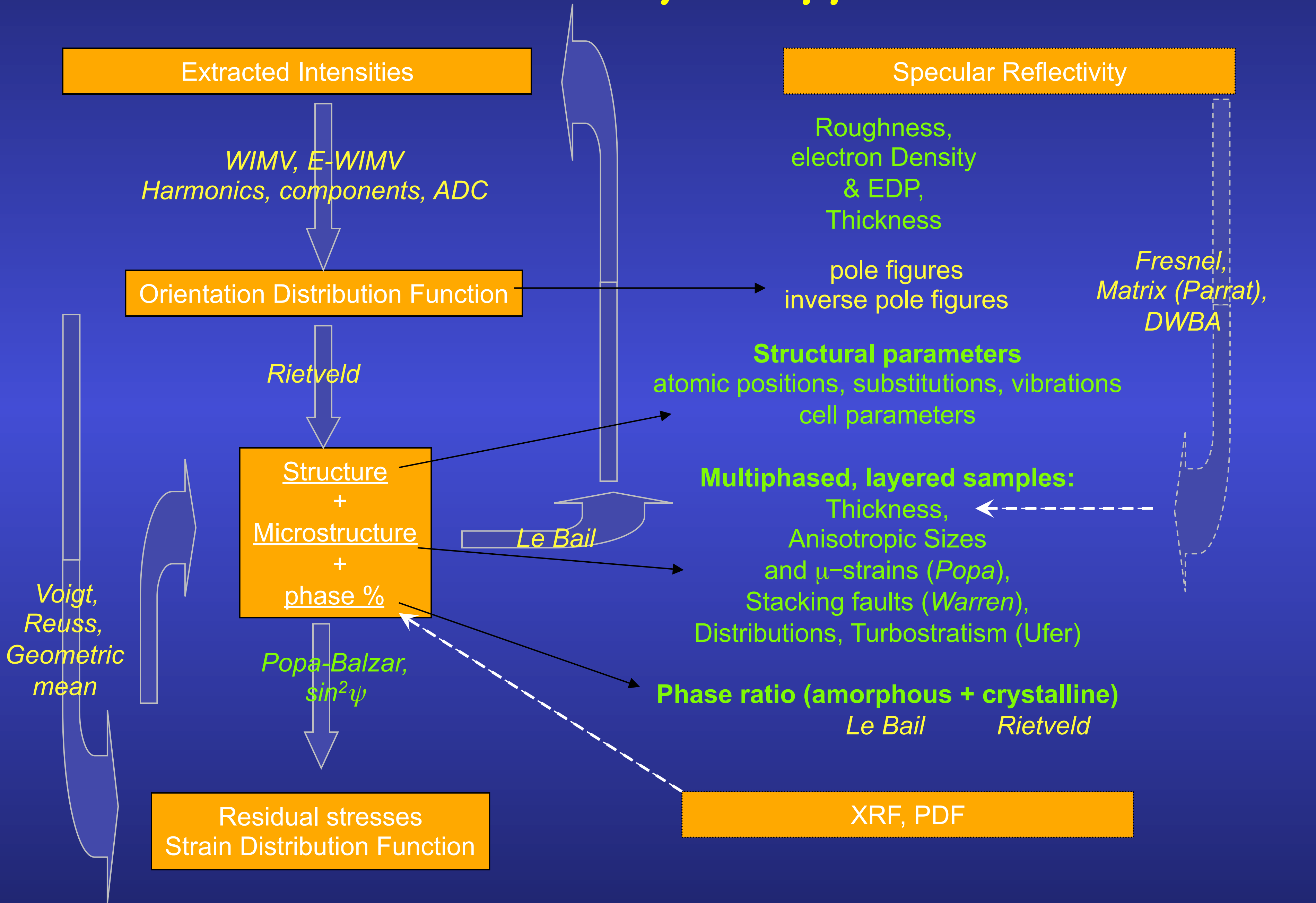
40 nm

EMT nanocrystalline zeolite



Ng, Chateigner, Valtchev, Mintova: *Science* **335** (2012) 70

Combined Analysis approach



Grinding to powderise another problem !

Grinding: removes angular relationship, adds correlations

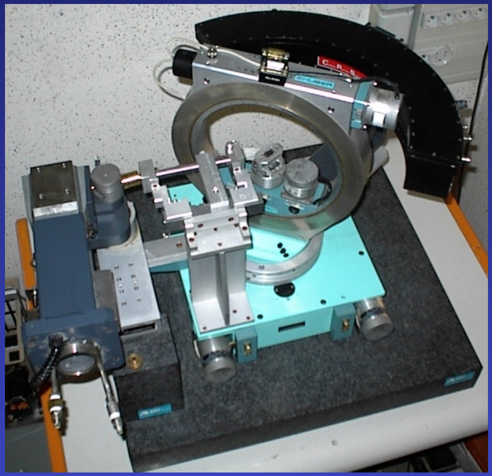
Texture:
- not measured
- removed ? hope to get a perfect powder

Strains, defaults, anisotropy … :
- some removed, some added

Same sample ?

Rare samples ?

Minimum experimental requirements



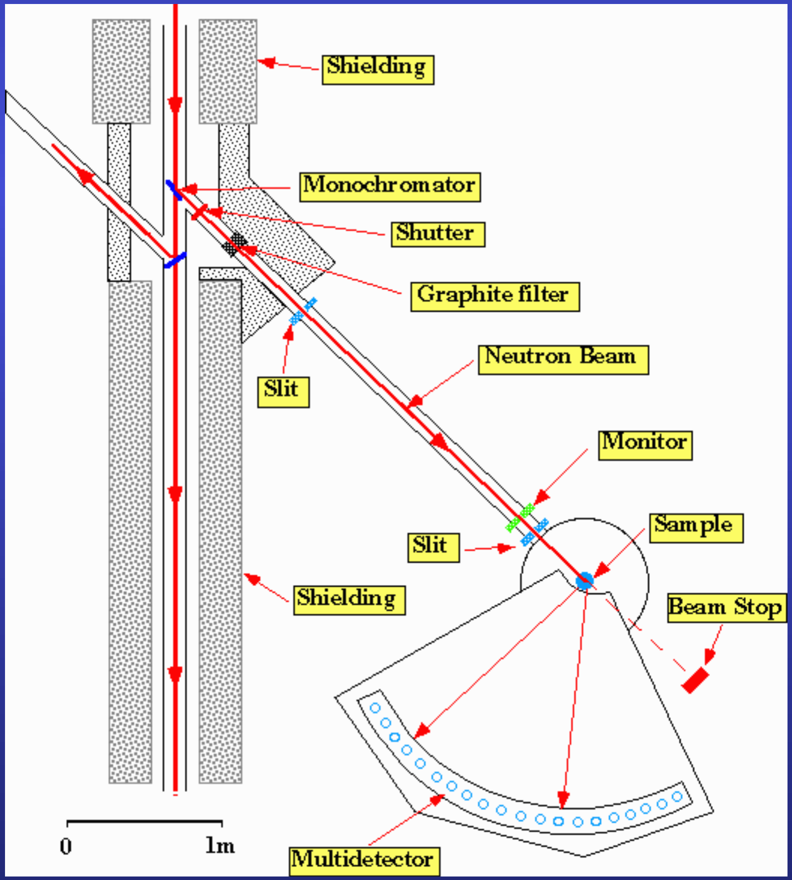
1D or 2D Detector + 4-circle diffractometer
(X-rays and neutrons)
CRISMAT, ILL

+

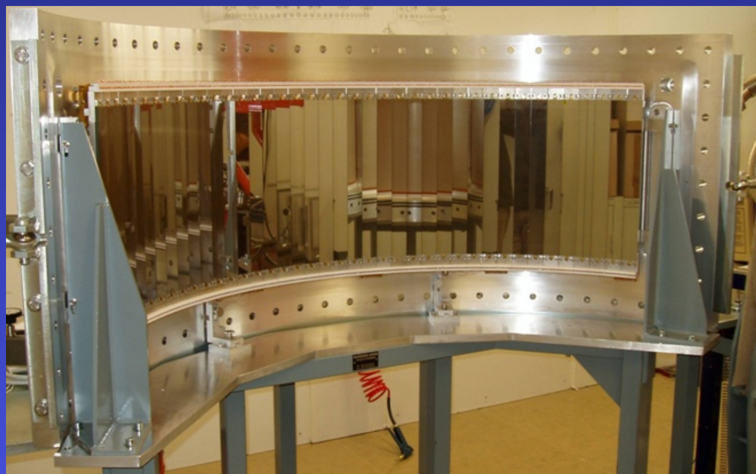
~1000 experiments (2θ diagrams)
in as many sample orientations

+

Instrument calibration
(peaks widths and shapes,
misalignments, defocusing …)



2D Curved Area Position Sensitive Detector

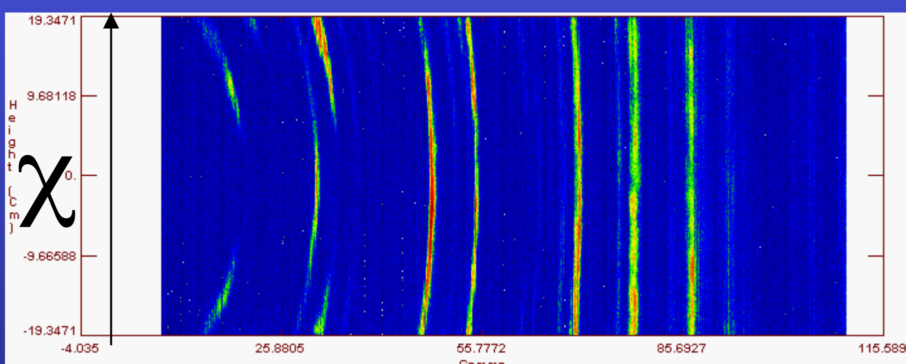


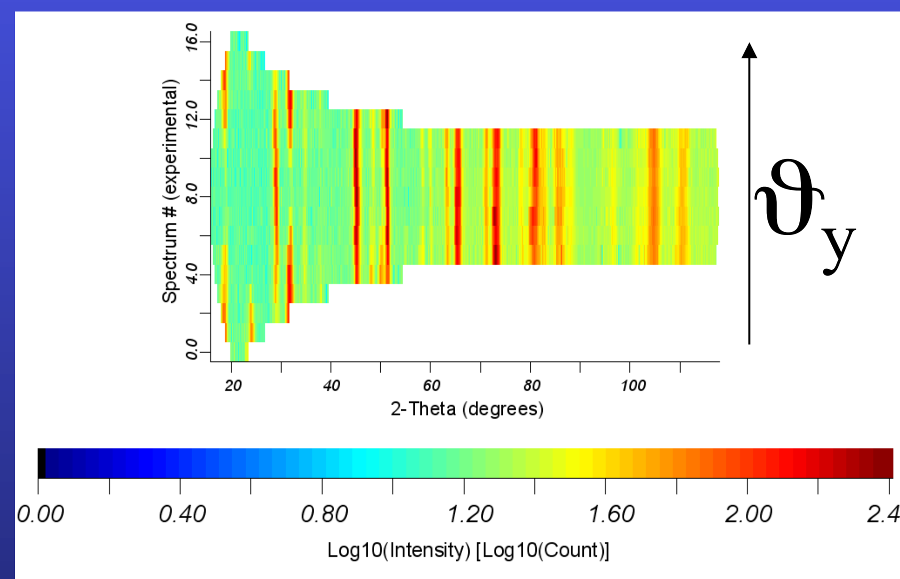
D19 - ILL

+

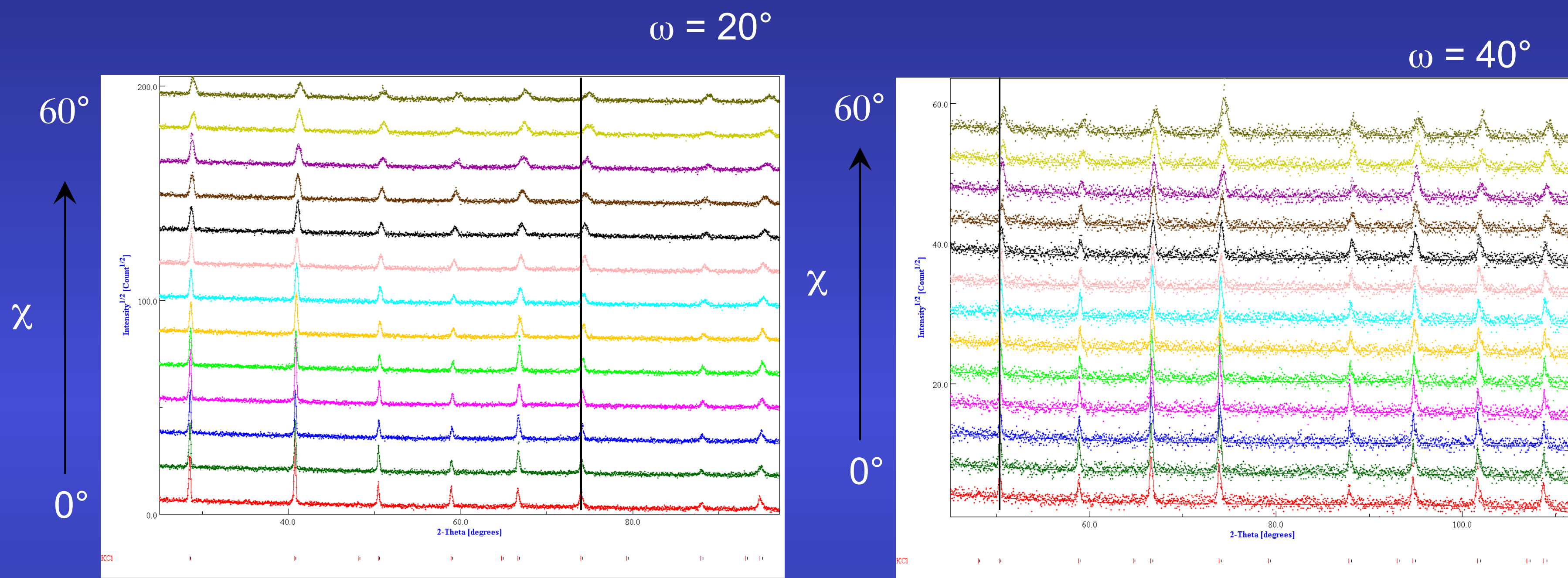
~100 experiments (2D Debye-Scherrer diagrams)

in as many sample orientations





Calibration



KCl, LaB_6 …

FWHM (ω, χ, 2θ, η …)
2θ shift
gaussianity
asymmetry
misalignments ...

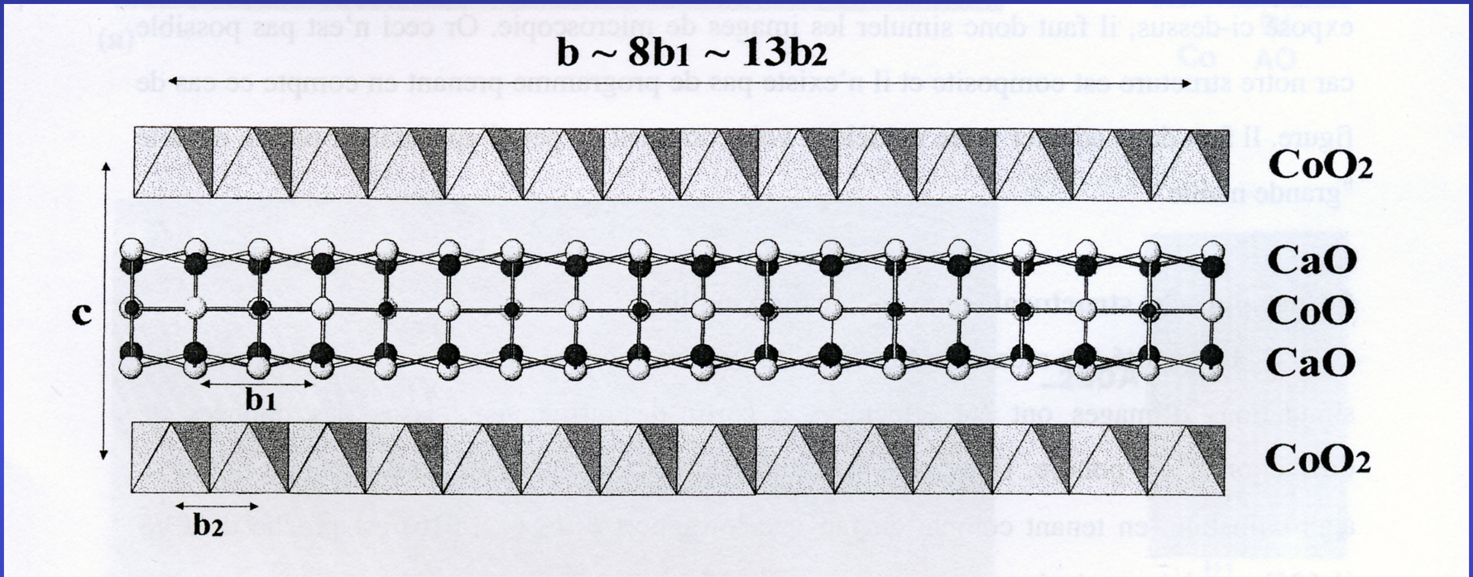
Minimization algorithms

- Can be fully used in the method (everywhere)

- Marquardt Least Squares (based on steepest decrease and Gauss-Newton)
  - Efficient, best with few parameters, near the solution
- Evolutionary computation (or genetic algorithm)
  - Slow, not efficient, requires a lot of resources
  - Unlimited number of parameters
  - Can start far from the solution
- Simulated annealing (the solution proceed like a random walk, but the walking step decreases as temperature decreases)
  - In between the Marquardt and evolutionary algorithms
- Simplex (generates n+1 starting solutions as vertices of a polygon, n number of parameters, and contract/expand the polygon around the minima)
  - Slow on convergence
  - Remains close to the solution, but explore more minima with respect to the Marquardt

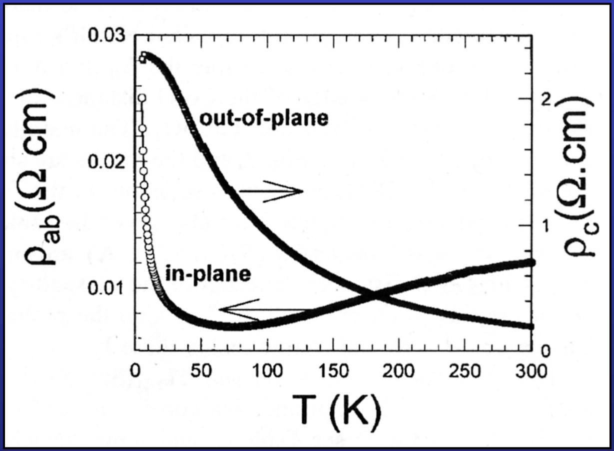
$Ca_3Co_4O_9$ thermoelectrics

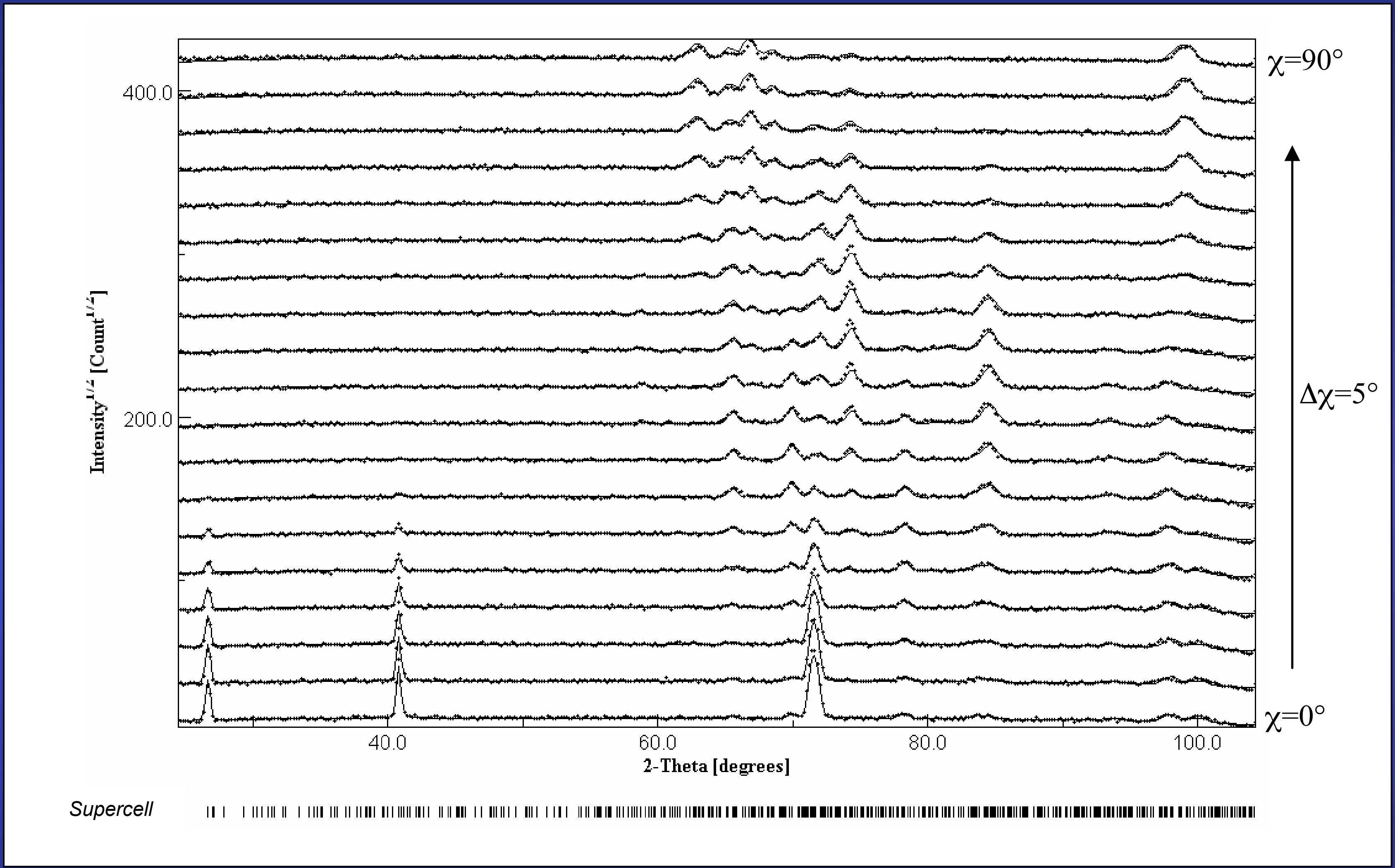
$Ca_3Co_4O_9$: Misfit lamellar and modulated Structure, with high thermopower



Two monoclinic sub-systems:
S1 with a ~ 4.8Å, b_1 ~ 4.5Å, c ~ 10.8Å et β ~ 98° (NaCl-type)
S2 with a ~ 4.8Å, b_2 ~ 2.8Å, c ~ 10.8Å et β ~ 98° (CdI_2-type)

$\Gamma = \sigma_{ab}/\sigma_c \sim 10$ → Texture

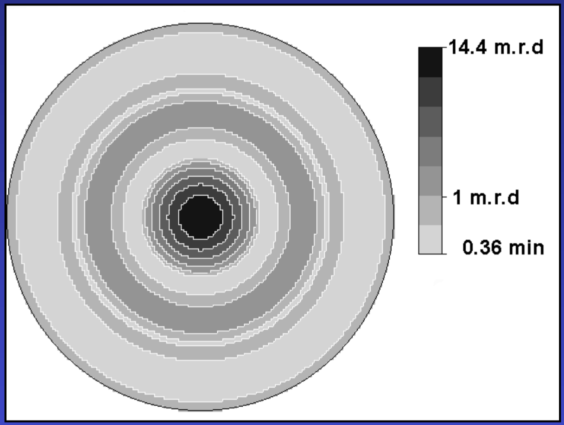




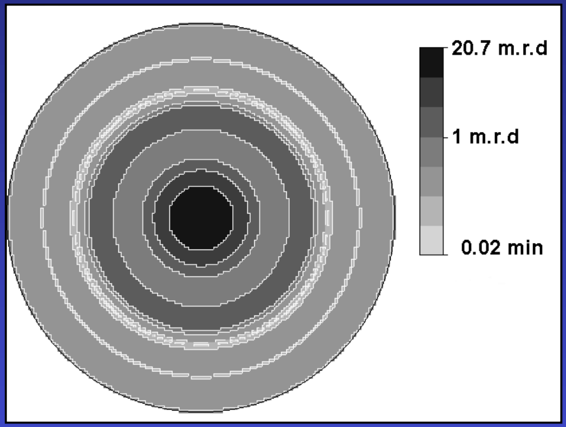
400.0
200.0
Intensity$^{1/2}$ [Count$^{1/2}$]
40.0
60.0
80.0
100.0
2-Theta [degrees]
χ=90°
Δχ=5°
χ=0°
Supercell

RP=19.7%, Rw=11.9%

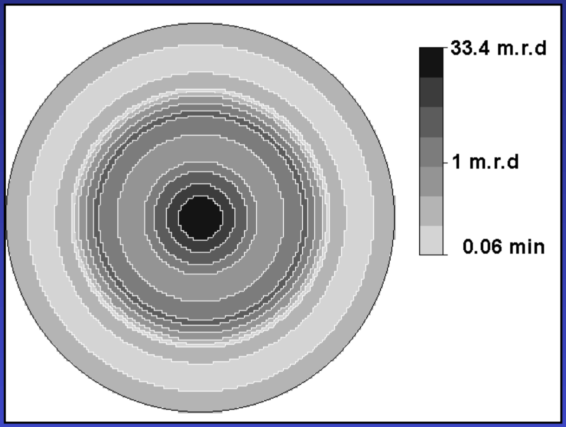
9.8 MPa for 2 h

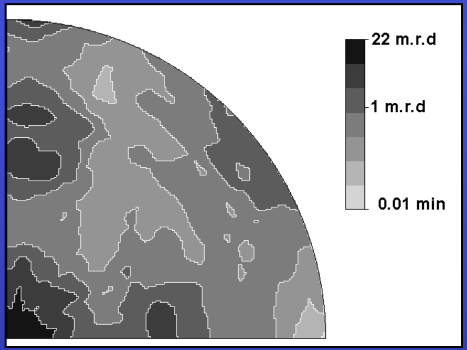


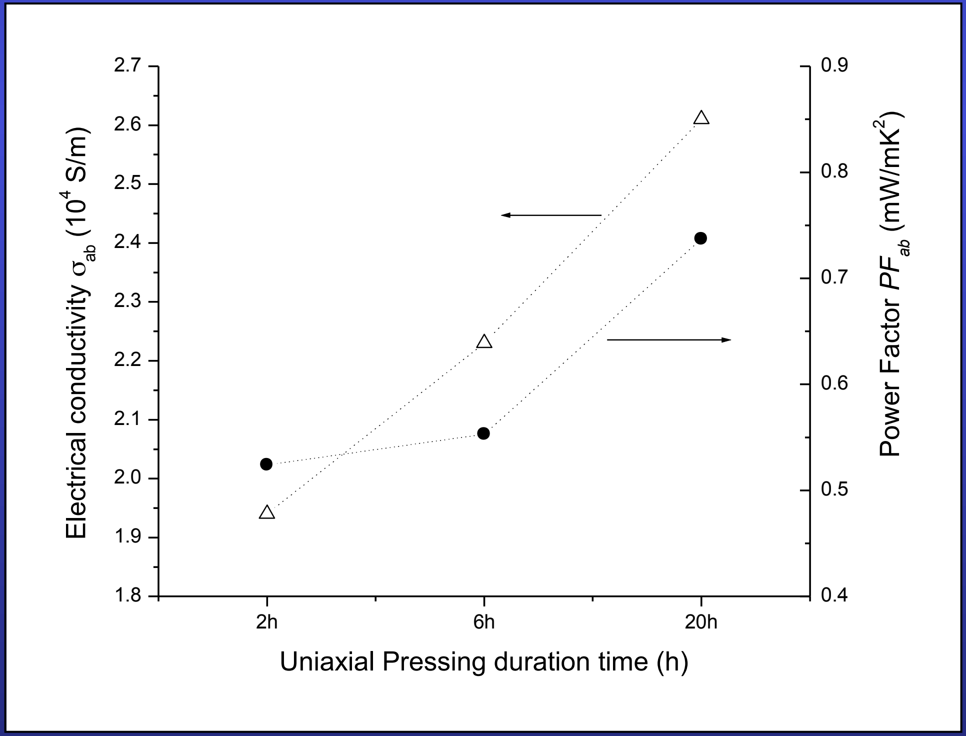
19.6 MPa for 6 h



19.6 MPa for 20 h



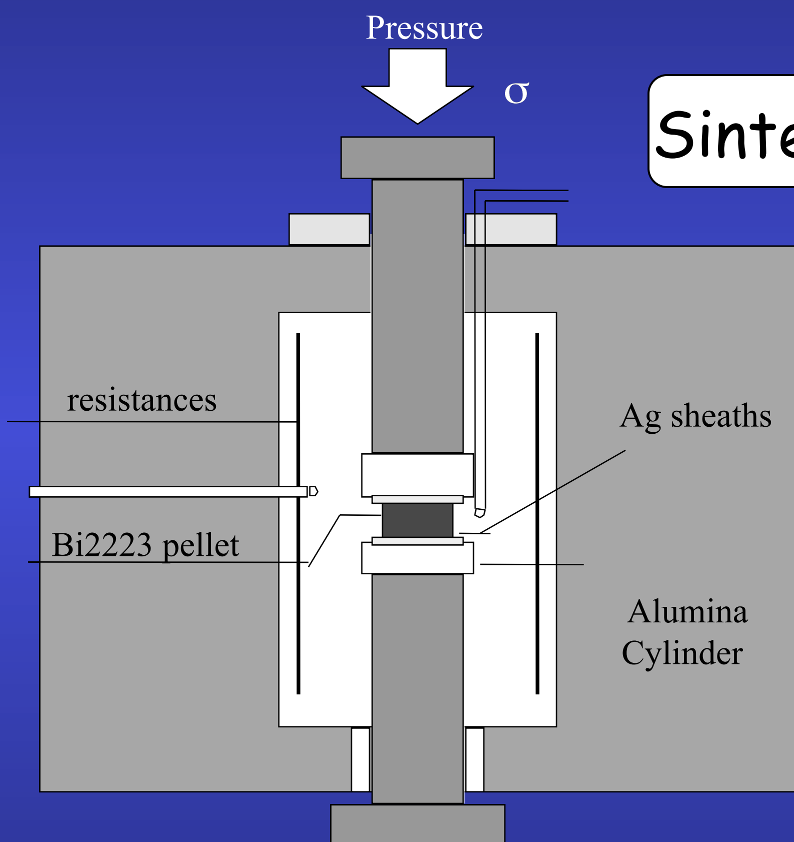




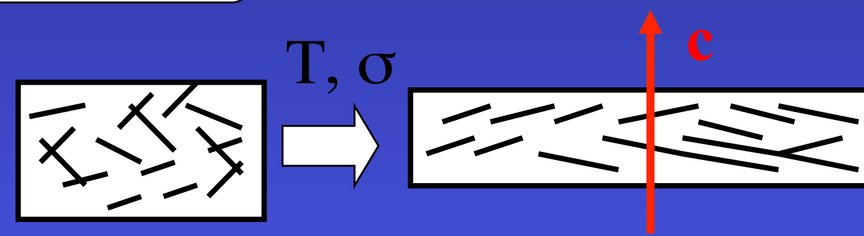
Templated Growth Method

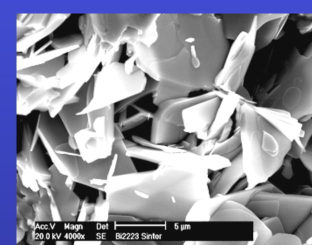
Bi2223 compounds

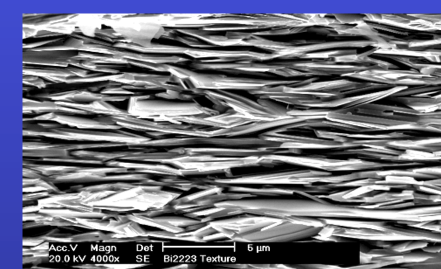
E. Guilmeau, PhD



Sinter-Forging

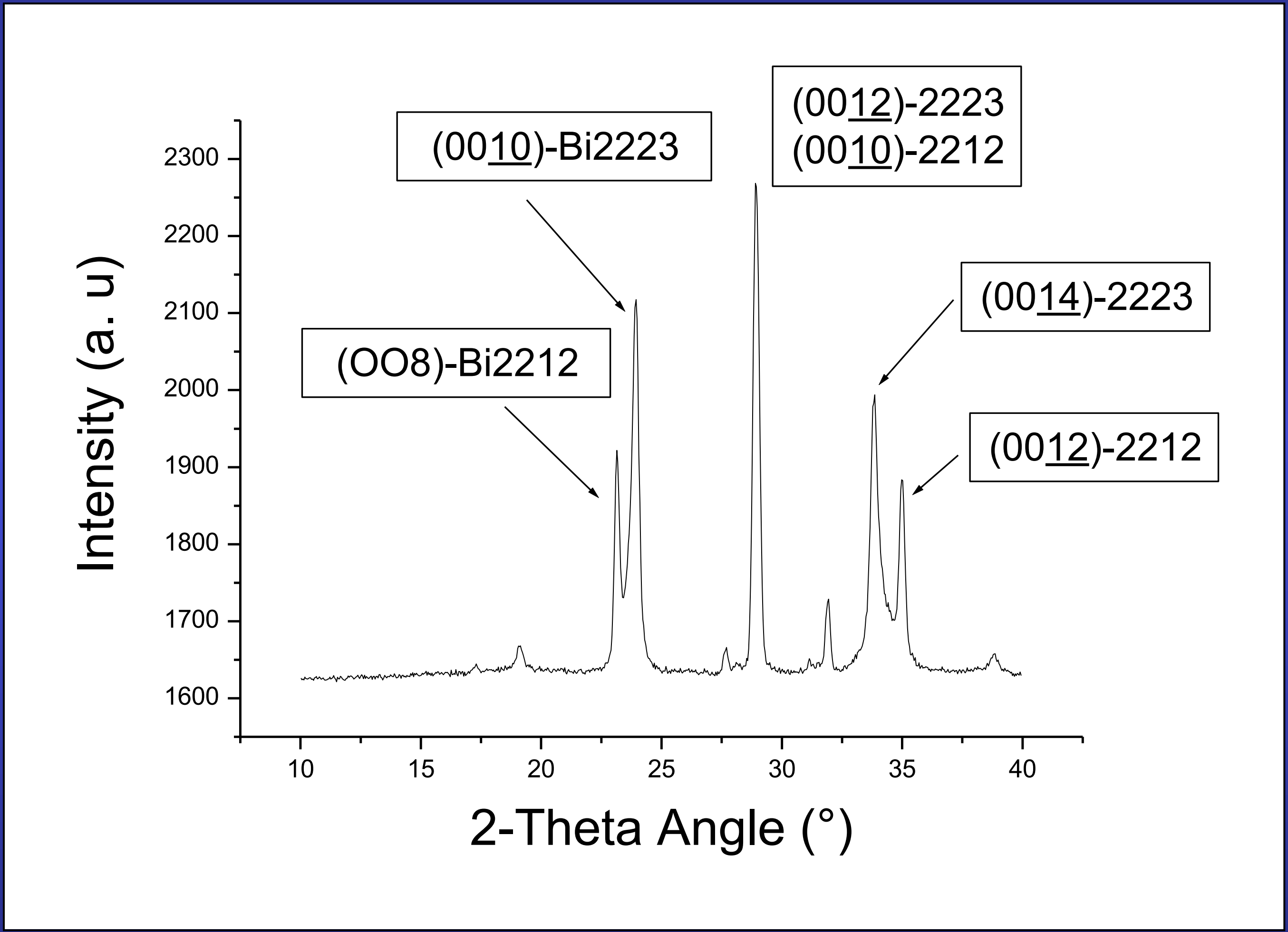






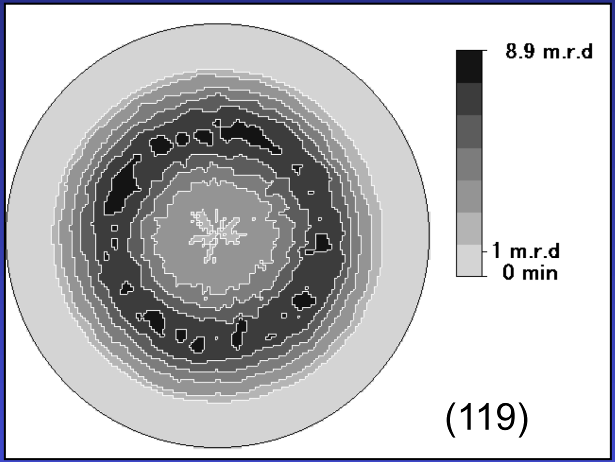
Grain alignment ⇒ ↗ Jc

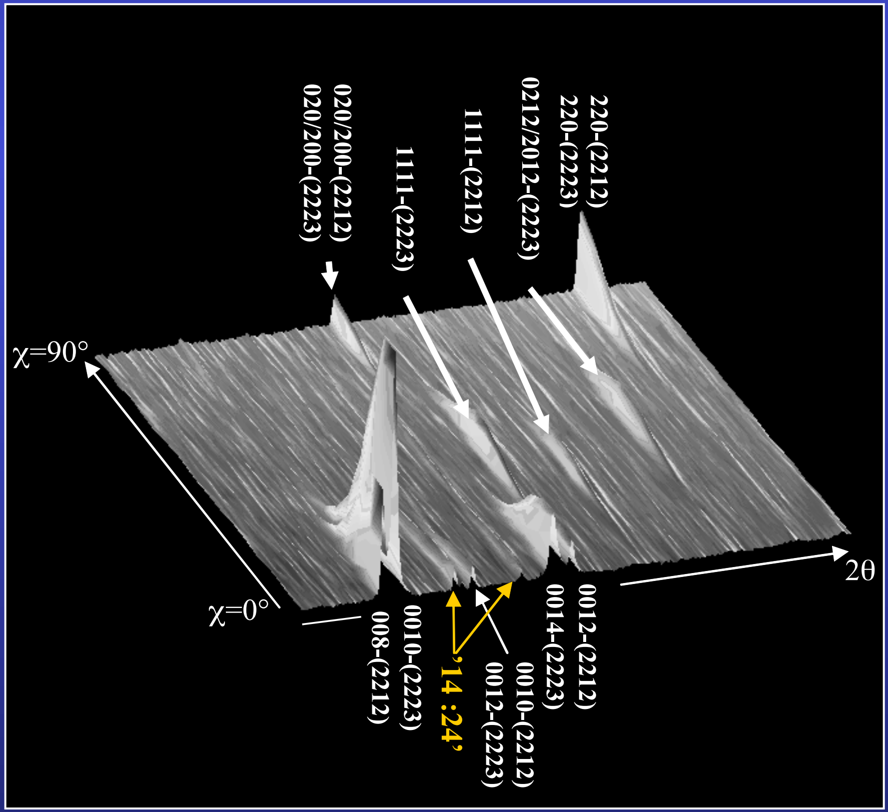
(00ℓ) Texture



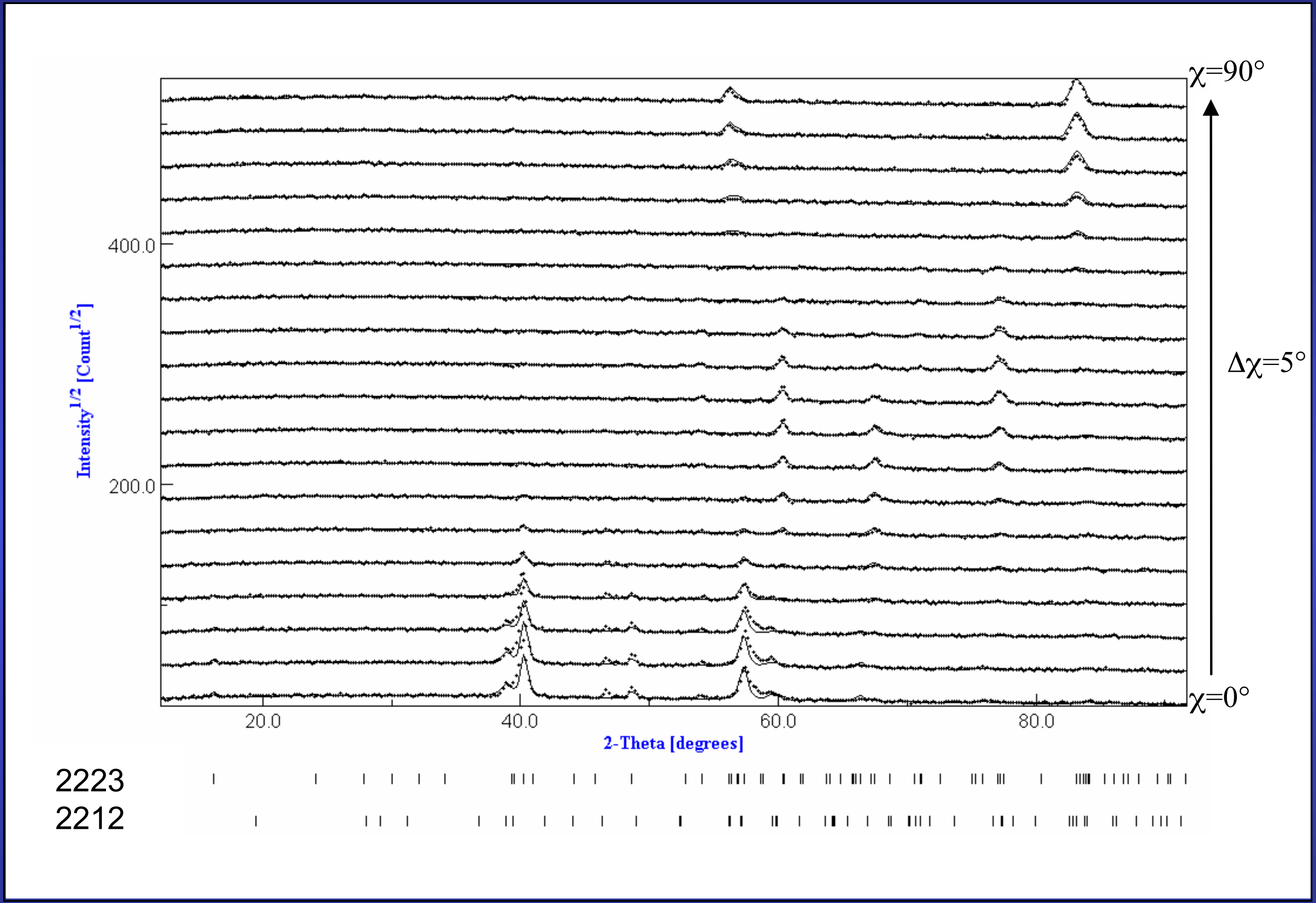
(0010)-Bi2223
(0012)-2223
(0010)-2212
(0014)-2223
(OO8)-Bi2212
(0012)-2212
Intensity (a. u)
2300
2200
2100
2000
1900
1800
1700
1600
10
15
20
25
30
35
40
2-Theta Angle (°)

Combined Analysis





- *Neutrons*
- Sample: ~70 mm^3
- 2θ patterns for χ=0° to 90°
- No φ rotation (fibre texture).



Rw=9.12
RP=16.24

Effect of the sinter-forging treatment on the texture development, crystal growth, transport properties

Sinter-forging dwell time (h)	Orientation Distribution Max (m.r.d.)		% Bi2223	Cell parameters (Å)		Crystallite size Bi2223 (nm)	Rb (%)	Rw (%)	Rexp (%)	RP0 (%)	RP1 (%)	J_c (A/cm^2)
	Bi2212	Bi2223		Bi2223	Bi2212							
20	21.8	20.7	59.9±1.3	a=5.419(3) b=5.391(3) c=37.168(3)	a=5.414(3) b=5.393(3) c=30.800(3)	205±7	7.56	11.1	4.55	17.74	10.56	12500
50	24.1	24.4	72.9±2.9	a=5.419(3) b=5.408(3) c=37.192(3)	a=5.416(3) b=5.396(3) c=30.806(3)	273±10	7.54	11.37	4.58	17.05	11.04	15000
100	31.5	25.2	84.4±4.6	a=5.410(3) b=5.405(3) c=37.144(3)	a=5.412(3) b=5.403(3) c=30.752(3)	303±10	5.4	8.04	3.69	13.54	9.31	19000
150	65.4	27.2	87.0±4.1	a=5.417(3) b=5.403(3) c=37.199(3)	a=5.413(3) b=5.407(3) c=30.792(3)	383±13	6.13	9.12	4.8	16.24	12.25	20000

↗ *Sinter-forging Time* ⇒ ↗ Texture strength, ↗ % Bi2223, ↗ Crystallite Size ⇔ ↗ J_c

E. Guilmeau et al., JAC

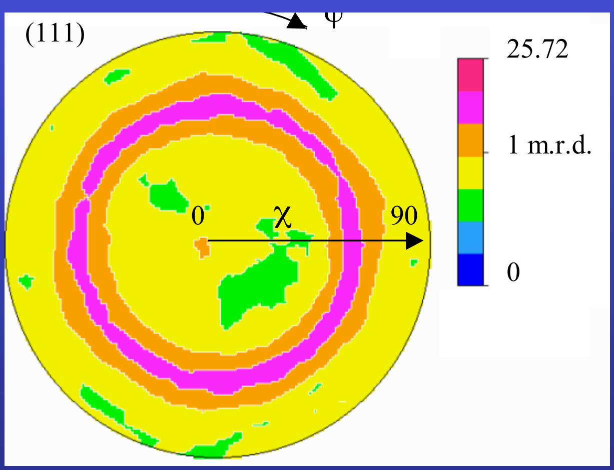
Ferroelectric PCT films

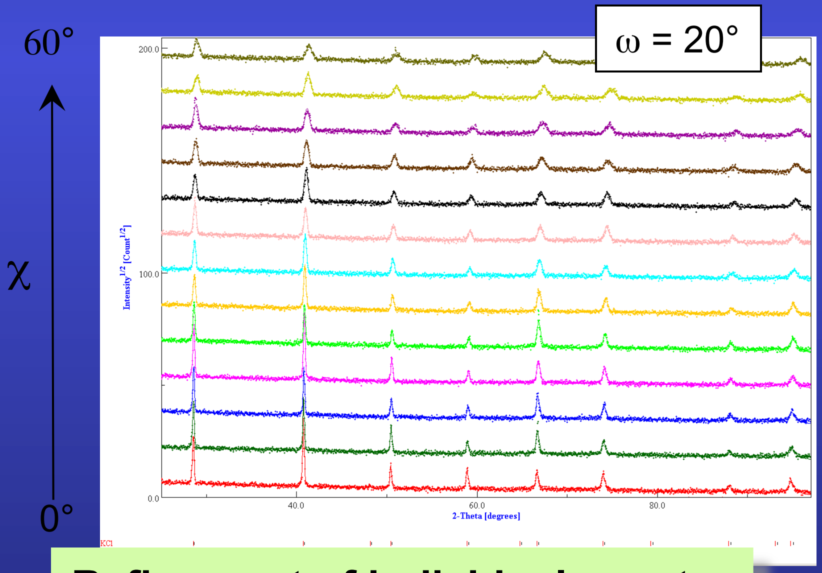
J. Ricote, Madrid

thin films:

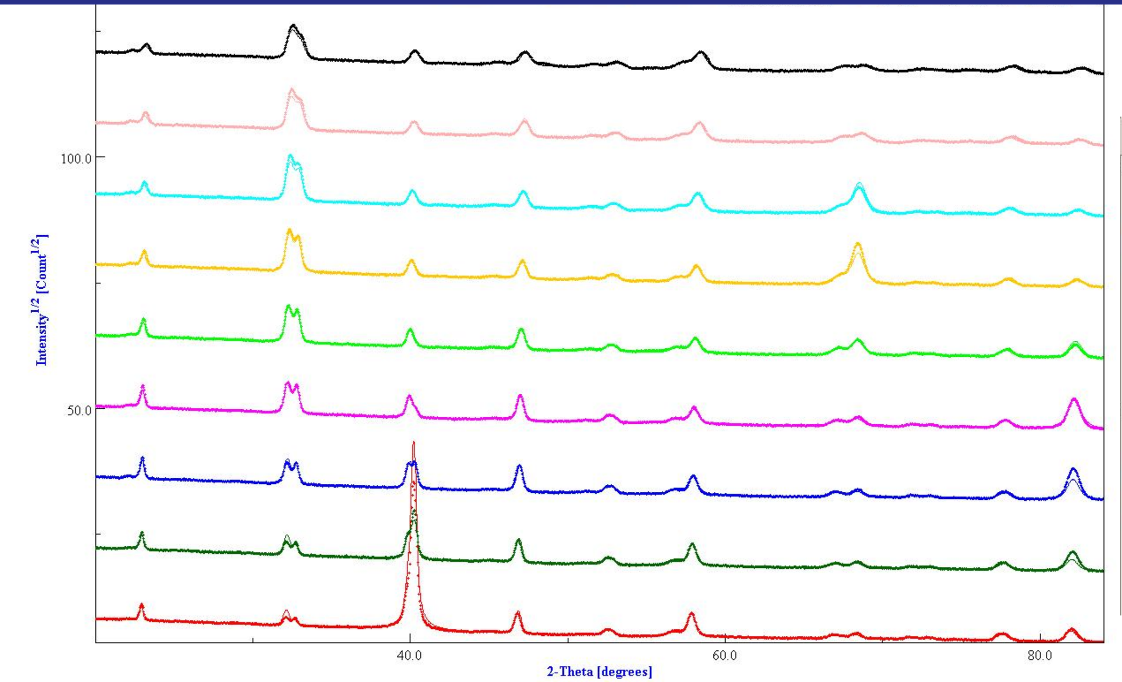
$(Ca_{0.24}Pb_{0.76})TiO_3$ sol-gel synthesised solutions deposited by spin coating on a substrate of $Pt/TiO_2/Si$, with and without a treatment at 650ºC for 30 min.

All films are crystallised at 700ºC for 50 s by Rapid Thermal Processing (RTP; 30ºC/s). A series is also recrystallised at 650ºC for 1 to 3 h.

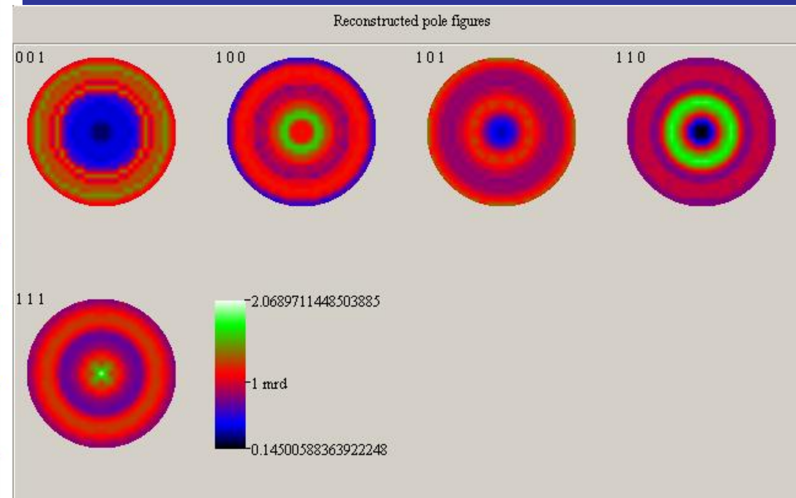




Refinement of individual spectra

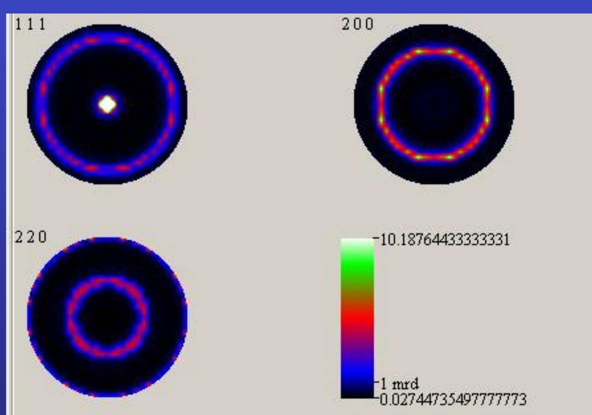


PCT



a = 3.9156(1) Å
c = 4.0497(3) Å
T = 2525(13) Å
t_{iso} = 390(7) Å
ε = 0.0067(1) rms

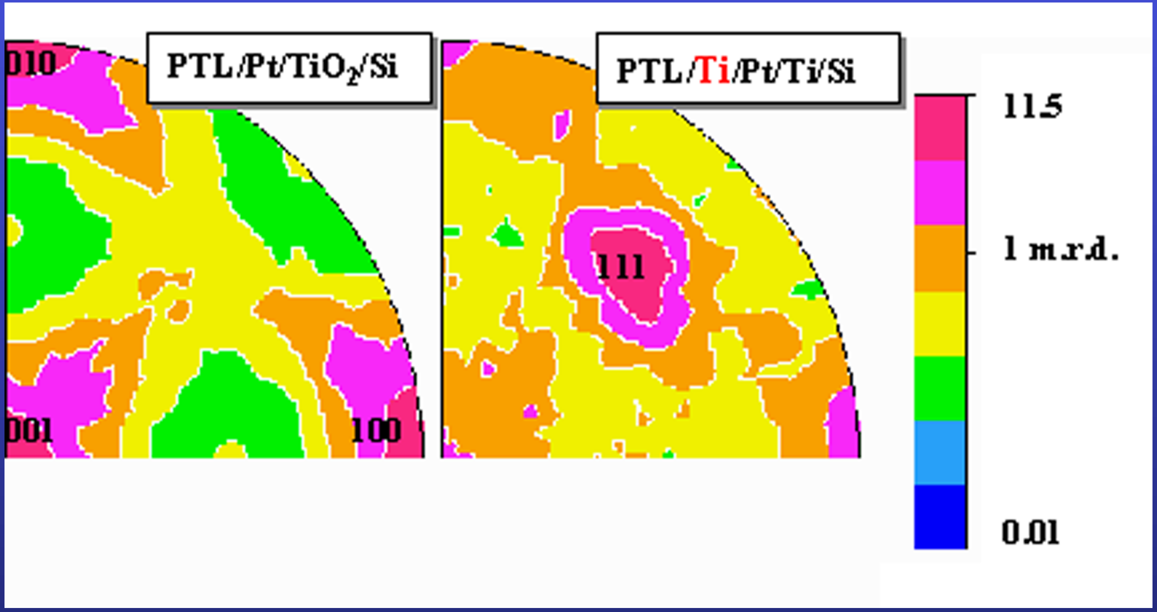
Pt



a = 3.9108(1) Å
T = 457(3) Å
t_{iso} = 458(3) Å
ε' = 0.0032(1) rms

R_W = 13%; R_B = 12%; R_{exp} = 22%.(Rietveld)
R_W = 5%; R_B = 6% (E-WIMV)

Atom	Occupancy	x	y	z
Pb	0.76	0.0	0.0	0.0
Ca	0.24	0.0	0.0	0.0
Ti	1.0	0.5	0.5	0.477(2)
O1	1.0	0.5	0.5	0.060(2)
O2	1.0	0.0	0.5	0.631(1)

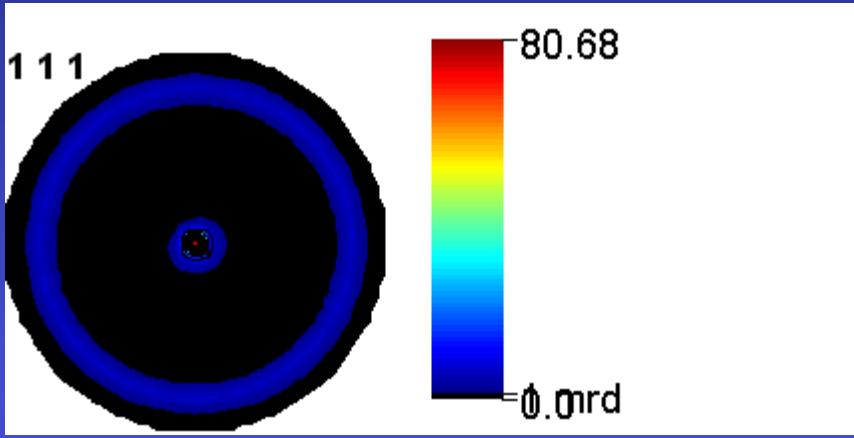


Compliance coefficients [10^{-3} GPa^{-1}]	$PbTiO_3$ single crystal (data set A)	Film random orientation	PCT-Si <001> contrib≈17%	PLT <001> contrib.≈49%	PCT-Mg <001> contrib.≈68%
s_{11}	6.5	10.1	10.5	10.0	9.7
s_{22}	6.5	10.0	10.5	10.0	9.7
s_{33}	33.3	9.8	9.0	10.3	11.3
s_{44}	14.5	13.2	12.8	12.9	13.1
s_{55}	14.5	13.2	12.8	13.0	13.1
s_{66}	9.6	13.4	14.0	13.5	12.7
s_{12}	-0.35	-3.3	-3.5	-3.2	-3.0
s_{21}	-0.35	-3.3	-3.5	-3.2	-3.0
s_{13}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{31}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{23}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{32}	-7.1	-3.2	-3.1	-3.4	-3.6
s_{33}/s_{11}	5.1	0.97	0.86	1.03	1.16
s_{13}/s_{12}	20.3	0.97	0.89	1.06	1.20

Geometric mean average + biaxial stress state

Ferroelectric PMN-PT films

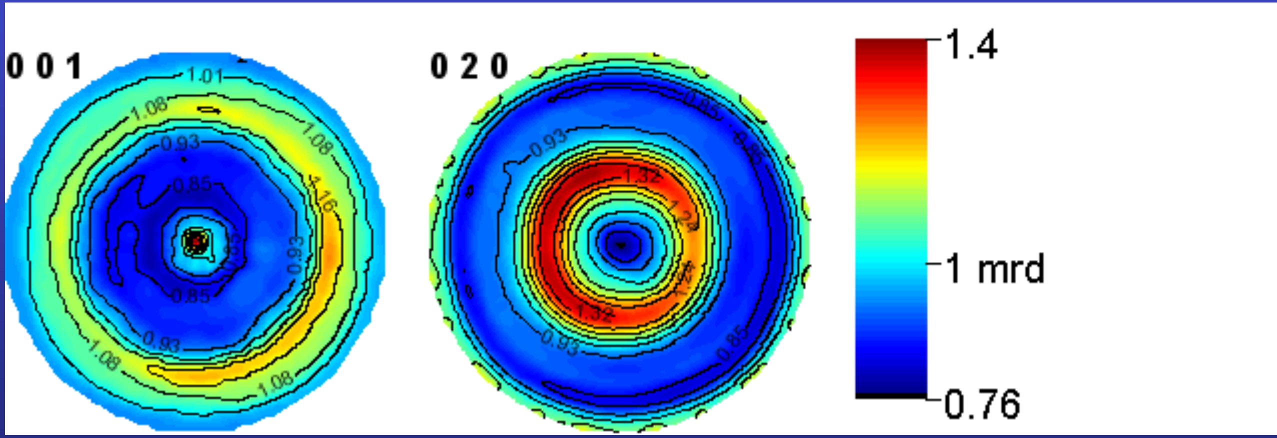
J. Ricote, DMF-Madrid



Pt

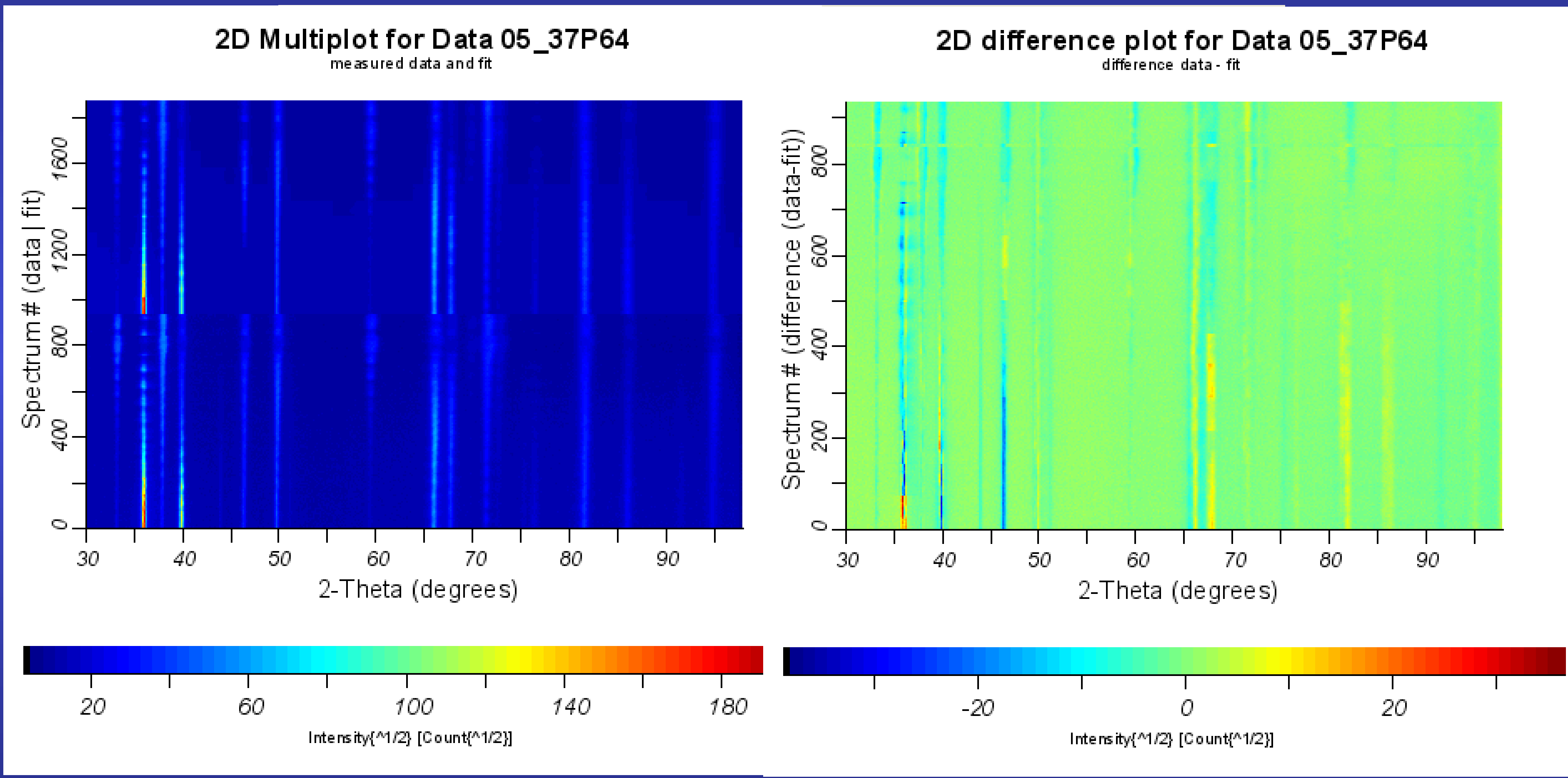
a = 3.91172(1) Å
T = 583(5) Å
t_{iso} = 960(1) Å
ε = 0.0032(1) rms
σ_{11}= 0.639(1) GPa
σ_{22}= 0.651(1) GPa
σ_{12}= -0.009(1) GPa

$Pb_{0.7}(Mg_{1/3}Nb_{2/3})O_3$-$Pb_{0.3}TiO_3$ /$Ti0_2$/Pt/Si-(100)



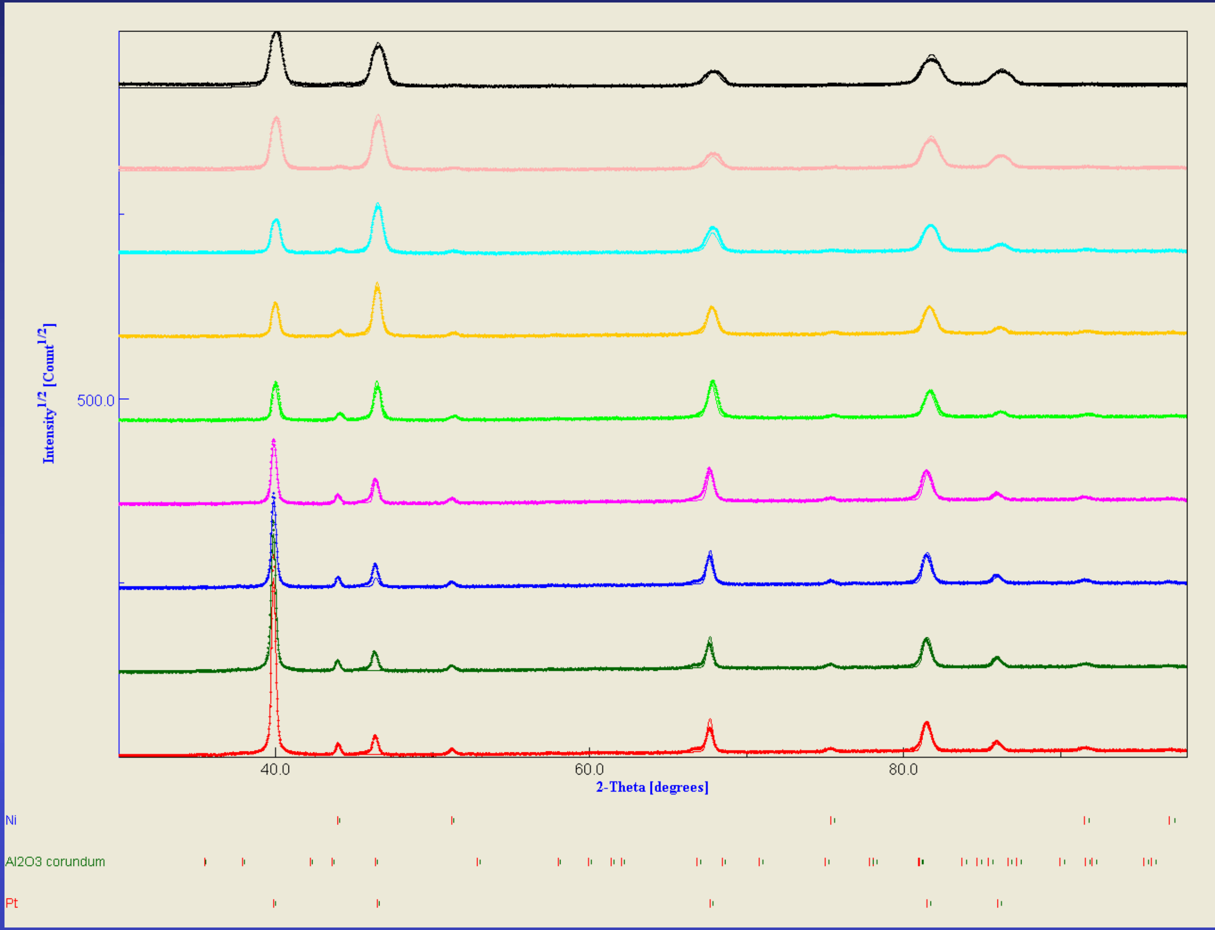
a = 5.67858(9) Å
b = 5.69038(9) Å
c = 3.99558(4) Å
β = 90.392(1) Å
T = 1322(9) Å
t_{iso} = 1338(2) Å
ε = 0.0067(1) rms

$AlN/Pt/TiO_x/Al_2O_3$/Ni-Co-Cr-Al



Rw (%) = 24.120445
Rexp (%) = 5.8517213

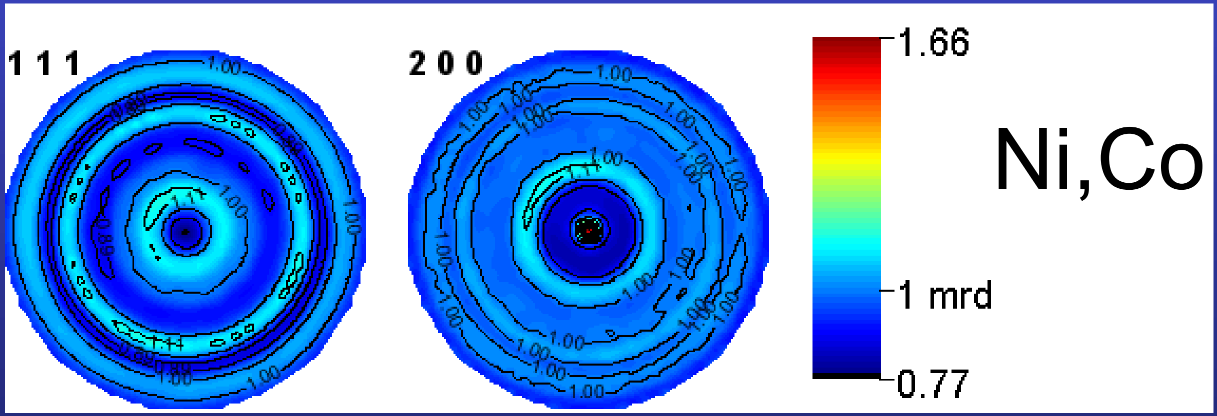
T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm



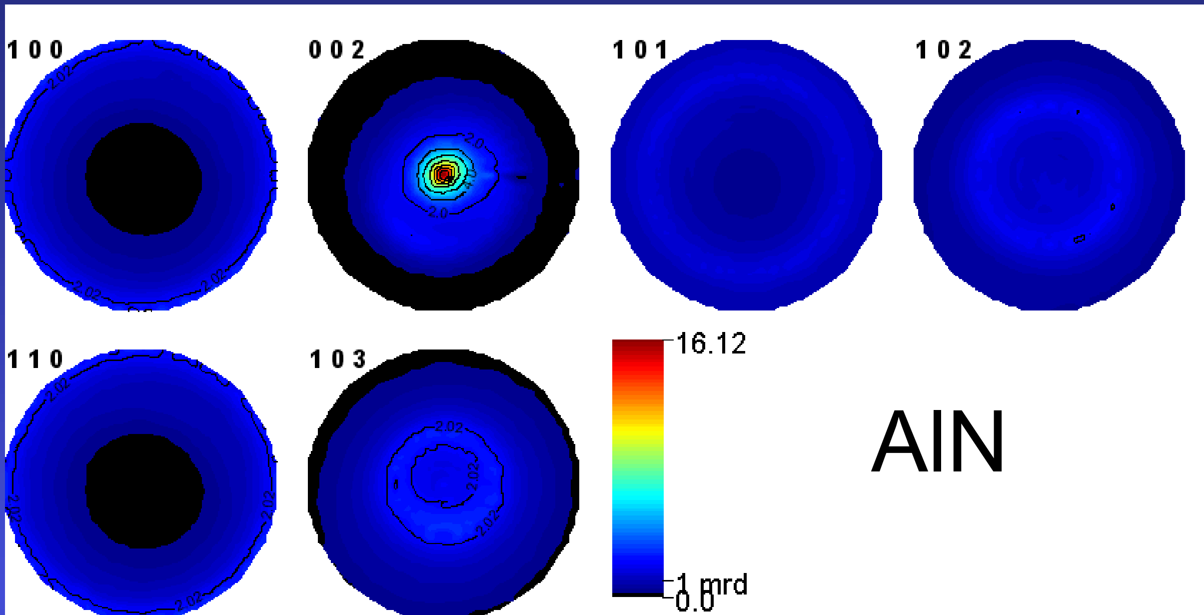
(χ,φ) randomly selected diagrams

Al_2O_3

a = 4.7562(6) Å
c = 12.875(3) Å
T= 7790(31) nm
<t> = 150(2) Å
<ε> = 0.008(3)

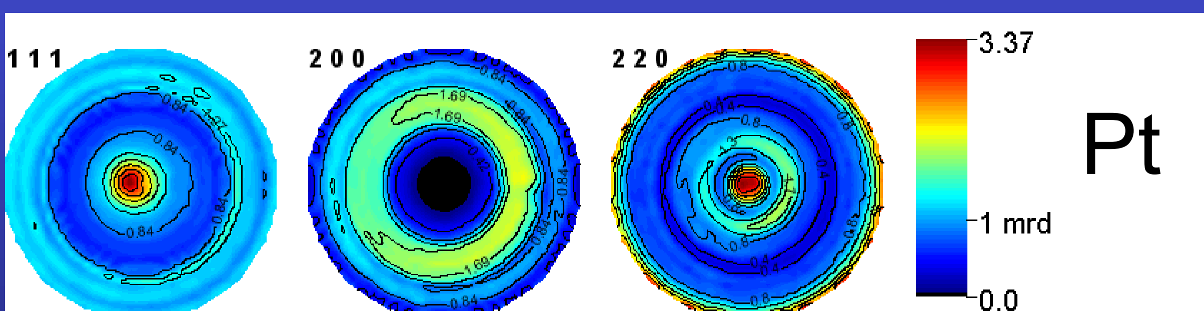


a = 3.569377(5) Å
<t> = 7600(1900) Å
<ε> = 0.00236(3)
σ_{11} = -328(8) MPa
σ_{22} = -411(9) MPa



Rw (%) = 4.1

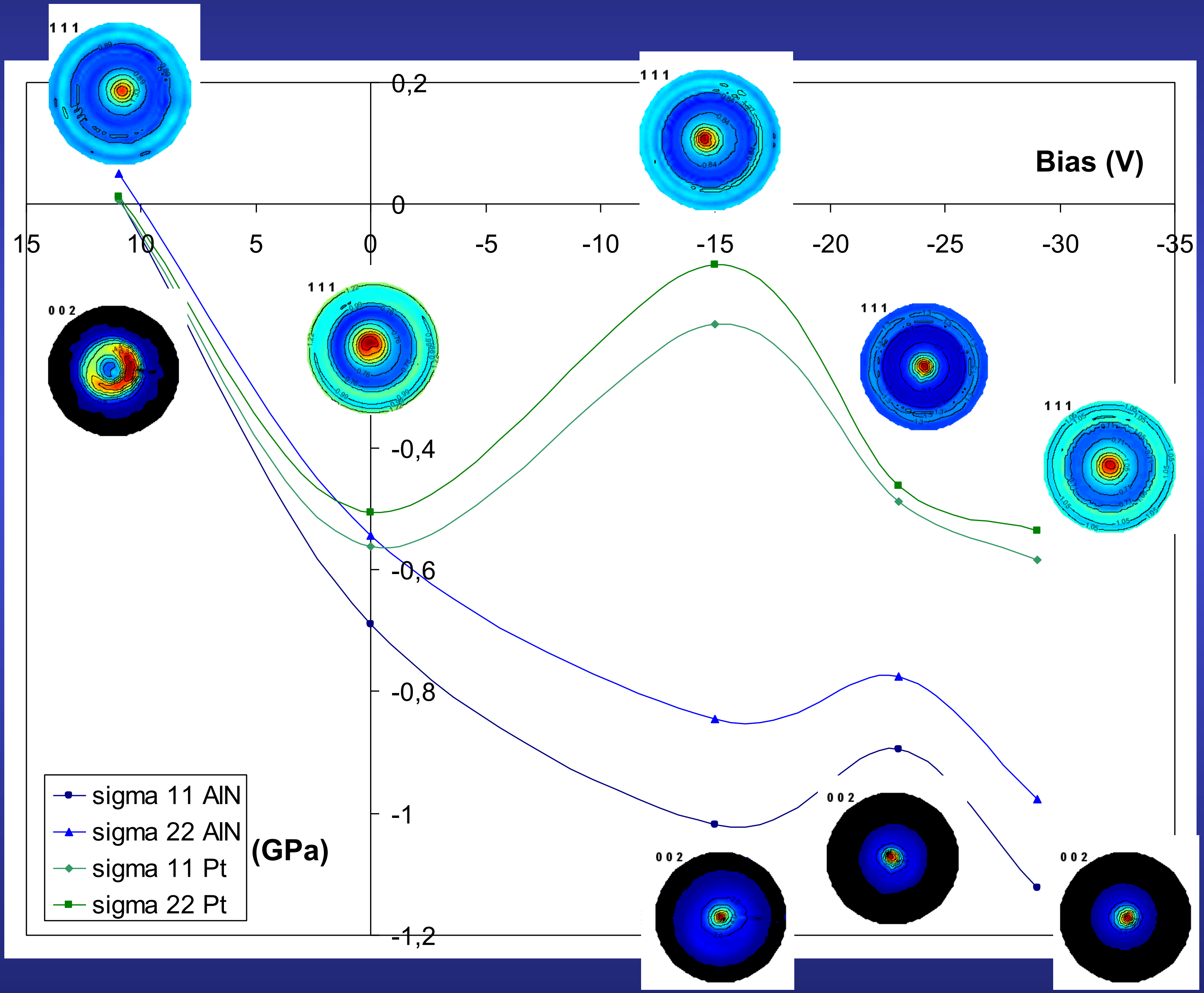
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa



Rw (%) = 33.3

a = 3.91198(1) Å
T = 1204(3) nm
<t> = 2173(10) Å
<ε> = 0.002410(3)
σ_{11} = -196.5(8)
σ_{22} = -99.6(6)

Substrate bias vs stress-texture evolution



Si nanocrystalline thin films

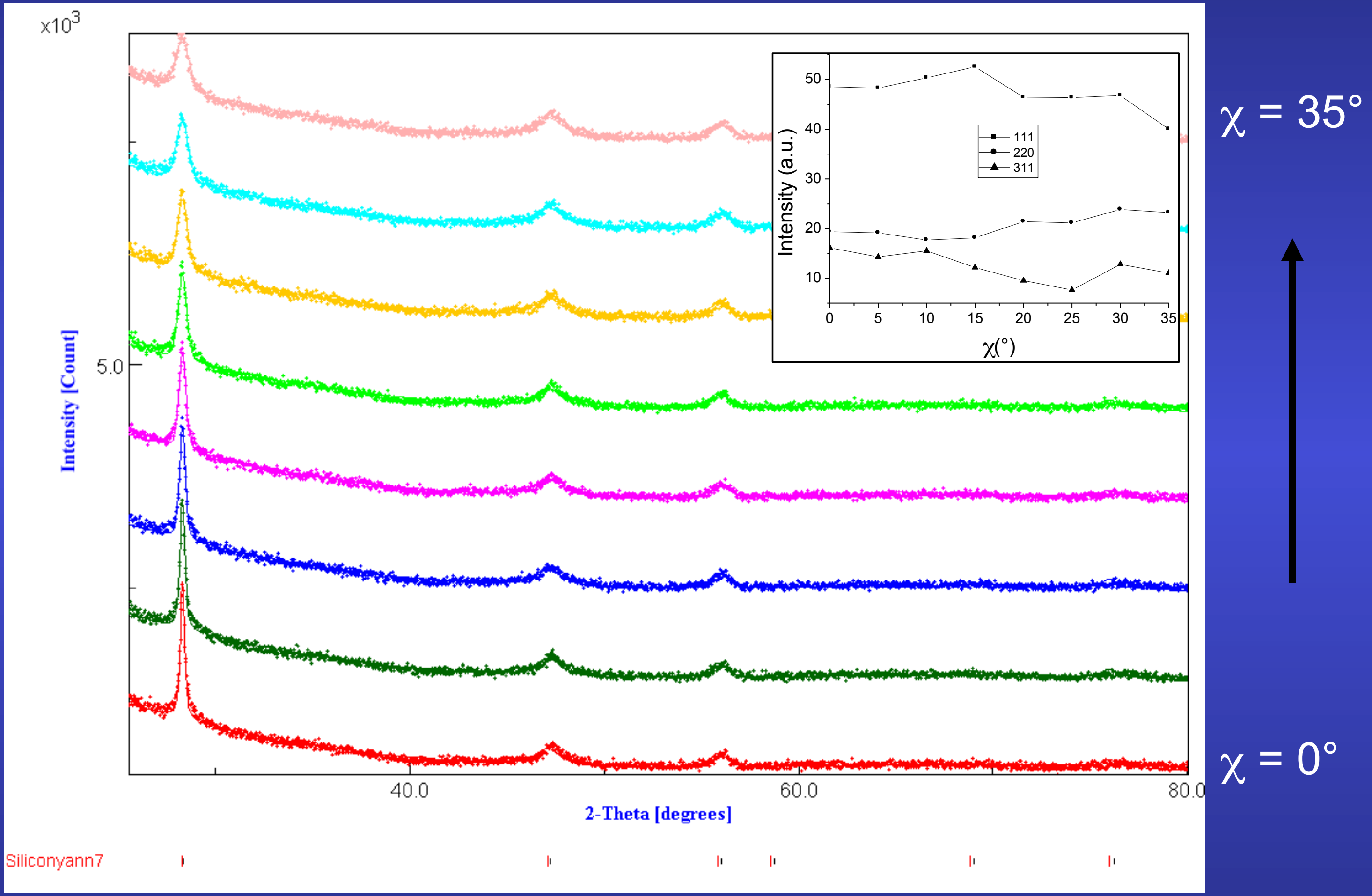
M. Morales, Caen

Silicon thin films deposition by reactive magnetron sputtering:

- power density 2W/cm^2
- total pressure: $p_{total} = 10^{-1}$ Torr
- plasma mixture: H_2 / Ar, pH_2 / p_{total} = 80 %
- temperature: 200°C
- substrates: amorphous SiO_2 (a-SiO_2)
  (100)-Si single-crystals
- target-substrate distance (d)
  - a-SiO_2 substrates: d = 4, 6, 7, 8, 10, 12 cm
    films A, B, C, D, E, F
  - (100)-Si: d = 6, 12 cm
    films G, H

Aim: quantum confinement, photoluminescence properties

Typical refinement

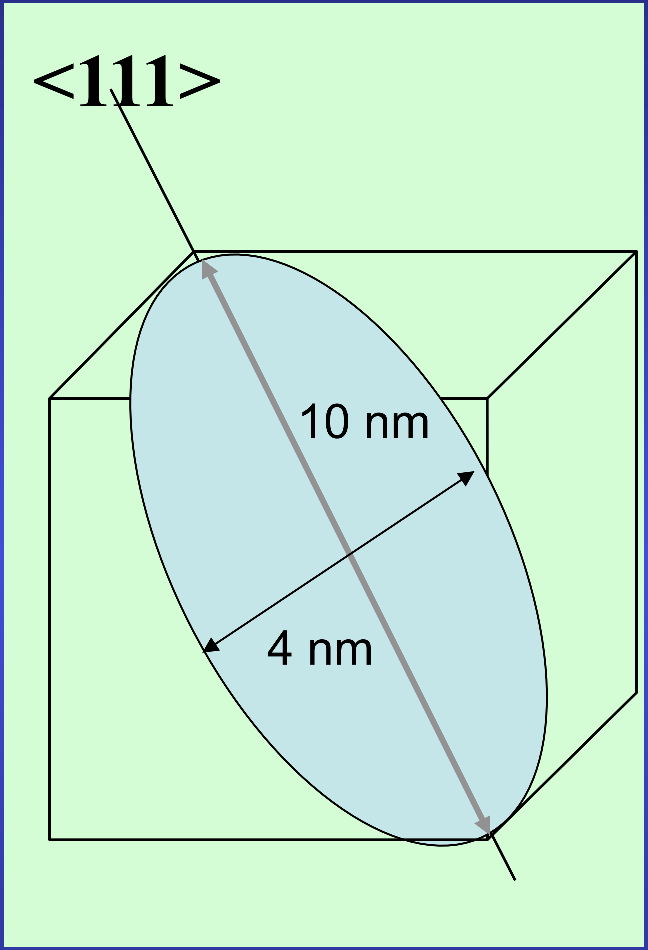


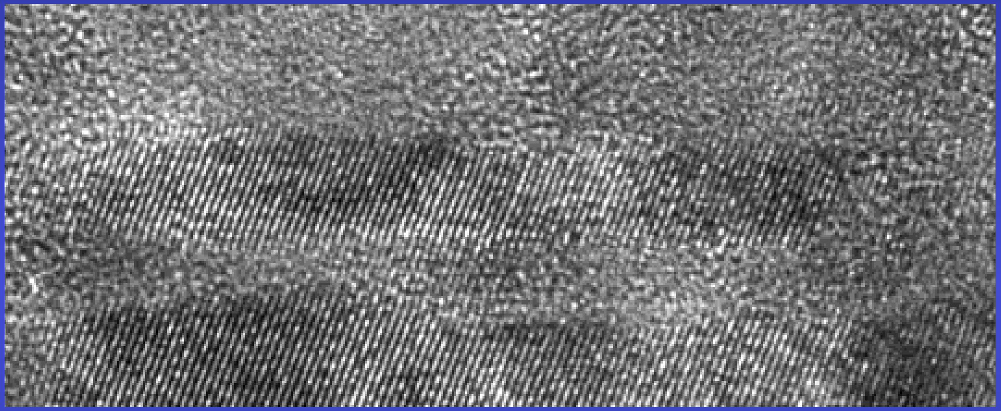
broad, anisotropic diffracted lines, textured samples

Refinement Results

Sample	d (cm)	a (Å)	RX thickness (nm)	Anisotropic sizes (Å)			Texture parameters			Reliability factors (%)			
				<111>	<220>	<311>	Maximum (m.r.d.)	minimum (m.r.d.)	Texture index F^2 (m.r.d^2)	RP_0	R_w	R_B	R_{exp}
A	4	5.4466 (3)	---	94	20	27	1.95	0.4	1.12	1.72	4.0	3.7	3.5
B	6	5.4439 (2)	711 (50)	101	20	22	1.39	0.79	1.01	0.71	4.9	4.3	4.2
C	7	5.4346 (4)	519 (60)	99	40	52	1.72	0.66	1.05	0.78	4.3	4.0	3.9
D	8	5.4461 (2)	1447 (66)	100	22	33	1.57	0.63	1.04	0.90	5.5	4.6	4.5
E	10	5.4462 (2)	1360 (80)	98	20	25	1.22	0.82	1.01	0.56	5.0	3.9	4.0
F	12	5.4452 (3)	1110 (57)	85	22	26	1.59	0.45	1.05	1.08	4.2	3.5	3.7
G	6	5.4387 (3)	1307 (50)	89	22	28	1.84	0.71	1.01	1.57	5.2	4.7	4.2
H	12	5.4434 (2)	1214 (18)	88	22	24	2.77	0.50	1.12	2.97	5.0	4.5	4.3

Mean anisotropic shape



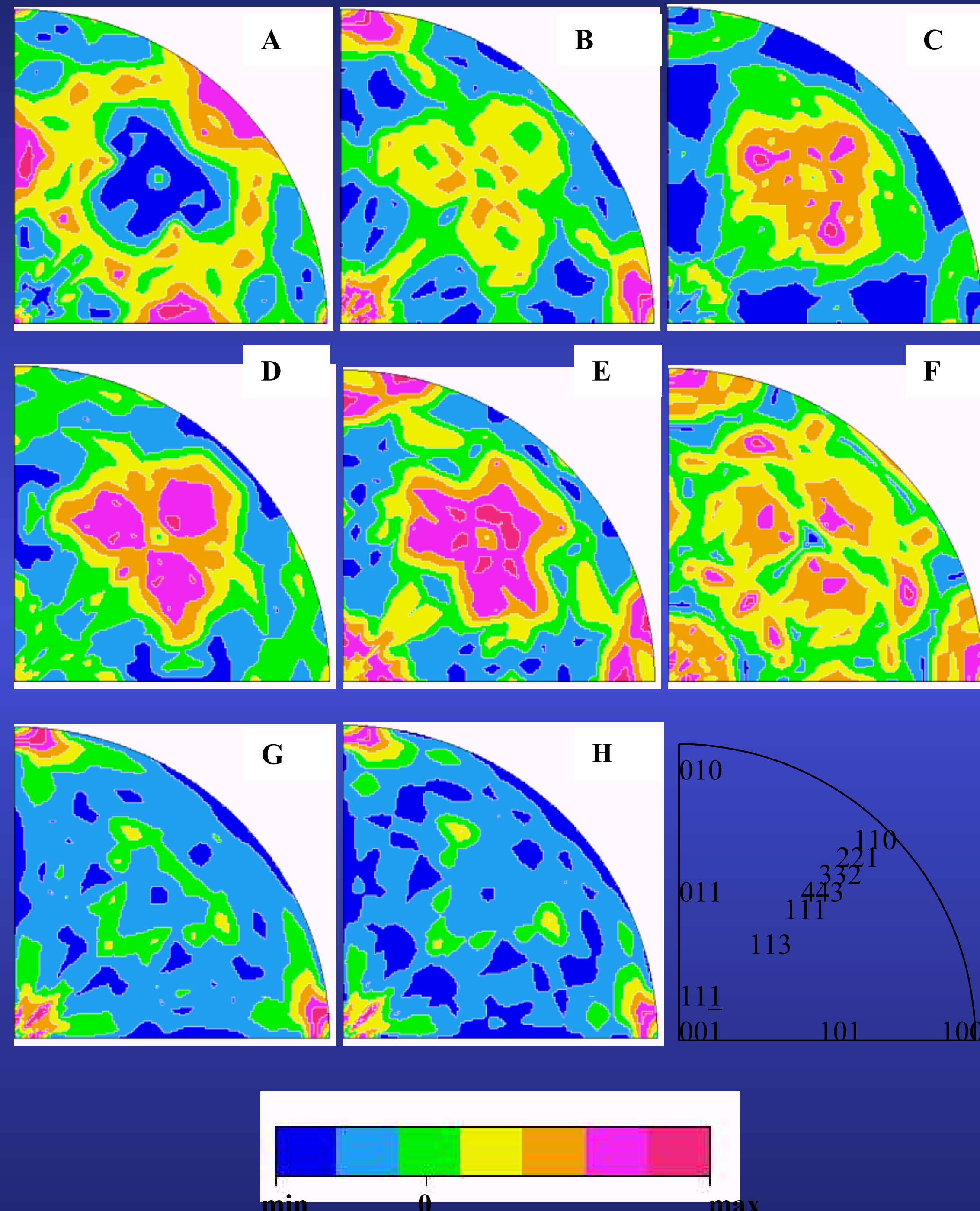


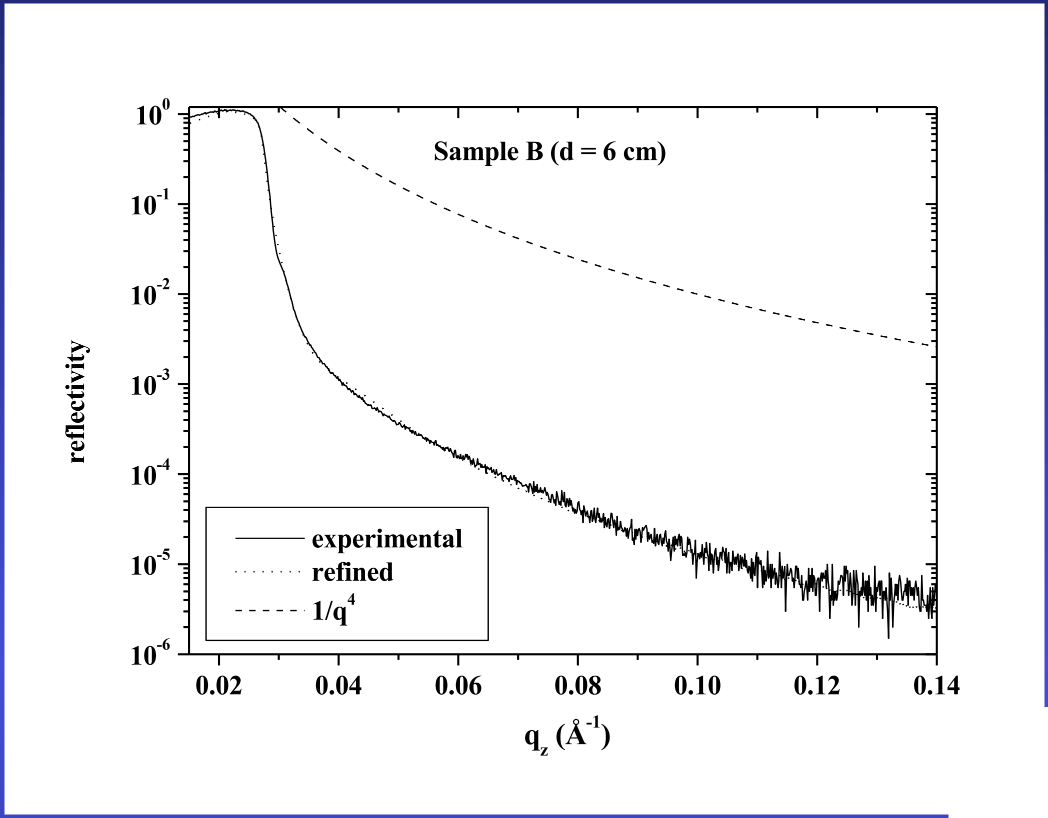
Schematic of the mean crystallite shape for Sample D represented in a cubic cell, as refined using the Popa approach and exhibiting a strong elongation along <111>, and TEM image

001 Inverse Pole Figures

a-SiO_2

(100)-Si



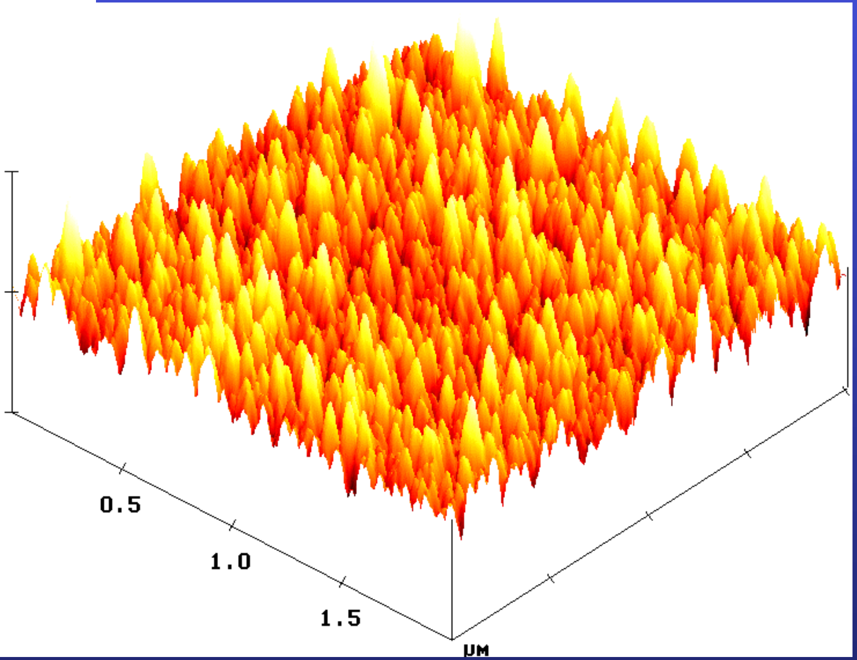


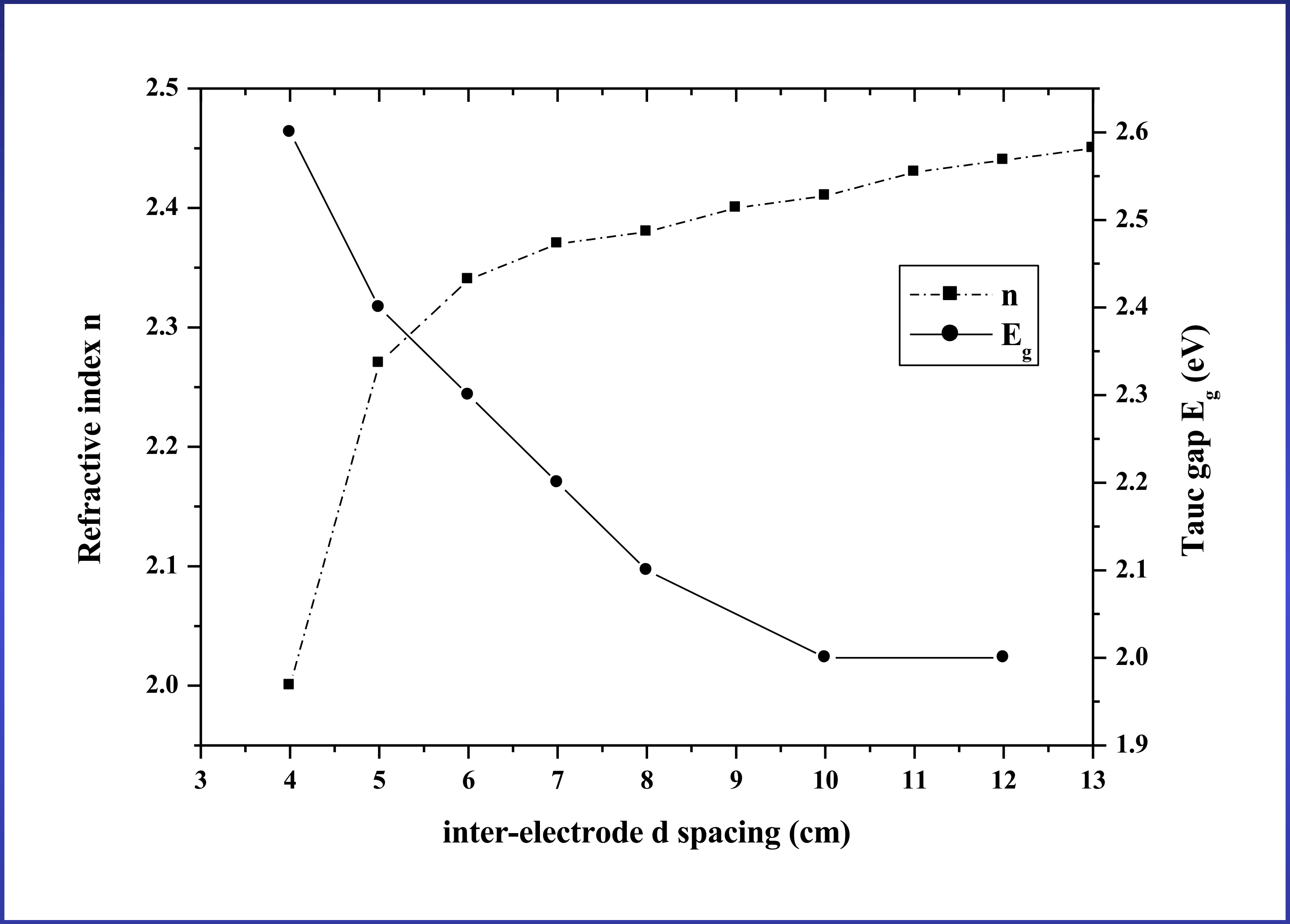
XRR:

Roughness governed

AFM:

homogeneous roughness



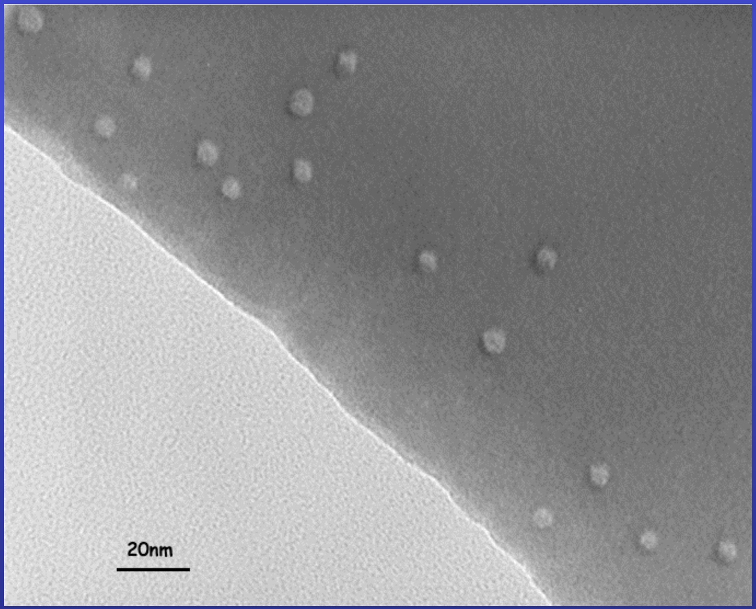


↬ Refractive index linked to film porosities:

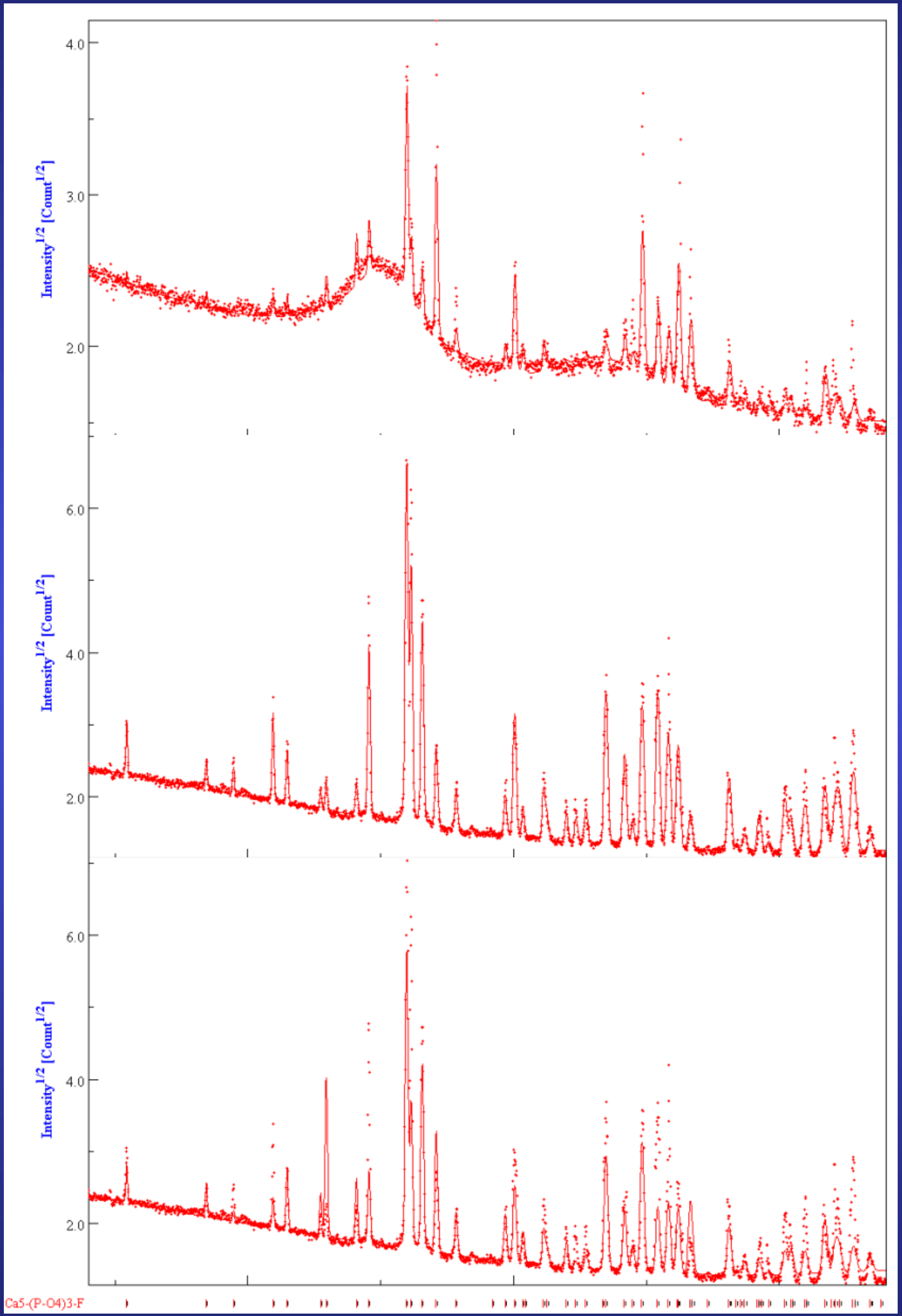
Larger target-sample distances: increased compacity due to lower nanopowder filling

Irradiated FluorApatite (FAp) ceramics

Self-recrystallisation under irradiation, depending on SiO_4 / PO_4 ratio (FAp / Nd-Britholite) and on irradiating species



TEM of FAp irradiated with 70 MeV, 10^{12} Kr cm^{-2} ions



texture corrected,

10^{13} Kr cm^{-2}

Virgin, with texture correction

Virgin, no texture correction

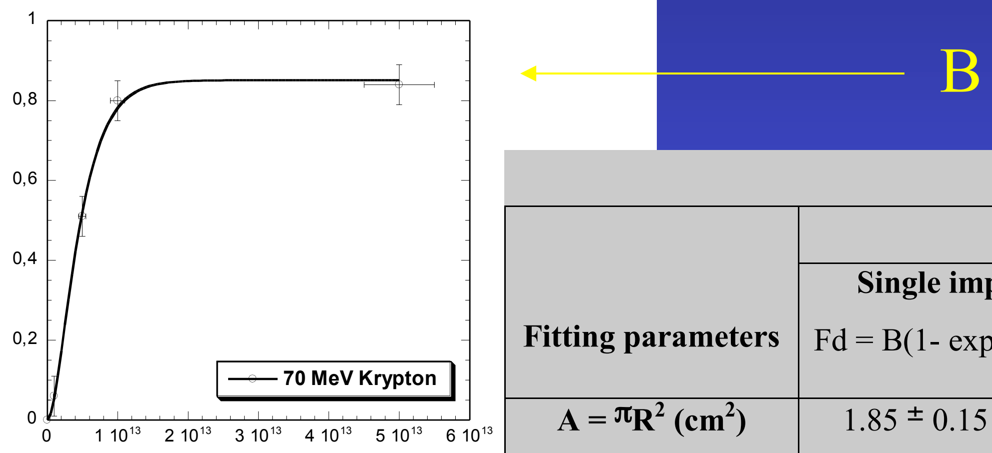
Fluence (ions.cm^{-2})	Vc/V (%)	A (Å)	c (Å)	<t> (nm)	$\Delta a/a_0$ (%)	$\Delta c/c_0$ (%)	R_w (%)	R_B (%)
0	100	9.3365(3)	6,8560(5)	294(22)	-	-	14.6	9.1
Kr								
10^{11}	100	-	-	-	-	-		
10^{12}	100	-	-	-	-	-		
5.10^{12}	49(1)	9.3775(9)	6.8912(8)	294(20)	0.44	0.53	24	15
10^{13}	20(1)	9.4236(5)	6.9105(5)	291(20)	0.94	0.82	9.9	6
5.10^{13}	14(1)	9.3160(4)	6.8402(5)	294(22)	-0.21	-0.22	10.5	5.9
I								
10^{11}	-	-	-	-	-	-		
5.10^{11}	86(2)	9.3603(3)	6.8790(5)	90(10)	0.26	0.35	23.9	15.1
10^{12}	-	-	-	-	-	-		
3.10^{12}	47(2)	9.3645(3)	6.8840(5)	91(6)	0.30	0.42	13.3	9
5.10^{12}	29.2(5)	9.3765(5)	6.8881(6)	77(11)	0.44	0.48	10.4	7.3
10^{13}	13.2(2)	9.3719(4)	6.8857(6)	82(9)	0.38	0.45	6.7	4.9

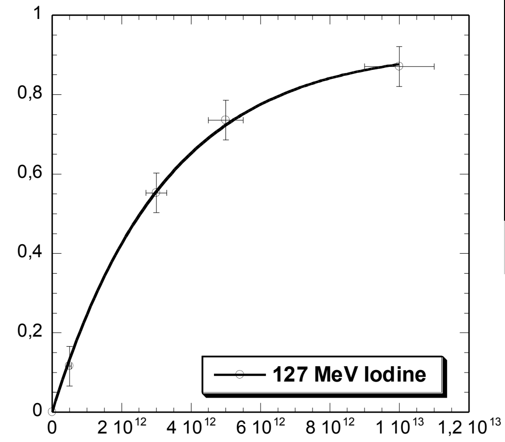
Single impact model associated to crystal size reduction

Cell parameters and volume increase, then relax

Amorphisation / recrystallisation competition: single or double impact

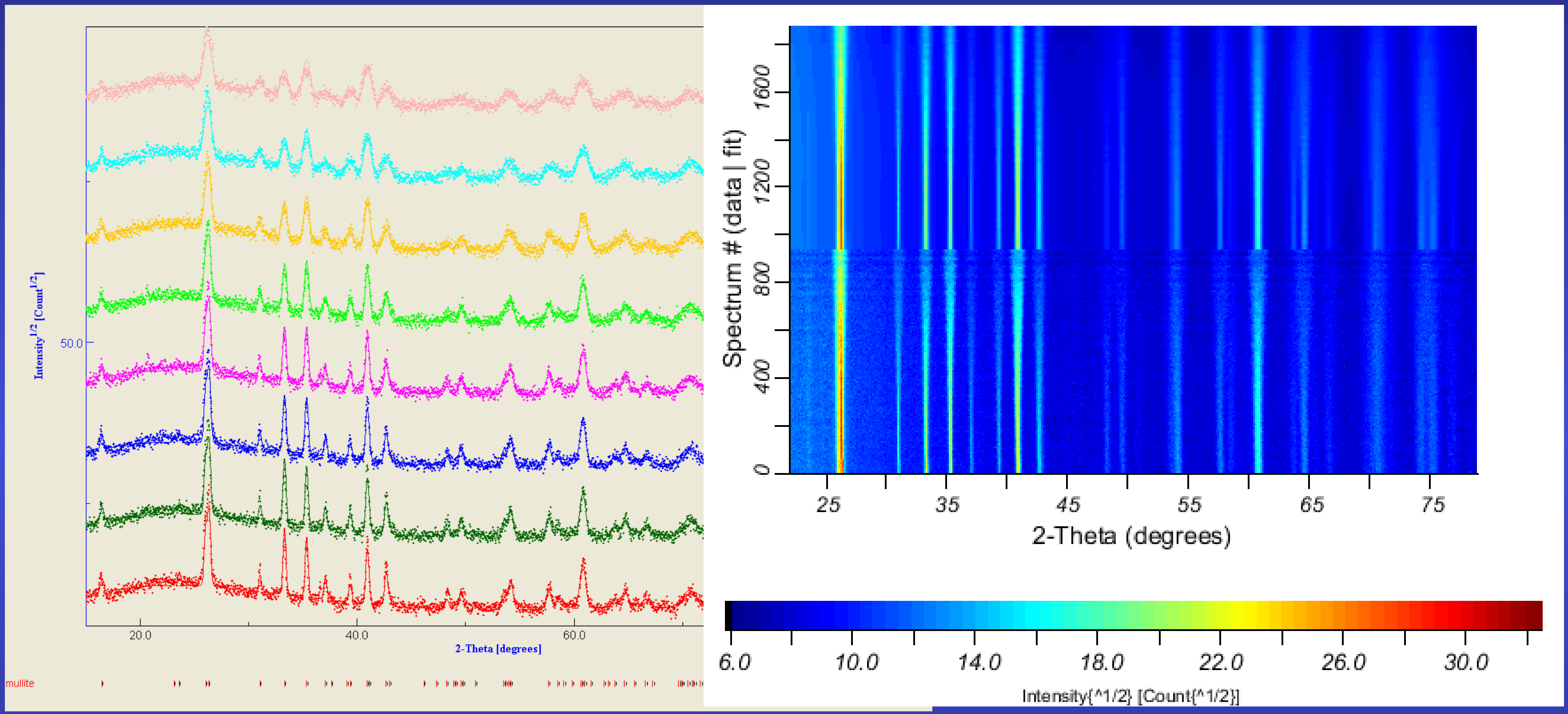
Amorphous/crystalline volume fraction (damaged fraction Fd = Va / V) as determined by x-ray diffraction





	Krypton		Iodine
Fitting parameters	**Single impact** Fd = B(1- exp(-Aϕt))	**Double impact** Fd = B(1 – (1+ Aϕt) exp(-Aϕt))	**Single impact** Fd = B(1- exp(-Aϕt))
A = πR^2 (cm^2)	1.85 ± 0.15 10^{-13}	4.1 ± 0.15 10^{-13}	3.3 ± 0.15 10^{-13}
Radius R (nm)	2.4 ± 0.2	3.6	3.2
B (Max.damage rate)	0.87	0.85 ± 0.2	0.92 ± 0.2
$\chi 2$	0.013	0.0006	0.0004

Mullite-silica composites

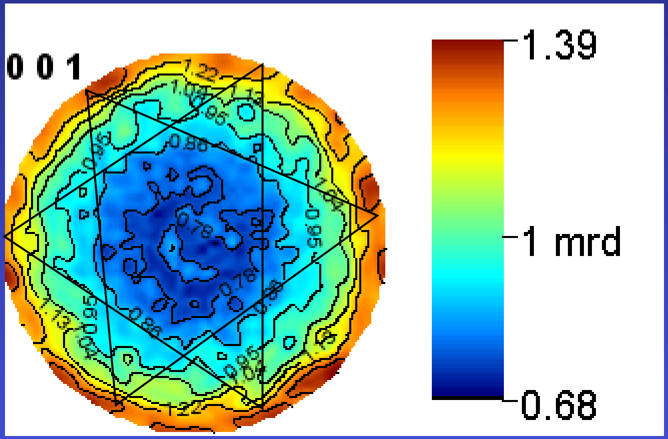


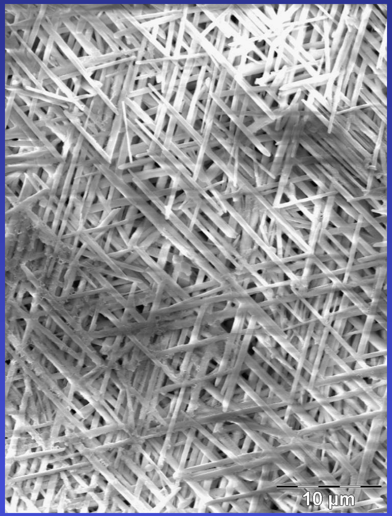
ODF: R_w = 4.87 %, R_B = 4.01 %

Rietveld: R_w = 12.90 %, GoF = 1.77

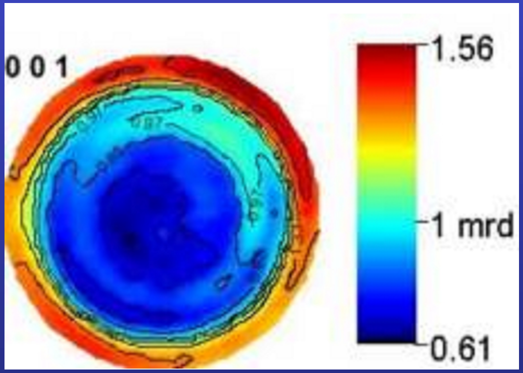
Mullite: a = 7.56486(5) Å; b = 7.71048(5) Å; c = 2.89059(1)Å

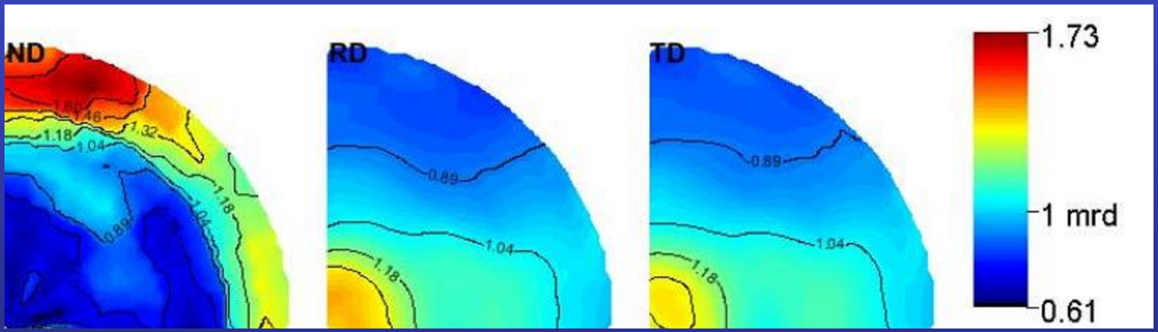
Uniaxially pressed

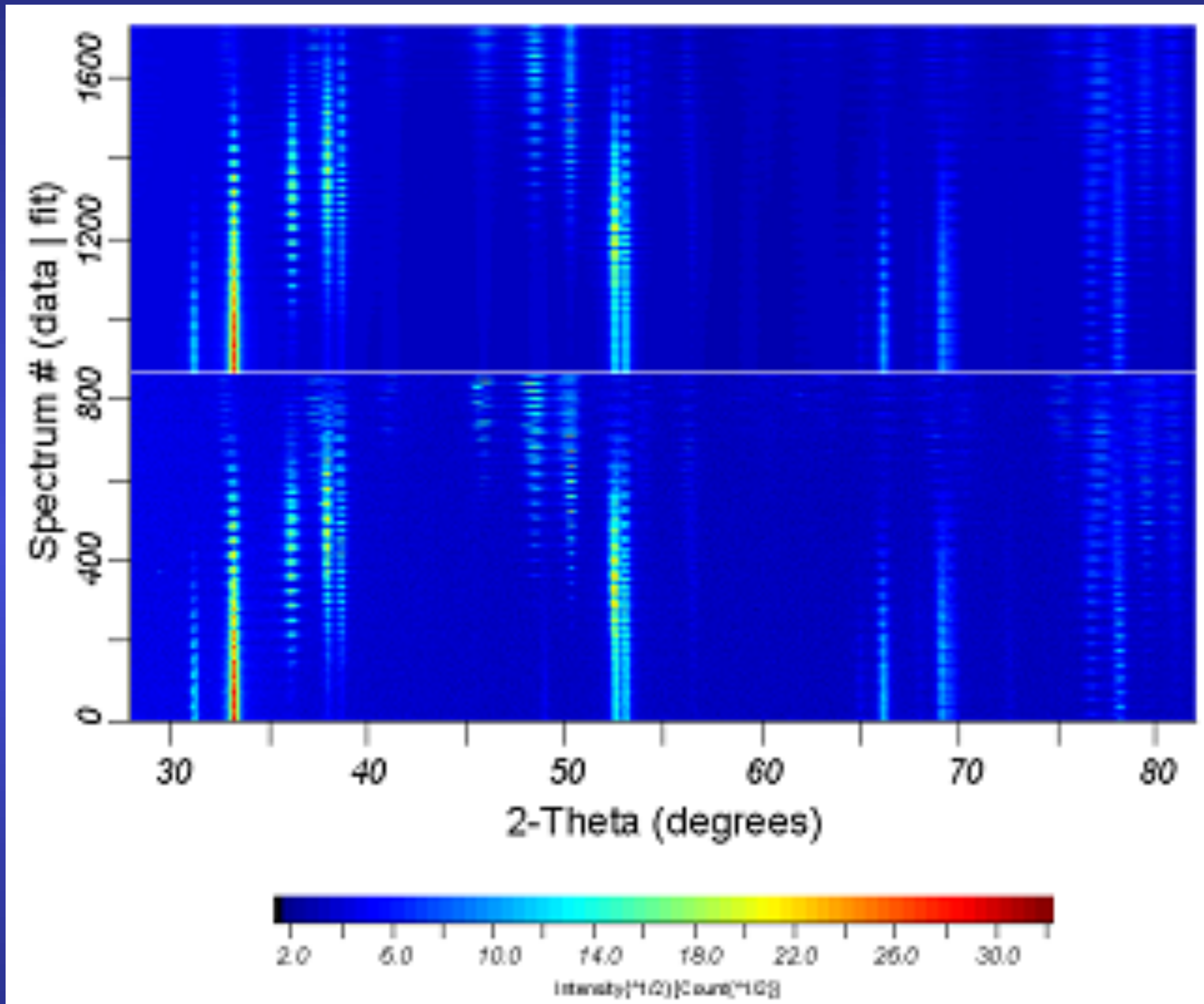




Centrifugated





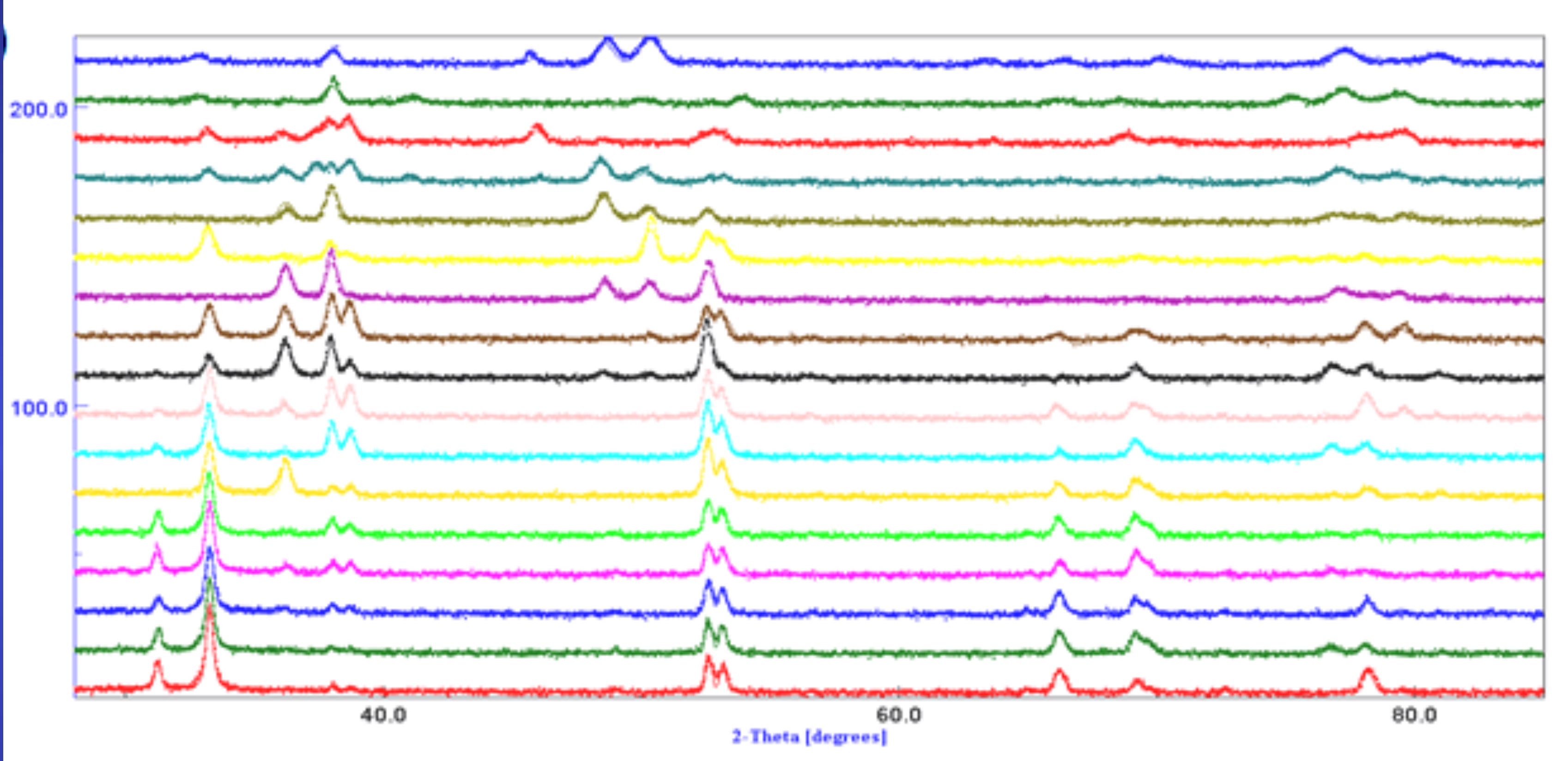


refined

experiments

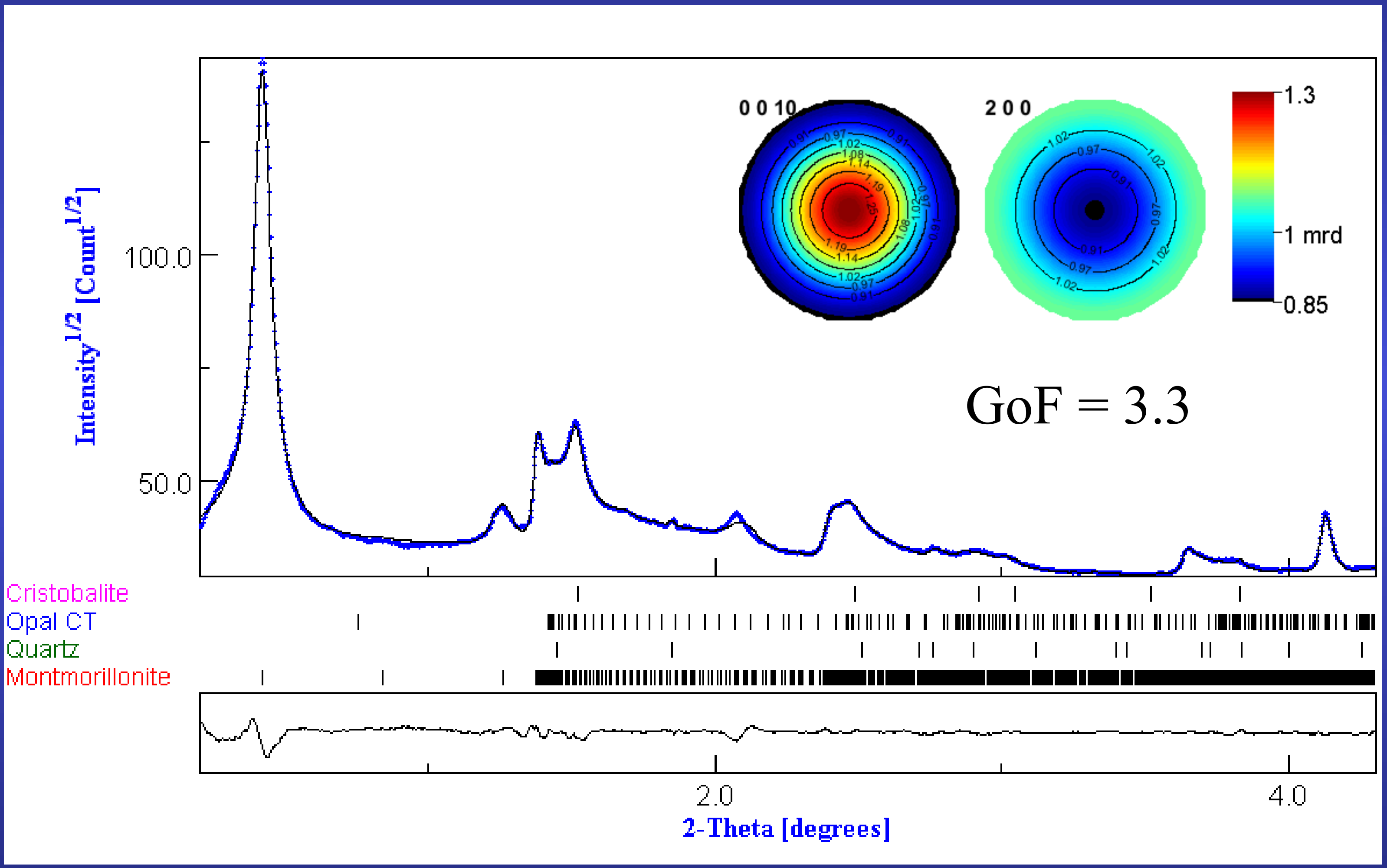
GoF:1,72
Rw: 28,0%
Rexp:21,3%

for all (χ,φ) sample orientations



IRC layer of *Charonia lampas lampas* for selected (χ,φ) sample orientations

Turbostratic phyllosilicate aggregates



V%
1.45(2)
6.6(1)
0.19(1)
91.8(3)

Specular reflectivity: **q**=(0,0,z)

- Fresnel:

$$R(\mathbf{q}) = \left| \frac{q_z - \sqrt{q_z^2 - q_c^2 + \frac{32 i \pi^2 \beta}{\lambda^2}}}{q_z + \sqrt{q_z^2 - q_c^2 + \frac{32 i \pi^2 \beta}{\lambda^2}}} \right|^2 \delta q_x \delta q$$

- matrix:

$$R^{flat} = \frac{r_{0,1}^2 + r_{1,2}^2 + 2 r_{0,1} r_{1,2} \cos 2 k_{Z,1} h}{1 + r_{0,1}^2 r_{1,2}^2 + 2 r_{0,1} r_{1,2} \cos 2 k_{Z,1} h}$$

- Born approximation:
  Electron Density Profile

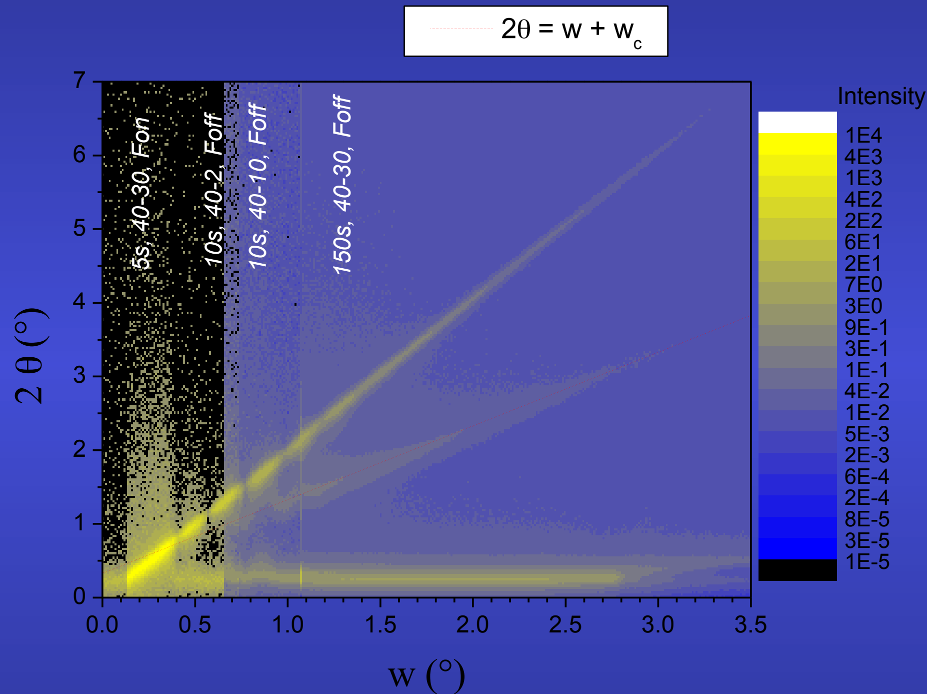
$$R(q_z) = r.r^* = R_F(q_z) \left| \frac{1}{\rho_s} \int_{-\infty}^{+\infty} \frac{d\rho(z)}{dz} e^{i q_z z} dz \right|^2$$

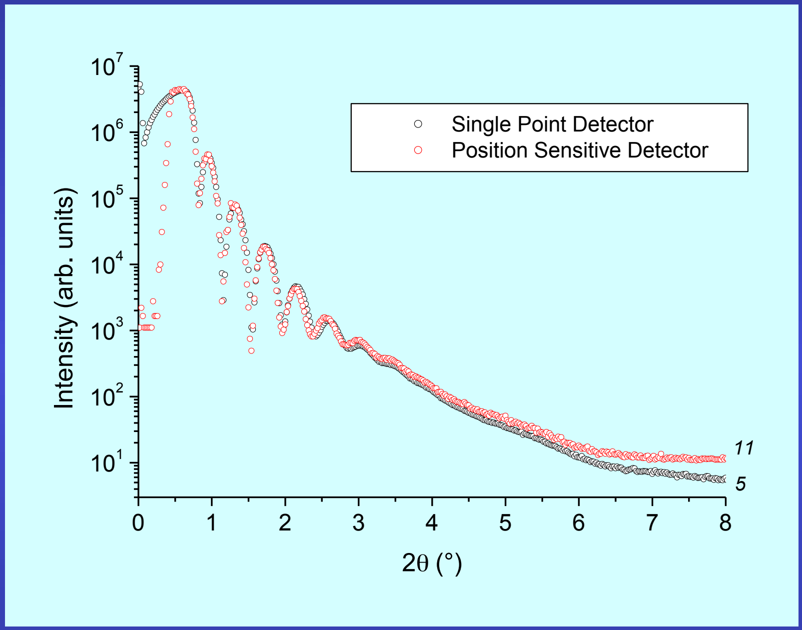
- Roughness:

$$R^{rough}(q_z) = R(q_z) \exp(-q_{z,0} q_{z,1} \sigma^2) \quad \text{Low-angles (reflectivity)}$$

$$S_R = 1 - p \exp(-q) + \mathrm{p} \exp\left(\frac{\mathrm{-q}}{\sin \theta} \right) \quad \text{high-angle (Suortti)}$$

CPS scans

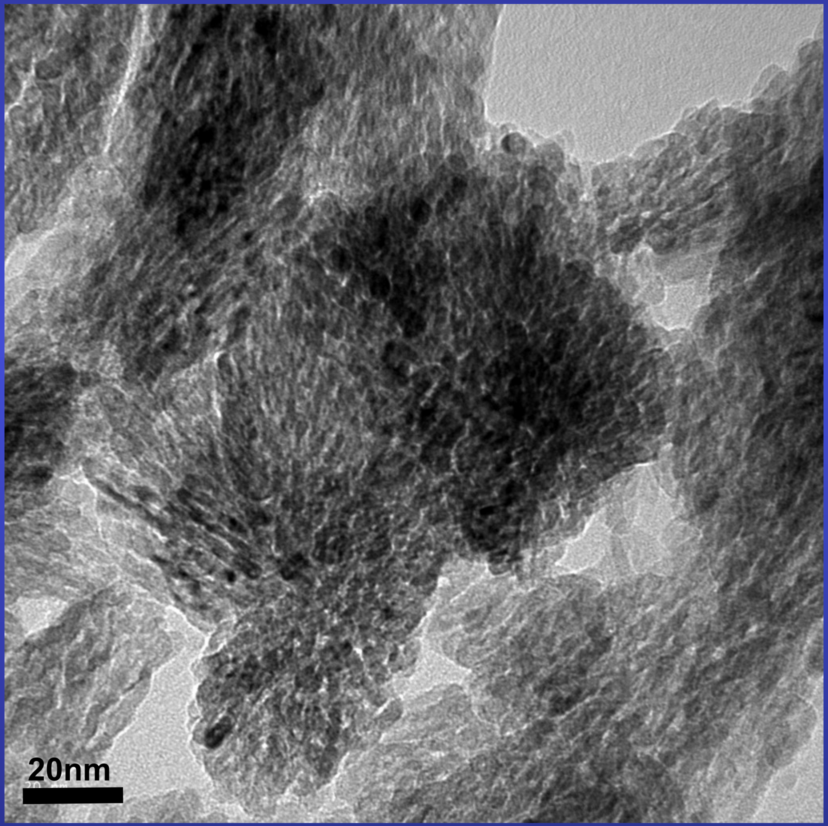


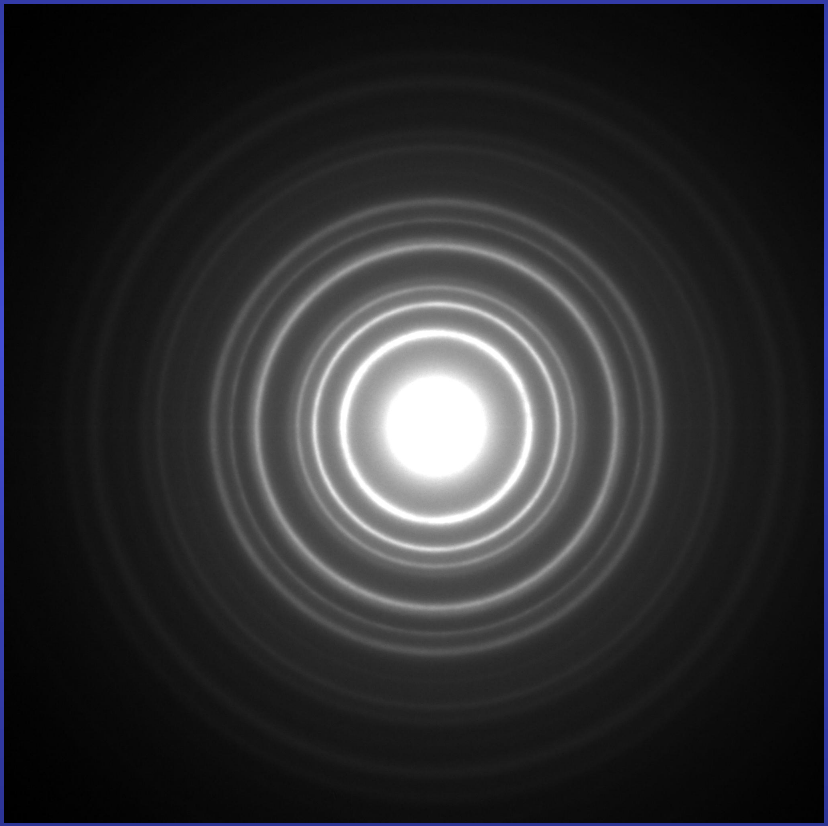


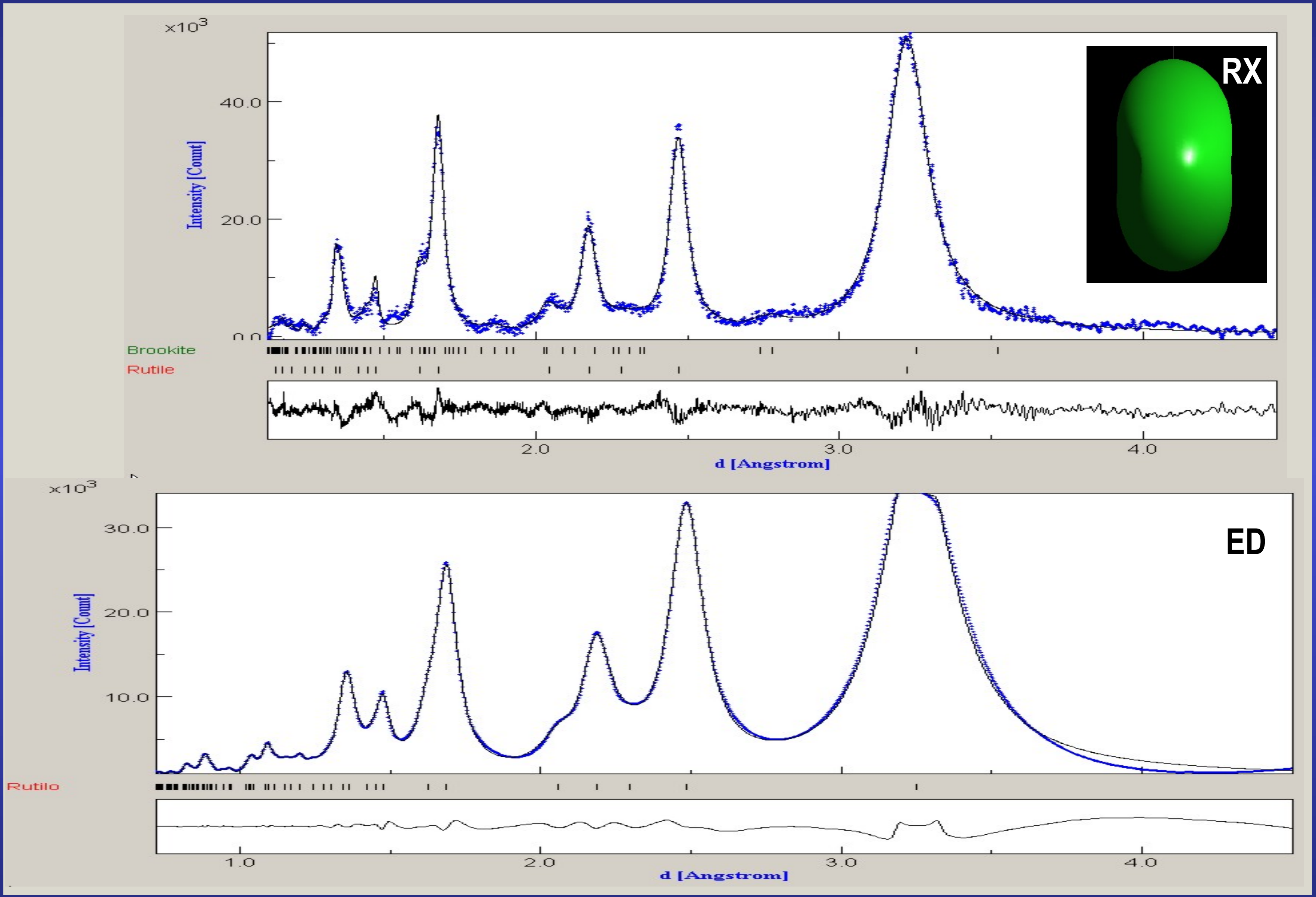
Useful for having bot specular and off-specular signals in one scan

Microstructure of nanocrystalline materials: TiO_2 rutile [(1)]

► *quantitative analysis of electron diffraction ring pattern ?*

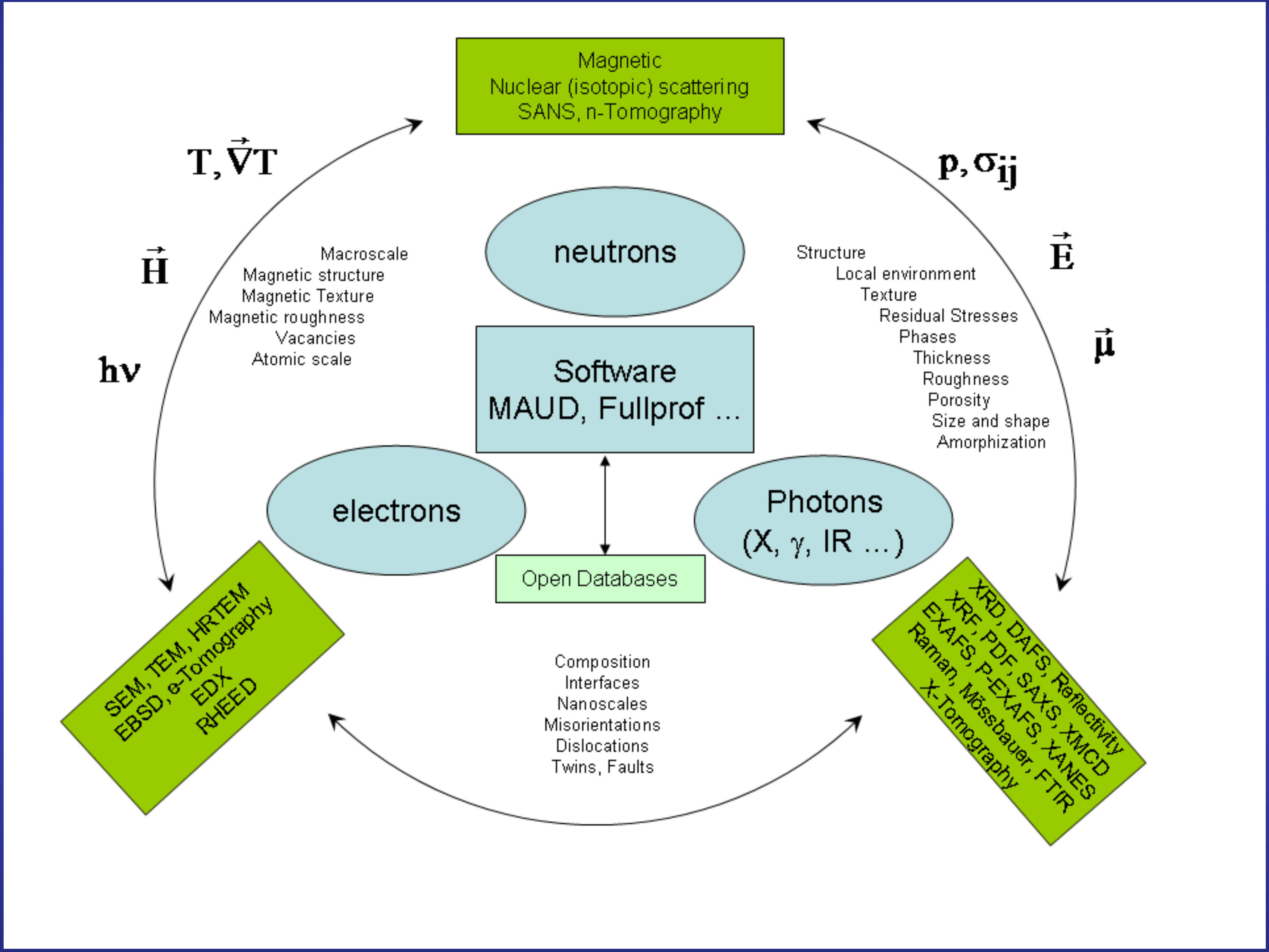






x10³
40.0
20.0
0.0
Intensity [Count]
RX
Brookite
Rutile
2.0
3.0
4.0
d [Angstrom]
x10³
30.0
20.0
10.0
Intensity [Count]
ED
Rutilo
1.0
2.0
3.0
4.0
d [Angstrom]

Why not more ?



Magnetic
Nuclear (isotopic) scattering
SANS, n-Tomography
$T, \vec{\nabla}T$
p, σ_{ij}
$\vec{H}$
$\vec{E}$
$h\nu$
$\vec{\mu}$
neutrons
Macroscale
Magnetic structure
Magnetic Texture
Magnetic roughness
Vacancies
Atomic scale
Structure
Local environment
Texture
Residual Stresses
Phases
Thickness
Roughness
Porosity
Size and shape
Amorphization
Software
MAUD, Fullprof …
electrons
Photons
(X, γ, IR …)
Open Databases
SEM, TEM, HRTEM
EBSD, e-Tomography
EDX
RHEED
XRD, DAFS, Reflectivity
XRF, PDF, SAXS, XMCD
EXAFS, P-EXAFS, XANES
Raman, Mössbauer, FTIR
X-Tomography
Composition
Interfaces
Nanoscales
Misorientations
Dislocations
Twins, Faults

Conclusions

a) A lot of dilemma are only apparent

b) Texture helps to resolve them: good for real samples

c) Anisotropy favours higher resolutions

d) Combined analysis may be a solution, unless you can destroy your sample or are not interested in macroscopic anisotropy ...

e) If you think you can destroy it, perhaps think twice

f) more information is always needed: why not more?

g) Combined Analysis (D. Chateigner Ed), Wiley-ISTE 2010