Combined Analysis for the characterisation of texture, microstructure and stresses of nanocrystalline thin layers

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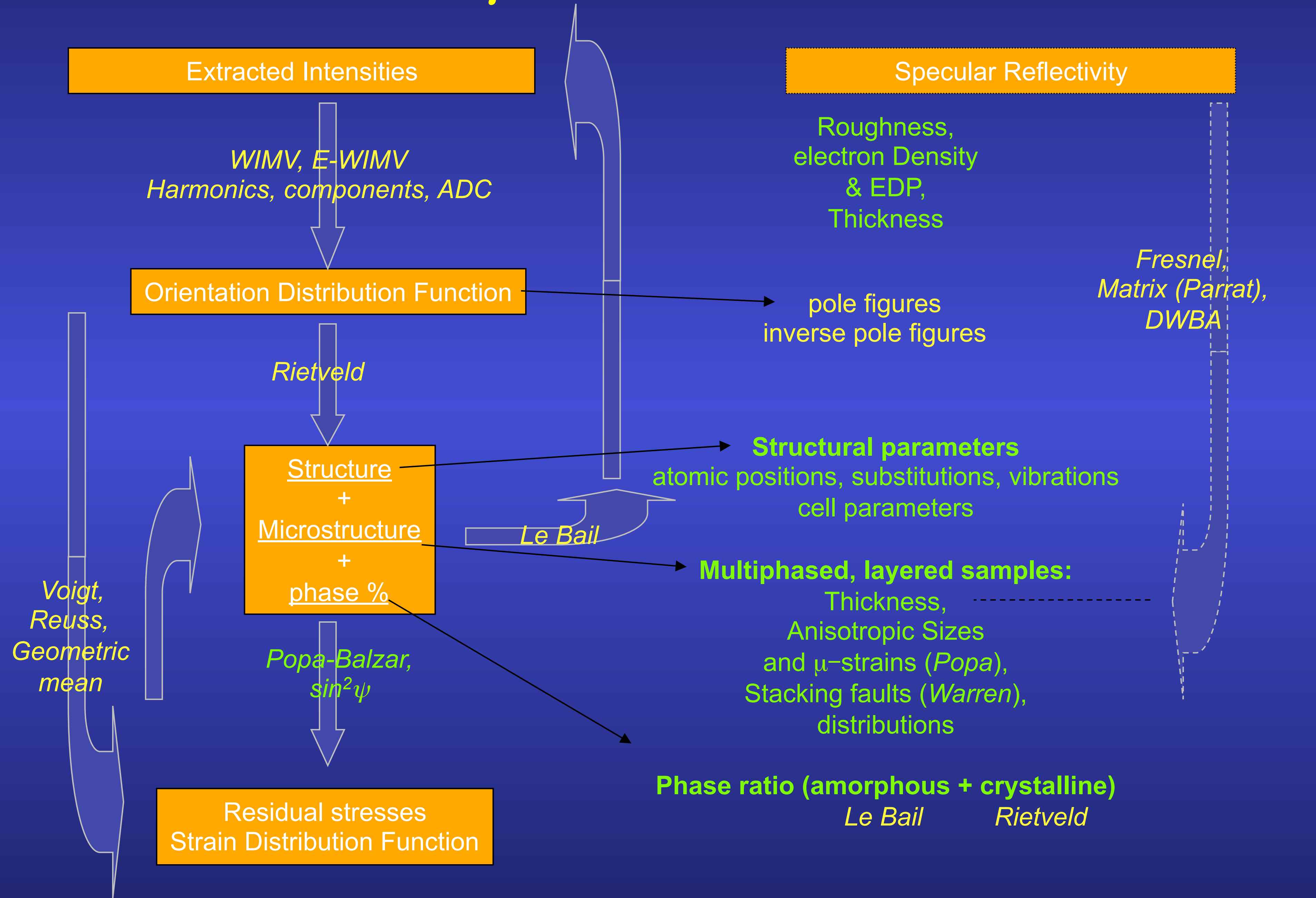
ZnSe films

nano-Si films

AlN/Pt/Ni(Co) films

Irradiated FAp ceramics

Implemented codes



Rietveld

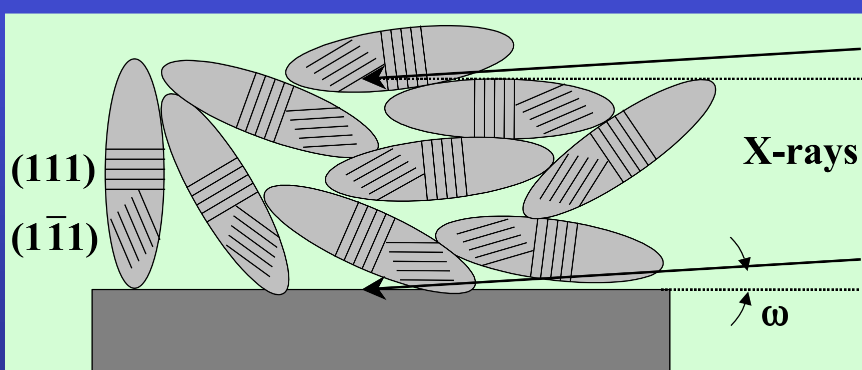
$$I_i^{calc}(\chi,\phi) = \sum_{n=1}^{Nphases} S_n \sum_k L_k \left|F_{k;n}\right|^2 S\left(2\theta_i - 2\theta_{k;n}\right) P_{k;n}(\chi,\phi) A + bkg_i$$

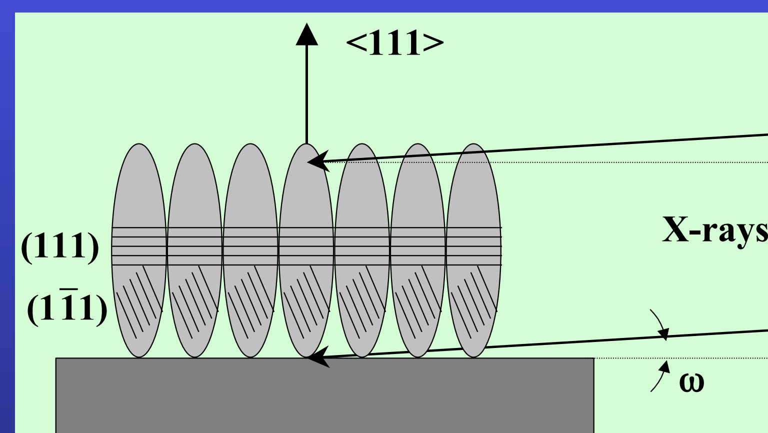
Texture

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

- ODF solved using E-WIMV, Standard functions, Harmonics, ADC or max entropy

Anisotropic sizes and microstrains



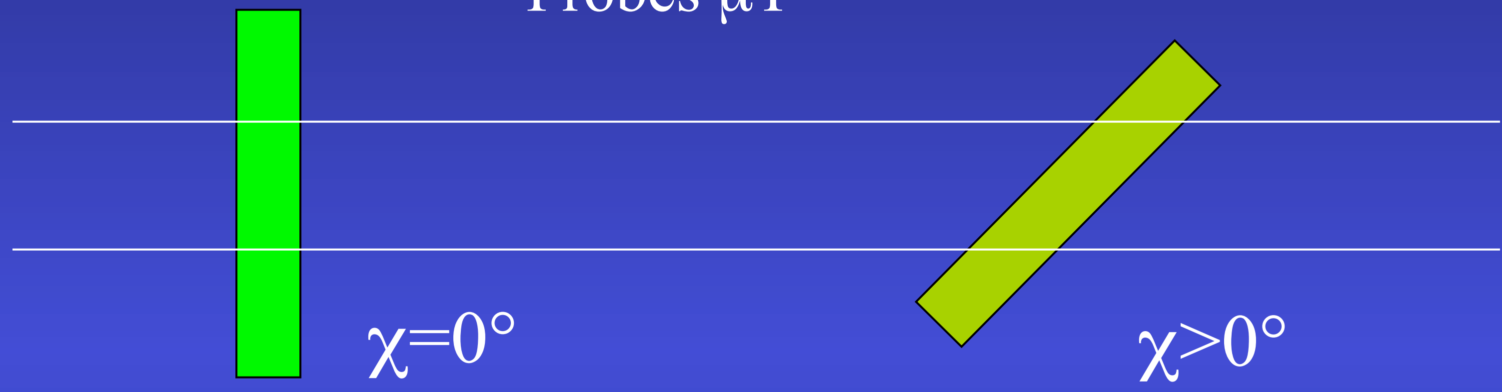


- Texture helps the "real" mean shape determination
- Determination by peak deconvolution + Popa formalism

Layering

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

Probes μT



Strain-Stress

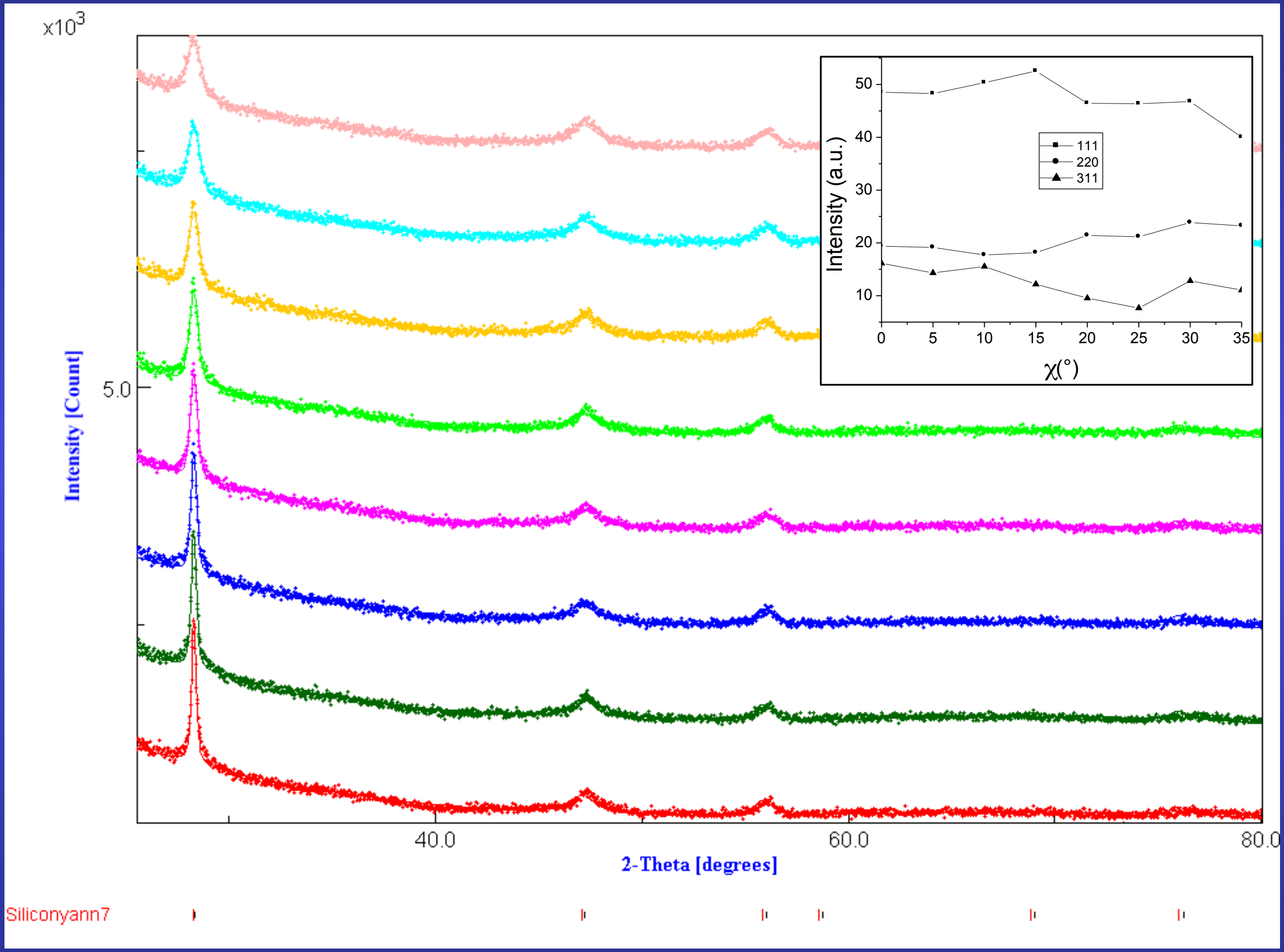
- Using the ODF and geometric mean approach
- Fitting the macrostress tensor

Si nanocrystalline thin films

Deposition: reactive magnetron sputtering (H_2 / Ar)
Low temperature: 200°C
Substrates: amorphous SiO_2 (a-SiO_2) and (100)-Si single-crystals
Varying Target-substrate distance (d)

Aim: quantum confinement, photoluminescence properties

Typical refinement



χ = 35°

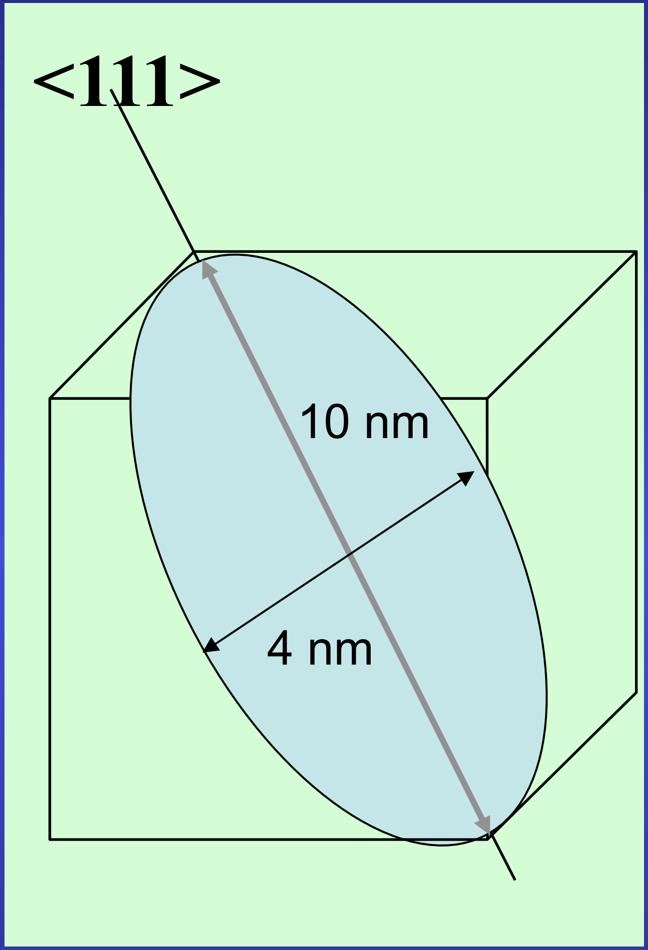
χ = 0°

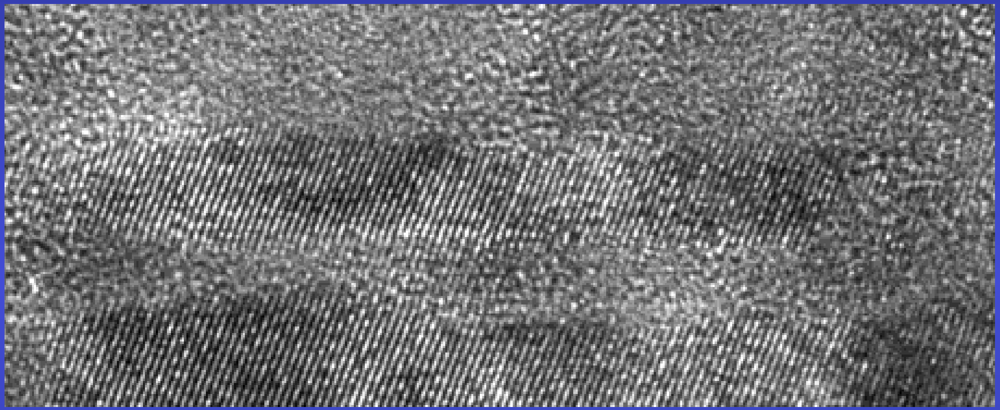
broad, anisotropic diffracted lines, textured samples

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



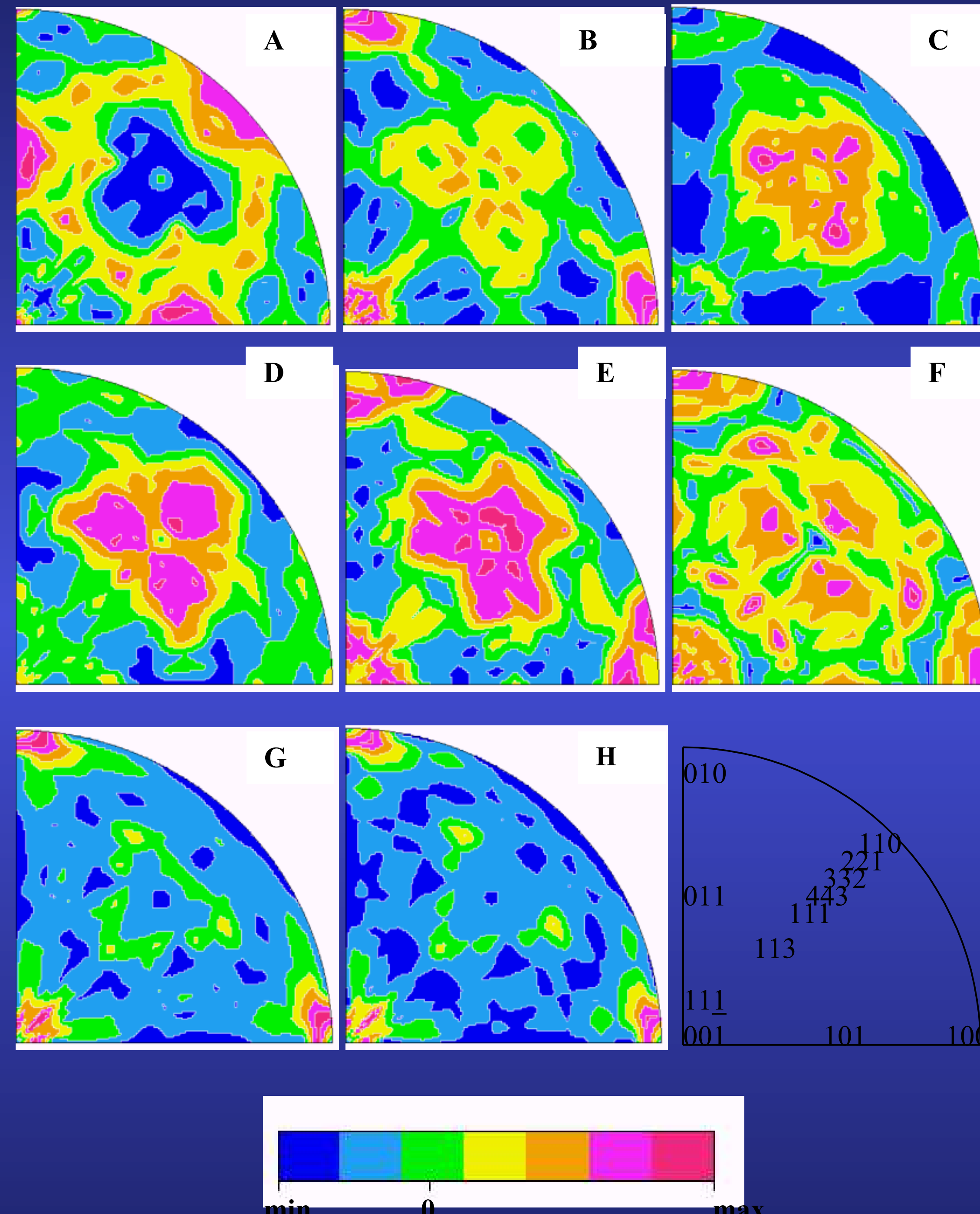


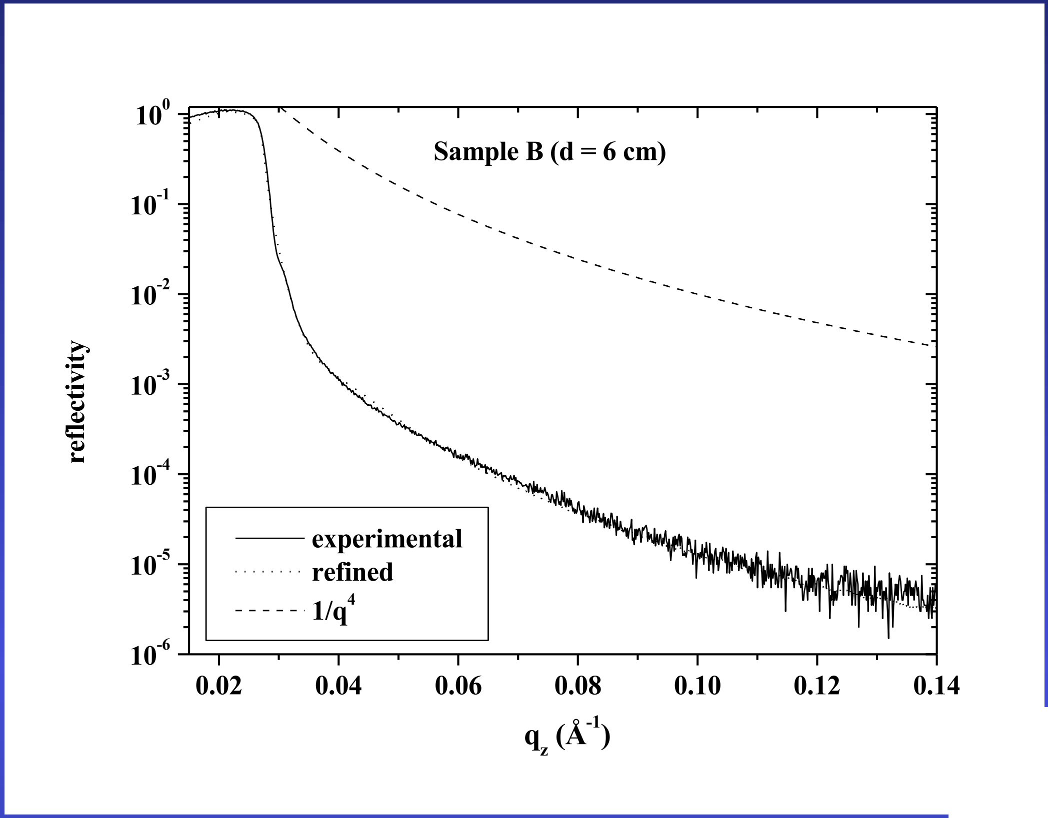
Schematic of the mean crystallite shape for Sample D represented in a cubic cell, as refined using the Popa approach and exhibiting a strong elongation along <111>, and TEM image

001 Inverse Pole Figures

a-SiO_2

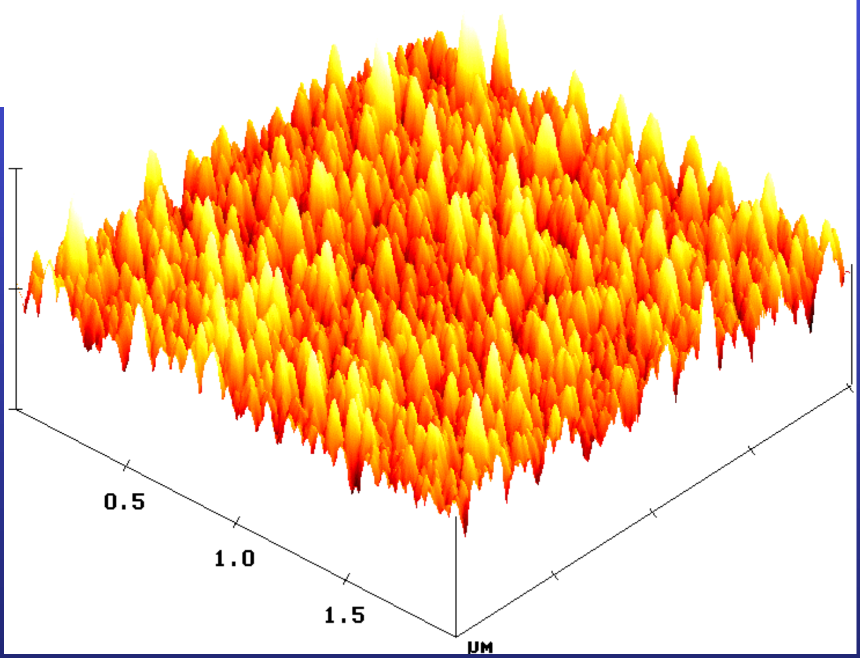
(100)-Si





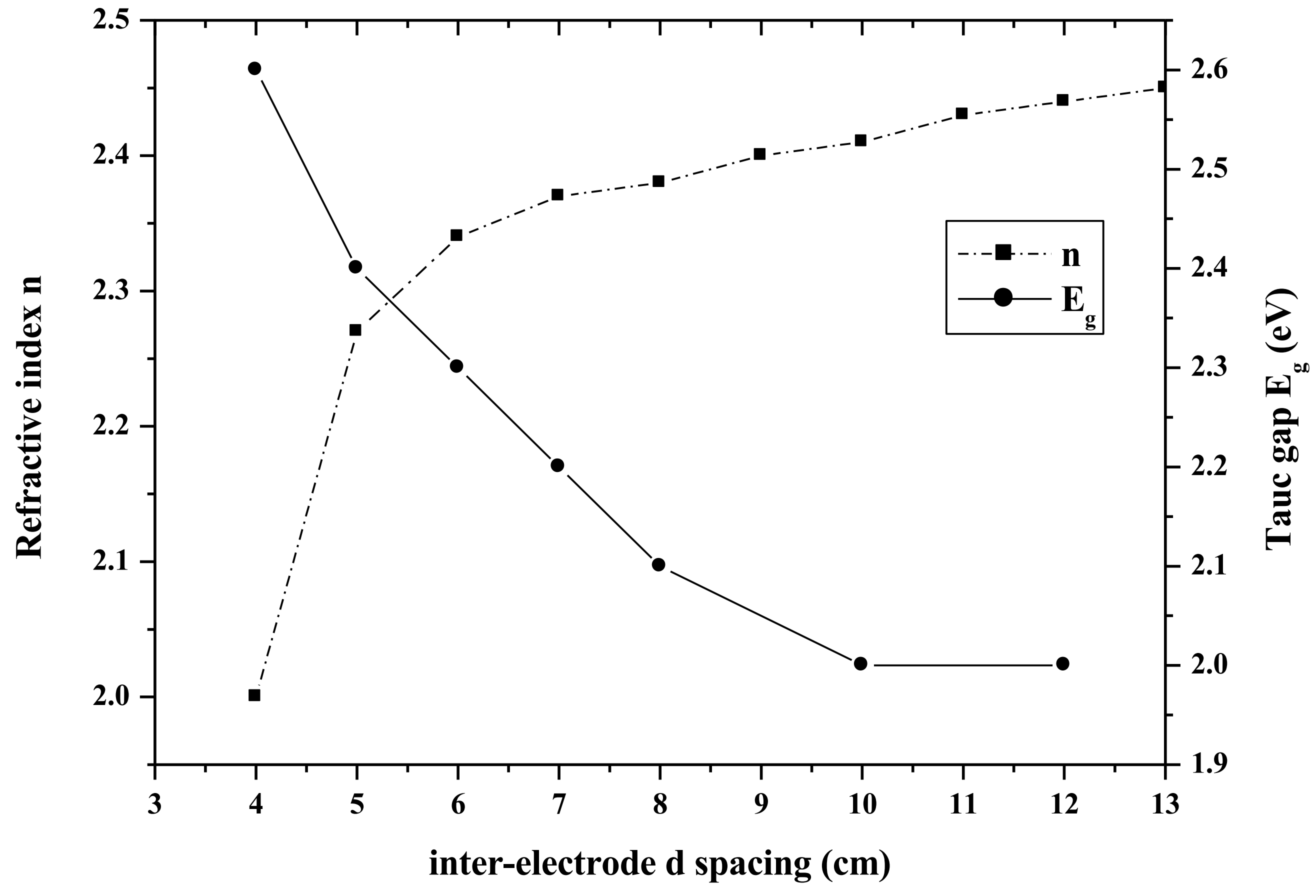
XRR:

Roughness governed



AFM:

homogeneous roughness

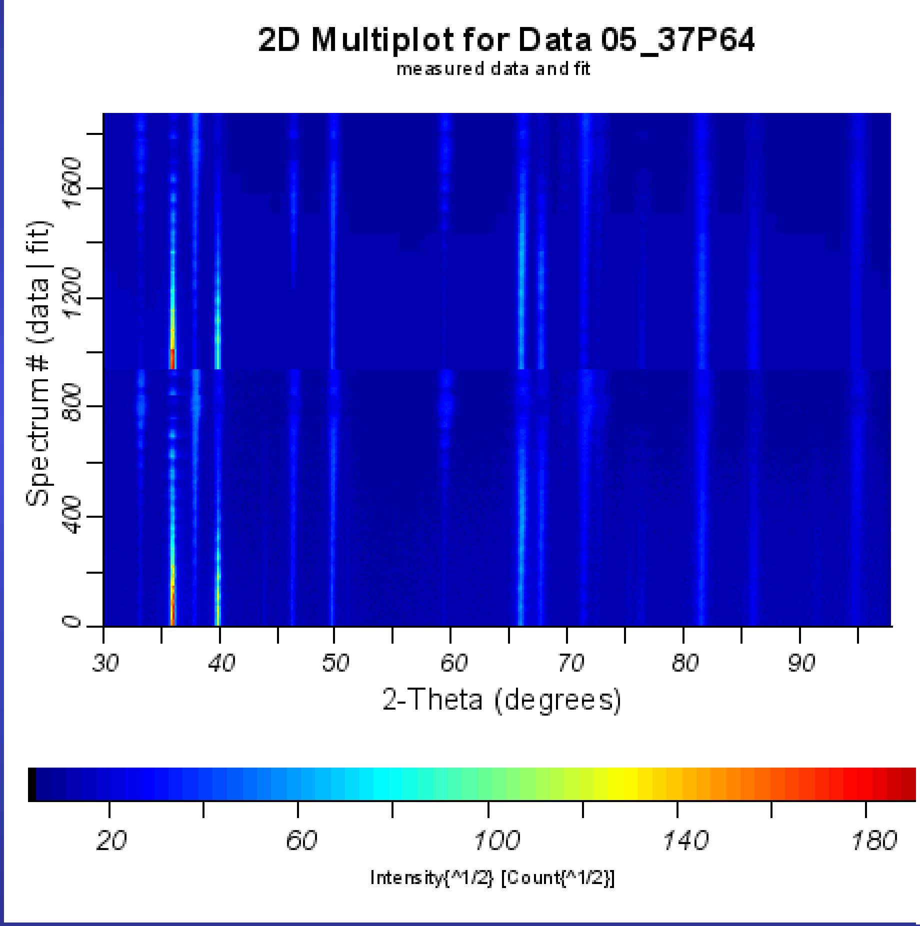


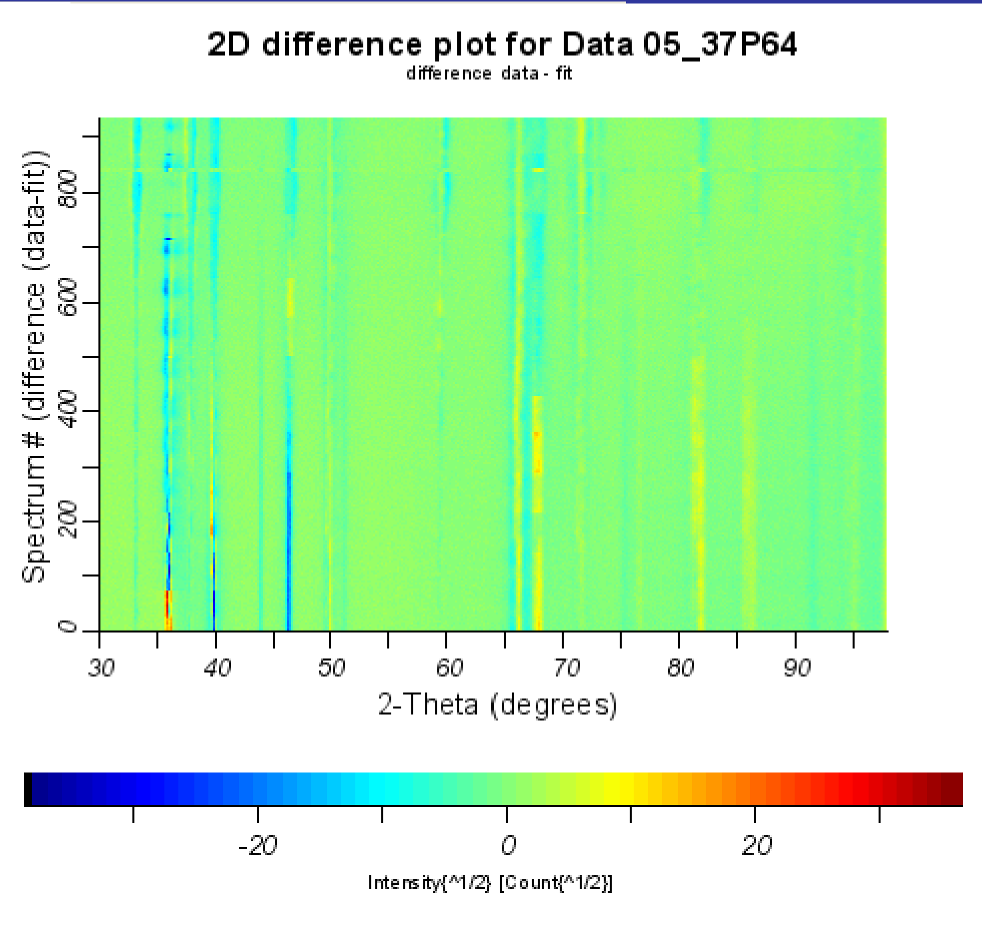
↳ Refractive index linked to film porosities:

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

AlN/Pt/TiO$_x$/Al$_2$O$_3$/Ni-Co-Cr-Al

E. Derniaux, PhD





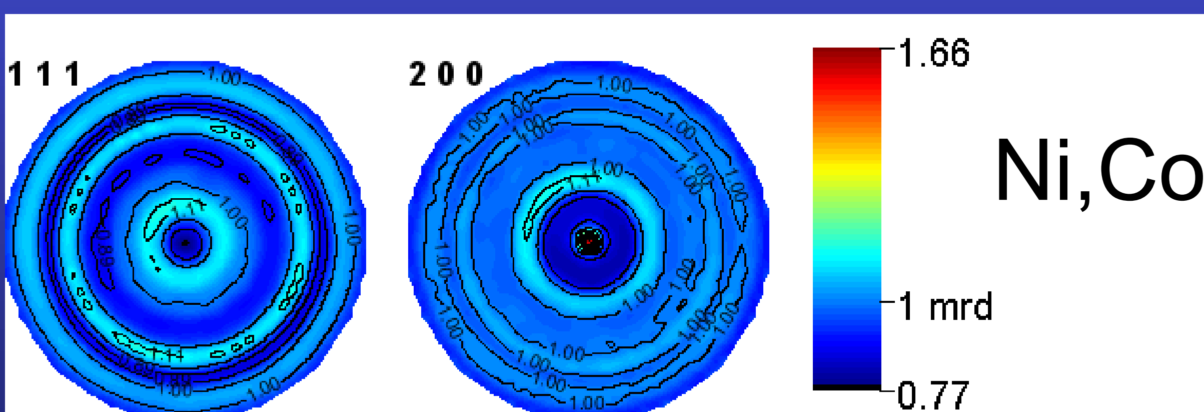
Rw (%) = 24.120445
Rexp (%) = 5.8517213

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

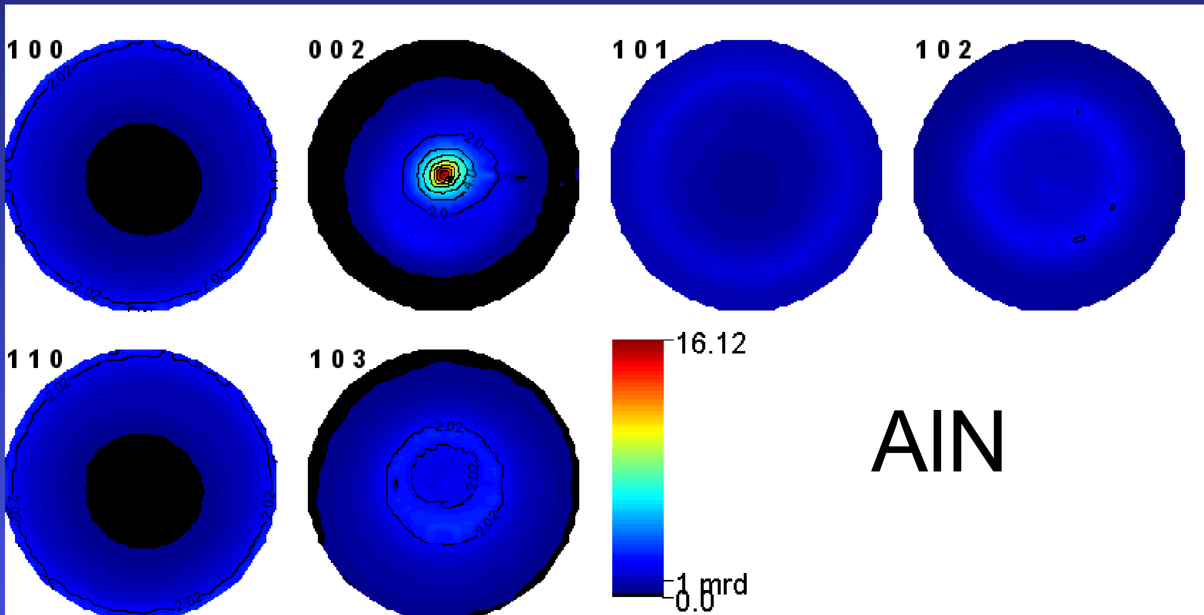
(χ,φ) randomly selected diagrams

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)

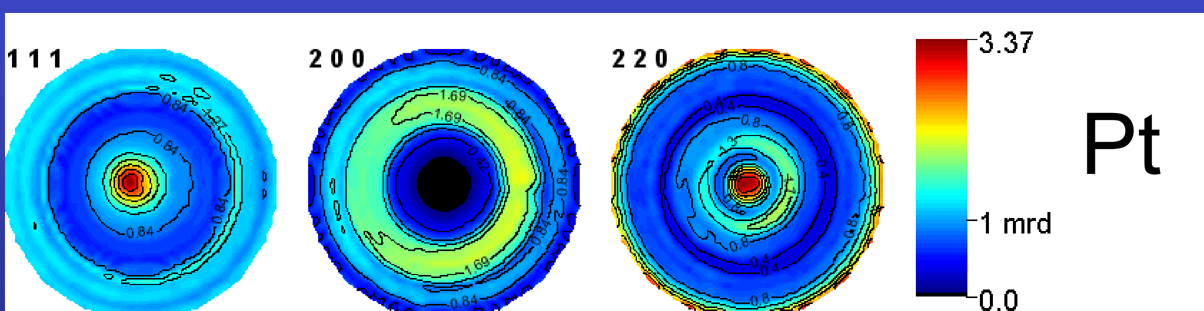


a = 3.569377(5) Å
<t> = 7600(1900) Å
<ε> = 0.00236(3)
σ_{11} = -328(8) MPa
σ_{22} = -411(9) MPa



Rw (%) = 4.1

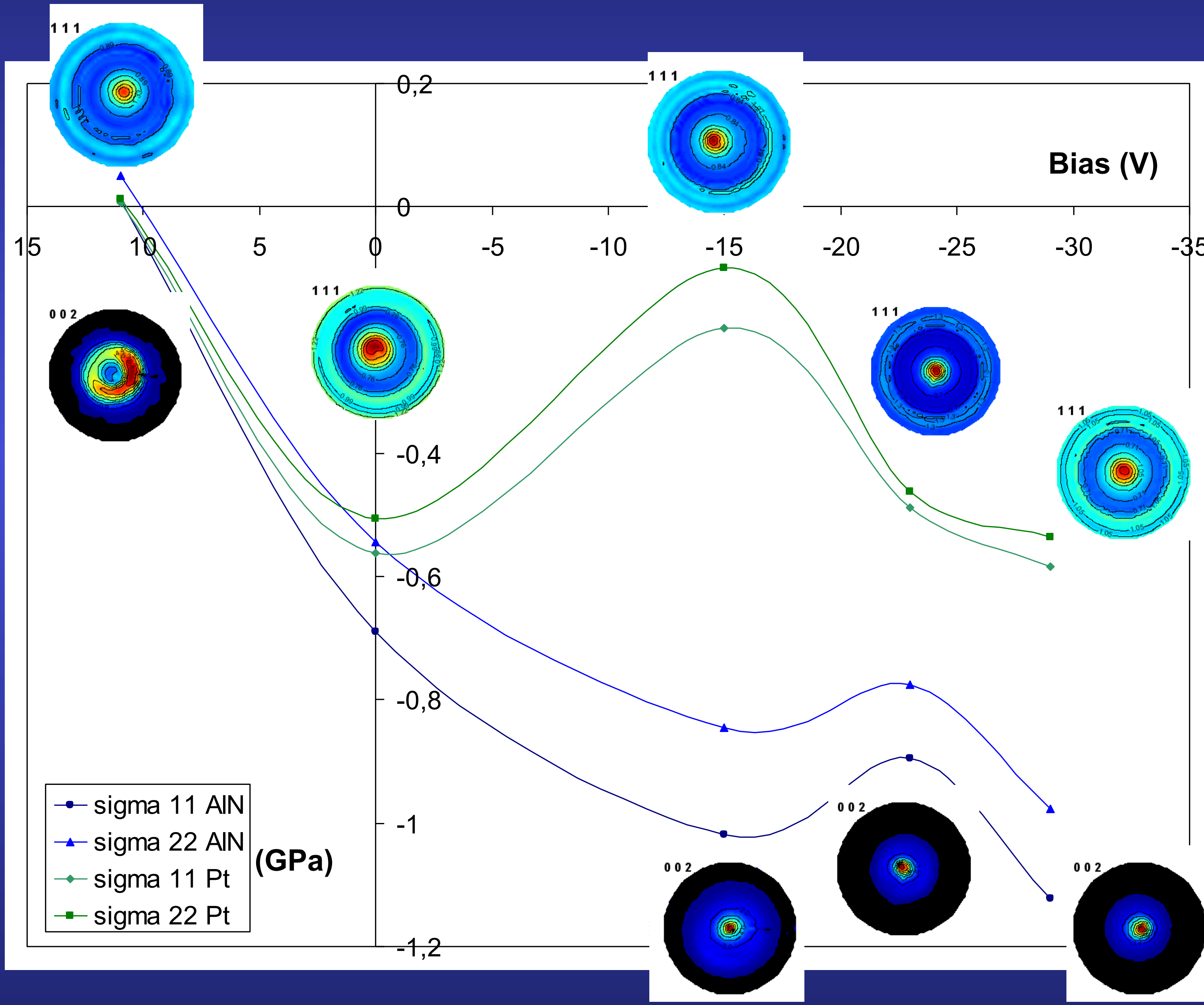
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa



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)

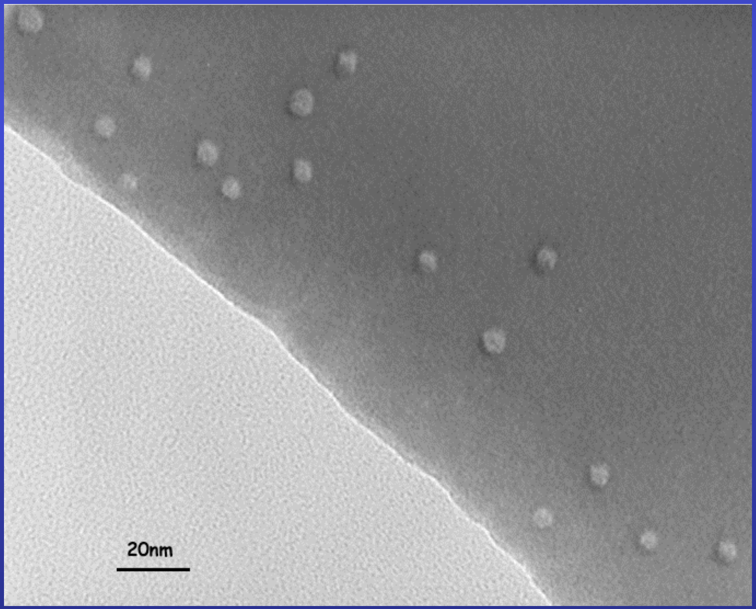
Substrate bias vs stress-texture evolution



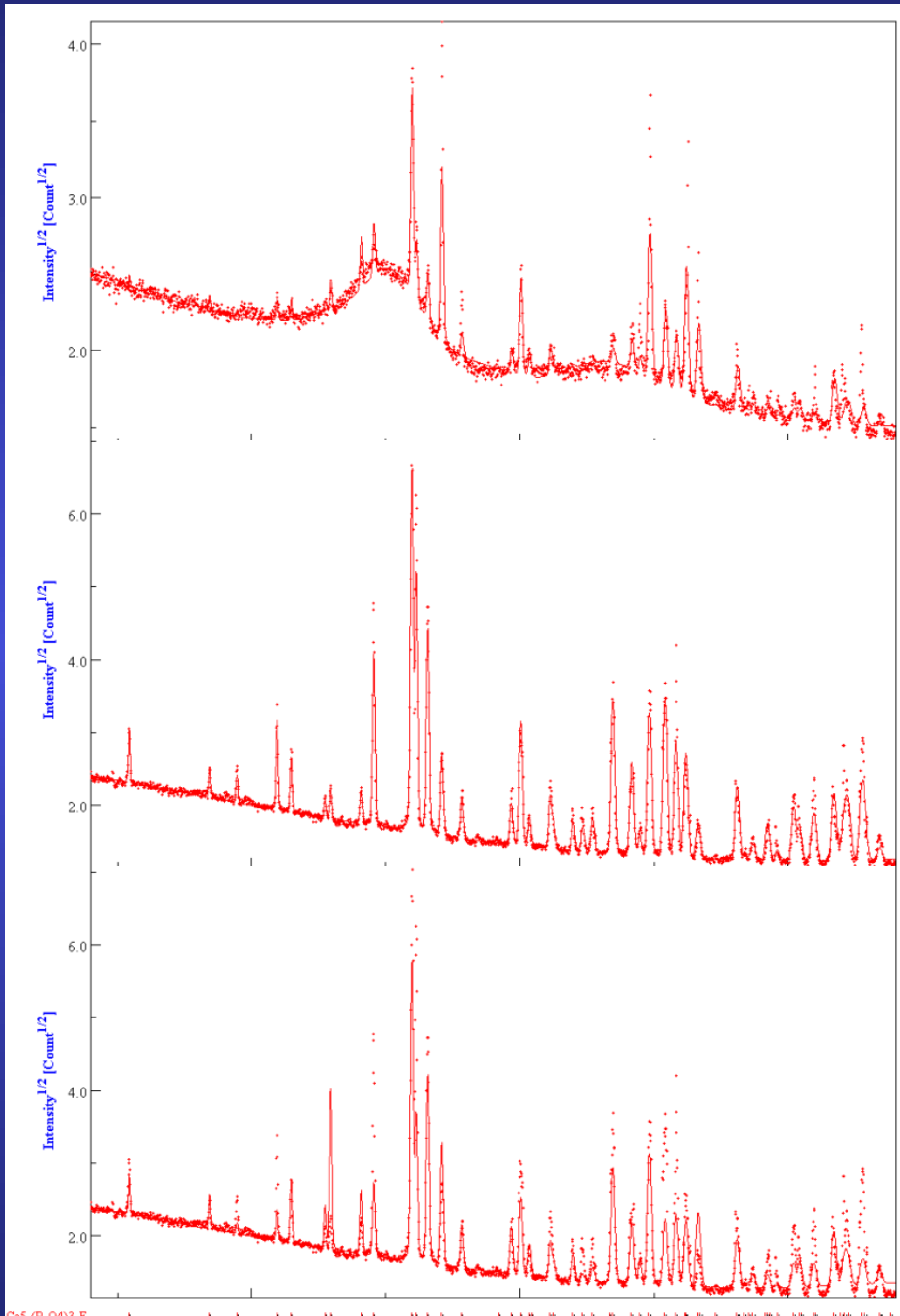
Irradiated FluorApatite (FAp) ceramics

S. Miro, PhD

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

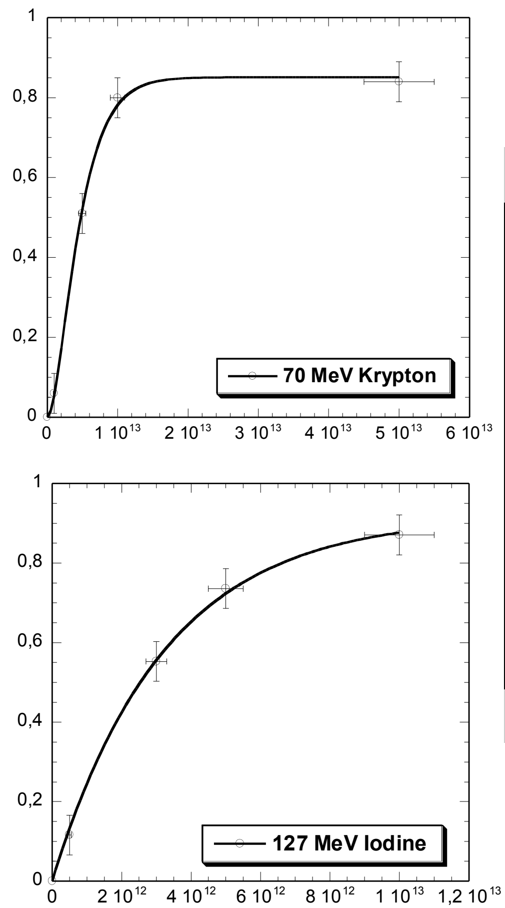
Fluence (ions.cm^{-2})	Vc/V (%)	A (Å)	c (Å)	<t> (nm)	$\Delta a/a_0$ (%)	$\Delta c/c_0$ (%)	R_w (%)	R_B (%)
0	100	9.3365(3)	6,8560(5)	294(22)	-	-	14.6	9.1
Kr								
10^{11}	100	-	-	-	-	-		
10^{12}	100	-	-	-	-	-		
5.10^{12}	49(1)	9.3775(9)	6.8912(8)	294(20)	0.44	0.53	24	15
10^{13}	20(1)	9.4236(5)	6.9105(5)	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



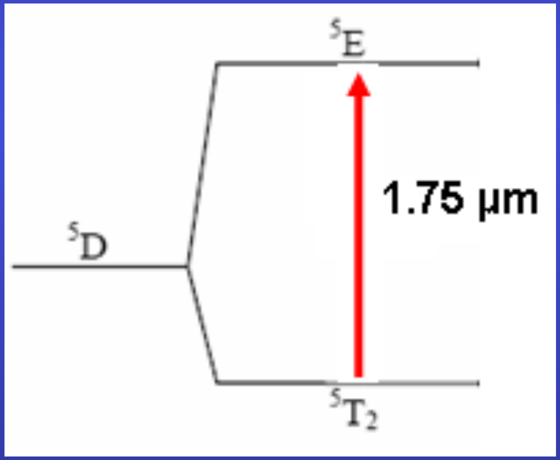
B

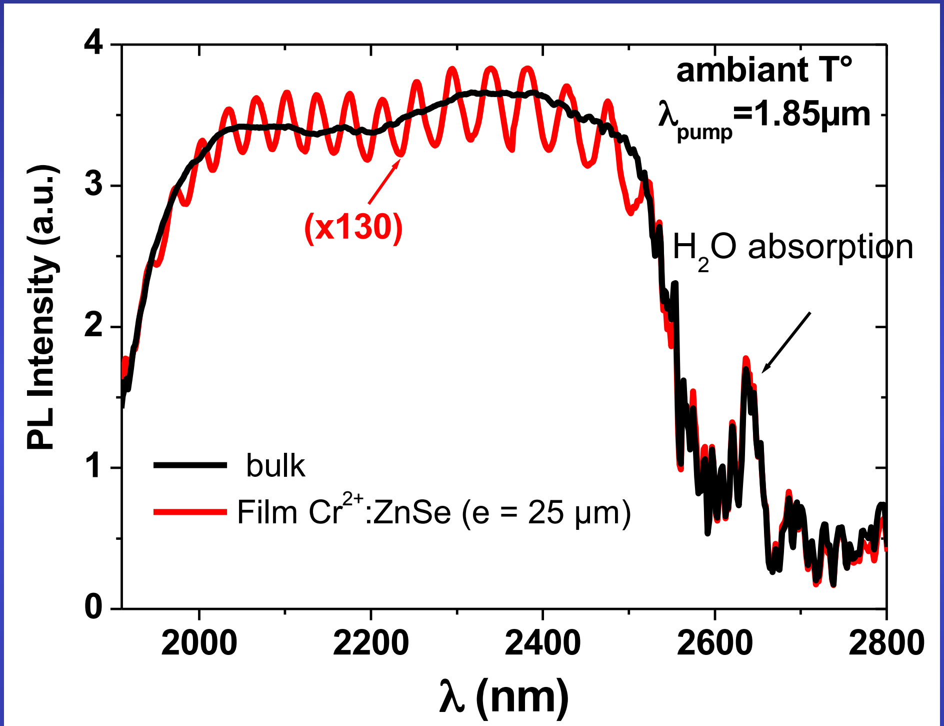
Fitting parameters	Krypton		Iodine
	Single impact $Fd = B(1- \exp(-A\phi t))$	Double impact $Fd = B(1 - (1+ A\phi t) \exp(-A\phi t))$	Single impact $Fd = B(1- \exp(-A\phi t))$
$A = \pi R^2$ (cm^2)	$1.85 \pm 0.15\ 10^{-13}$	$4.1 \pm 0.15\ 10^{-13}$	$3.3 \pm 0.15\ 10^{-13}$
Radius R (nm)	2.4 ± 0.2	3.6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

ZnSe:Cr^{2+} films
N. Vivet, PhD

conditions:

- ♦ $20 \le T_d \le 385°C$
- ♦ P_{RF} = 50-200W
- ♦ P_{Ar} = 0.5 Pa and 2 Pa
- ♦ d = 7 and 10 cm

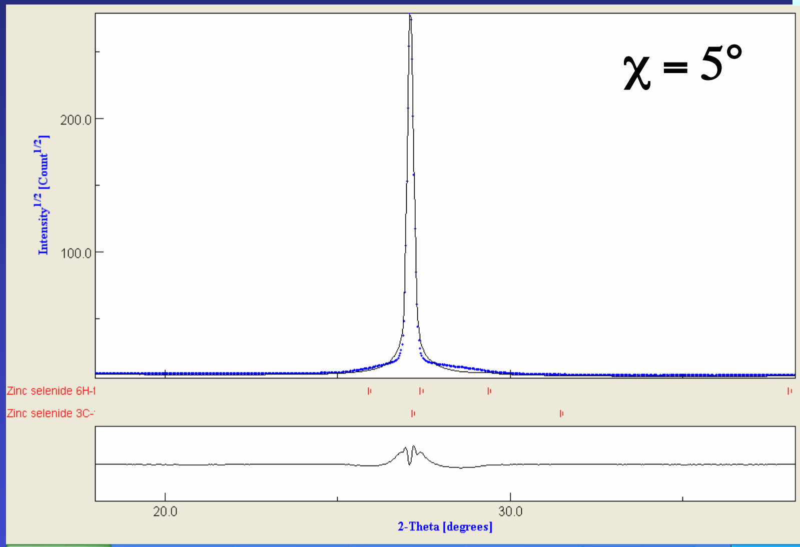


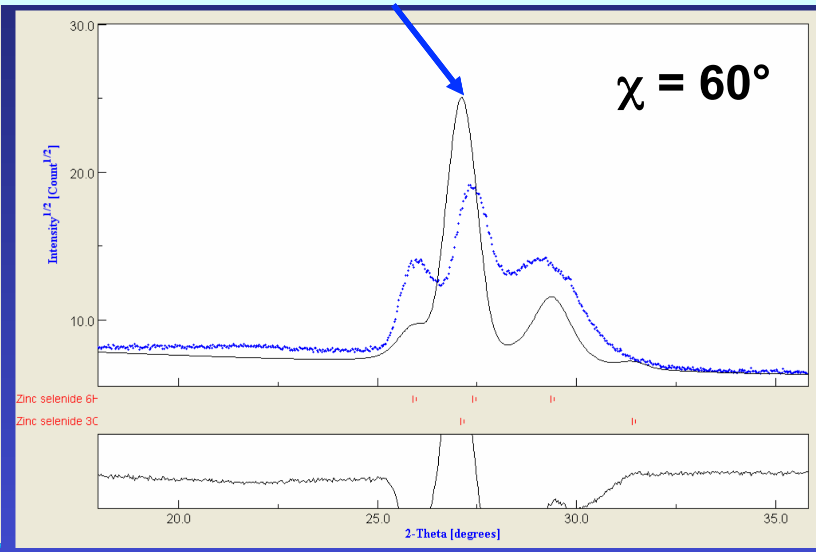


♦ **Large emission band centred at 2200nm: $^5E \rightarrow {}^5T_2$ transition (Cr^{2+})**

♦ **Single crystals and thin films: similar spectra**

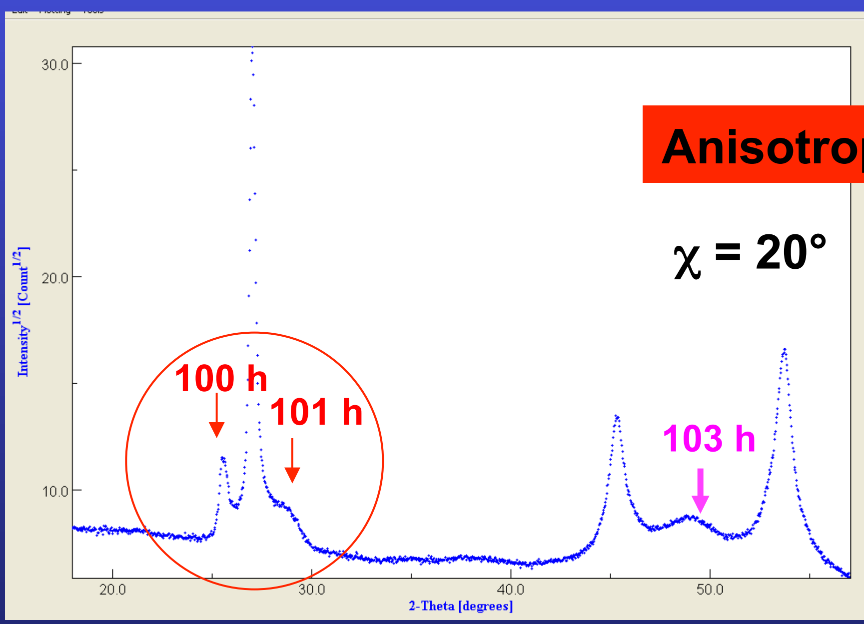
111 Peak shifts

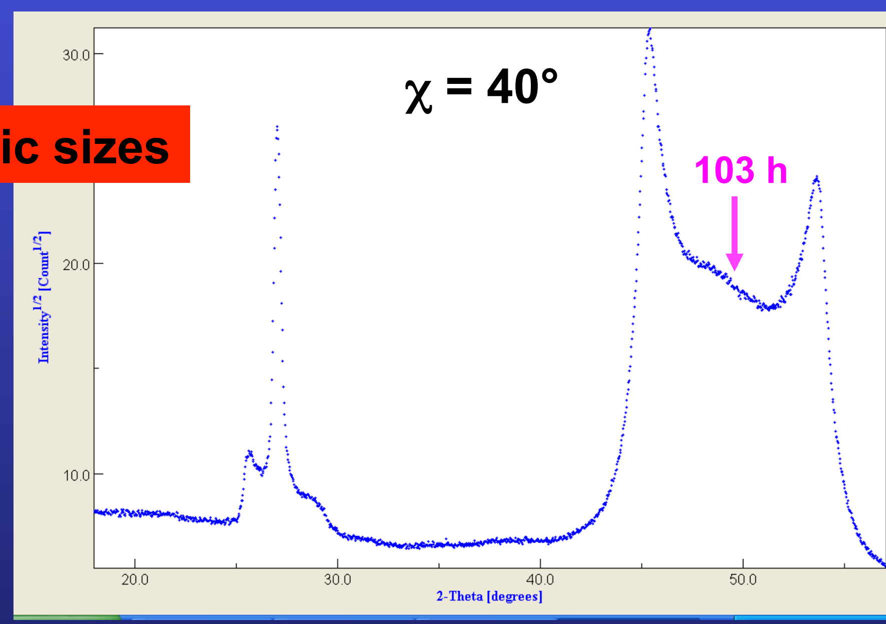




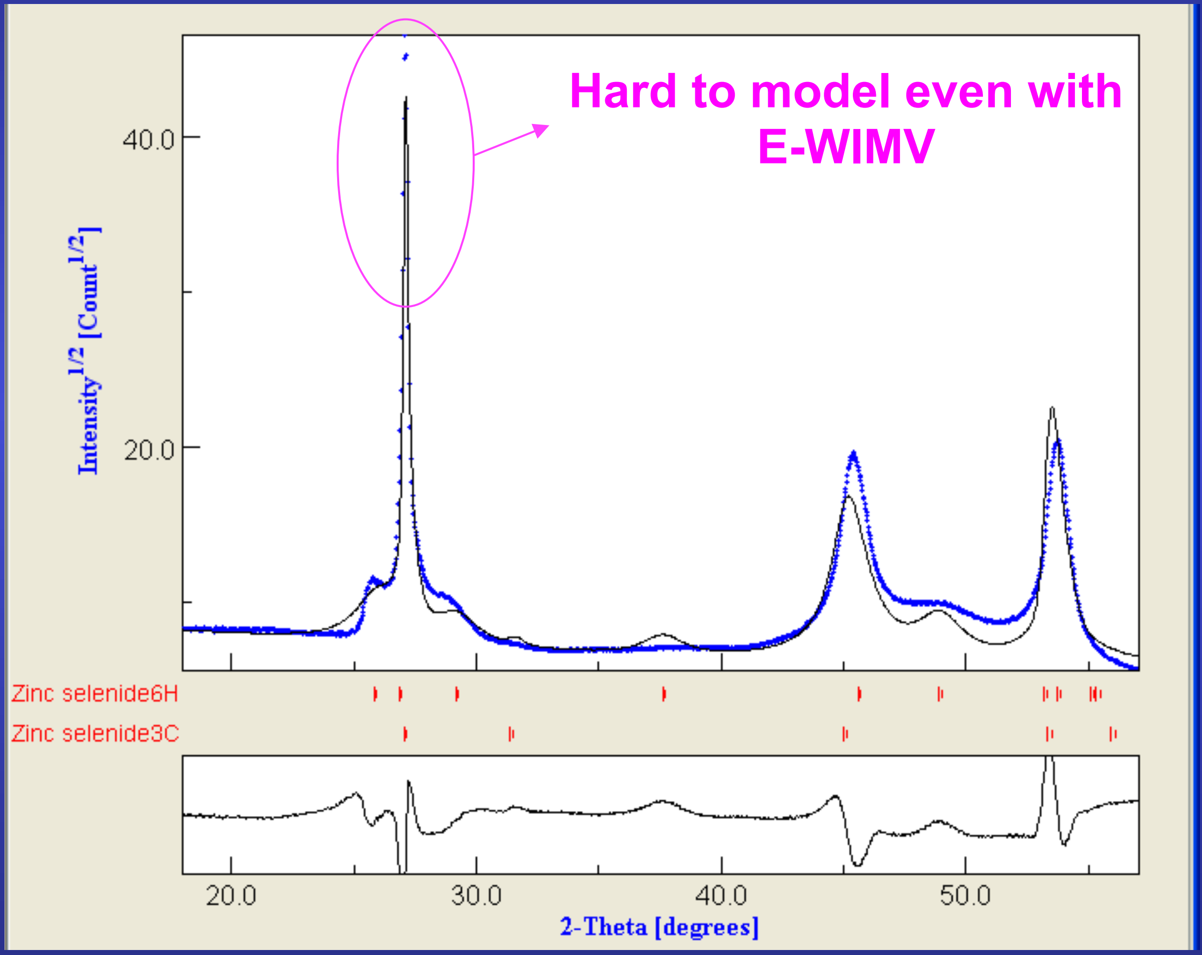
Residual stresses and/or stacking faults

Anisotropic sizes





Fibre Texture + 2 polytypes (6H and 3C) + anisotropic sizes + residual stresses and/or stacking faults + layering



Sum diagram: ω =13.65°, P_{RF} = 200W

Conclusions

a) Texture affects phase ratio and structure determination

b) Microstructure (crystallite size) affects texture (go to a)

c) Stresses shift peaks then affects structure and texture determination

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: local probes ...

g) www.ecole.ensicaen.fr/~chateign/texture/combined.pdf