Characterization of microstructure and crystallographic texture of ceramics

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Structure determination on real (textured) samples
Dilemma 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

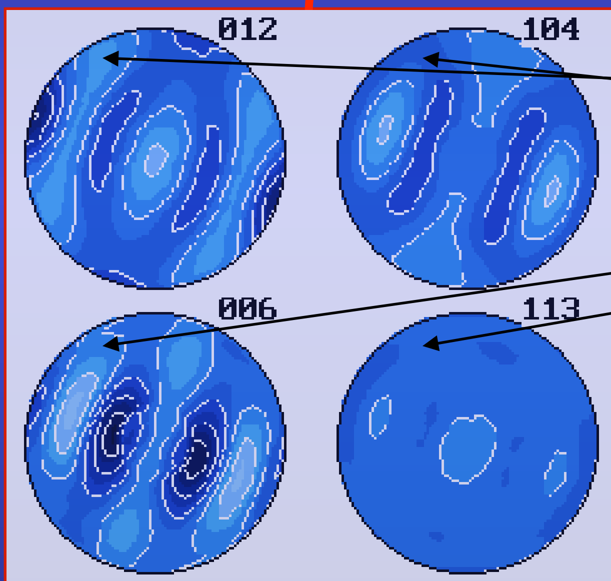
- work on the sum of all diagrams on average

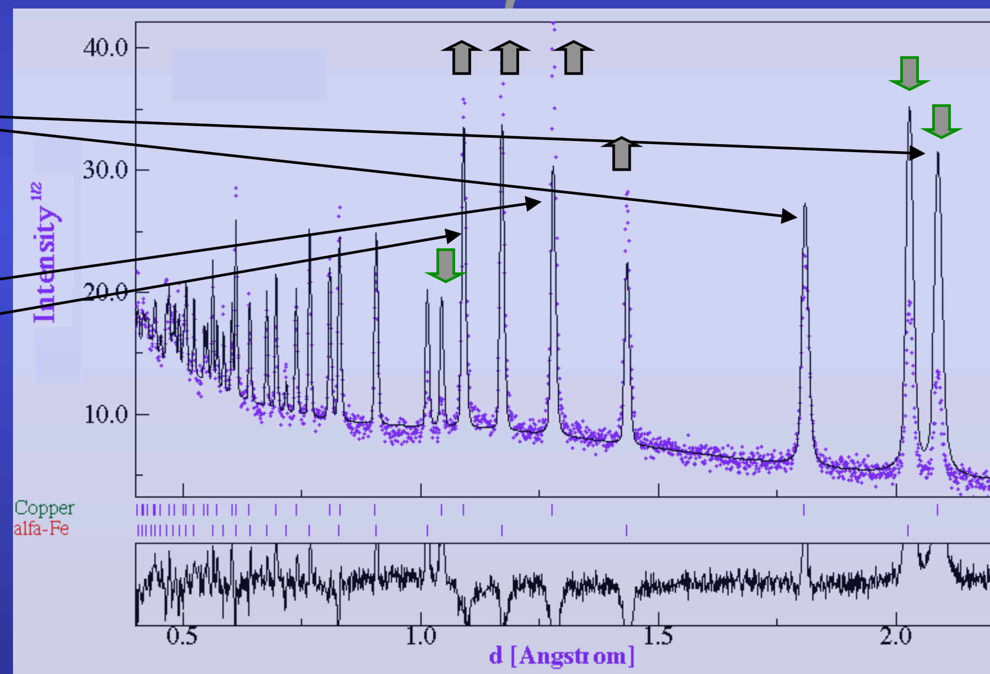
Texture from Spectra

Orientation Distribution Function (ODF)

From pole figures

From spectra





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

Residual Stresses shift peaks with y

Dilemma 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

Layered systems

Dilemma 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)

Phase and Texture
Dilemma 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)

Residual Stresses shift peaks with y
Dilemma 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
Dilemma 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

Combined Analysis approach

Extracted Intensities

WIMV, E-WIMV
Harmonics, components, ADC

Orientation Distribution Function

pole figures
inverse pole figures

Rietveld

Structure
+
Microstructure
+
phase %

Le Bail

Structural parameters
atomic positions, substitutions, vibrations
cell parameters

Multiphased, layered samples:
Thickness,
Anisotropic Sizes
and μ-strains (*Popa*),
Stacking faults (*Warren*),
Distributions, Turbostratism (Ufer)

Popa-Balzar,
$\sin^2\psi$

Voigt,
Reuss,
Geometric
mean

Residual stresses
Strain Distribution Function

Specular Reflectivity

Roughness,
electron Density
& EDP,
Thickness

Fresnel,
Matrix (Parrat),
DWBA

Phase ratio (amorphous + crystalline)
Le Bail *Rietveld*

Grinding to powderise another dilemma !

Grinding: removes angular relationship, adds correlations

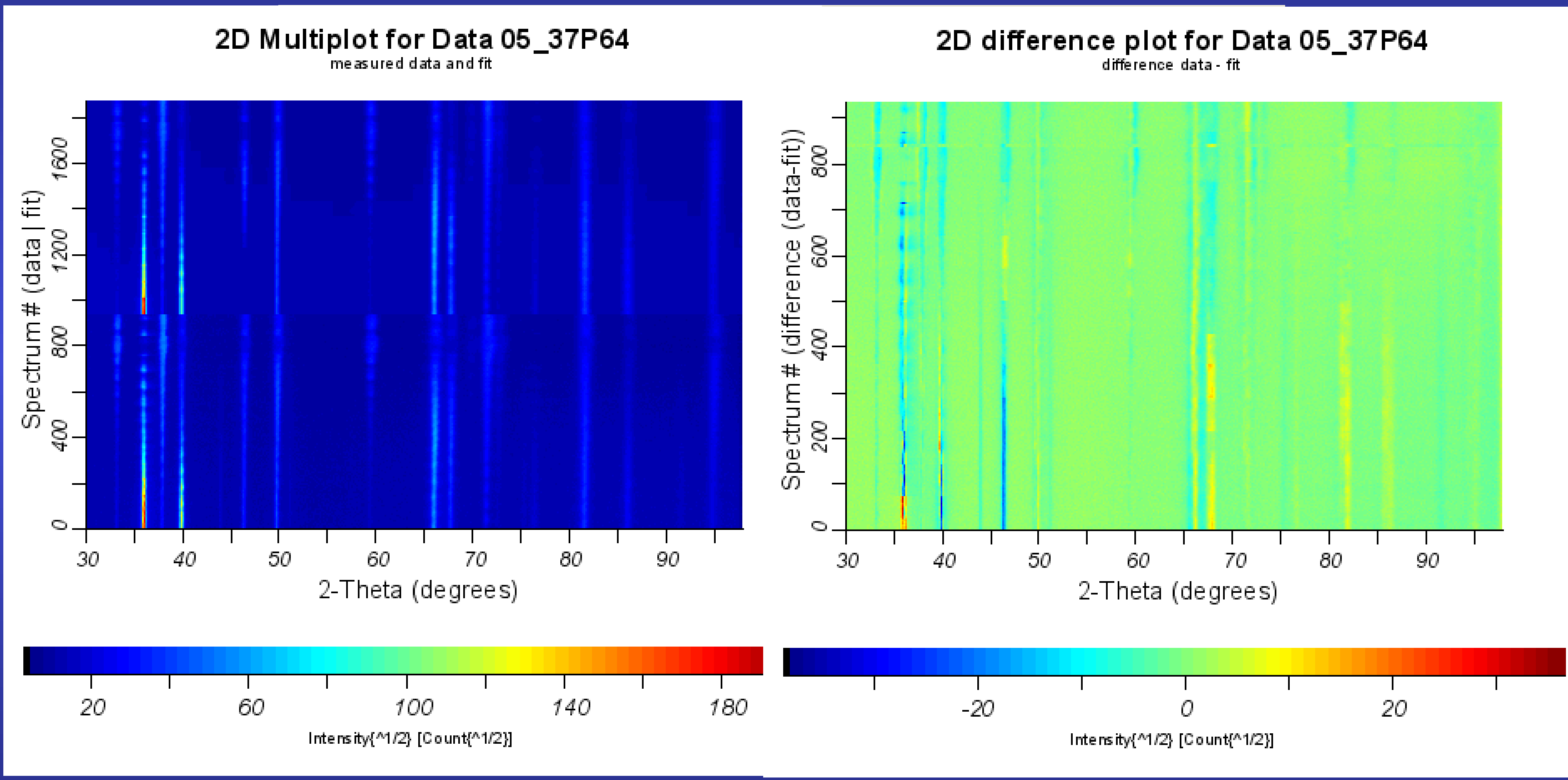
Texture:
- not measured
- removed ? hope to get a perfect powder

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

Same sample ?

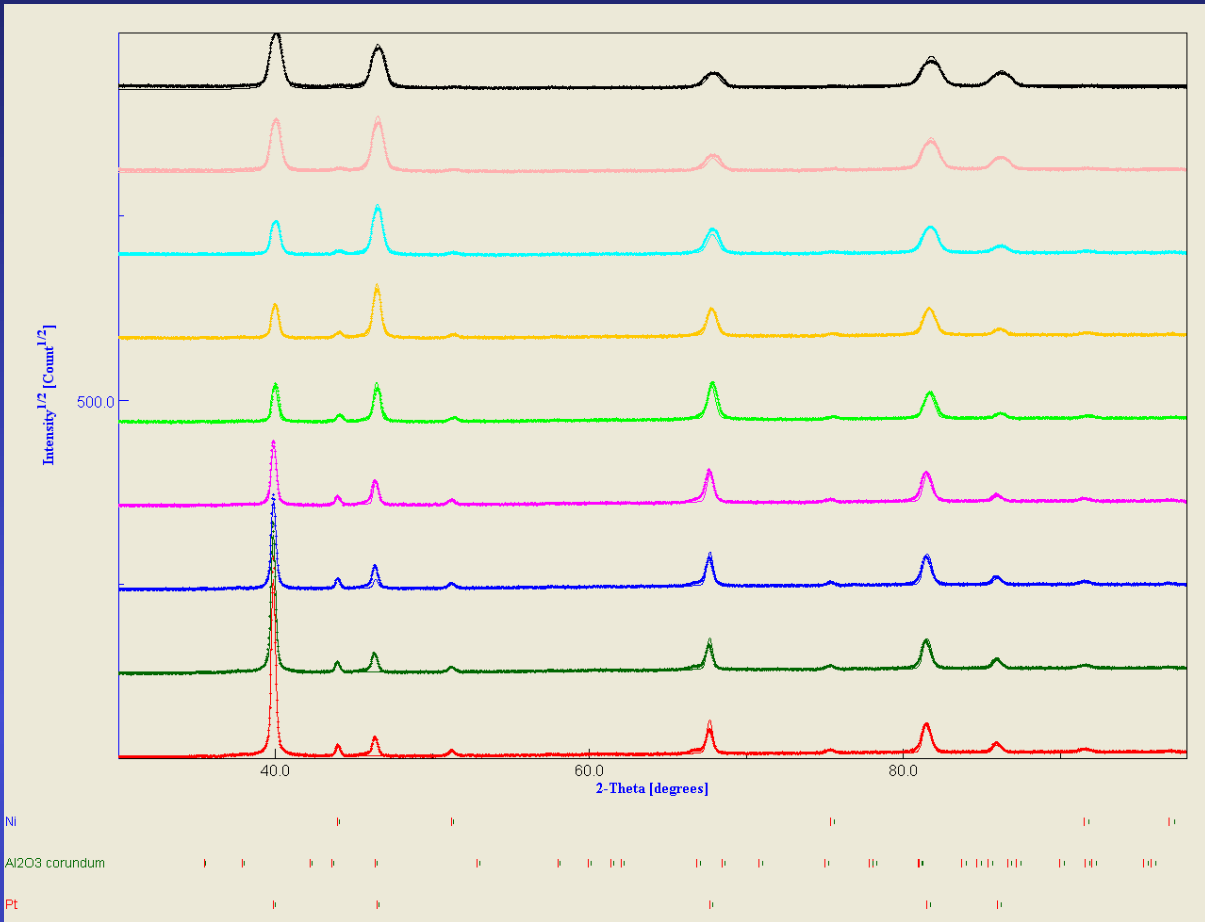
Rare samples ?

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



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

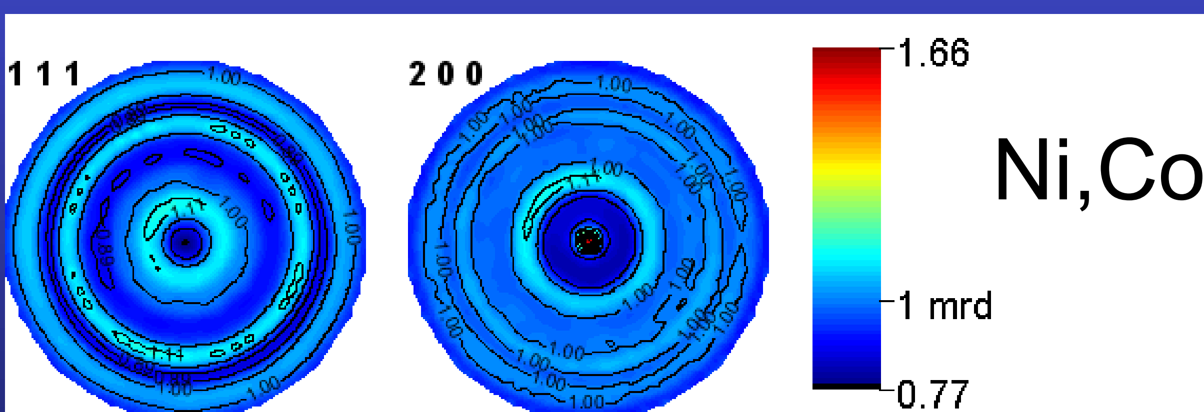
T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm



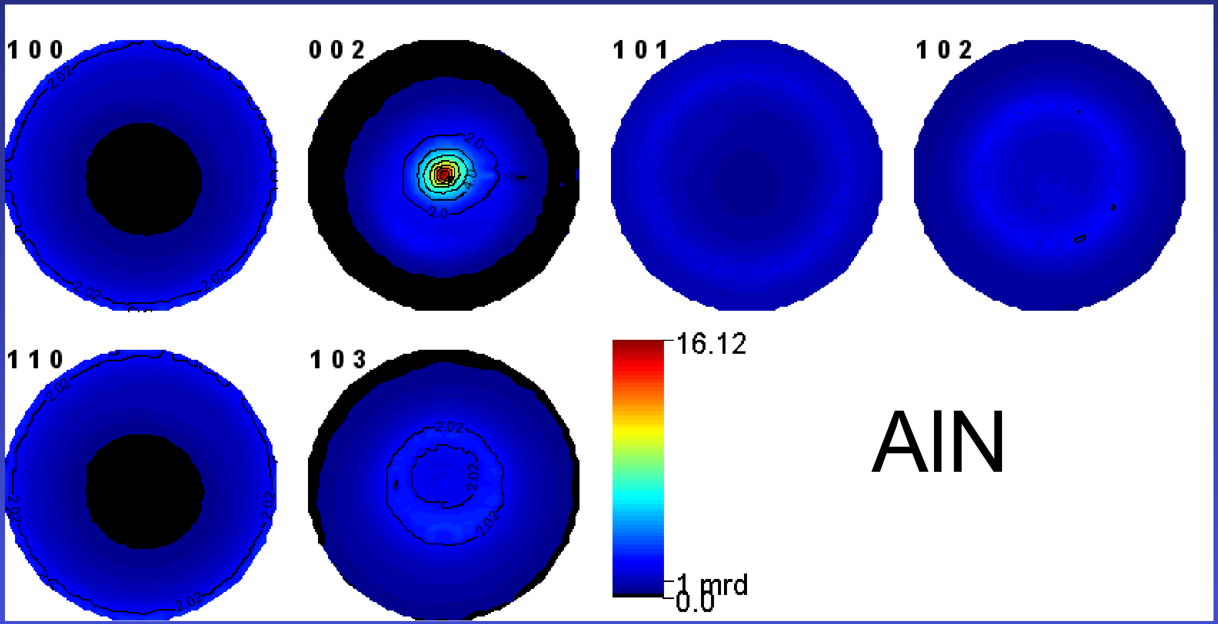
(χ,φ) randomly selected diagrams

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)

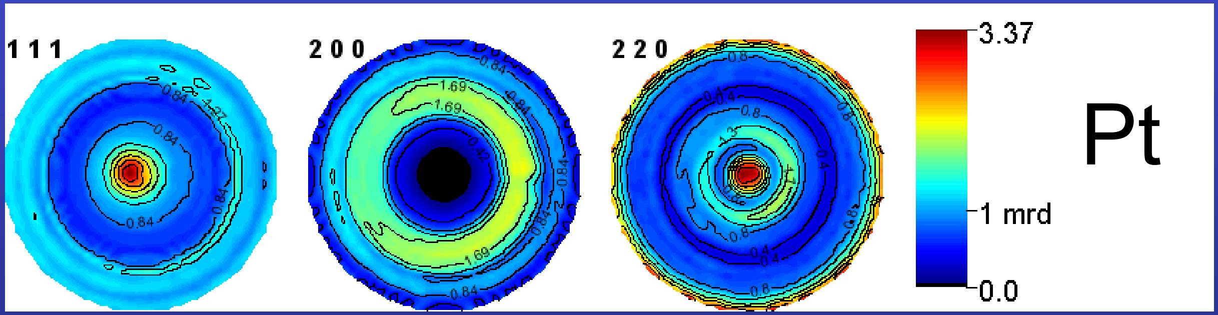


a = 3.569377(5) Å
<t> = 7600(1900) Å
<ε> = 0.00236(3)
σ_{11} = -328(8) MPa
σ_{22} = -411(9) MPa



Rw (%) = 4.1

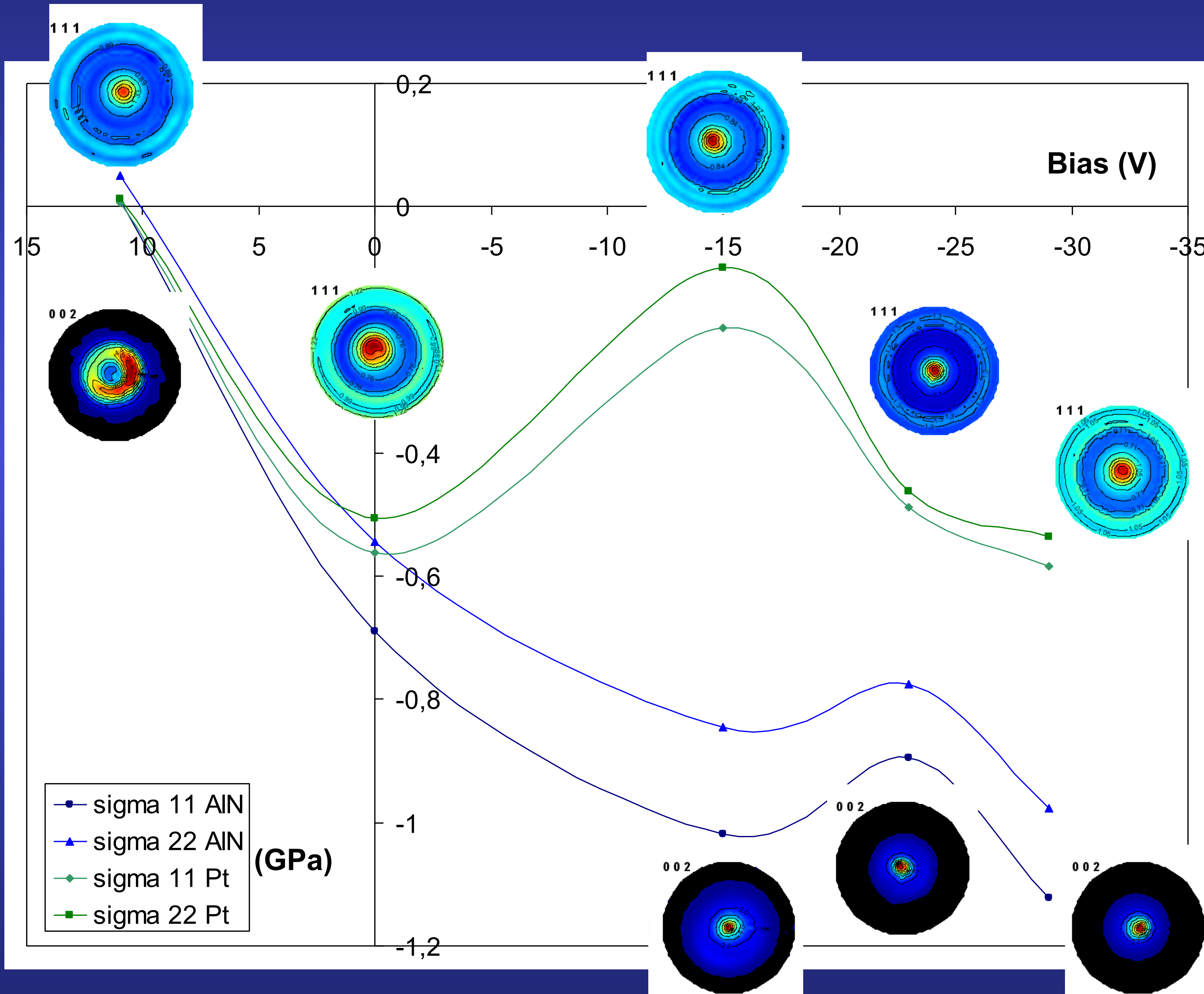
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<t> = 2404(8) Å
<ε> = 0.001853(2)
σ_{11} = -1019(2) MPa
σ_{22} = -845(2) MPa



Rw (%) = 33.3

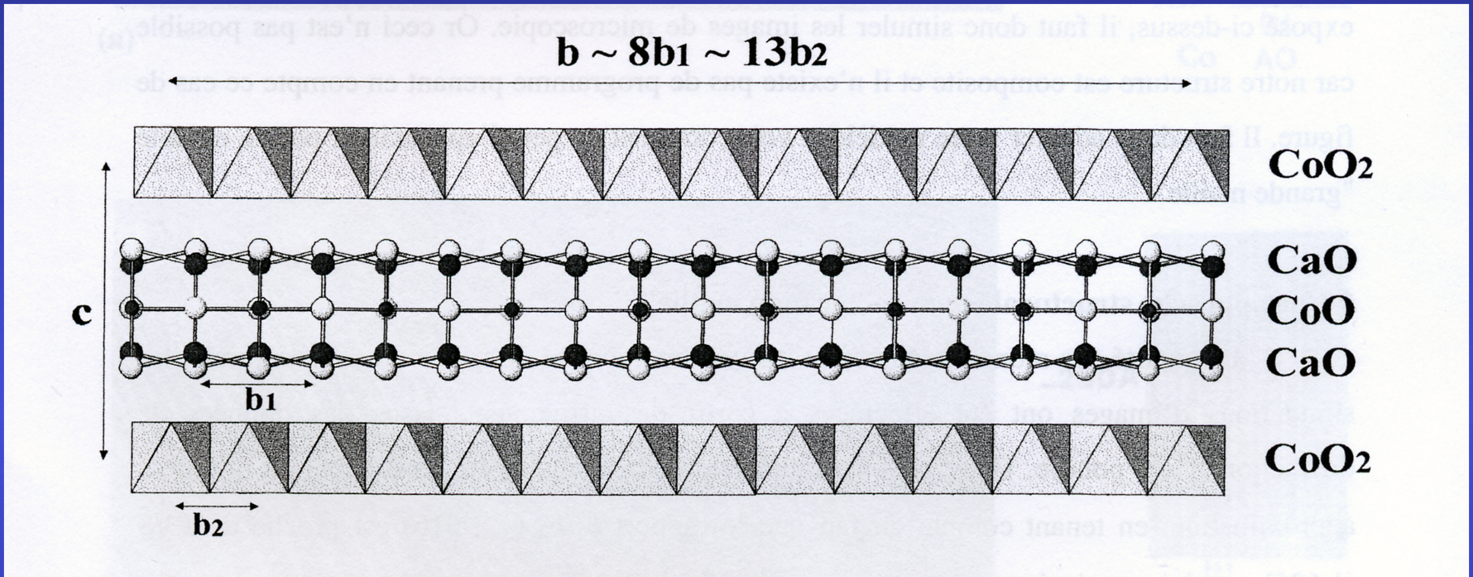
a = 3.91198(1) Å
T = 1204(3) nm
<t> = 2173(10) Å
<ε> = 0.002410(3)
σ_{11} = -196.5(8)
σ_{22} = -99.6(6)

Substrate bias vs stress-texture evolution



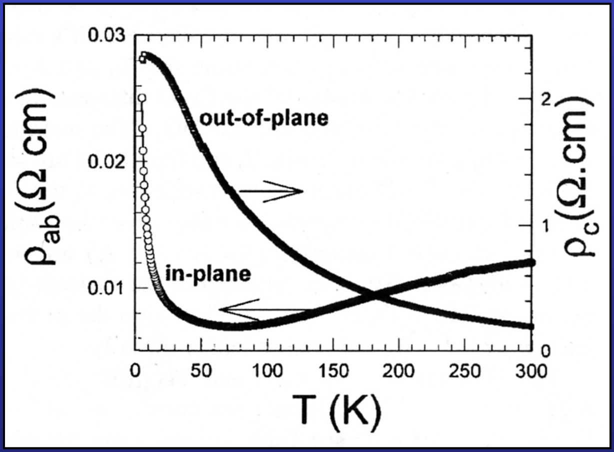
$Ca_3Co_4O_9$ thermoelectrics

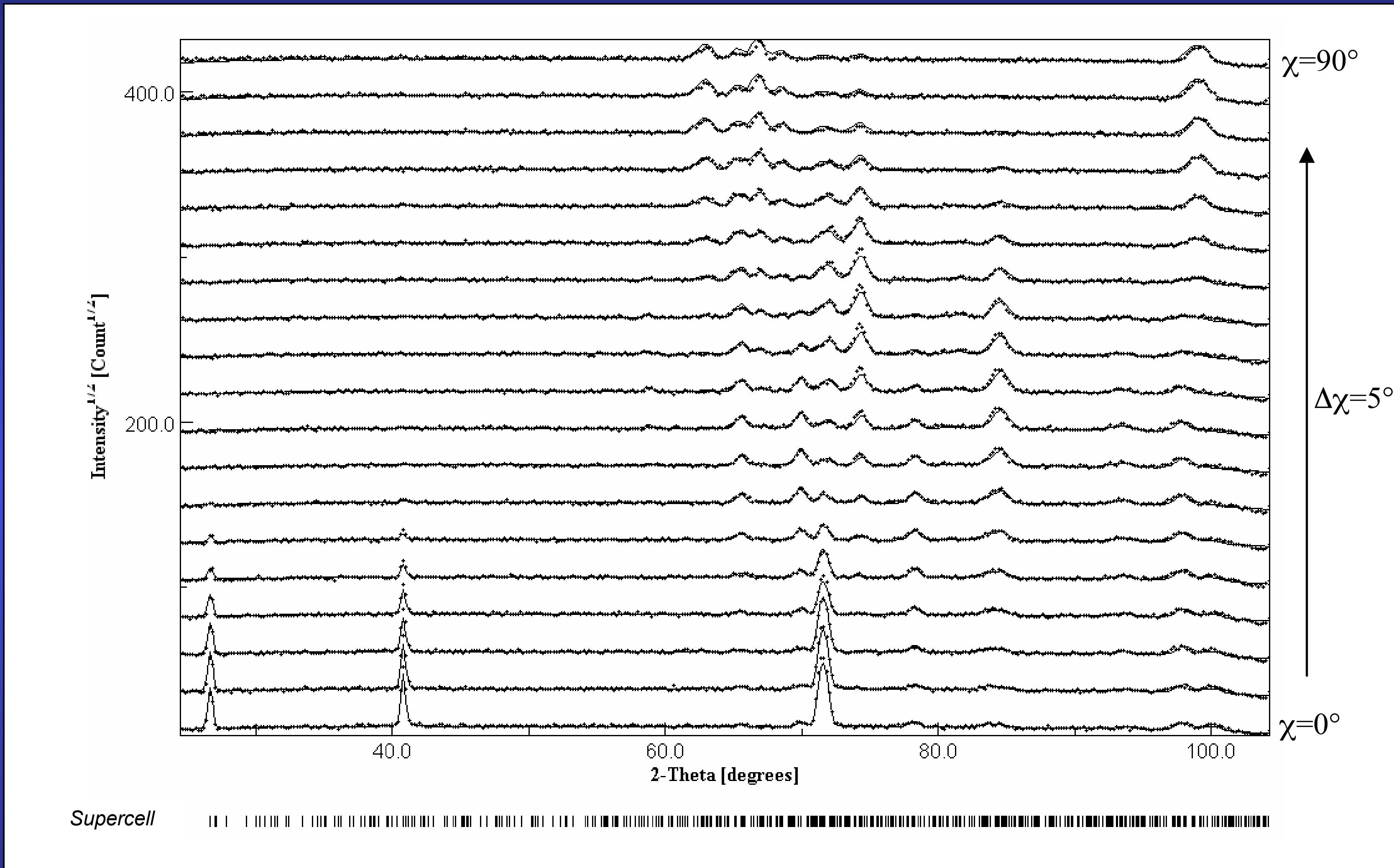
$Ca_3Co_4O_9$: Misfit lamellar and modulated Structure, with high thermopower



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)

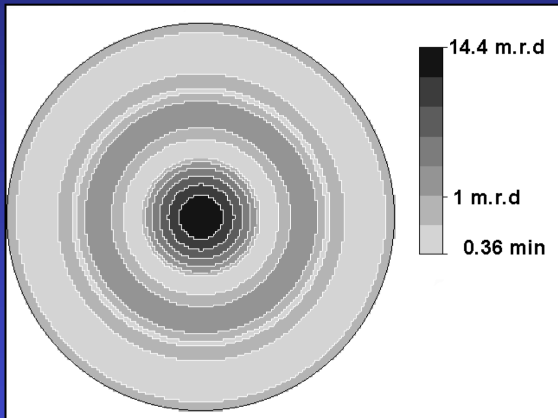
$\Gamma = \sigma_{ab}/\sigma_c \sim 10$ → Texture



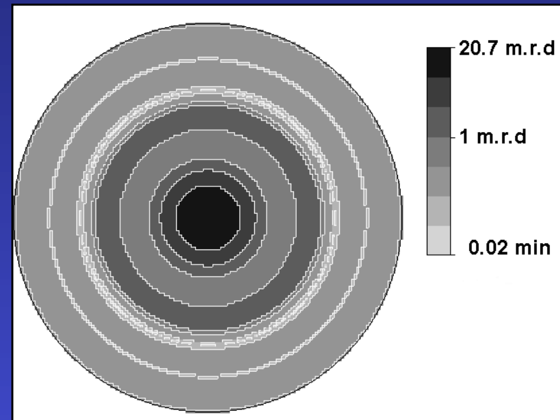

χ=90°
400.0
Intensity^1/2 [Count^1/2]
200.0
Δχ=5°
χ=0°
40.0
60.0
80.0
100.0
2-Theta [degrees]
Supercell

RP=19.7%, Rw=11.9%

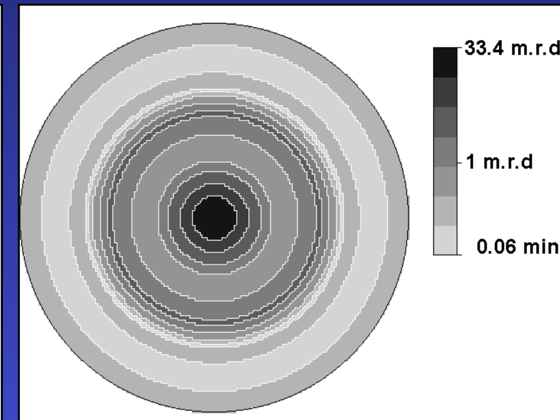
9.8 MPa for 2 h

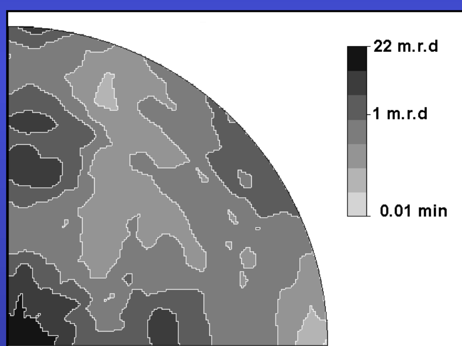


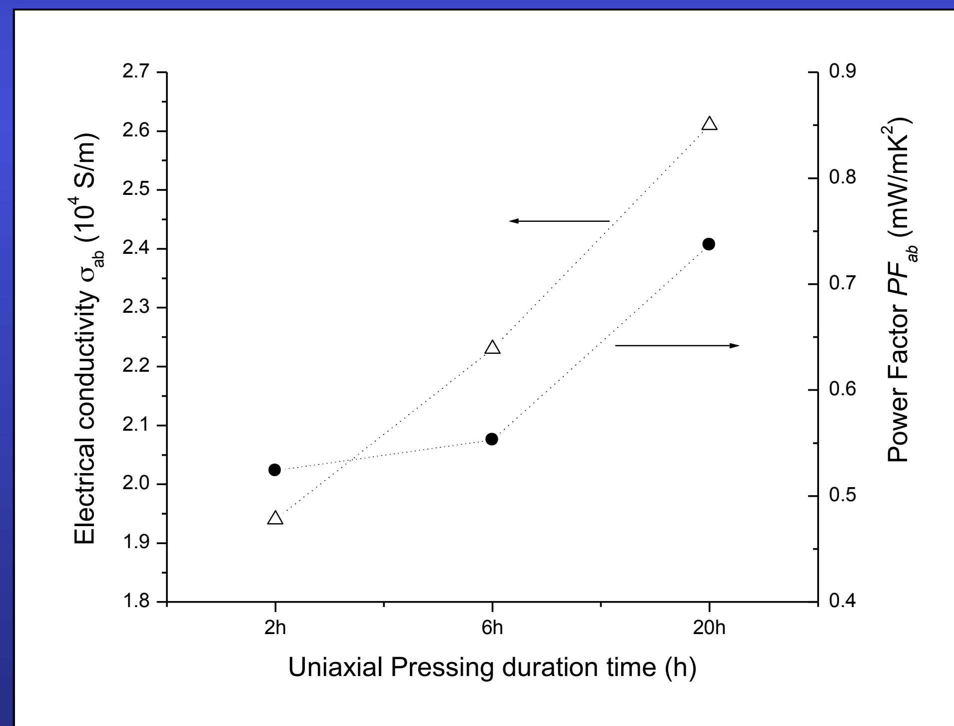
19.6 MPa for 6 h



19.6 MPa for 20 h







Templated Growth Method

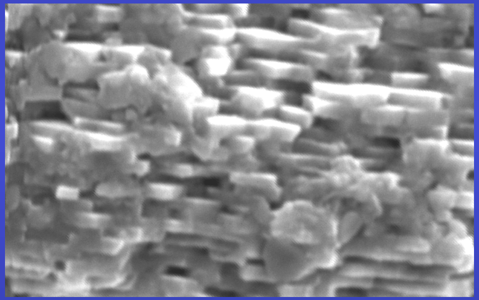
Aragonitic layers in mollusc shells

Gastropods

Crossed lamellar layers

Charonia lampas lampas (triton or trumpet cousin)

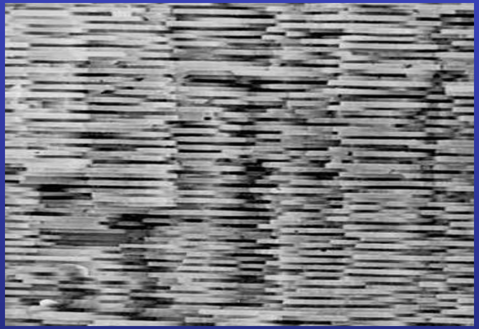
Columnar Nacre



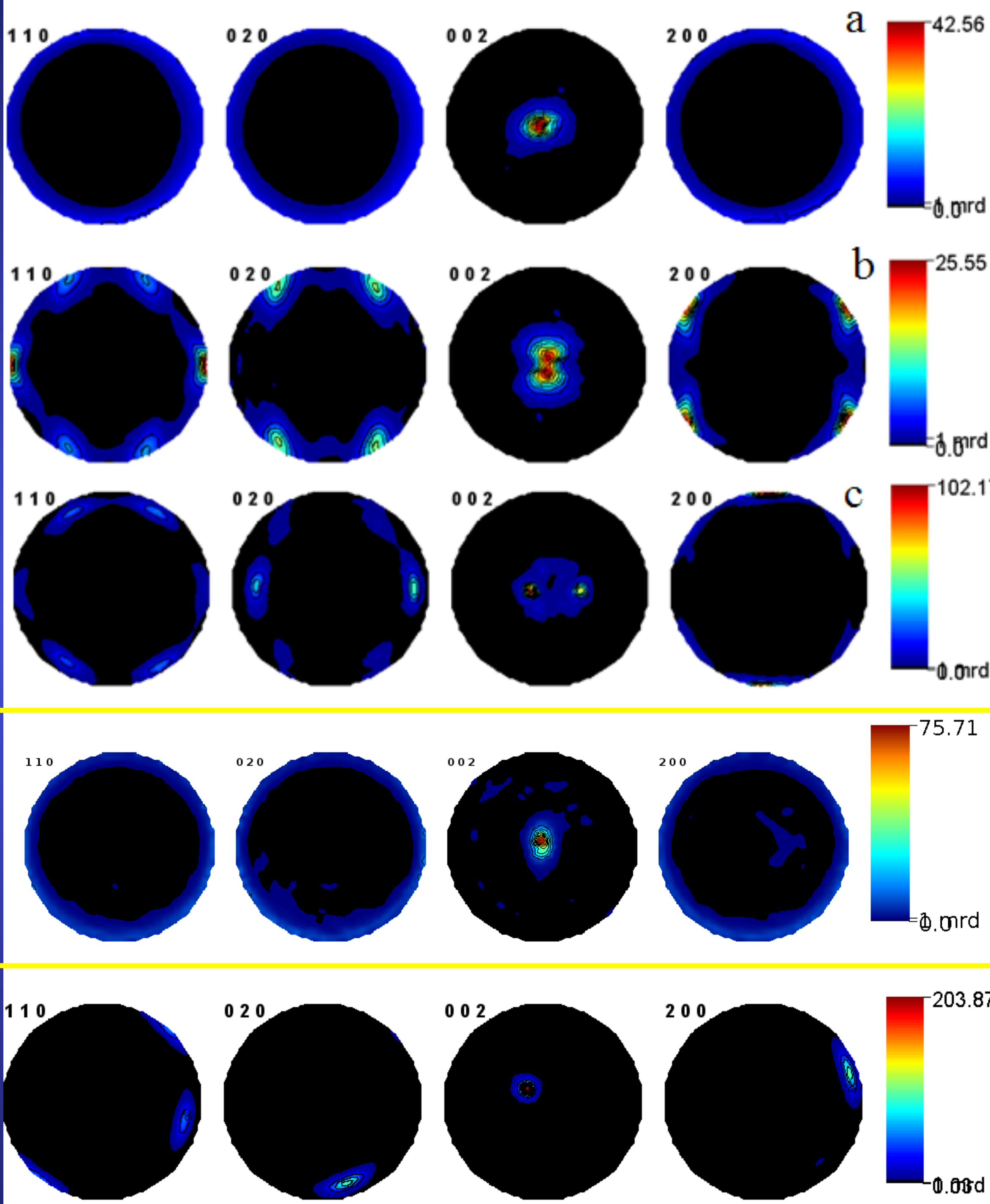
Haliotis tuberculata (common abalone)

Bivalves

Sheet Nacre



Pinctada maxima (Mother of pearl oyster)



Outer CL
43 mrd^2

Interm Radial CL
47 mrd^2

Inner Com CL
721 mrd^2

Inner Columnar Nacre
211 mrd^2

Inner Sheet Nacre
1100 mrd^2

Unit-cell distortions

	OCL	*Charonia* IRCL	ICCL	*Pinctada* ISN	*Haliotis* ICN
a (Å) b (Å) c (Å)	4,98563(7) 8,0103(1) 5,74626(3)	4,97538(4) 7,98848(8) 5,74961(2)	4,9813(1) 7,9679(1) 5,76261(5)	4,97071(4) 7,96629(6) 5,74804(2)	4.9480(2) 7.9427(6) 5.7443(6)
Δa/a Δb/b Δc/c	0,0047 0,0053 0,0004	0,0026 0,0026 0,0010	0,0038 0,0000 0,0033	0.0017 -0.0002 0.0007	-0.0029 -0.0032 0.0007
ΔV/V (%)	1,05	0,62	0,71	0.22	-0.60

Anisotropic cell distortion - depends on the layer
Only nacres exhibit (**a**,**b**) contraction
Due to inter- and intra-crystalline molecules
Distortions and anisotropies larger than pure intra- effect (Pokroy et al. 2007)

Elastic stiffnesses

Single crystal	**160**	**37.3**	**1.7**			
		87.2	**15.7**			
			84.8			
				41.2		
					25.6	
						42.7
ICCL	**96.5**	**31.6**	**13.7**			
		139	**9.5**			
			87.8			
				29.8		
					36.6	
						40.2
RCL	**130.1**	**32.6**	**10.3**			
		103.3	**14.1**			
			84.5			
				36.3		
					31.1	
						40.5
OCL	**111.1**	**32.9**	**13.2**			
		119	**11.8**			
			84.8			
				32.8		
					34.6	
						40.9

Atomic Structures

		Geological reference	*Charonia lampas* OCL	*Charonia lampas* IRCL	*Charonia lampas* ICCL	*Strombus decorus* mixture	*Pinctada maxima* ISN
Ca	y z	0.41500 0.75970	0.41418(5) 0.75939(3)	0.414071(4) 0.76057(2)	0.41276(9) 0.75818(8)	0.4135(7) 0.7601(8)	0.41479 (3) 0.75939 (2)
C	y z	0.76220 -0.08620	0.7628(2) -0.0920(1)	0.76341(2) -0.08702(9)	0.7356(4) -0.0833(2)	0.7607(4) -0.0851(7)	0.7676 (1) -0.0831 (1)
O1	y z	0.92250 -0.09620	0.9115(2) -0.09205(8)	0.9238(1) -0.09456(6)	0.8957(3) -0.1018(2)	0.9228(4) -0.0905(9)	0.9134 (1) -0.09255 (7)
O2	x y z	0.47360 0.68100 -0.08620	0.4768(1) 0.6826(1) -0.08368(6)	0.4754(1) 0.68332(9) -0.08473(5)	0.4864(3) 0.6834(2) -0.0926(1)	0.4763(6) 0.6833(3) -0.0863(7)	0.4678 (1) 0.68176 (7) -0.09060 (4)
$\Delta Z_{C\text{-}O1}$ (Å)		**0.05744**	**0.00029**	**0.04335**	**0.1066**	**0.031**	**0,054**

Carbonate group aplanarity specific to a given layer

Aplanarity decreases from inner to outer shell layers (CL layers)

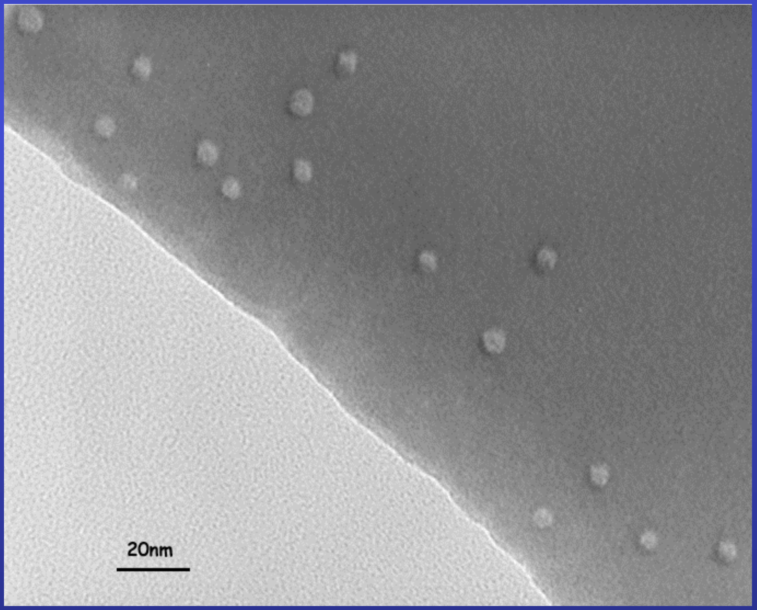
-> up to quite ΔZ=0 outside (nearly the calcite value)

Average aplanarity on the whole shell = geological reference (Strombus)

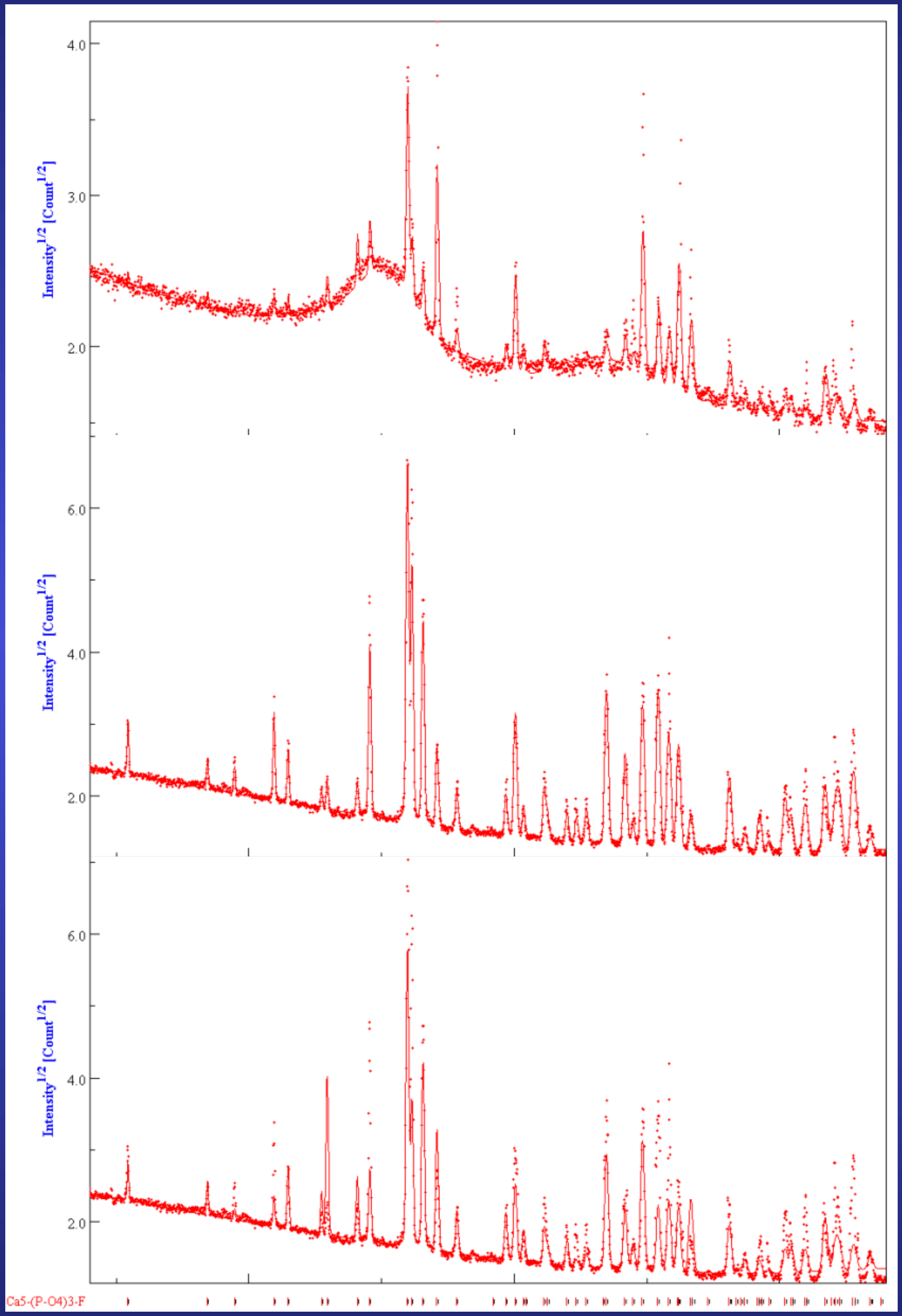
In Haliotis nacre: large ΔZ=0.08, + strong anisotropy: less stable nacre

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



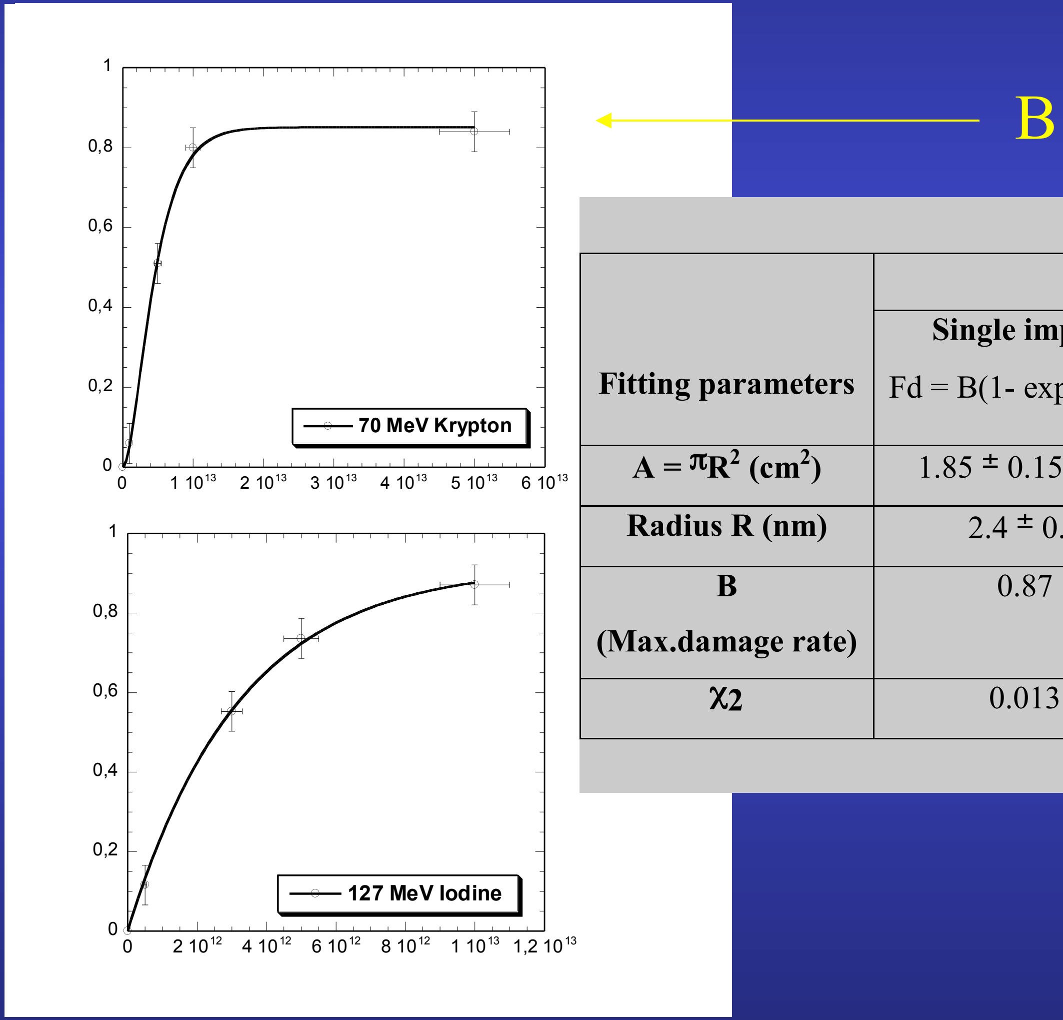
texture corrected,

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

Virgin, with texture correction

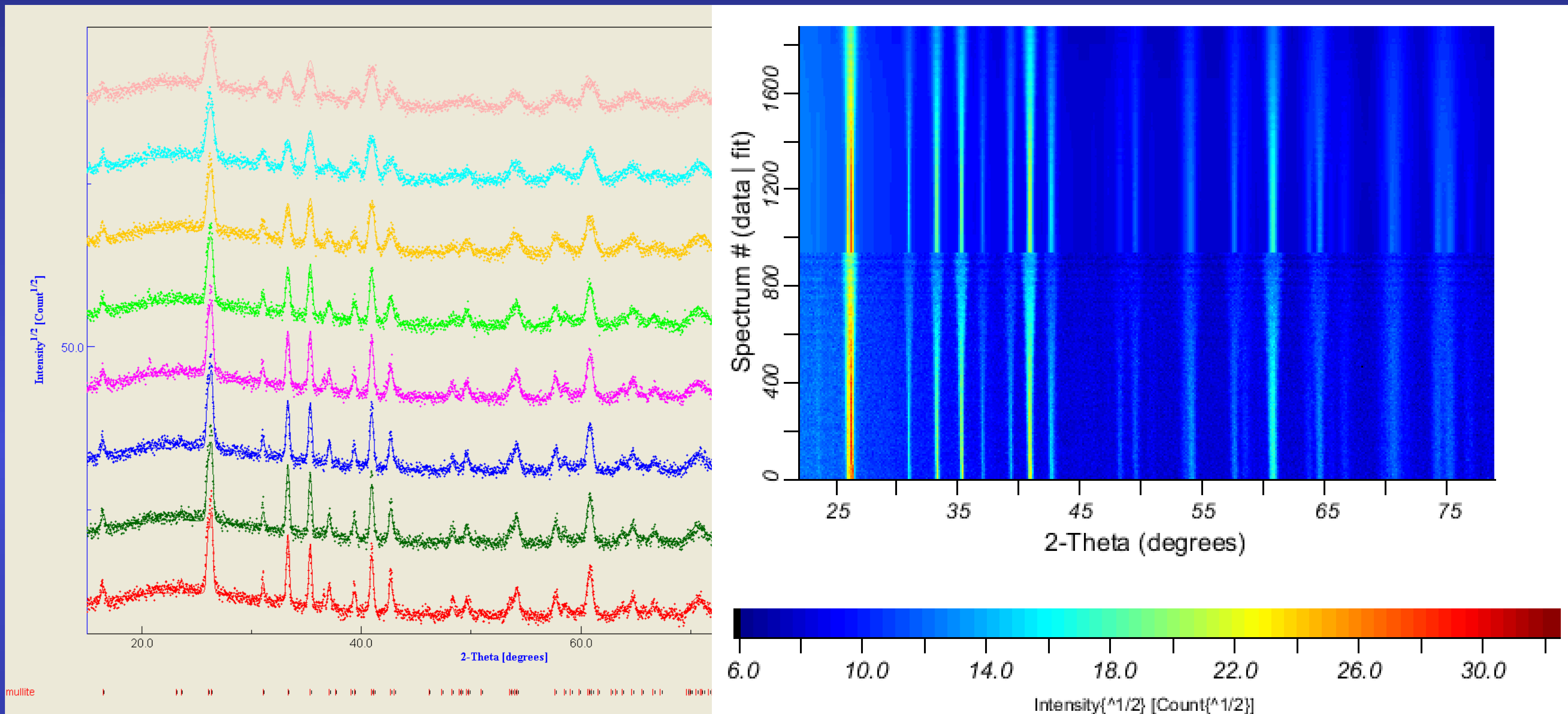
Virgin, no texture correction

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



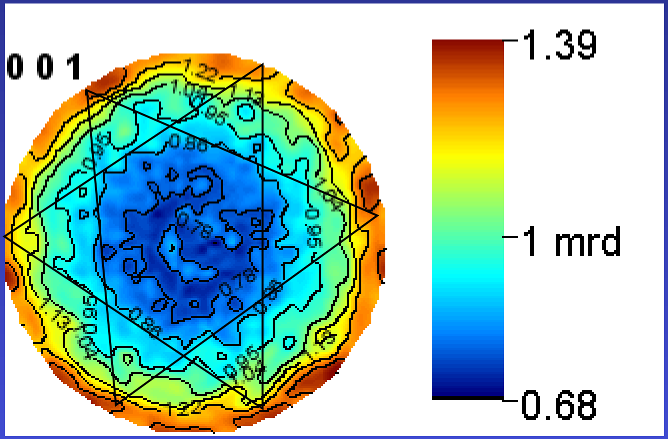
Fitting parameters	Krypton		Iodine
	Single impact	Double impact	Single impact
	Fd = B(1- exp(-Aϕt))	Fd = B(1 – (1+ Aϕt) exp(-Aϕt))	Fd = B(1- exp(-Aϕt))
$A = \pi R^2$ (cm²)	$1.85 \pm 0.15\ 10^{-13}$	$4.1 \pm 0.15\ 10^{-13}$	$3.3 \pm 0.15\ 10^{-13}$
Radius R (nm)	2.4 ± 0.2	3.6	3.2
B (Max.damage rate)	0.87	0.85 ± 0.2	0.92 ± 0.2
$\chi 2$	0.013	0.0006	0.0004

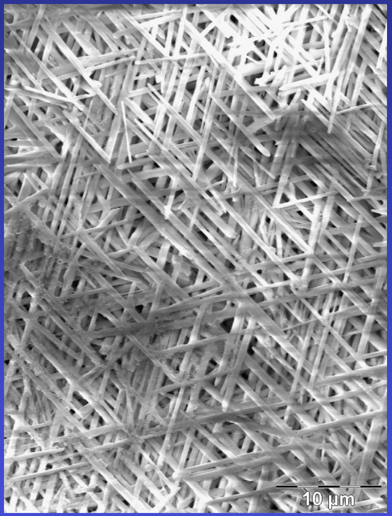
Mullite-silica composites



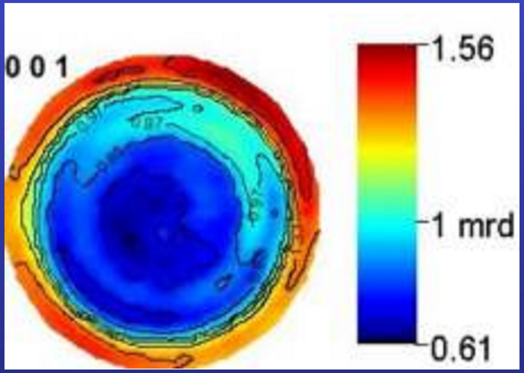
ODF: R_w = 4.87 %, R_B = 4.01 %
Rietveld: R_w = 12.90 %, GoF = 1.77
Mullite: a = 7.56486(5) Å; b = 7.71048(5) Å; c = 2.89059(1)Å

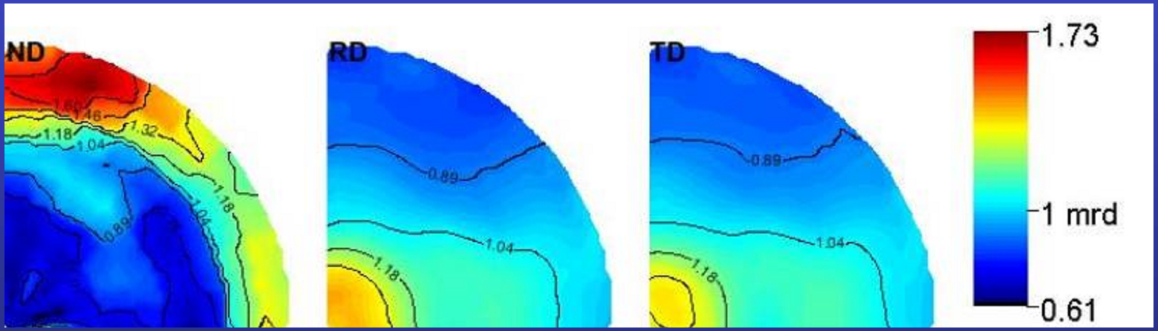
Uniaxially pressed



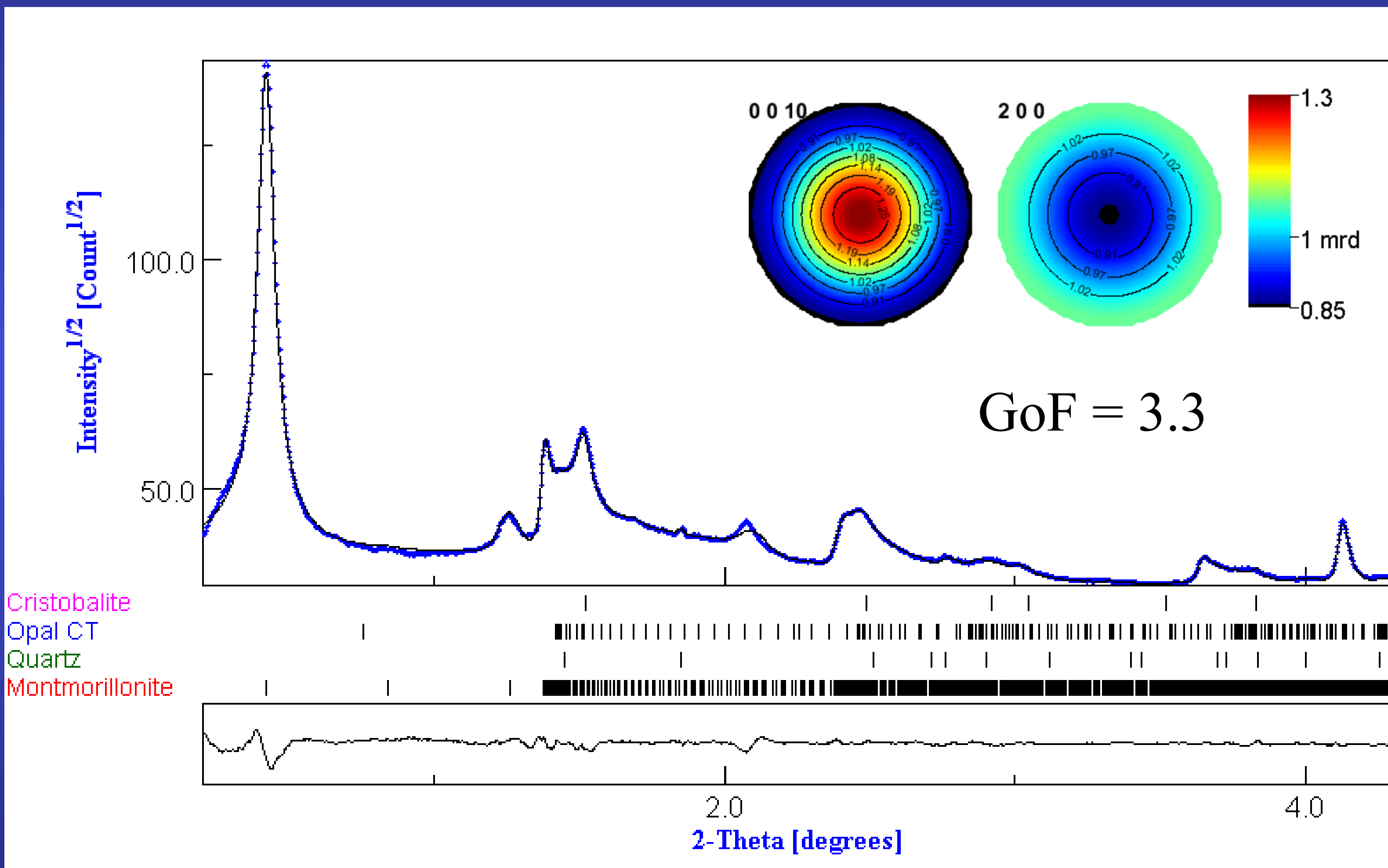


Centrifugated





Turbostratic phyllosilicate aggregates



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

Structural distortions in aragonitic biogenic ceramic composites

Aplanarity of carbonate groups in $CaCO_3$

$\Delta Z_{C\text{-}O1} = c(z_C - z_{O1})$

Calcite	Biogenic aragonite	Mineral aragonite
0 Å	*Intermediate ?*	*0.05744 Å*

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