Combined Analysis: structure, microstructure, texture, stresses, phase, reflectivity

Daniel Chateignier
IUT-Univ. Caen Basse-Normandie
CRISMAT-ENSICAEN (Caen-France)

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Structure determination on real (textured) samples

Dilemma 1

Structure and QTA: correlations: $f(g)$ and $|F_h|^2$ 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

$|F_h|^2$:
- 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 \( \mu \)
- unknown effective thickness (porosity)
Phase and Texture

Dilemma 4

Phase and QTA: correlations: \( f(g), S_\Phi \)

\( f(g) \):
- angular relationships
- plays on individual spectra
- essential to operate on textured sample

\( S_\Phi \):
- 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 $\Psi$
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
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?
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 ...)

[Diagram of a diffractometer setup]
2D Curved Area Position Sensitive Detector

D19 - ILL

+ ~100 experiments (2D Debye-Scherrer diagrams) in as many sample orientations
$\text{AlN/Pt/TiO}_x/\text{Al}_2\text{O}_3/\text{Ni-Co-Cr-Al}$

$\text{Rw} \, (\%) = 24.120445$
$\text{Rexp} \, (\%) = 5.8517213$

$T(\text{AlN}) = 14270(3) \, \text{nm}$
$T(\text{Pt}) = 430(3) \, \text{nm}$
(χ,φ) randomly selected diagrams

\begin{align*}
\text{Al}_2\text{O}_3 \\
a &= 4.7562(6) \text{ Å} \\
c &= 12.875(3) \text{ Å} \\
T &= 7790(31) \text{ nm} \\
\langle t \rangle &= 150(2) \text{ Å} \\
\langle \varepsilon \rangle &= 0.008(3)
\end{align*}

\begin{align*}
\text{Ni,Co} \\
a &= 3.569377(5) \text{ Å} \\
\langle t \rangle &= 7600(1900) \text{ Å} \\
\langle \varepsilon \rangle &= 0.00236(3) \\
\sigma_{11} &= -328(8) \text{ MPa} \\
\sigma_{22} &= -411(9) \text{ MPa}
\end{align*}
Rw (%) = 4.1
a = 3.11203(1) Å
c = 4.98252(1) Å
T = 14270(3) nm
<\text{t}> = 2404(8) Å
<\varepsilon> = 0.001853(2)
\sigma_{11} = -1019(2) MPa
\sigma_{22} = -845(2) MPa

Rw (%) = 33.3
a = 3.91198(1) Å
T = 1204(3) nm
<\text{t}> = 2173(10) Å
<\varepsilon> = 0.002410(3)
\sigma_{11} = -196.5(8)
\sigma_{22} = -99.6(6)
Substrate bias vs stress-texture evolution

- \( \sigma_{11\text{ AlN}} \)
- \( \sigma_{22\text{ AlN}} \)
- \( \sigma_{11\text{ Pt}} \)
- \( \sigma_{22\text{ Pt}} \)
Aragonitic layers in mollusc shells

Gastropods

Crossed lamellar layers

Charonia lampas lampas (triton or trumpet cousin)

Columnar Nacre

Bivalves

Sheet Nacre

Haliotis tuberculata (common abalone)

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

<table>
<thead>
<tr>
<th></th>
<th>Charonia</th>
<th>Pinctada</th>
<th>Haliotis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OCL</td>
<td>IRCL</td>
<td>ICCL</td>
</tr>
<tr>
<td>a (Å)</td>
<td>4.98563(7)</td>
<td>4.97538(4)</td>
<td>4.9813(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.0103(1)</td>
<td>7.98848(8)</td>
<td>7.9679(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.74626(3)</td>
<td>5.74961(2)</td>
<td>5.76261(5)</td>
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<tr>
<td>Δa/a</td>
<td>0.0047</td>
<td>0.0026</td>
<td>0.0038</td>
</tr>
<tr>
<td>Δb/b</td>
<td>0.0053</td>
<td>0.0026</td>
<td>0.0000</td>
</tr>
<tr>
<td>Δc/c</td>
<td>0.0004</td>
<td>0.0010</td>
<td>0.0033</td>
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<tr>
<td>ΔV/V (%)</td>
<td>1.05</td>
<td>0.62</td>
<td>0.71</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Elastic Stiffnesses</th>
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<tbody>
<tr>
<td>Single crystal</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
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<tr>
<td>ICCL</td>
<td>96.5</td>
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<tr>
<td>RCL</td>
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<td></td>
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<tr>
<td>OCL</td>
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</table>
## Atomic Structures

<table>
<thead>
<tr>
<th></th>
<th>Geological reference</th>
<th>Charonia lampas OCL</th>
<th>Charonia lampas IRCL</th>
<th>Charonia lampas ICCL</th>
<th>Strombus decorus mixture</th>
<th>Pinctada maxima ISN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>y</td>
<td>0.41500</td>
<td>0.41418(5)</td>
<td>0.414071(4)</td>
<td>0.41276(9)</td>
<td>0.4135(7)</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>0.75970</td>
<td>0.75939(3)</td>
<td>0.76057(2)</td>
<td>0.75818(8)</td>
<td>0.7601(8)</td>
</tr>
<tr>
<td>C</td>
<td>y</td>
<td>0.76220</td>
<td>0.7628(2)</td>
<td>0.76341(2)</td>
<td>0.7356(4)</td>
<td>0.7607(4)</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>-0.08620</td>
<td>-0.0920(1)</td>
<td>-0.08702(9)</td>
<td>-0.0833(2)</td>
<td>-0.0851(7)</td>
</tr>
<tr>
<td>O1</td>
<td>y</td>
<td>0.92250</td>
<td>0.9115(2)</td>
<td>0.9238(1)</td>
<td>0.8957(3)</td>
<td>0.9228(4)</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>-0.09620</td>
<td>-0.09205(8)</td>
<td>-0.09456(6)</td>
<td>-0.1018(2)</td>
<td>-0.0905(9)</td>
</tr>
<tr>
<td>O2</td>
<td>x</td>
<td>0.47360</td>
<td>0.4768(1)</td>
<td>0.4754(1)</td>
<td>0.4864(3)</td>
<td>0.4763(6)</td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>0.68100</td>
<td>0.6826(1)</td>
<td>0.68332(9)</td>
<td>0.6834(2)</td>
<td>0.6833(3)</td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>-0.08620</td>
<td>-0.08368(6)</td>
<td>-0.08473(5)</td>
<td>-0.0926(1)</td>
<td>-0.0863(7)</td>
</tr>
<tr>
<td>ΔZ_{C-O1} (Å)</td>
<td></td>
<td>0.05744</td>
<td>0.00029</td>
<td>0.04335</td>
<td>0.1066</td>
<td>0.031</td>
</tr>
</tbody>
</table>

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.
Virgin, no texture correction

texture corrected,

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

Virgin, with texture correction

Virgin, no texture correction
Amorphous/crystalline volume fraction (damaged fraction $F_d = \frac{V_a}{V}$) as determined by x-ray diffraction

### Fitting parameters

<table>
<thead>
<tr>
<th></th>
<th>Krypton</th>
<th>Iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single impact</td>
<td>Double impact</td>
</tr>
<tr>
<td>$F_d = B(1 - \exp(-A\Phi t))$</td>
<td>$F_d = B(1 - (1 + A\Phi t) \exp(-A\Phi t))$</td>
<td>$F_d = B(1 - \exp(-A\Phi t))$</td>
</tr>
<tr>
<td>$A = \pi R^2$ (cm$^2$)</td>
<td>$1.85 \pm 0.15 \times 10^{-13}$</td>
<td>$4.1 \pm 0.15 \times 10^{-13}$</td>
</tr>
<tr>
<td>Radius $R$ (nm)</td>
<td>$2.4 \pm 0.2$</td>
<td>$3.6$</td>
</tr>
<tr>
<td>$B$ (Max. damage rate)</td>
<td>$0.87$</td>
<td>$0.85 \pm 0.2$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>$0.013$</td>
<td>$0.0006$</td>
</tr>
</tbody>
</table>
**Turbostratic phyllosilicate aggregates**

GoF = 3.3

V%  
1.45(2)  
6.6(1)  
0.19(1)  
91.8(3)
$\text{Al}_2\text{O}_3$ « standard » powder from Almelo

2$\theta$-scans:
GoF = 1.92
$R_W = 15.60 \%$
$R_B = 11.94 \%$

$\theta$–$2\theta$-scans:
GoF = 1.86
$R_W = 16.11 \%$
$R_B = 12.40 \%$

15 diagrams x 5 mn (fibre texture): 1.25 h
936 diagrams x 5 mn (non symmetric texture): 3.25 days
-70 microns x shift in $\chi$
And texture !!
Cyclic-fibre texture assumed
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
Merci de votre attention !

M. Morales, L. Lutterotti