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 $|F_h|^2$ are different!

$f(g)$:
- Angularly constrained: $[h_1 k_1 l_1]^*$ and $[h_2 k_2 l_2]^*$ 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
**Combined Analysis approach**

- **Extracted Intensities**
  - Orientation Distribution Function
    - Orientation Distribution Function
      - Rietveld
        - Structure + Microstructure + phase %
          - Popa-Balzar, \( \sin^2 \psi \)
            - Residual stresses Strain Distribution Function
              - Voigt, Reuss, Geometric mean
    - WIMV, E-WIMV Harmonics, components, ADC
      - Specular Reflectivity
        - Roughness, electron Density & EDP, Thickness
          - pole figures inverse pole figures
        - Structural parameters atomic positions, substitutions, vibrations
          - Structural parameters cell parameters
            - Multiphased, layered samples:
              - Thickness, Anisotropic Sizes and \( \mu \)-strains (Popa), Stacking faults (Warren), Distributions, Turbostratism (Ufer)
                - Phase ratio (amorphous + crystalline)
                  - Le Bail Rietveld
        - Fresnel, Matrix (Parrat), DWBA
          - Combined Analysis approach
            - Le Bail Volgy, Rieuss, Geometric mean
              - Residual stresses Strain Distribution Function
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$_2$O$_3$/Ni-Co-Cr-Al

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

T(AlN) = 14270(3) nm
T(Pt) = 430(3) nm
\((\chi, \varphi)\) randomly selected diagrams

**Al\(_2\)O\(_3\)**

- \(a = 4.7562(6) \text{ Å}\)
- \(c = 12.875(3) \text{ Å}\)
- \(T = 7790(31) \text{ nm}\)
- \(<t> = 150(2) \text{ Å}\)
- \(<\varepsilon> = 0.008(3)\)

**Ni, Co**

- \(a = 3.569377(5) \text{ Å}\)
- \(<t> = 7600(1900) \text{ Å}\)
- \(<\varepsilon> = 0.00236(3)\)
- \(\sigma_{11} = -328(8) \text{ MPa}\)
- \(\sigma_{22} = -411(9) \text{ MPa}\)
Rw (%) = 4.1

\[\begin{align*}
a &= 3.11203(1) \, \text{Å} \\
c &= 4.98252(1) \, \text{Å} \\
T &= 14270(3) \, \text{nm} \\
\langle t \rangle &= 2404(8) \, \text{Å} \\
\langle \varepsilon \rangle &= 0.001853(2) \\
\sigma_{11} &= -1019(2) \, \text{MPa} \\
\sigma_{22} &= -845(2) \, \text{MPa}
\end{align*}\]

Rw (%) = 33.3

\[\begin{align*}
a &= 3.91198(1) \, \text{Å} \\
c &= 4.98252(1) \, \text{Å} \\
T &= 1204(3) \, \text{nm} \\
\langle t \rangle &= 2173(10) \, \text{Å} \\
\langle \varepsilon \rangle &= 0.002410(3) \\
\sigma_{11} &= -196.5(8) \, \text{MPa} \\
\sigma_{22} &= -99.6(6)
\end{align*}\]
Substrate bias vs stress-texture evolution

![Graph showing the relationship between substrate bias and stress-texture evolution for different materials such as AlN and Pt. The graph includes polar plots for different stress levels and bias values. The y-axis represents stress (GPa) ranging from 0 to -1.2, while the x-axis represents bias (V) ranging from -15 to -35. The graph includes lines for sigma 11 AlN, sigma 22 AlN, sigma 11 Pt, and sigma 22 Pt.]
Ca$_3$Co$_4$O$_9$ thermoelectrics

Ca$_3$Co$_4$O$_9$: Misfit lamellar and modulated Structure, with high thermopower

Two monoclinic sub-systems:

S1 with $a \sim 4.8 \text{Å}$, $b_1 \sim 4.5 \text{Å}$, $c \sim 10.8 \text{Å}$ et $\beta \sim 98^\circ$ (NaCl-type)

S2 with $a \sim 4.8 \text{Å}$, $b_2 \sim 2.8 \text{Å}$, $c \sim 10.8 \text{Å}$ et $\beta \sim 98^\circ$ (CdI$_2$-type)

$\Gamma = \frac{\sigma_{ab}}{\sigma_c} \sim 10$

Texture
\( \chi = 0^\circ \)

\( \Delta \chi = 5^\circ \)

\( \chi = 90^\circ \)

Supercell

\[ \text{RP}=19.7\%, \text{Rw}=11.9\% \]
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

<table>
<thead>
<tr>
<th></th>
<th>OCL</th>
<th>Charonia</th>
<th>Pinctada</th>
<th>Haliotis</th>
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<td></td>
<td>IRCL</td>
<td>ICCL</td>
<td>ISN</td>
<td>ICN</td>
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<tr>
<td>a (Å)</td>
<td>4,9863(7)</td>
<td>4,97538(4)</td>
<td>4,9813(1)</td>
<td>4,97071(4)</td>
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<td>b (Å)</td>
<td>8,0103(1)</td>
<td>7,98848(8)</td>
<td>7,9679(1)</td>
<td>7,96629(6)</td>
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<tr>
<td>c (Å)</td>
<td>5,74626(3)</td>
<td>5,74961(2)</td>
<td>5,76261(5)</td>
<td>5,74804(2)</td>
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<tr>
<td>Δa/a</td>
<td>0,0047</td>
<td>0,0026</td>
<td>0,0038</td>
<td>0,0017</td>
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<tr>
<td>Δb/b</td>
<td>0,0053</td>
<td>0,0026</td>
<td>0,0000</td>
<td>-0.0002</td>
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<tr>
<td>Δc/c</td>
<td>0,0004</td>
<td>0,0010</td>
<td>0,0033</td>
<td>0,0007</td>
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<tr>
<td>ΔV/V (%)</td>
<td>1,05</td>
<td>0,62</td>
<td>0,71</td>
<td>0,22</td>
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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

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<th>Single crystal</th>
<th>160</th>
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<th>1.7</th>
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<th>1.7</th>
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<td>87.2</td>
<td>15.7</td>
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<td></td>
<td>ICCL</td>
<td>96.5</td>
<td>31.6</td>
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<td>139</td>
<td>9.5</td>
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<td></td>
<td>31.6</td>
<td>103.3</td>
<td>14.1</td>
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<td>32.6</td>
<td>103.3</td>
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<tr>
<td></td>
<td>RCL</td>
<td>130.1</td>
<td>10.3</td>
<td>36.3</td>
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<td>132.6</td>
<td>36.3</td>
<td>31.1</td>
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<td>32.6</td>
<td>36.3</td>
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<td></td>
<td>OCL</td>
<td>111.1</td>
<td>13.2</td>
<td>13.2</td>
<td>32.8</td>
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## 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>
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<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>
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<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>
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<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>
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<tr>
<td>ΔZ\text{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
texture corrected, 10^{13} \text{ Kr cm}^{-2}

Virgin, with texture correction

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

![Graphs showing the amorphous/crystalline volume fraction for 70 MeV Krypton and 127 MeV Iodine.](image)

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

GoF = 3.3

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$_3$

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

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