Tomography and Precession Diffraction for 3D Structural Analysis of Nanocrystals

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Electrons: $10^3$ x stronger interaction with matter compared to x-rays

1D – data but probing the bulk

Powder X-ray diffraction

Crystal size

mm µm nm

Single crystal X-ray diffraction

Single crystal electron diffraction

3D – data but limited to the selected crystal
Information available from electron diffraction

- single crystals in polyphasic samples
- phase analysis
- crystal orientation

- cell parameters
- possible space groups
- existence of centrosymmetry
- structure analysis

- superstructures
- twinning
- Stress/strain measurements
- disorder, defects, dislocations

→ HRTEM

Excitation error s:
crystal cannot be oriented fully
(precision ↔ radiation damage)

Dynamical scattering:
Strong in oriented zones → wrong intensities, violated extinction rules
CBED: Use of dynamical effects, thick specimens >200 Å
Moving the Ewald sphere: Double diffraction reduction and reflection integration

Double diffraction along systematic row: e.g. (001) and (003) forbidden

On-Zone

Off-Zone
Measured and (Multislice) simulated precession patterns (L.D. Marks, Sinclair Northwestern Univ. USA)

Example: Natural Mineral $\text{Al}_2\text{SiO}_5$ Orthorhombic Pnnm with 32 atoms/unit cell (Andalusite)

- **Bragg’s Law Simulation**
- **Experimental**
- **Multislice**

With increasing precession angle:
- Exponential decay of forbidden reflections
- Linear decay of e.g. non-forbidden (002) reflection

Rate of decay is relatively invariant of the crystal thickness

$$I = A \exp(-D\phi)$$

Courtesy L.D. Marks,
Precession diffraction angle

- increase of the number of diffraction spots intercepted by the Ewald sphere
- integration over the reflection intensity and reduction of the excitation error effect
- reducing the effect of slight misorientation of the sample
- reduction of the dynamical effects and the diffraction dependency on the thickness of the sample

Increasing precession angle $\rightarrow$ increasing resolution in diffraction pattern (i.e. more diffraction spots are seen).

Example: Mayenite [111] $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  Space group: $I43d$
Advantages of nanodiffraction

- free control over the beam size
- we do not unnecessarily damage the sample
- possible to move the beam over the crystal
- we are sure about the area we are collecting the information from
A-Star Acquisition

Acquisition of precession electron diffraction spot patterns

Orientation map

Phase map

Mg-Cu-Gd partly recrystallized metallic glass with Mg₃Cu and Cu₂Gd crystalline precipitates

Strain map

Pt particles, Prof. P. Ferreira, J. Ganesh, Univ Texas at Austin USA
JEOL 2010 FEG (1 nm resolution)


Non-precessed  precessed
Crystallographic Orientation and Phase Identification

Template generation using Diffgen of all possible simulated orientations (every $1^\circ$) within stereographic triangle for given crystal lattice(s) and symmetry.

The degree of matching between experimental patterns and simulated templates is given by a correlation index; highest value corresponds to the adequate orientation/phase.
Identification example: nanocrystalline Cu

250 x 200 pixel data acquisition: ~ 5 min

Typical software data analysis time

cubic: 5-15 min

hexagonal, tetragonal: x 3-4 more time

Diffraction pattern

(nanocrystalline cubic copper)

correlation index = 585

Correlation index map

Orientation map of severely deformed copper

NBD step 20 nm
Different microscopes

Zeiss Libra 200

0.3° precession

NO FILTER

Zeiss Libra 200 FE

100 mrad

0.3° precession

ZERO LOSS FILTER

filter Libra 200 FE: 100 mrad acceptance angle (ΔE = 10 eV)

more information

visualize precisely high order/resolution reflections

M. Gemmi, IIT Pisa
Drug Delivery applications & Texture of nanoparticles

Orientation mapping with 10nm resolution

Matching of each collected pattern with a generated data bank

1 Fe₃O₄ nanoparticle (vertical view)

Several Fe₃O₄ nanoparticles self assembled (lateral view)

Unpublished results Courtesy of M Gemmi IIT Pisa Italy.
Nanoparticle (50 nm) phase identification

Orientation map precession 0.3º

PHASE map precession 0.3º

Magnetite or maghemite ??

$Fd\bar{3}m$

$P4_{1}32 \gamma-\text{Fe}_{2}\text{O}_{3}$

Fe$_3$O$_4$

cubic 8.32 A

cubic 8.32 A

ALL Nanoparticles

REVEALED AS

magnetite (RED)
INDEX and create virtual dark and bright field maps

Diffraction Pattern viewer with virtual aperture

Virtual dark field image
TEM orientation imaging: Phase maps with and without precession

3 existing phases: only possible to distinguish by precession

Orientation map

- Austenitic matrix with fcc structure (a=3.58 Å)
- Stacking faults with hexagonal structure (a=2.57 c=4.08 Å)

When stacking faults cross themselves, they produce locally a martensite structure (a=2.87 Å)

Crystal phase map

- Non-precessed
- Precession 0.4°

VBF
In-situ ASTAR STEM characterization In-situ Orientation Imaging ncAu

map 0: 0% strain
initial state

map 7: 4.6% strain
beginning of loading

map 9: 6.5% strain
middle of loading

map 11: 9.7% strain
raptured

A. Kobler, H. Hahn, C. Kübel, *Ultramicroscopy* 2013, online
3d data: Traditional approach – tilt series of oriented diffraction patterns

$\zeta$-phase Pigment Red 53:2

Ab initio structure solution by direct methods from PED data

**single zone**

Determination of Nb atom positions
Cell parameters: $a = 27.15\ \text{Å}$, $b = 21.60\ \text{Å}$, $c = 3.95\ \text{Å}$, space group $\text{Pbam}$

*Ab initio determination of the framework structure of the heavy-metal oxide $\text{Cs}_x\text{Nb}_{2.54}\text{W}_{2.46}\text{O}_{14}$ from 100 kV precession electron diffraction data*, Weirich et al., *Ultramicroscopy* **106** 164–175 (2006)

**3D data**

10 single zone patterns
Cell parameters: $a = b = 5.06\ \text{Å}$, $c = 32.54\ \text{Å}$, space group $\text{P-3c1}$
refined on Synchrotron XRPD data


Reflection intensities and corrections

\[ I(g) = \int |F(g) \sin(\pi ts_z)/(\pi s_z)|^2 ds_z \]

\( s_z \) taken appropriately over the Precession Circuit
\( t \) is crystal thickness (column approximation)
\( \phi \) is total precession angle

\[ I(g) = |F(g)|^2 L(g, t, \phi) \]

Lorentz Correction: \( L(g, t, \phi) = g \sqrt{1 - \left( \frac{g}{2R_0} \right)^2} \)


Blackman 2 Beam approximation:

\[ I_{\text{Blackman}}(t) = \int_0^{A_z} J_0(2x) dx; \quad A_g(k) \propto tF(k) \]

Multislice Calculation:

\[ s_z^{\text{eff}} = \left( s_z^2 + \frac{1}{\xi_g^2} \right)^{1/2} \]

\[ \xi_g = \frac{\pi V_c \cos \theta_B}{\lambda F_g} \]
Completeness of diffraction data

Tilt series: Prominent zones from oriented single crystal selected

- Unaccessible area 20°-60°
- Quick and easy (off-zone diffraction: no crystal orientation needed)
- Enhanced number of intensities
ADT data collection sequence – with and without precession

Select a crystal → Image → Diffraction → Tilt series

Nanodiffraction:
- crystals down to 30nm
- agglomerated samples
- beam sensitive samples

Tilt (1°)

Tilt around an arbitrary axis → off-zone data

- significantly less dynamical effects
- further enhancement of the number of independent intensities

Completeness of the reciprocal space is crucial for structure determination
Taking care of camera length calibration

The additional focussing introduces rotation and contraction/expansion of the pattern → change of the camera length.

Nanodiffraction  Nanodiffraction pattern  focus into spotty pattern using the diffraction lens  overlay
Tomography of the reciprocal space - ADT

**Real Space Tomography**


**Reciprocal Space Tomography**

±60° = 121 diffraction patterns
Approx. 2h data collection time

3D reconstructed reciprocal space

Bi$_{12}$O$_{17}$Cl$_2$: superstructure

Li$_2$O/Al$_2$O$_3$/WO$_3$: disordered
Steps necessary to reconstruct the reciprocal space

Crystal tracking by beam shift $\rightarrow$ diffraction shift (SAED small, NED more sensitive)

Finding the correct tilt axis
Importance of correct tilt axis
ADT – cell parameter determination using difference vector space

Cell parameter determination by Clusteranalysis

Error of approx. 2% and triclinic cells directly accessible

Dataset h,k,l Int for „ab-initio“ structure solution using X-ray programs

Peakintegration after fine background subtraction

No further correction is performed on the extracted electron diffraction data

Indexing the facets: Silikalit-I and 50nm Au nanorod

Wang et al. 1999
Carbó-Argibay et al. 2010
Katz-Boon H et al. 2011
Barite (BaSO₄):

a = 8.884 Å, b = 5.458 Å, c = 7.153 Å, V = 346 Å³
Space group Pnma found directly by SIR08, only minor extinction violations

355 of 375 possible reflections at 0.7 Å resolution
95% coverage of reciprocal space
### Structure solution of known structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Resolution</th>
<th>Completeness</th>
<th>Sample applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barite ( \text{BaSO}_4 )</td>
<td>Pnma</td>
<td>0.08 nm</td>
<td>~70% triclinic</td>
<td>Smallest crystal used: ~300 nm organics</td>
</tr>
<tr>
<td>Calcite ( \text{CaCO}_3 )</td>
<td>R-3c</td>
<td>0.06 nm</td>
<td>~90% monoclinic</td>
<td>~ 30 nm inorganics</td>
</tr>
<tr>
<td>ZnSb ( \text{Pbca} )</td>
<td></td>
<td></td>
<td></td>
<td>Largest analysed volume: 33000 Å³</td>
</tr>
<tr>
<td>Mullite ( \text{Al}_6\text{Si}<em>2\text{O}</em>{13} )</td>
<td>Pbam</td>
<td></td>
<td></td>
<td>Largest number of independent atoms: 90</td>
</tr>
<tr>
<td>Natrolite ( \text{Na}_2\text{Al}_2\text{Si}<em>3\text{O}</em>{10}\cdot2\text{H}_2\text{O} )</td>
<td>Fdd2</td>
<td></td>
<td></td>
<td>Agglomerated and embedded samples</td>
</tr>
<tr>
<td>10-CNBA ( \text{C}_29\text{NH}_17 )</td>
<td>P21/c</td>
<td>0.08 nm</td>
<td>≤0.01 nm</td>
<td>Polyphasic materials</td>
</tr>
<tr>
<td>Basolite ( \text{C}_6\text{H}_4\text{CuO}_5 )</td>
<td>Fm-3m</td>
<td></td>
<td></td>
<td>Highly beam sensitive material</td>
</tr>
<tr>
<td>NLO-organic ( \text{C}_20\text{O}_3\text{NH}_15 )</td>
<td>Pca2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IM-5 ( \text{Si}<em>{288}\text{O}</em>{576} )</td>
<td>Cmce</td>
<td>0.06 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5/Silikalit ( \text{Pnma} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_4)Ti(<em>6)O(</em>{14} )</td>
<td>Cm</td>
<td>0.08 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(_2)WO(_7 )</td>
<td>Cmce</td>
<td>0.06 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Diffraction data quality:**

- Completeness of diffraction space:
  - ~70% triclinic
  - ~90% monoclinic
- Resolution:
  - ~0.08 nm organics
  - ~0.06 nm inorganics
- Average deviation of atomic positions (comparison ADT - X-ray): ≤0.01 nm
- Good detectability of light atoms

**Sample applicability:**

- Smallest crystal used:
  - ~300 nm organics
  - ~ 30 nm inorganics
- Largest analysed volume: 33000 Å³
- Largest number of independent atoms: 90
- Agglomerated and embedded samples
- Polyphasic materials
- Highly beam sensitive material
Principle of tomography

Projected potential

Reconstructed image

Object

Tomographic reconstruction

Real space

Image plane

projection of potential

Reciprocal space

Backfocal plane

FT of potential
Missing cone problem: ZSM-5 (twinned crystals)

Pnma: $a = 20.1 \, \text{Å}$, $b = 19.9 \, \text{Å}$, $c = 13.4 \, \text{Å}$, $V= 5360 \, \text{Å}^3$
2288 indep. reflections, completeness 79% mainly reflections in direction $a^*$ are missing

Completeness 100%
Theoretical data

Completeness 79%
Experimental data

12 T sites; 10-member rings
Si/O determined „ab initio“; Na by fourier map; EDX confirms small amount of Na
Detectability of atoms

Electron radiation:  - atoms are less distinguishable
                  - light atoms are better visible next to heavy atoms

Elemental analysis (EDX) can deliver composition information

Si/Al: distinguishable via bond lengths
Si/(Ge, Ti, ...): chance to find major

Carbamazepine Polymorph III: Solution
„direkt methods“ from SIR14

1,5-diaminoanthraquinone (DAAQ) - organic dye

40° ADT data: two atoms missing

found in Literature: solved from zonal PED data and XRPD

120° ADT data: all atoms detected
Si/Ge Zeolite + organic structure-directing agent, framework density 11.4 T-atoms /1000 Å³

3 sets of 12-ring channels of 6.8 Å × 6.1 Å cloverleaf-like channels formed by 28-rings along c axis; pore diameters: 21.9 Å × 19.6 Å

**Delta-recycling**: Rius, J. (2012)
MOFs – highly beam sensitive material

MFU-4long

Bi(BTB): twinned crystals

Fm-3m, a=32.0 Å, V = 32,768 Å³, resolution 1.3 Å, R(F)=32%, max. deviation to XRPD = 0.21 Å

Problem: olivine and garnet + small crystals of a third unknown phase

New high-pressure phase synthesized in MgO-Al₂O₃-SiO₂-H₂O system

Not detected by optical microscope and by X-ray powder diffraction.

Re-synthesized after structure solution and refined versus x-ray powder data

High pressure – boron oxo nitride ($\text{B}_6\text{N}_4\text{O}_3$)


Triangular platelets <50nm (EELS: B:N:O = 6:4:3)
Charoite - Murun Massif in Yakutiya, Sakha Republic, Siberia, Russia

- asbestos-like fibres typically around 200 nm diameter
- two phases: fibre axes almost parallel, a and b differently oriented
- fibres are laterally separated by an amorphous phase

Charoite-90: space group P2₁/m
a=31.96 Å, b=19.64 Å, c=7.09 Å, β=90°

Charoite-96: space group P2₁/m
a=32.11 Å, b=19.67 Å, c=7.23 Å, β=95.9°

I. Rozhdestvenskaya et al., *Mineralogical Magazin*, 74(1), 159-177 (2010)
Hydroxyapatite – enamel and dentine $\text{Ca}(2)_6\text{Ca}(1)_4(\text{PO}_4)_6(\text{OH})_2$

ADT analysis on 3 enamel and 2 dentine crystals deliver best solutions for $P6_3$.

Contrast differences: 02-21 and 02-2-1 02-22 and 02-2-2

→ No mirror perpendicular to c

Bi-sulfate incrustations, oxidation of bismuthinite (Bi$_2$S$_3$) Alfenza mine, Italy

Monoclinic spacegroup $Pc$ or $P2_1/c$; $a=22.0$, $b=16.7$, $c=15.9$ Å, $\beta=102.9^\circ$, strong disorder along a*

$\Rightarrow$ Structure could not be solved

Hexagonal $P6_3mc$, $P-62c$ or $P6_3/mmc$, $a=9.6$, $c=15.3$ Å

$\text{Bi}_{9-x}\text{Te}_x(\text{OH})_6\text{O}_8$ clusters and $\text{SO}_4$ groups

EDX reveals only for this phase a small amount of Te

Zeolite beta - stacking disorder visualized by ADT

Polytype A:
$P4_{1}22$
$a = 12.66 \, \text{Å} \\
c = 26.41 \, \text{Å}$

Polytype B:
$C2/c$
$a = 17.90 \, \text{Å}, b = 17.92 \, \text{Å} \\
c = 26.41 \, \text{Å}, \beta = 114.8^\circ$
Vaterite – superstructure solved ab-initio by direct methods

Structure explains all features observed in the Raman spectrum

Space group C2/c

views down [010] and [103] (equivalent to [001] in the previous hexagonal structure models)

Space group C-1

Conclusion

**Minerals:**
- Sarrabusite: \(S_2^{1+x}Bi_{9-x}Te_x(OH)_6O_8(SO_4)_2\) [1]
- Charoite-90/96
- Chukanovit
- Cannonit

**Phosphates:**
- \(SrP_3N_5O\)
- \(Ba_6Br_3P_{12}N_{17}O_9\)

**Organic-inorganic hybrids:**
- ECS-3, ECS-5

**Intermetallic nanophases:**
- \(Zn_8Sb_7\)

**Oxides:**
- \(Na_2W_4O_{13}\)
- \(Li_2Ti_3NiO_8\)
- \(NaHTi_3O_7\cdot H_2O\)
- \(Na_2Ti_6O_{13}\)

**Ca-compounds:**
- Vaterite \(CaCO_3\)
- \(Ca_5Si_6O_{17}\cdot 5H_2O\)
- \(Ca_5(PO_4)_3(OH)\)

**High pressure phases:**
- HP hydrous Al-pyroxene \((Mg_2Al(OH)_2AlSiO_6)\)

**Organic:**
- Pharmaceuticals
- Amides
- Dyes

**Zeolites:**
- ITQ-43, ITQ-45, ITQ-N
- ZSM-5, ZSM-25,
- Zeolite beta

**Metal Organic Frameworks (MOF):**
- MUF-4l
- Bi(BTB)

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**Metal Organic Frameworks (MOF):**
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The group

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Photo: Dr. Peter Müller, MIT, Cambridge, MA
Acknowledgment

Cooperation:
- Max Otten, FEI, Eindhoven, Netherlands
- Wolfgang Tremel, Universität Mainz, Germany (Vaterit)
- Avelino Corma, Instituto de Tecnologia Quimica, Valencia, Spain (ITQ-43)
- Giovanna Vezzalini, University of Modena and Reggio Emilia and Rossella Arletti, University of Torino, Italy (ZSM-5)
- Ch. Bärlocher, ETH Zürich, Switzerland (IM-5)
- Dirk Volkmer, Dimitry Denysenko, University of Ulm, Germany (MFU-4long)
- Norbert Stock, University of Kiel (CAU), Germany (Bi(BTB))
- Wulf Depmeier, Michael Czank, University of Kiel, Germany and Ira Rozhdestvenskaya, University of Moskow, Russia (Charoite)
- Mauro Gemmi, Stefano Poli, University of Milano, Italy (Hapy)

Financial Support:
Stiftung Rheinland-Pfalz Innovation SFB 625 SPP 1415

Thank you for your attention