MCX
(Material characterization by X-ray diffraction)

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X-ray Diffraction (XRD)

X-ray Powder Diffraction (XRPD)
• What is X-ray Diffraction
• Basics of Crystallography
• What is powder diffraction
• How measure XRPD
• Why perform powder diffraction at synchrotrons
• Why and when use XRPD

• Instrumentation at synchrotron: MCX beamline for powder diffraction
• Applications of SR-XRPD (case of study)
**Oxford dictionary:**

**diffraction**

the process by which a beam of light is spread out as a result of passing through a narrow aperture or across an edge (an obstacle), typically accompanied by interference between the wave produced.

This phenomenon originate when the wave encounter an obstacle that is of comparable in size to its wavelength

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**Diffraction**

- Wave Diffraction

  Wide gap compared to wavelength results in waves traveling straight on or rectilinear propagation.

  ![Wide gap](image)

  \[ \lambda \]

- Narrow gap waves spread out beyond the gap. This spreading is called diffraction.

  Diffraction is most obvious when the gap is approximately the same size as the wavelength of the wave.

  ![Narrow gap](image)

  \[ \lambda \]
The wavelength of X rays are similar to the distance between atoms.
- The electrons in an atom coherently scatter light, producing secondary spherical waves. This phenomenon is known as elastic scattering and the electron is known as the scatterer.

  The strength with which an atom scatters light is proportional to the number of electrons around the atom.

Crystals are regular arrays of atoms characterized by the long range order.
The electrons in an atom coherently scatter light, producing secondary spherical waves. This phenomenon is known as elastic scattering and the electron is known as the scatterer.

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Crystals are regular arrays of atoms characterized by the long range order.
A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law.

\[ 2dsin\theta = n\lambda \]

- \( d \) is the spacing between diffracting planes.
- \( \theta \) is the incident angle.
- \( n \) is any integer.
- \( \lambda \) is the wavelength of the incident beam.
Deriving Bragg’s Law: $n\lambda = 2d\sin\theta$

Constructive interference occurs only when

1. $n\lambda = AB + BC$
2. $AB = BC$
3. $n\lambda = 2AB$
4. $AB = d\sin\theta$
5. $n\lambda = 2d\sin\theta$
6. $\lambda = 2d_{hkl}\sin\theta_{hkl}$
X-ray diffraction by crystals
What is a Crystal?
A crystal consists in an ordered **three dimensional** arrangement of atoms, molecules or ions. This can be imagined as the stacking of bricks in a wall (resembling to a two dimensional ordered arrangement of bricks!).

<table>
<thead>
<tr>
<th>2D Ordered Arrangement of Bricks</th>
<th>3D Ordered Arrangement of atoms</th>
</tr>
</thead>
</table>

![2D Ordered Arrangement of Bricks](image1.png)  
![3D Ordered Arrangement of atoms](image2.png)
What is a unit-cell and lattice?

A **unit-cell** is the smallest building block of a crystal and is representative unit of the repetitive motifs in the crystal structure.

**Unit cell** of a crystalline structure is defined by:

- $a$, $b$, and $c$ (length) and $\alpha$, $\beta$, and $\gamma$ angles between $a$, $b$, and $c$ which can be determined by XRD.

**Lattice** is the geometrical basis of all the crystals. A lattice can be considered as a regular and infinite arrangement of points/atoms where in each point/atom has the same surrounding environment. This is equally applicable in two and three dimensional space.
What is a unit-cell and lattice?
A **unit-cell** is the smallest building block of a crystal and is representative unit of the repetitive motifs in the crystal structure.

**Unit cell** of a crystalline structure is defined by:

\[ a, b \text{ and } c \text{ (length) and } \alpha, \beta \text{ and } \gamma \text{ angles between } a, b \text{ and } c \text{ which can be determined by XRD}. \]

**Lattice** is the geometrical basis of all the crystals. A lattice can be considered as a regular and infinite arrangement of points/atoms where in each point/atom has the same surrounding environment. This is equally applicable in two and three dimensional space.
Types of Lattice Structures

1. Primitive Unit Cells
   - Face-Centered Cubic (FCC) Lattice Structure
   - Body-Centred Cubic (BCC) Lattice structure
   - Hexagonal Closest Packed (HCP) Lattice Structure
Types of Crystal Systems

- **Simple Cubic**: $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$
- **Tetragonal**: $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$
- **Orthorhombic**: $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$
- **Hexagonal**: $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
- **Rhombohedral**: $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$
- **Monoclinic**: $a = b \neq c$, $\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$
- **Triclinic**: $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$
There are only 14 independent 3D lattices!

**Bravais lattices**

<table>
<thead>
<tr>
<th>System/Axes/Angles</th>
<th>Unit Cells</th>
</tr>
</thead>
</table>
| **Cubic** 
  \( a = b = c \) 
  \( \alpha = \beta = \gamma = 90^\circ \) | Simple | Face-centered | Body-centered |
| **Tetragonal** 
  \( a = b \neq c \) 
  \( \alpha = \beta = \gamma = 90^\circ \) | Simple | Body-centered |
| **Orthorhombic** 
  \( a \neq b \neq c \) 
  \( \alpha = \beta = \gamma = 90^\circ \) | Simple | Body-centered | Base-centered | Face-centered |
| **Monoclinic** 
  \( a \neq b \neq c \) 
  \( \alpha = \gamma = 90^\circ; \beta \neq 90^\circ \) | Simple | Base-centered |
| **Triclinic** 
  \( a \neq b \neq c \) 
  \( \alpha \neq \beta \neq \gamma \neq 90^\circ \) | | |
| **Hexagonal** 
  \( a = b \neq c \) 
  \( \alpha = \beta = 90^\circ; \gamma = 120^\circ \) | | |
| **Rhombohedral** 
  \( a = b = c \) 
  \( \alpha = \beta = \gamma \neq 90^\circ \) | | |
• Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal.
  – These crystallographic planes are identified by **Miller indices** \( (hkl) \)
NaCl Crystal example

Basics of Crystallography

FCC

Na Cl

(200)

(220)

Wavelength: 1.54056

2 theta
55.008, 102.27
h, k, l = 3, 1, 1
What is a powder?

- A powder is a sample that consists of many small crystallites with a wide range of different orientations in space.
  - Ideally, a random and uniform distribution of orientations
- Only some small fraction of the crystallites in the sample are in the correct orientation to contribute to the diffracted intensity in a given peak

Only crystallites that fulfill Bragg’s law contribute to diffraction
What is powder diffraction

From single crystal to Powder Diffraction

- Single crystal
- Full powder average
What is powder diffraction?
Amorphous materials like glass do not have a periodic array with long-range order, so they do not produce a diffraction pattern.

Three phase of SiO$_2$ are chemically identical. Quartz and cristobalite have two different crystal structures.
How measure XRPD?

1) Production

Source of radiation
- X-Ray tube
- Syncrotron Radiation
- Neutron
- … electron diffraction (not treated here)

2) Diffraction

3) Detection

4) Interpretation?

*n* \(\lambda = 2d\sin\theta\)

Diffraction occurs only when Bragg's Law is satisfied. Condition for constructive interference from planes with spacing *d*.
The result of a diffraction experiment is a diffractogram in which is reported the trend of the intensity of the diffracted radiation as a function of 2θ.

The intensity of radiation diffracted depends on how much the crystalline planes are densely populated and how much the atoms are rich in electrons.
How measure XRPD?

4) Interpretation?

\[ I_{hkl} \propto |F_{hkl}|^2 \]

The structure factor \( F_{hkl} \) sums the results of scattering from all the atoms in the unit cell to form a diffraction peaks from the \((hkl)\) planes of atoms.

The amplitude of scattered light is determined by:

- Where the atoms are on the atomic planes
- this is expressed by the fractional coordinates \(x_j y_j z_j\)

What atoms are on the atomic planes?

- \(f_j\), that measures the X-ray scattering power of each atom.
How measure XRPD?

4) Interpretation?

- Background
  - Sample
  - Scattering from sample holder, air, ...

- Incoherent scattering:
  - Compton scattering

- Amorphous fraction
  (local order/disorder)

- Reflections
  - Position
  - Intensity
  - Profile (FWHM, peak shape)
    - Instrument function
    - Sample broadening

  - Lattice parameters
  - Space group

  - Proof of phase purity
  - Thermal expansion
  - Compressibility
  - Phase changes

  - Crystal structure:
    - Atomic positions
    - Temperature factor
    - Occupancy (Disorder)
    - Texture

  - Qualitative/quantitative phase analysis

- Real structure:
  - Stress
  - Strain
  - Crystallite size
  - Domain Size
How measure XRPD?

4) Interpretation?

Intensity

No Preferred Orientation

Preferred Orientation

incident x-ray

reflected x-ray

incident x-ray

reflected x-ray

All planes detected equally

One plane detected preferentially

No preferred orientation - correct intensity ratios
Preferred orientation - highly skewed intensity ratios
How measure XRPD?

4) Interpretation?

Background
- Sample
- Scattering from sample holder, air, ...

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Profile function
- Instrument broadening
- Sample broadening
4) Interpretation?

The diffraction peak we see is a result of various broadening ‘mechanisms’ at work.

Full Width at Half-Maximum (FWHM) is typically used as a measure of the peak ‘width’.
Why perform powder diffraction at synchrotrons

- High intensity
- Highly monochromatic parallel beam
- Energy tunability

Higher resolution
Faster measurements
New types of experiments

- *Ab initio* determination of crystal structures
- Quantitative detection of small amounts of polymorphic phases
- Resonant scattering experiments
- Time-resolved experiments
- *In situ* experiments (P, T, …)
- Microdiffraction
Why perform powder diffraction at synchrotrons

Transmission geometry

- synchrotron white beam
- monochromator
- parallel beam
- sample in capillary
- detector
- scan
- 2θ
Why perform powder diffraction at synchrotrons

Reflection geometry
Why and When use XRPD

- Phase identification - Qualitative phase analysis (search match procedures)
- Quantitative Phase Analysis (QPA)
- Determination of the crystal structure (ab initio solution and refinement)
- Crystal domain size / shape and reticular defect analysis (LPA)
- Determining Preferred Orientations (Texture Analysis)
- Amorphous phase and total diffusion analysis - PDF analysis
- Analysis of residual stresses

... and more
Rietveld method

Minimize differences between calculated and observed pattern by least-squares method

\[
\Phi = \sum_{i=1}^{n} w_i \left( Y_i^{\text{obs}} - Y_i^{\text{calc}} \right)^2
\]

\[
\Phi = \sum_{i=1}^{n} w_i \left( Y_i^{\text{obs}} - \left( b_i + K \sum_{j=1}^{m} I_j y_j(x_j) \right) \right)^2
\]

- \( b_i \) is the background at the \( i^{\text{th}} \) data point.
- \( K \) is the phase scale factor.
- \( m \) is the number of Bragg reflections contributing to the intensity of the \( i^{\text{th}} \) reflection.
- \( I_j \) is the integrated intensity of the \( j^{\text{th}} \) Bragg peak.
- \( y_i(x_i) \) is the peak shape function.
Why and When use XRPD

<table>
<thead>
<tr>
<th>Effect in diffraction pattern</th>
<th>Origin in crystal structure model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wrong peak positions</td>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td></td>
<td>Sample height displacement</td>
</tr>
<tr>
<td></td>
<td>Zero-shift</td>
</tr>
<tr>
<td>Wrong absolute intensities</td>
<td>Weight fraction (scaling)</td>
</tr>
<tr>
<td>Wrong relative intensities</td>
<td>Preferred orientation</td>
</tr>
<tr>
<td></td>
<td>Grainy sample</td>
</tr>
<tr>
<td></td>
<td>Atomic species / Substitutions / Vacancies</td>
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<tr>
<td></td>
<td>Atomic coordinates</td>
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<td></td>
<td>Site occupancies</td>
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<tr>
<td></td>
<td>Thermal displacement parameters</td>
</tr>
<tr>
<td>Wrong peak width</td>
<td>Crystallite size</td>
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<tr>
<td></td>
<td>Micro-strain</td>
</tr>
<tr>
<td></td>
<td>Surface roughness</td>
</tr>
<tr>
<td></td>
<td>Transparency</td>
</tr>
</tbody>
</table>
Why and When use XRPD
XRD is applicable only to crystalline material

Bragg law \[ 2dsin\theta = n\lambda \]

XRD pattern is a fingerprint of the material

From the XRD pattern we can extract a lot of information