Basic X-ray Powder Diffraction (XRPD)

- Solid-State, Material Science
  - Crystalline (Scattering : diffraction)
  - Non-crystalline (Scattering)
- Analytical Tool
- Qualitative and Quantitative Analysis
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern
- Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width
- *in-situ* Experiments
  - evaluate all properties above as a function of time, temperature, and gas environment
The parameters that define a unit cell are:

- \( a, b, c \) = unit cell dimensions along \( x, y, z \) respectively
- \( \alpha, \beta, \gamma \) = angles between \( b,c (\alpha); a,c (\beta); a,b (\gamma) \)
# Shapes of unit cells

All the possible shapes of a unit cell are defined by **7 crystal systems**, which are based on the relationship among \( a, b, c \) and \( \alpha, \beta, \gamma \),

<table>
<thead>
<tr>
<th>Condition</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a = b = c; \alpha = \beta = \gamma = 90^\circ )</td>
<td>Cubic system</td>
</tr>
<tr>
<td>( a = b \neq c; \alpha = \beta = \gamma = 90^\circ )</td>
<td>Tetragonal system</td>
</tr>
<tr>
<td>( a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ )</td>
<td>Orthorhombic system</td>
</tr>
<tr>
<td>( a = b = c; \alpha = \beta = \gamma \neq 90^\circ )</td>
<td>Rhombohedral system</td>
</tr>
<tr>
<td>( a = b \neq c; \alpha = \beta = 90^\circ; \gamma = 120^\circ )</td>
<td>Hexagonal system</td>
</tr>
<tr>
<td>( a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta )</td>
<td>Monoclinic system</td>
</tr>
<tr>
<td>( a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ )</td>
<td>Triclinic system</td>
</tr>
</tbody>
</table>
Crystalline materials are characterized by the orderly periodic arrangements of atoms.

- The unit cell is the basic repeating unit that defines a crystal.
- 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)**.
The atoms in a crystal are a periodic array of coherent scatterers and thus can diffract X-rays.

- Diffraction occurs when each object in a periodic array scatters radiation coherently, producing concerted constructive interference at specific angles.
- The electrons in an atom coherently scatter X-rays.
  - The electrons interact with the oscillating electric field of the X-ray.
- Atoms in a crystal form a periodic array of coherent scatterers.
  - The wavelength of X rays are similar to the distance between atoms.
  - Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- X-Rays are also reflected, scattered incoherently, absorbed, refracted, and transmitted when they interact with matter.
Scattering of X-rays by crystallographic planes
We need to consider how X-rays are diffracted by parallel crystallographic planes

X-rays diffracted in phase will give a signal. "In phase" means that the peak of one wave matches the peak of the following wave.

**Diffraction occurs ONLY when the distance travelled by the parallel X-rays are an integer of the wavelength.**
The diagram shows only two scattering planes, but implicit here is the presence of many parallel, identical planes, each of which is separated from its adjacent neighbor by a spacing $d$.

Constructive interference (diffraction) occurs when $(A+B)/\lambda = n$. The integer $n$ refers to the order of diffraction. For $n = 1$, $(A+B) = \lambda$ and for $n = 2$, $(A+B) = 2\lambda$ etc.
The two X-ray beams travel at different distances. This difference is related to the distance between parallel planes.

We connect the two beams with perpendicular lines (CD and CF). CE (interplanar distance) gives two equivalent right triangles.

\[
\sin \theta = \frac{DE}{d} \quad d \sin \theta = DE \quad DE = EF \quad d \sin \theta = EF
\]

\[
2d \sin \theta = EF + DE = \text{distance travelled by the bottom wave}
\]
This condition is met when the distance equals an integer multiple of the wavelength, called order of diffraction, \( n \). The final equation is the BRAGG’S LAW

\[
 n\lambda = 2d \sin \theta
\]

Data are collected by using X-rays of a known wavelength. The sample is rotated so that the angle of diffraction changes.

When the angle is correct for diffraction a signal is recorded.

With modern X-ray **diffractometers** the signals are converted into peaks.
Bragg’s law is a simplistic model to understand what conditions are required for diffraction.

\[ \lambda = 2d_{hkl} \sin \theta \]

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta} \]

- For parallel planes of atoms, with a space \( d_{hkl} \) between the planes, constructive interference only occurs when Bragg’s law is satisfied.
  - In our diffractometers, the X-ray wavelength \( \lambda \) is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle \( \theta \).
  - Additionally, the plane normal must be parallel to the diffraction vector
    - Plane normal: the direction perpendicular to a plane of atoms
    - Diffraction vector: the vector that bisects the angle between the incident and diffracted beam

- The space between diffracting planes of atoms determines peak positions.
- The peak intensity is determined by what atoms are in the diffracting plane.
- For Atomic/Molecular distances in Å the wavelength for diffraction \( \lambda \) is \( \sim 1\text{Å} \)
CHARACTERIZATION OF THE STRUCTURE OF SOLIDS

Three main diffraction techniques $\sim \lambda$ Å:

- **X-ray diffraction**
  - Single crystal
  - *Powder*
- Electron diffraction
- Neutron diffraction

**Principles of X-ray diffraction**

X-rays are passed through a crystalline material and the patterns produced give information of size and shape of the unit cell.

X-rays passing through a crystal will be bent at various angles: this process is called **diffraction**.

X-rays interact with electrons in matter, i.e. are scattered by the electron clouds of atoms.
The angles at which x-rays are diffracted depends on the distance between adjacent layers of atoms or ions. X-rays that hit adjacent layers can add their energies constructively when they are “in phase”. This produces dark dots on a detector plate.
Single-Crystal (radial + spatial) (single orientation)

Polycrystalline (preferred orientations)

Powder (radial) (random orientations)
THE POWDER TECHNIQUE

An X-ray beam diffracted from a lattice plane can be detected when the x-ray source, the sample and the detector are correctly oriented to give Bragg diffraction.

A powder or polycrystalline sample contains an enormous number of small crystallites, which will adopt all possible orientations randomly.

Thus for each possible diffraction angle there are crystals oriented correctly for Bragg diffraction.

Each set of planes in a crystal will give rise to a cone of diffraction.

Each cone consists of a set of closely spaced dots each one of which represents a diffraction from a single crystallite.
Formation of a powder pattern

• Samples can be powder, sintered pellets, coatings on substrates, engine blocks, ...

• If the crystallites are randomly oriented, and there are enough of them, then they will produce a continuous Debye cone.

• In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point; thus giving the appearance of a discrete diffraction peak.

![Diagram of powder sample and Debye cone](image)

Figure 3.9. The intersection of $d^{*}_{100}$ vectors from a powder with the Ewald sphere.
Experimental Methods

To obtain X-ray diffraction data, the diffraction angles of the various cones, $2\theta$, must be determined.

The main techniques are: Debye-Scherrer camera (photographic film) or powder diffractometer.

\[ \theta + \theta = 2\theta \]
Powder diffractometers typically use the Bragg-Brentano geometry.

- The incident angle, $\theta$, is defined between the X-ray source and the sample.
- The diffracted angle, $2\theta$, is defined between the incident beam and the detector angle.
- The incident angle $\theta$ is always $\frac{1}{2}$ of the detector angle $2\theta$.
- In a $\theta:2\theta$ instrument the tube is fixed, the sample rotates at $\theta$ $^\circ$/min and the detector rotates at $2\theta$ $^\circ$/min.
- In a $\theta:\theta$ instrument the sample is fixed and the tube rotates at a rate $-\theta$ $^\circ$/min and the detector rotates at a rate of $\theta$ $^\circ$/min.
- Powder, crystals in random orientations
- Goniometer swings through many angles
- Enough crystals, enough angles, get enough diffraction to determine material
Essential Parts of the Diffractometer

- X-ray Tube: the source of X Rays
- Incident-beam optics: condition the X-ray beam before it hits the sample
- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
- The sample & sample holder
- Receiving-side optics: condition the X-ray beam after it has encountered the sample
- Detector: count the number of X Rays scattered by the sample
Monochromators remove unwanted wavelengths of radiation from the incident or diffracted X-ray beam.

- Diffraction from a crystal monochromator can be used to select one wavelength of radiation and provide energy discrimination.
- An incident-beam monochromator might be used to select only Kα1 radiation for the tube source.
- A diffracted-beam monochromator may be used to remove fluoresced photons, Kβ, or W-contamination photons from reaching the detector.
Detectors

• point detectors
  – observe one point of space at a time
    • slow, but compatible with most/all optics
  – scintillation and gas proportional detectors count all photons, within an energy window, that hit them
  – Si(Li) detectors can electronically analyze or filter wavelengths

• position sensitive detectors
  – linear PSDs observe all photons scattered along a line from 2 to 10° long
  – 2D area detectors observe all photons scattered along a conic section
  – gas proportional (gas on wire; microgap anodes)
    • limited resolution, issues with deadtime and saturation
  – CCD/Phosphors
    • limited in size, expensive
  – solid state real-time multiple semiconductor strips
    • high speed with high resolution, robust
Powder Diffractometer
Preparing a powder specimen

- An ideal powder sample should have many crystallites in random orientations
  - the distribution of orientations should be smooth and equally distributed amongst all orientations
- If the crystallites in a sample are very large, there will not be a smooth distribution of crystal orientations. You will not get a powder average diffraction pattern.
  - crystallites should be $<10\mu m$ in size to get good powder statistics
- Large crystallite sizes and non-random crystallite orientations both lead to peak intensity variation
  - the measured diffraction pattern will not agree with that expected from an ideal powder
  - the measured diffraction pattern will not agree with reference patterns in the Powder Diffraction File (PDF) database
Ways to prepare a powder sample

• Top-loading a bulk powder into a well
  – deposit powder in a shallow well of a sample holder. Use a slightly rough flat surface to press down on the powder, packing it into the well.
    • using a slightly rough surface to pack the powder can help minimize preferred orientation
    • mixing the sample with a filler such as flour or glass powder may also help minimize preferred orientation
    • powder may need to be mixed with a binder to prevent it from falling out of the sample holder
      – alternatively, the well of the sample holder can be coated with a thin layer of Vaseline
• Dispersing a thin powder layer on a smooth surface
  – a smooth surface such as a glass slide or a zero background holder (ZBH) may be used to hold a thin layer of powder
    • glass will contribute an amorphous hump to the diffraction pattern
    • the ZBH avoids this problem by using an off-axis cut single crystal
  – dispersing the powder with alcohol onto the sample holder and then allowing the alcohol to evaporate, often provides a nice, even coating of powder that will adhere to the sample holder
  – powder may be gently sprinkled onto a piece of double-sided tape or a thin layer of Vaseline to adhere it to the sample holder
    • the double-sided tape will contribute to the diffraction pattern
  – these methods are necessary for mounting small amounts of powder
  – these methods help alleviate problems with preferred orientation
  – the constant volume assumption is not valid for this type of sample, and so quantitative and Rietveld analysis will require extra work and may not be possible
Important characteristics of samples for XRPD

• a flat plate sample for XRPD should have a smooth flat surface
  – if the surface is not smooth and flat, X-ray absorption may reduce the intensity of low angle peaks
  – parallel-beam optics can be used to analyze samples with odd shapes or rough surfaces
• Densely packed
• Randomly oriented grains/crystallites
• Grain size less than 10 microns
• ‘Infinitely’ thick
The detector records the **angles** at which the families of lattice planes scatter (diffract) the x-ray beams and the **intensities** of the diffracted x-ray beams.

The detector is scanned around the sample along a circle, in order to collect **all** the diffracted X-ray beams.

The angular positions \(2\theta\) and intensities of the diffracted peaks of radiation (**reflections or peaks**) produce a two dimensional pattern.

Each reflection represents the x-ray beam diffracted by a family of lattice planes \((hkl)\).

This pattern is characteristic of the material analysed (**fingerprint**).
APPLICATIONS AND INTERPRETATION OF X-RAY POWDER DIFFRACTION DATA

Information is gained from:

**Number and positions (2θ) of peaks**
- Crystal class
- Lattice type
- Cell parameters

**Intensity of peaks**
- Types of atoms
- Position of atoms

**Information gained:**
- Identification of unknown phases
- Determination of phase purity
- Determination and refinement of lattice parameters
- Determination of crystallite size
- Structure refinement
- Investigation of phase changes
Basic ideas of chemical analysis by X-ray diffraction

- **Qualitative analyses** -- the goal is to determine what phases are present
- **Quantitative analyses** -- the goal is to determine how much of each phase is present
- Note that diffraction methods determine *phases*, not elements
- Diffraction methods have the advantage that the sample does not have to be dissociated, dissolved, or otherwise changed (non-destructive).
The powder diffraction pattern as a “fingerprint”

• Experience has shown that the ensemble of $d$-spacings ($d=\lambda/2\sin\theta$) and intensities (“$I$”s) are sufficiently distinctive in order to identify phases
• “Uniqueness” is not a problem, particularly when combined with common sense
• Phase determination can be performed by a comparison of a set of experimental $d$’s and $I$’s with a database of $d$-$I$ files
• $d$-spacings are independent of wavelength
• Intensities are relative (most intense = 100)
Identification of compounds

The powder diffractogram of a compound is its ‘fingerprint’ and can be used to identify the compound

Powder diffraction data from known compounds have been compiled into a database (PDF) by the Joint Committee on Powder Diffraction Standard, (JCPDS)

‘Search-match’ programs are used to compare experimental diffractograms with patterns of known compounds included in the database

This technique can be used in a variety of ways
PDF - Powder Diffraction File

A collection of patterns of inorganic and organic compounds

Data are added annually (2006 database contains 186,107 entries)
Example of Search-Match Routine
Outcomes of solid state reactions

\[ 2\text{SrCO}_3 + \text{CuO} \rightarrow \text{SrCuO}_2 \quad ? \quad \text{Sr}_2\text{CuO}_3 \]

Product: \(\text{SrCuO}_2\)?  
Pattern for \(\text{SrCuO}_2\) from database

Product: \(\text{Sr}_2\text{CuO}_3\)?  
Pattern for \(\text{Sr}_2\text{CuO}_3\) from database
Example: Mannitol

Polymorph I

Polymorph II

Polymorph III

Evaporation from a binary mixture of solvents*

Spot plate evaporation method
A saturated solution of D-Mannitol in ethanol and water is prepared

<table>
<thead>
<tr>
<th>well</th>
<th>EtOH/H₂O</th>
<th>well</th>
<th>EtOH/H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/0</td>
<td>5</td>
<td>8/2</td>
</tr>
<tr>
<td>2</td>
<td>50/1</td>
<td>6</td>
<td>7/3</td>
</tr>
<tr>
<td>3</td>
<td>20/1</td>
<td>7</td>
<td>6/4</td>
</tr>
<tr>
<td>4</td>
<td>9/1</td>
<td>8</td>
<td>5/5</td>
</tr>
</tbody>
</table>

Mannitol: Results

%Ethanol

Polymorph I

Polymorph II

Polymorph III

Raman of Mannitol Polymorphs

Polymorph III

Polymorph II

Polymorph I
Quantitative analysis of multiphase mixtures

• Basic assumption: the diffracted intensity from a particular phase in a multiphase mixture is proportional to the concentration of that phase in the mixture

• The intensity diffracted by a single-phase powder specimen in a diffractometer is given by:

\[
I = \left( \frac{I_0 A \lambda^3}{32\pi r} \right) \left[ \left( \frac{\mu_0}{4\pi} \right)^2 e^4 \right] \left( \frac{1}{v^2} \right) \left| F \right|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M} \frac{2\mu}{2\mu}
\]

• Fortunately we can simplify this expression to:

\[
I_\alpha = \frac{K_1 c_\alpha}{\mu_{\text{mixture}}}
\]

We can cancel out the unknown \( K_1 \) if we can measure the ratio of \( I_\alpha \) to some reference line.
Methods for quantitative phase analyses

• **External standard method** – compare the experimental line intensity from the mixture to a line from a pure phase

• **Direct comparison method** – compare the experimental line intensity from the mixture to a line from another phase in the mixture

• **Internal standard method** – compare the experimental line intensity from the mixture to a foreign material mixed with the sample
Internal standard method

- A diffraction peak from the phase (whose volume fraction is being determined) is compared with a peak from a standard substance (thus restricted to powders)

\[ I_\alpha = \frac{K_3 c'_\alpha}{\mu_m} = \text{intensity from phase a} \]

\[ I_s = \frac{K_4 c_s}{\mu_m} = \text{intensity from one line of the standard} \]

Dividing we get:

\[ \frac{I_\alpha}{I_s} = \frac{K_3 c'_\alpha}{K_4 c_s} \]

\[ c_s = c'_\alpha K \frac{I_s}{I_\alpha} \]

- This method can be extended to multi-component mixtures
- By mixing known concentrations of phase \( \alpha \) and a constant concentration of a suitable standard and measuring the ratio \( I_\alpha/I_s \) we can establish a calibration curve for measuring \( \alpha \) in an unknown specimen
In-Situ Example

Reaction of $SO_2$ with Ni(BME-DACH)*

Ni(BME-DACH) $\rightleftharpoons$ BROWN SOLID $\leftrightarrow$ ORANGE SOLID

*M. Darensbourg et.al. (2004) Inorg. Chem. Accepted for publication
TGA of Ni(BME-DACH).xSO$_2$

NiL.2SO$_2$

NiL.SO$_2$

NiL
Effusion of SO2 : Ni(BME-DACH).2SO2

First 30mins
NiL.2SO2 → NiL.1SO₂

16 hr
NiL.1SO₂ → NiL

APS : Room Temperature in air
Dynamic X-ray Powder Diffraction
6 hour experiment. Ni(BME-DACH) 2SO2

- Conditions
- Starting material: Ni(BME-DACH) 2SO2
- Temp. 300K (Oxford)
- Dry Nitrogen Flow (20 l/min)
- Fine particles (< 5 microns)
- ~ 100 µgrams
- nylon loop
- no grease or oil
- data collected every 4 mins
- experiment: 6 hours
Wide Angle X-ray Scattering of Concentrated Solutions

50% NMe$_4$Cl in H$_2$O
Sealed in a 0.3mm PET tube