**X-Ray Diffraction**

- Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles.

- The electrons in an atom coherently scatter light.
  - We can regard each atom as a coherent point scatterer.
  - The strength with which an atom scatters light is proportional to the number of electrons around the atom.

- The atoms in a crystal are arranged in a periodic array and thus can diffract light.

- Amorphous materials do not have a periodic array with long-range order, so they do not produce a diffraction pattern.

- The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal.
A diffraction pattern depends on the crystal structure of the material and is unique like a fingerprint

The 3 phases of SiO₂ are chemically equivalent

Quartz and Cristobalite are both crystalline but have two different crystal structures
- Different arrangement of Si and O atoms.
- Quartz and Cristobalite have long-range atomic order

Glass is amorphous
- No long-range atomic order
- Produces only broad peaks
Crystalline materials are characterized by the long-range orderly periodic arrangement of atoms

- The unit cell is the basic repeating unit that defines the crystal structure
- The lattice parameters describe the size of the unit cell \((a, b, c, \alpha, \beta, \gamma)\)
- The unit cell repeats in all dimensions to fill space and produce the macroscopic grains or crystals of the material
Diffraction peaks are associated with planes of atoms

• Parallel planes of atoms intersect the unit cell and are described by Miller indices \((hkl)\)

• The distance between parallel planes of atoms is described by a vector, \(d_{hkl}\), that extends from the origin to the crystallographic plane \((hkl)\). \(d_{hkl}\) is normal to the plane.
Bragg’s Law

- Bragg’s Law provides a simplistic model to understand what conditions are required for diffraction

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

- For parallel planes of atoms, with a space \( d_{hkl} \) between the planes, Bragg’s law is satisfied when the diffracted beams remain in-phase, i.e. the distance \( CB+BD \) equals an integral number of wavelengths.

- Additionally, the plane normal \([hkl]\) must be parallel to the diffraction vector, \( s \)
  - Plane normal \([hkl]\): the direction perpendicular to a plane of atoms
  - Diffraction vector \( s \): the vector that bisects the angle between the incident and diffracted beam

- The x-ray wavelength \( \lambda \) is fixed, therefore a family of planes produces a diffraction peak only at a specific angle \( 2\theta \)
Position and Intensity of a diffraction peak are determined by the structure of the molecule

• **Position:** determined by the distance, \(d\), between parallel planes
  - Some planes may be equivalent because of symmetry
    - In a cubic molecule (100), (010) and (001) are equivalent
    - Expect fewer peaks in higher symmetry samples

• **Intensity:** determined by the arrangement of atoms
  - The structure factor \(F_{hkl}\) sums the result of scattering from all the atoms in the unit cell to form a diffraction peak from the \((hkl)\) planes of atoms
  
  \[
  F_{hkl} = \sum_{j=1}^{n} N_j f_j \exp\left[2\pi i (hx_j + ky_j + lz_j)\right]
  \]

  - The amplitude of scattered light is determined by:
    - Where the atoms are on the atomic planes
      - This is expressed by the factional coordinates \(x_j y_j z_j\)
    - What atoms are on the atomic planes
      - The scattering factor \(f_j\) quantifies scattering by the group of electrons in each atom
      - \(F_j\) is equal to the number of electrons around the atom at \(0^\circ\theta\) and drops off as \(\theta\) increases
      - \(N_j\) is the fraction of every equivalent position that is occupied by atom \(j\)
Diffraction patterns are collected as $2\theta$ vs absolute intensity, but can be reported as $d_{hkl}$ vs relative intensity

- The peak position in degrees $2\theta$ depends on the wavelength (Cu, Co, Mo etc)
  - Bragg’s law $[n\lambda = 2d_{hkl}\sin\theta]$ is used to convert observed $2\theta$ to $d_{hkl}$

- The absolute intensity of a peak will vary with instrumental and experimental parameters
  - Relative intensities should be instrument independent
    - To calculate relative intensity, divide the absolute intensity of every peak by the absolute intensity of the most intense peak, and then convert to a percentage. The most intense peak of a phase is therefore the “100% peak”
  - Peak areas are more reliable than peak heights as a measure of intensity

<table>
<thead>
<tr>
<th>No.</th>
<th>2-theta (deg)</th>
<th>d (ang)</th>
<th>Height (cps)</th>
<th>FWHM (deg)</th>
<th>Int. (cps deg)</th>
<th>Rel. int. (a.u.)</th>
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<td>1</td>
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<td>320(23)</td>
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<td>3.3422</td>
<td>3500(76)</td>
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</table>
Diffractometers typically use Bragg-Brentano geometry

- The incident angle, $\omega$, is the angle between the x-ray source and the sample
- The diffraction angle, $2\theta$, is the angle between the incident beam and the detector
- The incident angle $\omega$ is always $\frac{1}{2}$ of the detector angle $2\theta$
  - In a $\theta:\theta$ instrument the sample is fixed, the tube rotates at $-\theta^\circ$ and the detector rotates at $\theta^\circ$
  - In a $\theta:2\theta$ instrument the tube is fixed, the sample rotates at $\theta^\circ$ and the detector rotates at $2\theta^\circ$
- The diffraction vector, $s$, is always normal to the surface of the sample
A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

At 20.6 °2θ, Bragg’s law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.
A polycrystalline sample should contain thousands of randomly oriented crystallites. Therefore, all possible diffraction peaks should be observed.

- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract.
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.
The “ideal” powder sample contains **tens of thousands of randomly oriented crystallites** so that every diffraction peak is the product of x-rays scattering from an equal number of crystallites

- **“Non-ideal” samples:**
  - Does not contain tens of thousands of crystallites:
    - Poor particles statistics
    - Random error in peak intensities
  - Crystallites are not randomly oriented:
    - Preferred orientation (plate, needle)
    - Systematic error in peak intensities

- Small sample quantities pose a problem because the sample size limits the number of crystallites that can contribute to the measurement
- Irradiating a larger volume of material can help ensure that a statistically relevant number of grains contribute to the diffraction pattern
- Spinning sample: increase number of crystallites contributing to the pattern
- Proper sample prep: crush sample, make sure it’s well mixed
Preparing a Powder Sample

• **Top loading a bulk powder into a well:**
  - Deposit the powder in a shallow well of the 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

• **For small sample quantities:**
  - **Zero background holders**
    - Glass or aluminum sample holders will contribute an amorphous hump or peaks to the diffraction pattern if the sample cannot cover the entire surface
    - The ZBH avoids this problem by using an off-axis cut single crystal

• **Dispersing a thin powder layer on a smooth surface**
  - Dispersing the powder with alcohol on the holder then allowing the alcohol to evaporate can provide 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 (tape/vaseline can contribute to the pattern)

• **These methods may alleviate problems with preferred orientation**

• **‘Constant volume assumption’ is not necessarily valid for thin films or small sample quantities on a ZBH**
Applications of PXRD:

• **Phase Composition of a Sample:**
  - The diffraction pattern for every phase is unique: like a fingerprint
  - The diffraction pattern of a mixture is the sum of the scattering from each component phase

• Phases with the same chemical composition can have very different diffraction patterns
Phase Composition of a Sample

- Use the **position** and **relative intensity** of a series of peaks to match experimental data to the reference patterns in a database.

- The International Center for Diffraction Data’s **Powder Diffraction File (PDF)** database contains diffraction patterns for over 300,000 crystalline phases.

- Software programs can be used to determine what phases are present in a sample by comparing the experimental diffraction data to all of the patterns in the database.

- The PDF card for an entry contains lots of useful information, including literature references.
Quantitative Analysis

• With high quality data, you can determine how much of each phase is present in a sample

• Prepare a standard calibration curve:
  • The ratio of peak intensities varies linearly as a function of weight fractions for any two phases in a mixture
  • \( \frac{I_a}{I_b} = K \frac{X_a}{X_b} \)
  • Need to know the constant of proportionality (slope)

• Reference Intensity Ratio (RIR):
  • Fast and gives semi-quantitative results
  • \( K = \frac{RIR_a}{RIR_b} \)

• Whole pattern fitting/Rietveld refinement:
  • More accurate but more complicated analysis
  • Requires atomic positions from crystal structures

*Quantitative analysis may not be possible where the constant volume assumption is not met
Variable Temperature Experiments:

• Monitor changes in the diffraction pattern/structure of a material as the sample is heated or cooled
Parallel-Beam Experiments:

- In typical Bragg-Brentano (focusing) geometry the diffracted x-ray beam converges at the focal point of the detector producing sharp, well-defined diffraction peaks.

- If the source, detector, and sample are not all on the focusing circle, the diffracted x-ray beam will not converge at the correct position for the detector and errors will appear in the data.

- **Sample displacement errors:** observed peak position is incorrect
  - Sample holder is over- or under-filled
  - Samples with rough shapes or odd surfaces

- **Parallel-beam optics** eliminates all sources of error associated with the focusing circle
  - Reduced beam size means less intensity and longer experiments
Other Applications of PXRD:

- **Unit Cell and Lattice Parameter Refinement**
  - By accurately measuring peak positions over a long range of 2theta, you can determine the unit cell parameters of your sample
  - Alloying, doping, temperature and pressure, etc.. can create changes in lattice parameters that you may want to quantify

- **Determine bulk purity of a sample characterized by single crystal x-ray diffraction**
  - Can calculate expected powder pattern from single crystal data and compare to experimental powder pattern of the bulk material

- **SAXS (Small Angle X-ray Scattering)**
  - Determine particle/pore size of nanoparticles

- **Micro Area Stage for sample mapping**
  - X, Y mapping of a sample using a very small beam
In the lab:

• Overview of the powder diffractometers
• Sample prep demonstration
• Set up a quick experiment
• Answer questions