

Powder Diffraction Methods

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Information Contained in a Diffraction Pattern

- Peak Positions
 - Crystal System
 - Space Group Symmetry
 - Translational Symmetry
 - Unit Cell Dimensions
 - Qualitative Phase Identification
- Peak Intensities
 - Unit Cell Contents
 - Point Symmetry
 - Quantitative Phase Fractions
- Peak Shapes & Widths
 - Crystallite Size (2-200 nm)
 - Non-uniform microstrain
 - Extended Defects (stacking faults, antiphase boundaries, etc.)

Qualitative Analysis

- The powder diffraction pattern of a known phase should act as a "fingerprint" which can be used to identify the phase.
- Computer "search-match" algorithms are used to compare experimental pattern with ICDD database of known compounds
- As of 1994 the International Centre for Diffraction Data (ICDD) database contained over 60,000 entries
- Can be used for multiphase mixtures
- Can be used to identify polymorphic mixtures

Quantitative Analysis

- By measuring changes in the unit cell dimensions it is sometimes possible to determine composition through Vegards law (i.e. Na_{1-x}K_xCl)
- Weight fractions of multiphase mixtures can be determined using a variety of methods, but the Rietveld method is the most commonly used approach.
- Care must be taken when phases have significantly different densities or crystallite sizes
- With care, accuracy is typically within a few percent, and the lower limit of detection can be less than 1%
- See "Outcomes of the International Union of Crystallography Commission on Powder Diffraction round robin on quantitative phase analysis: samples 1a to 1h" Madsen IC, Scarlett NVY, Cranswick LMD, Lwin T, J. Appl. Crystallography 34, 409-426 (2001)

Structural Data from Powder Diffraction Data

- Why not use single crystal methods?
 - It may difficult to obtain a single crystal
 - Usable form of a material may be polycrystalline
 - Problems with twinning or phase transitions
- What types of structures can be analyzed?
 - Typically 5-15 crystallographically distinct atoms
 - Good data may allow 50-75 cryst. distinct atoms
- What type of data is best?
 - High resolution is important (monochromatic and/or synchrotron radiation is best)
 - Neutron data can be very useful for finding light atoms



Limitations of Powder Diffraction for Structure Determination

- The 3D set of diffraction spots obtained from a single crystal experiment is condensed into 1D in powder diffraction pattern. This leads to both accidental and exact peak overlap, and complicates the determination of individual peak intensities.
- Crystal symmetry cannot be seen directly from diffraction pattern.
- Multiphase mixtures can be problematic.
- Preferred orientation can lead to inaccurate peak intensities.



Steps to Structure Solution

- Index the diffraction pattern to determine crystal system and unit cell dimensions
- Analyze systematic absences in order to determine space group (at least narrow the list)
- Whole pattern fitting to obtain accurate unit cell dimensions and peak shape parameters
- Input approximate structural model
- Allow atomic positions, occupancies and displacement parameters to refine in order to optimize the fit to the observed diffraction pattern (<u>Rietveld refinement</u>)

How do I obtain the Approximate Structure Model?

Empirical Methods

- Look for isostructural compounds
 - Search the powder diffraction file (JCPDS)
 - Search the inorganic crystal structure database (ICSD)
 - Search the Cambridge Database
- Derive structural models using Z, the constraints of space group symmetry and chemical intuition

ab-initio Structure Solution

- Reciprocal Space (Traditional) Methods
- Real Space Methods



Rietveld Refinements

- What is the goal of a Rietveld refinement?
 - To obtain an accurate crystal structure
- What is the basic idea of a Rietveld refinement?
 - To fit the entire diffraction pattern at once, optimizing the agreement between calculated and observed patterns
- What input is needed to carry out a Rietveld refinement?
 - Correct space group symmetry
 - Reasonably accurate unit cell dimensions
 - Approximate starting positions for the atoms



Intensity (Arb. Units)

Rietveld Refinement of TbBaFe₂O₅ using Neutron Powder Data



Crystal Structure TbBaFe₂O₅



Fe^{III}-O Distances O(x) 2 × 1.965(4) Å O(y) 2 × 1.975(1) Å O(z) 1 × 1.895(6) Å

Fe^{II}-O Distances

- O(x) 2 × 2.134(4) Å
- $O(y) 2 \times 1.962(1) \text{ Å}$
- O(z) 1 × 2.046(5) Å

Magnetic Structure TbBaFe₂O₅



Peak Shape Analysis

Peak broadening comes from several sources

- Instrumental effects
- Finite crystallite (not particle) size (< 100-500 nm)
- Strain (atoms deformed from ideal positions in a nonuniform manner)
- Extended defects (terminate "crystal" and lead to size broadening)

Methods of extracting size & strain information

- Scherrer formula (average size, neglects strain)
- Integral breadth methods (provide average values of size and strain)
- Peak shape methods (provide size and strain distributions)

Correcting for Instrumental Effects

- To do an accurate analysis for size and/or strain effects one must accurately account for instrumental broadening. The manner of doing this differs depending upon the peak shape.
 - Lorentzian

$$\begin{split} \beta_{\text{obs}} &= \beta_{\text{size}} + \beta_{\text{strain}} + \beta_{\text{inst}} \\ \{\beta_{\text{obs}} - \beta_{\text{inst}}\} &= \beta_{\text{size}} + \beta_{\text{strain}} \end{split}$$

Gaussian

 $\beta_{obs}^{2} = \beta_{size}^{2} + \beta_{strain}^{2} + \beta_{inst}^{2}$ $\{\beta_{obs}^{2} - \beta_{inst}^{2}\} = \beta_{size}^{2} + \beta_{strain}^{2}$

- Voigt, Pseudo-Voigt
 - Generally it is necessary to first deconvolute into gaussian and lorentzian fractions before subtracting out the instrumental effects.

Finite Crystallite Size

- A perfect crystal would extend in all directions to infinity, so we can say that no crystal is perfect due to it's finite size. This deviation from perfect crystallinity leads to a broadening of the diffraction peaks. However, above a certain size (100-500 nm) this type of broadening is negligible.
- Crystallite size is a measure of the size of a coherently diffracting domain. Due to the presence of polycrystalline aggregates crystallite size is not generally the same thing as particle size.
- Other techniques for measuring size, measure the particle size rather than the crystallite size
 - BET
 - Light (Laser) Scattering
 - Electron Microscopy (SEM)



Scherrer (1918) first observed that small crystallite size could give rise to line broadening. He derived a well known equation for relating the crystallite size to the broadening, which is called the "Scherrer Formula"

$$\mathsf{D}_{\mathsf{v}} = \mathsf{K}\lambda/\{\beta \cos \theta\}$$

- D_v = Volume Weighted crystallite size
- K = Scherrer constant, somewhat arbitrary value that falls in the range 0.87-1.0. I usually assume K = 1.
- λ = The wavelength of the radiation
- β = The integral breadth of a reflection (in radians 2 θ) located at 2 θ .

Extended Defects

- Extended defects disrupt the atomic arrangement of a crystal, typically along a 2D plane. These defects effectively terminate a crystallographically ordered domain of the crystal. Thus as far as x-rays are concerned one crystal ends and a new crystal begins at the extended defect.
- Crystallite size analysis on a sample containing extended defects can be used to estimate the ordered domain size (the size of the region between defects) in the same manner that XRD is used to determine crystallite size.
- Types of extended defects
 - Stacking faults (ABCABCABCCBACBACBA...)
 - Dislocations in "layered" materials (graphite, MoS₂, clays, ZrNCI, etc.)
 - Antiphase boundaries, which arise in partially ordered materials (Cu₃Au, Sr₂AlTaO₆)



Lattice Strain (Microstrain)

- Strain is a term used more often in engineering than in chemistry. Strain is defined as the deformation of an object divided by it's ideal length, △d/d. In crystals there we can observe two types of strain
 - Uniform strain
 - Non-uniform strain
- Uniform strain causes the unit cell to expand/contract in an isotropic way. This simply leads to a change in the unit cell parameters and shift of the peaks. <u>There is no</u> <u>broadening associated with this type of strain</u>.
- Non-uniform strain leads to systematic shifts of atoms from their ideal positions and to peak broadening. This type of strain arises from the following sources:
 - Point defects (vacancies, site-disorder)
 - Plastic deformation (cold worked metals, thin films)
 - Poor crystallinity



Strain Broadening

Stokes and Wilson (1944) first observed that strained or imperfect crystals containing line broadening of a different sort, than the broadening that arises from small crystallite size.

$$\varepsilon_{str} = \beta / \{4 \tan \theta\}$$

- ε_{str} = weighted average strain
- β = The integral breadth of a reflection (in radians 20) located at 20.
- Note that "size" and "strain" broadening show a different θ dependence. This provides a way to separate the two effects.

Williamson-Hall Analysis Simplified Integral Breadth Methods

Williamson and Hall (1953) proposed a method for deconvoluting size and strain broadening by looking at the peak width as a function of 20. Here I derive the Williamson-Hall relationship for the Lorentzian peak shape, but it can derived in a similar manner for the Gaussian peak shape

 $\{\beta_{obs} - \beta_{inst}\} = \lambda / \{D_v \cos \theta\} + 4 \epsilon_{str} \{\tan \theta\}$ $\{\beta_{obs} - \beta_{inst}\} \cos \theta = \lambda / D_v + 4 \epsilon_{str} \{\sin \theta\}$

To make a Williamson-Hall plot

- Plot $\{\beta_{obs} \beta_{inst}\}\cos \theta$ on the y-axis (in radians 2 θ)
- Plot 4 sinθ on the x-axis
- If you get a linear fit to the data you can extract
 - the crystallite size from the y-intercept of the fit
 - the strain from the slope of the fit

Williamson-Hall Plot



A Williamson-Hall plot for Pb₂ScTaO₆. The size extracted from the eveneven-even reflections gives the volume weighted crystallite size, while the size extracted from the odd-odd-odd reflections gives the volume weighted size of the regions over which the Sc and Ta atoms are well ordered.

References

Elements of X-ray Diffraction

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