Information obtainable from XRPD

1) Peak Positions

- (a) Crystal system
- (b) Unit Cell Size (Lattice Constants)

2) Peak Intensities

- (a) Unit Cell Contents (Atomic Positions, etc.)
- (b) Quantitative Phase Determination

3) Peak Shapes

- (a) Crystallite Size
- (b) Nonuniform Strain
- (c) Extended Defects

Phase Identification & Lattice Constant Determination

A) Phase Identification

1) Compare the observed spectrum to a library (JCPDS) containing diffraction patterns of known compounds

2) Index the peaks from known lattice constants

B) Lattice Constant Determination

- 1) Lattice Constant Refinement
 - a) Least squares refinement of individually fit peaks
 - b) Whole pattern fitting

2) Autoindexing

- a) Internal standard critical
- b) Unidentified impurities significantly reduce the probability of success

Structure Determination

- Determine the Crystal System and Lattice Constants (By indexing the peaks in the diffraction pattern)
- Identify the Space Group (Using the systematic absences)
- 3) Determine an Approximate Structure
 - a) Empirical Methods
 - b) Ab Initio Approach
- 4) Refine the Approximate Structure (Using the Rietveld refinement method)
- 5) Test and compare alternative models

Sources of Peak Broadening

1) Instrumental Broadening

- a) Nonideal optics
- b) Wavelength dispersion
- c) Specimen transparency
- d) Misalignment
- 2) Finite Crystallite Size
- 3) Strain
 - a) Uniform strain (shifts peaks)
 - b) Nonuniform strain (broadens peaks)

4) Extended Defects

- a) Stacking faults
- b) Antiphase boundaries

Integral Breadth Methods

- 1) Size Broadening (Scherrer Formula)
 - $\beta = \kappa \lambda / D \cos \theta$

 β = Peak width (in radians)

 λ = X-ray wavelength

D = Crystallite size (volume average)

K = Scherrer constant (1.0 <u>> K > 0.89</u>)

2) Strain Broadening

 $\beta = 4\epsilon \tan \theta$

 β = Peak width (in radians)

 ε = Strain ($\Delta I/I$)

3) Williamson-Hall Plot

 β (sample) = β (size) + β (strain)

 $\beta = \lambda / D \cos \theta + 4 \epsilon \tan \theta$

 $\beta \cos\theta = \lambda / D + 4 \epsilon \sin\theta$

In order for the peak widths to linearly combine a Lorentzian peak profile is necessary.

Gaussian peaks add together as squares { β^2 (sample) = β^2 (size) + β^2 (strain)}.

Note that in order to carry out a proper analysis one should use the integral breadth values for the peak width (the integral breadth is the width of a rectangle with the same area and height as the peak).

Fourier Methods

Warren-Averbach Method

The entire peak profile is described by a Fourier series. The cosine Fourier coefficients, which describe symmetric broadening, are then used for further analysis. The peak shape of a standard material which shows no broadening is also determined and subsequently used to deconvolute the instrumental and sample broadening effects. At least two reflections must be used in the analysis. Because the entire peak profile is used this approach has both advantages and disadvantages when compared to the Williamson-Hall technique.

Advantages vs. the Williamson-Hall Method

- Produces crystallite size distribution.
- More accurately separates the instrumental and sample broadening effects.
- Gives a length average size rather than a volume average size.

Disadvantages vs. the Williamson-Hall Method

- More prone to error when peak overlap is significant (in other words it is much more difficult to determine the entire peak shape accurately, than it is to determine the integral breadth or FWHM).
- Typically only a few peaks in the pattern are analyzed.

Neutron Powder Diffraction

1) Neutrons are scattered by nuclei instead of electrons.

This leads to a completely different scattering power distribution for the elemets. This is extremely useful for determining positions of light atoms in compounds containing both light and heavy atoms.

2) The absorption coefficients for neutrons are much smaller than they are for x-rays.

This results in much greater penetration depths for neutrons (i.e. 25 mm depth for neutrons compared with 25 μ m depth for x-rays). This is advantageous in reducing errors such as matrix effects and preferred orientation, but can be disadvantageous in that larger samples are needed.

3) Scattering factors do not decrease with 2θ .

This increases the information content of the high angle region of the diffraction pattern.

4) Resolution is typically lower than found in high resolution x-ray diffraction.

This can be problematic if there is considerable peak overlap. On the other hand, peak shapes are more easily modeled.