XRDUG Session I

Design and Set-up of XRD Experiments

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SESSION 1

Design and Set-up of XRD Experiments

1. Define what you want to learn about your sample and what XRD technique will provide this knowledge. Various examples of XRD data are presented in fig. 1-5. Fig. 1-Single Phase LaB_6, Fig. 2-Multiphase Material, Fig. 3-Peak Broadening in Brass Annealed and Cold Worked, Fig.4-PMN-PT Single Crystal He Ion Implanted Effects of Annealing, Fig.5-Increased Background Scattering (E.A.Laitila volume 23, issue 2, page 96 Powder Diffraction Journal)

- Phase ID (Major and/or Minor Phases, Peak Overlap)
- Lattice Parameter (Lattice Mismatch, Solute Content)
- Quantitative Phase Analysis
- Peak Profile Analysis (Micro-strain, Particle size, Dislocation Density)
- Order Parameters (Short and Long Range Order)
- Structure Determination
- Site Occupancy Studies (Type of Atoms on Sites – Atom Coordinates)
- Texture Analysis
- Residual Stress Measurements
- Thin Film Analysis (Grazing Incidence Diffraction, Thin Film Thickness)
- High Temperature Diffraction
- Phase Diagram Determination
- Any structural change could potentially be measured.
- etc..

2. Sample Preparation.

- Make sure that the method of sample preparation does not interfere with the property you are trying to measure.

    - Classic example; when analyzing diffraction peak profiles polishing without etching a sample. The high dislocation densities introduced by polishing will have a large effect on the diffraction peaks, increasing the width of the peak profiles; remember x-rays are diffracted from a thin surface layer.

- Rule of thumb is to repeat the last polishing step followed by a macroscopic etch, 3 times. Depends if sample is ductile or brittle. Ductile samples are more susceptible to dislocation formation from polishing.

- Large grain size or particle size can drastically alter the population of hkl planes parallel to the surface (remember only planes parallel to the sample surface are observed in a diffractometer), affecting the relative intensities of your diffraction pattern. Test for this effect by changing the sample position in the holder and repeating the diffraction measurement, large changes in intensity could indicate grain size effects (See Figure 6 and 7).

- Size of the sample and the area of irradiation of the sample at the 2θ of interest is very important to understand, beam overlap over the sides of the sample can result in a loss of intensity information. (See Figure 8).

- Beware of the material the sample is mounted in, can diffraction from this material interfere with your results (See Figure 9-12)?

3. Sample Mounting

- Most common source of error in 2θ position in a diffractometer is sample displacement error.

- The sample mounting surface or plane, for the standard sample holder, is located under the lip of the goniometer sample holder for the Scintag θ/θ diffractometer and the three pins located on the underside of the fixed portion of the sample holder on the Siemens D500 diffractometer, this surface is the focal or reference plane of the diffractometer.

- The surface of the sample must be in this plane, otherwise peak shifts in the diffraction spectrum can occur (See Figure 13). This type of peak shift error is referred to as a sample displacement error.

  - If the sample is below the focal plane the peaks shift to lower 2θ angles.
  - If the sample surface is above this plane the peaks will shift to higher 2θ angles.

- In powder diffraction, provided the sample holder is inserted properly and the powder if loaded properly, the surface of the powder sample holder corresponds to the focal plane.

- For polycrystalline solid samples the top surface of the sample holder corresponds to the focal plane, typically the sample surface is held in this plane by modeling clay. **Important note; a special weight must be placed on top of the glass slide used to put sample in the focal plane defined by the holder for a minimum of 5 minutes to ensure no displacement error due to the clay relaxation constant (See Figure 14).**

- Use the long side drifted holder for scans below 15° 2θ when using standard beam slits (1mm and 2mm).

- If you have a single crystal sample you must consult with me prior to doing any work, improper generator settings can damage the detector.

- Small quantities of powders can be mounted on "zero background" holders, these are quartz single crystals cut so not atomic planes are parallel to the surface. Two kinds are available one that mounts on clay and the other that mounts directly into the instrument holder. The direct mount holder may cause a small displacement error since the sample will be displaced based on the thickness of the powder.

4. Determine the scan range.

    - Use JCPDS powder diffraction file to determine peak positions for all possible phases. Note all XRD computers have a digital JCPDS database.

        - Estimate phases from knowledge of sample, processing history, chemical composition, phase diagram, etc..

        - Estimate phases for unknown samples from chemical information provided by x-ray fluorescence spectrometry or other methods.

    - Determine minimum scan range that will define information you need.

        Guidelines In General:

        - Need 3 most intense peaks for positive phase ID (depends on complexity of sample).

        - In some cases data can be collected in separate 2θ ranges, thereby decreasing the data collection time.

        - Determine what peaks provide the information you require.

        - How many peaks are required for your particular analysis?

            Examples:

            - Quantitative volume fractions minimum need is 2 peaks.

            - Fourier analysis of peak broadening, minimum need is two orders of diffraction peaks for each crystallographic direction of interest, e.g. {111}-{222}

5. Determine the type of diffraction scan to perform.

    - Many variations and types of diffraction scans can be performed, dictated by the type of structural analysis to be performed, only limit is the imagination and knowledge of theory.

    - Typically, to preserve the parafocusing condition, $\theta/2\theta$ step scans or continuous scans are performed:

        - Step scan used for quantitative analysis, move $\Delta 2\theta$, accumulate counts for some preset time.

        - Continuous scan used for qualitative analysis or to run quick scans, goniometer continuously moves at a defined scan rate and integrates intensity (averaging effect) over some $\Delta 2\theta$ referred to as the chopper increment or step size. Runs faster than a step scan but could introduce a time delay in the data due to fast scan rates and/or distort data due to integration over a 2θ range.

    - Other types of scans:

        - Grazing incidence: tube is fixed at a low angle with detector scanned through 2θ range (Bragg-Brentano parafocusing geometry no longer applies).

        - Rocking curves: detector is fixed on Bragg peak, sample is scanned a few degrees around Bragg peak.

        - Residual stress: scan a particular (hkl) plane, change the sample angular relationship to the incident beam.

        - Texture: fix detector on Bragg peak and move the sample in 3-D space.

        - etc.

6. Determine step size or chopper increment (step scan, continuous scan typically 0.03° 2θ).

   - Need to determine FWHM (full width at half maximum intensity) of diffraction peaks:

# of data pts in 2θ above FWHM = FWHM/(step size or chopper increment)

For quantitative and peak profile analysis this should be 7-15. Can be less for phase ID, etc.

- Estimate by knowledge of your material:
  - Well annealed material (minimal structural defects) sharp peaks typically less than 0.1° 2θ. (See Figure 15 and 16).
  - Cold worked material, structural defects, solid solutions, broad peaks greater than 0.3° 2θ, can be several degrees. (See Figure 17).
  - Brittle/ductile phases of material that has been mechanically processed. (See Figure 18).
- Determine experimentally:
  - Manual operation of XRD unit, if available, to move the goniometer over a peak and measure.
  - Run a rapid scan (a few minutes long) over some peaks of interest to determine FWHM.

- Step size might be important when trying to resolve overlapping peaks, or obtaining accurate peak information, e.g. FWHM, position, area, etc.

Example:

- The peak parameters of position, FWHM, and area are given in Table 1 for two scans of LaB_6 standard (shown in Figure 15 and 16) using step sizes of 0.005° and 0.05°.

Table 1 Comparison of Peak Parameters of LaB6 Using Different Step Size

Step Size (2θ)	Position (2θ)	FWHM (degrees)	Area
0.05	67.5435	0.1000	78.1
0.005	67.5458	0.0748	70.6
0.03	67.5432	0.0765	69.4
0.02	67.5445	0.0728	68.7
0.01	67.5449	0.0758	70.6
0.05	30.3657	0.1000	270.8
0.005	30.3726	0.0681	241.3
0.03	30.3681	0.0715	245.1
0.02	30.3694	0.0688	250.4
0.01	30.3701	0.0695	245.5

7. Determine the preset time (also referred to as count time) in seconds at each step, or the scan rate in °/minute for a continuous scan.

- X-ray photon production is random in time; therefore the error in a counting rate measurement is governed by the laws of random probability.

- Using a constant x-ray intensity and position, the number of x-ray photons counted for a fixed time in repeated measurements, will have a Gaussian distribution about the true value N_t, which is obtain by averaging many measurements.

$$\therefore \text{ Relative } \sigma = \frac{\sqrt{N}}{N} \times (100) = \frac{100}{\sqrt{N}}\%$$

$$\therefore \text{ Probable error} = 0.67 \text{ (relative } \sigma) = \frac{67}{\sqrt{N}}\%$$

N = x-ray photons counted or number of counts (Intensity (cps) X preset time)

  - The error depends only on the number of x-ray photons counted not on their rate. However, the higher the rate the faster a total count can be achieved.

- Typically, interested in the diffracted peak intensity above background, look at N_P(number of counts for the peak) and N_B (number of counts for the background):

$$\therefore \text{Relative } \sigma_{P\text{-}B} = \frac{(N_P + N_B)^{1/2}}{(N_P - N_B)}$$

  - The probable error in the measured intensity of a diffraction peak above background increases as the background intensity increases.

  - The probable error in the measured intensity of a diffraction peak above background increases as the ratio of N_P/N_B decreases or N_P decreases.

- Increasing preset time or decreasing scan rate does not alter the diffraction event but only improves the statistical quality of the data (See Figure 19).

- In general, the preset count time or scan rate is determined by the type of analysis that is to be performed on the diffraction data:

    - Qualitative analysis: typically use a small preset time (1 sec.) fast scan rate (1 °/min. or 2 °/min.), Although much faster scan rates can be used.

    - Quantitative analysis: Typically use a larger preset time or slower scan rate, the value depends on the quality of data needed.
        - If peaks of interest have high count rates can run faster scan rates.

        - Peak position, usually can run higher rate scans.

        - Peak profile analysis usually requires large preset times.

- In reality, the preset time or scan rate are generally determined by the total amount of scan time available:

    - Should limit long scans to 12 hours if possible, reach a point of diminishing returns beyond counting times of 20-30 sec./step.

    - Estimated scan time for step scan :

      Scan Time = (number of data pts.) X (preset time)

      number of data pts. = (scan range 2θ) / (step size)

    - Scan time for continuous scan:

      Scan Time = (scan range 2θ) / (scan rate)

8. Determine optimum slit size for experiment:

- Slits determine 2θ spatial resolution, by establishing the diffraction optics.

- Increasing resolution decreases intensity.

- An important role of the beam slit is to define area of irradiation (See Figure 20).

- Receiving slit defines amount of 2θ circle observed at any given point, affects angular resolution, and thus affects resolution of d-spacings (See Figure 13).

- Slits typically used in Scintag θ/θ diffractometer are 1 and 2 mm beam slits and 0.5 and 0.3 receiving slits (See figures 21, 22, 23).

- Slits typically used in the Siemens D500 are 1° beam slits, 0.05° receiving slit and 0.15° monochromator slit (size defines range of wavelengths).

- Sollar slits increase resolution which decreases FWHM of diffraction profiles and affects low angle side of low angle peaks (See Figure 20).

- Grazing incidence diffraction use a long collimator, with a fine plate spacing, and a small incident angle to look near the surface of a sample or thin films. Note this takes the instrument out of the parafocusing mode.

- Understand that the diffractometer optical inefficiencies add to the peak breadth of the incident $Cuk_{\alpha1}$ and $Cuk_{\alpha2}$ radiation, therefore it is important, in most cases, to correct a peak profile analysis for instrumental broadening (See Figure 3, 15, 17).

- The diffraction optics play an important role in the determination of optimum step size due to their effect on the FWHM of diffraction profiles.

9. The most important objective should be to understand your material and run your experiments in a manor to maximize your information and minimize your scan time, above all else strive to do scans right the first time to minimize repeat scans on the same sample.