DICP Course 2 - Dalian, 2012 POWDER X-RAY DIFFRACTION Part III – POWDER DIFFRACTOMETRY Supported by the Chinese Academy of Sciences Charles Kappenstein, Professor Emeritus, University of Poitiers, France

DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES











Outline of the course

1. – SOURCE OF X-RAYS *1.1. – X-ray tube* 1.2. – White radiation 1.3. – Characteristic lines 1.4. – Take-off angle **2. - DETECTION OF X-RAYS 3. – SAMPLING 4. – SIZE OF THE IRRADIATED AREA 5. – DIFFRACTOMETER 6. – CORRECTIONS** 7. – QUANTITATIVE ANALYSIS **8. – PEAK PROFILE ANALYSIS** 9. – DATA TREATMENT

1.1. – X-ray tube

Electrons are emitted from a heated tungsten filament (thermoelectronic effect) They are accelerated by a high potential difference \rightarrow high speed They hit a target (anode, W, Cu, Mo, Co, Cr) \rightarrow strong deceleration

emission of electromagnetic waves
 in all directions
 or 4 circular beryllium windows

Operating conditions Filament current: 3 A Electronic current: 40 mA High voltage: 40 kV Power: 1600 W



1.1. – X-ray tube

Electrons are emitted from a heated tungsten filament (thermoelectronic effect) They are accelerated by a high potential difference \rightarrow high speed They hit a target (anode, W, Cu, Mo, Co, Cr) \rightarrow strong deceleration



X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, <u>Cu</u>, AI, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

1.1. – X-ray tube

Plot of the intensity of the emitted beam versus the wavelength

Main features:

- sharp cut-off
- continuous radiations (white radiation)
- very intense and narrow peaks



1.2. – White radiation

The radiation corresponds to the emission of electromagnetic waves linked to the sudden deceleration of the electrons when they hit the target

Independent of the nature of the target Kinetic energy of one electron E_C

$$E_C = mv^2/2 = eV$$

m = mass of the electron
v = speed of the electron
e = charge of the electron
V = voltage

Kinetic energy is converted into radiation Energy hv and heat Q

$$E_{C} = hv + Q$$

maximum photon energy when Q = 0 $E_C = hv_{max} = hc/\lambda_{min} = eV$ $\Rightarrow \lambda_{min} = hc/eV$ for $V = 40 \text{ kV} \Rightarrow \lambda_{min} = 0.31 \text{ Å}$



1.2. – White radiation

Yield $hv/E_{c} \sim 0.5$ % very low

The most part of kinetic energy is transformed into heat
→ the temperature of the target increases → need to cool the target with water

Maximum of the white radiation for about 1.5 λ_{min}

Power of commercially available X-ray tube: 300 to 2700 W

How to increase the power:

- rotating anode up to 10 000 W
- synchrotron radiation



Depends on the nature of the target

 \rightarrow quantum origin: electronic transition in the core levels of the target atoms

 \rightarrow core electrons are ejected \rightarrow atom in an higher energy state

→ relaxation process to a lower energy state with simultaneous emission of photon See figure











Figure 3. Electronic configuration and photon emission.

From electron configurations, we have the following possible transitions:



 $\lambda(K_{\alpha 1}) = 1.34000$ $\lambda(K_{\alpha 2}) = 1.34439$ A average value $\lambda(K_{\alpha}) = 1.54186$ Å $\lambda(K_{\beta}) = 1.39222$ Å

We want monochromatic radiation

- use of a filter to eliminate K_{β} line
- use of a monochromator to eliminate K_{β} line (generally back monochromator)
- use of a monochromator to eliminate $K_{\alpha 2}$ line (generally front monochromator)



Characteristic X-ray Lines

 $K\beta$ and $K\alpha 2$ will cause extra peaks in XRD pattern, and shape changes, but can be eliminated by adding filters.

----- is the mass absorption coefficient of Zr.

1.4. – Take-off angle

Angle τ between the plane defined by the target and the X-ray beam crossing the window. Mean value: 6 $^\circ$ to 12 $^\circ$



Outline of the course

- 1. SOURCE OF X-RAYS
- **2. DETECTION OF X-RAYS**
- 2.1. Proportional scintillation detector
- 2.2. Linear detector
- **2.3.** Counting statistics
- 2.4. Standard deviation and intensity
- 2.5. Stability of the X-ray source
- 3. SAMPLING
- 4. SIZE OF THE IRRADIATED AREA
- **5. DIFFRACTOMETER**
- **6. CORRECTIONS**
- 7. QUANTITATIVE ANALYSIS
- **8. PEAK PROFILE ANALYSIS**
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Scintillator screen converts X-rays to visible light which is then converted to electrical signals in an photodiode array detector.

2.2. – 1D Linear detector

1 D detector in use for plate sample



2.2. – 1D Linear detector

PIXcel3D detector
four modes:
0D mode: point detector
1D mode: line detector
2D mode: area detector
3D mode: computed tomography (CT) detector



2.2. – 1D curved detector (Inel company)



2.3. – Counting statistics

Units: counts (c) or counts per second (cps) We repeat the measure → Gaussian statistics –Normal distribution





$$\rho = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{x-M}{\sigma}\right)^2\right]$$

with ρ : frequency for a measurement M: mean value σ : standard déviation Probability to have the value in the range M $\pm \alpha\sigma$:

| 68.2 % | for $\alpha = 1$ |
|--------|--------------------|
| 95.4 % | for $\alpha = 2$ |
| 99 % | for $\alpha = 2.6$ |



2.3. – Counting statistics

For a counting, N is the best estimate, σ is the estimation of the standard deviation:

$$\sigma = \sqrt{N}$$

If we repeat the measurement n times:

$$\sigma = \frac{\sqrt{N}}{\sqrt{n}}$$

Signal / noise ratio:

$$\frac{N}{\sigma} = \sqrt{N} . \sqrt{n}$$

How to define the best strategy for a given powder?
→ it depends on the profile of the diffraction peaks

2.4. – Standard deviation and intensity: Statistical background

Figure 5. Background analysis. A) XRD plot of Al sample-holder in the range 45 to 140 ° 2 θ . B) enlargement of the range 85 to 95 ° 2 θ . Step 0.02 ° ; dwell time 1 s ; slit aperture 1 °.

2.4. – Standard deviation and intensity: Statistical background

Statistic functions \Rightarrow level of statistical noise in the background 20 ranges between diffraction peaks (see previous figures) Mean count level approximately 100 \Rightarrow statistical standard deviation of the order of $100^{1/2} = 10$ The results:

| 2θ range | 50 to 60 $^\circ$ | 85 to 95 ° | 100 to 110 $^{\circ}$ | 120 to 135 $^{\circ}$ |
|-----------------------|-------------------|------------|-----------------------|-----------------------|
| Point number | 501 | 501 | 501 | 751 |
| Minimum | 67 | 63 | 64 | 68 |
| Maximum | 124 | 123 | 122 | 137 |
| Mean | 94.24 | 92.51 | 92.90 | 97.11 |
| Exp. std deviation | 9.91 | 9.85 | 9.78 | 10.07 |
| $(\text{mean})^{1/2}$ | 9.71 | 9.62 | 9.64 | 9.85 |

 \rightarrow Very good agreement between experimental value and calculated value (mean)^{1/2}

2.5. – Stability of the X-ray source

Due to fluctuations of the X-ray tube For a given count number, the fluctuations will increase the standard deviation $\sigma(N)$

Assumption $h \sim 10^{-3}$ for a good stability

For N = 10⁶ counts → σ(N) ~ 10³
 → hN ~ 10³ same magnitude order
 → influence of fluctuations and risk of saturation of the detector

For N = 10⁴ counts $\rightarrow \sigma(N) \sim 10^2$ $\rightarrow hN \sim 10^1 \ll \sigma(N)$

it is not useful to make a measurement for a long time
possibility of systematic errors due to aging of the tube

Outline of the course

1. – SOURCE OF X-RAYS 2. - DETECTION OF X-RAYS 3. – SAMPLING 3.1. – Sample preparation 3.2. – Different sample holders **4. – SIZE OF THE IRRADIATED AREA 5. - DIFFRACTOMETER 6. - CORRECTIONS** 7. – QUANTITATIVE ANALYSIS **8. – PEAK PROFILE ANALYSIS** 9. – DATA TREATMENT

3.1. – Sample preparation

Preparing a good representative powder specimen

- An ideal powder sample should have:
- sufficient number of crystallites
- total random orientations, smooth distribution equally distributed amongst all orientations
- enough sample for sufficient intensity

 \rightarrow crystallites should be in the range 5 to 10µm in size to get good powder statistics The raw powder has to be milled very carefully in an agate mortar, using a pestle. Possibility of use a mechanical mill.

Large crystallite sizes + non-random crystallite orientations → peak intensity variation
 Measured intensities will not agree with reference patterns in the Powder Diffraction File (PDF) database

For one grain with a size of 1 mm \rightarrow how many grains with a size of 10 μ m? \rightarrow 10⁶ grains !!

3.1. – Sample preparation

Preferred orientation

- crystallites: plate or needle like shapes \rightarrow very difficult to adopt random orientations
- top-loading: powder pressed into a holder \rightarrow preferred orientation
- metal sheets or wires \rightarrow almost always preferred orientation due to manufacturing process
- for samples with systematic orientation, XRD can be used to quantify the **texture**

Different types of sample holders

- Plastic
- Glass
- Metal
- Silicon wafer: (511) face

For sample holder with a cavity: determine the volume and dimensions of the cavity Weight the mass of the sample. Then determine the apparent density

Avoid the possibility of preferential orientation of the crystallites

 \rightarrow random orientation is the best

 \rightarrow the surface has to be well defined: the best is to erase the excess with a razor blade

Different types of sample holders

Materials Characterization Lab www.mri.psu.edu/mcl

Different types of sample holders

Side Drift Mount

Assembled

Disassembled

Designed to reduce preferred orientation – great for clay samples, (and others with peaks at low 2-theta angles)

Materials Characterization Lab www.mri.psu.edu/mcl

Different sample holders have been measured in the same conditions to determine the level of the corresponding background:

aluminum,

glass,

silicon wafer...

Fig. Aluminum, glass, glass covered by grease. Step 0.02 °, dwell time 1 s, slit aperture 1 °.

Varying irradiated area of the sample

- the area illuminated by the X-ray beam varies as a function of:
 - incident angle of X rays
 - divergence angle of the X rays

• at low angles, the beam might be wider than your sample
→ "beam spill-off"

→ Constant irradiated volume

Outline of the course

- 1. SOURCE OF X-RAYS
- 2. DETECTION OF X-RAYS
- 3. SAMPLING
- 4. SIZE OF THE IRRADIATED AREA
- 4.1. Sample holder
- 4.2. Determination of the length L
- 4.3. Determination of the width l
- **5. DIFFRACTOMETER**
- 6. CORRECTIONS
- 7. QUANTITATIVE ANALYSIS
- **8. PEAK PROFILE ANALYSIS**
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4.1. – Sample holder

The cavity in the center of the sample holder contains the solid to be examined:

- cylindrical form with fixed diameter and depth
- parallelepiped form with dimensions specifically defined by the user.

→ Irradiated area must correspond only to the powder and not to the sample holder.
 The sample holder is kept in the focal plane by means of pins or clamp.
 The irradiated surface displays a rectangular shape with length L and width l.

4.2. – Determination of the length L

Length L depends on δ (aperture slit) and θ angle between sample holder and X-ray beam relation between these values:

 $L = R\delta / \sin\theta$

- R : radius of the goniometer circle = FC
- δ : aperture slit in <u>radian</u>
- θ : Bragg angle

4.2. – Determination of the length L

The result of this relation is given for different slit aperture angles.

Lengths determined experimentally, sample holder covered with X-ray fluorescent sheet; → visual examination to see the irradiated zone for different slit angle values. The results (dots) agree well with the calculated curves

| | slit angle | 0.1 ° | 0.3 ° | 1 ° |
|-----------------------------|---------------|---------|--------------|-----------------------|
| 2θ min for L = 20 mm | | | 6 ° | 20 ° |
| 2θ min for L = 10 mm | | 4 ° | 12 ° | 36 ° |
| These values have to be c | considered as | a rough | guide before | e making experiments. |

4.3. – Determination of the width l

Sample holder symmetrically masked by cardboard pieces constant length (L = 20 mm) and variable width (l = 0 to 34 mm). (111) peak of aluminum metal was recorded for each cardboard mask Results given in the figure which shows the integrated intensity versus the width l.

The curve displays two ranges :

from 0 to 14 mm with a linear increase of the intensity above 16 mm with a constant intensity.

 \rightarrow useful width 16 - 18 mm (depends on the apparatus).

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Bragg-Brentano geometry Goniometer (or measuring circle) defined by the middle of the sample E, the beam focus F and the detector D

 θ -2 θ goniometer: the X-ray source is fixed and the sample and detector are moving. The sample rotates by an angle θ , whereas the detector rotates by an angle 2 θ

 θ - θ goniometer: the sample is fixed and the source and detector are moving. Radius of the goniometer circle: R (must be known)

The beam is diverging from the focus and limited by an aperture slit

Bragg-Brentano geometry θ -2 θ

θ -2 θ Brucker powder diffractometer

A Modern Automated X-ray Diffractometer

Bragg-Brentano geometry

θ -2 θ Rigaku double powder diffractometer

Bragg-Brentano geometry θ -2 θ Rigaku double powder diffractometer \rightarrow back-monochromator

Bragg-Brentano geometry

θ - θ PANalytical powder diffractometer

Cu K α , Ni filter, PIXcel detector (3 °, 2 θ)

Bragg-Brentano geometry

5.2. – Focusing circle

Bragg-Brentano geometry Focusing circle defined by F (source focus), E (sample) and D (detector) Radius $r = R/(2 \sin\theta)$ Depends on the angle θ

5.3. – Aperture slits

Define the length L of the irradiated area The width l is constant and depends on the X-ray tube and the slits Fixed slit \rightarrow L varies Variable slit \rightarrow L constant

linear focus F with width l

 $L = R\delta / sin\theta$

5.3. – Aperture slits

Define the length L of the irradiated area The width l is constant and depends on the X-ray tube and the slits Fixed slit \rightarrow L varies Variable slit \rightarrow L constant

$L = R\delta / \sin\theta$

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6.1. – Zero correction

Instrumental sources of errors

- Error in zero 2θ position
- Instrument misalignement
- Speciment displacement
- Peak distorsion due to $K_{\alpha 2}$ wavelength

Zero correction

- Systematic error due to the alignment of the apparatus
- Must be checked regularly and indicated

6.2. – Sample displacement $\Delta = -2s \cos\theta / R \text{ (radian)}$ S: amount of displacement, R: goniometer radius $2\theta_{\text{corrected}} = 2\theta_{\text{exp}} + 180\Delta/\pi (^{\circ})$

6.2. – Sample displacement

$\Delta = -2s \cos\theta / R$ (radian)

 $2\theta_{\text{corrected}} = 2\theta_{\text{exp}} + 180\Delta/\pi$ (°)

– sample not on the focusing circle (or in the center of the goniometer circle)
– greatest systematic source of error in most data

Ex.: at 28.4 ° 2 θ , s = 0.006", R = 200 mm \Rightarrow peak shift of 0.08° peak shift?

- Can be minimized by using a zero background sample holder

Can be corrected by using an internal calibration standard
Can be eliminated by using parallel-beam optics

6.3. – Sample absorption

Mean path length of X-rays: $2/\mu$

 d_m = mean penetration depth (depends on the diffraction angle) Irradiated volume: $V = length * width * depth = L * l * d_m$

We have to calculate dm $2/\mu = AE' + E'B = 2d_m/\sin\theta$ $d_m = \sin\theta/\mu$

Remember $L = R\delta/\sin\theta$ volume $V = R^*\delta^*1 / \mu = constant$

Two limiting cases:

- μ is large: d_m < thickness t of the powder \rightarrow displacement s = $d_m/2$
- μ is small: d_m > thickness t of the powder \rightarrow displacement s = t/2

6.4. – Other sources of errors

- Axial divergence
- divergence of the X-ray beam in plane with the sample
- asymmetric broadening of the peak toward low 2theta angles
- peak shift: negative below 90° 2theta and positive above 90°
- reduced by Soller slits and/or capillary lenses
- Flat specimen error
- The entire surface of a flat specimen cannot lie on the focusing circle
- Creates asymmetric broadening toward low 2theta angles
- Reduced by small divergence slits; eliminated by parallel-beam optics
- Poor counting statistics
- not sufficient randomly oriented crystallites, as assumed
- sample might be textured or have preferred orientations
- Creates a systematic error in peak intensities
 Some peaks might be entirely absent
- The sample might have large grain sizes

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7.1. – Simple quantitative evaluation using the RIR or I/Icor data

The Reference Intensity Ratio (RIR) method scales all diffraction data to a standard. By convention, corundum α -Al₂O₃ is used as the international reference and The scale factor is defined by: Intensity Analyte / Intensity Corundum = I / Ic

On PDF sheets we have an RIR or I/Icor value This corresponds to the intensity ratio of a mixture 50 wt.-% species + 50 wt.-% corundum

We have to take the largest diffraction peaks of both phases

How to perform the calculation for two phases in a mixture?

| Example of Powder Diffraction File | Date: 2012-3-31 Time: 18:02:26 | File: 00-048-1773 |
|------------------------------------|--|---------------------|
| | <u>Name and formula</u> | |
| | Reference code: | 01-070-0363 |
| | ICSD name: | Barium Cobalt Oxide |
| | Empirical formula: | BaCoO ₃ |
| | Chemical formula: | BaCoO ₃ |
| | Crystallographic para | <u>meters</u> |
| | (rveta) evetem. | Heragonal |
| | Space group: | P63/mmc |
| | Space group number: | 194 |
| | a (?): | 5.6450 |
| | b (?): | 5.6450 |
| | с (?): | 4.7520 |
| | Alpha ("): | 90.0000 |
| | Beta ("): | 90.0000 |
| | Gamma ("): | 120.0000 |
| | Calculated density (g/cm^3): | 6.18 |
| | Measured density (g/cm^3): | 6.10 |
| | Volume of cell (10 ⁶ pm ³): | 131.14 |
| | Z: | 2.00 |
| | BIB. | 6 76 |

7.1. – Simple quantitative evaluation using the RIR or I/Icor data

Example of Powder Diffraction File

Subfiles and Quality

| Inorganic |
|----------------|
| Corrosion |
| ICSD Pattern |
| Calculated (C) |
| |

<u>Comments</u>

| ICSD | collection | code: | 000922 | 2 | | | |
|------|------------|-------|--------|-----------|-----------|-----|------------|
| Test | from ICSD: | | Calc. | density | unusual | but | tolerable. |
| | | | At lea | ast one 1 | [F missi] | ng. | |

References

| Primary reference: | Calculated f. | rom ICSD | usi | ng POWD-12++, | (1997) | | | | |
|--------------------|---------------|----------|-----|---------------|------------|-----|----------|-----|------|
| Structure: | Taguchi, H., | Takeda, | Υ., | Kanamaru, F. | , Shimada, | М., | Koizumi, | M., | Acta |
| | Crystallogr., | Sec. B, | 33 | , 1298, (197 | 7) | | | | |

| 7.1. – Simple quantitative evaluation us | sing | the | RI | R or | I/Icor | data | | |
|--|-------------|-------------|----|------|---------|-------------|--------|---|
| Example of Powder Diffraction File | <u>Peak</u> | <u>list</u> | | | | | | |
| | No. | h | k | 1 | d [A] | 2Theta[deg] | I [%] | |
| | 1 | 1 | 0 | 0 | 4.88871 | 18.131 | 1.4 | |
| | 2 | 1 | 0 | 1 | 3.40748 | 26.131 | 100.0 | |
| | 3 | 1 | 1 | 0 | 2.82250 | 31.675 | 82.3 · | _ |
| | 4 | 2 | 0 | 0 | 2.44436 | 36.738 | 1.9 | |
| | 5 | 0 | 0 | 2 | 2.37600 | 37.834 | 8.1 | |
| | 6 | 2 | 0 | 1 | 2.17365 | 41.511 | 55.3 | |
| | 7 | 1 | 0 | 2 | 2.13698 | 42.257 | 25.8 | |
| | 8 | 2 | 1 | 0 | 1.84776 | 49.276 | 0.3 | |
| | 9 | 1 | 1 | 2 | 1.81770 | 50.147 | 5.0 | |
| | 10 | 2 | 1 | 1 | 1.72215 | 53.140 | 18.6 | |
| | 11 | 2 | 0 | 2 | 1.70374 | 53.760 | 18.9 | |
| | 12 | 3 | 0 | 0 | 1.62957 | 56.420 | 11.6 | |
| | 13 | 3 | 0 | 1 | 1.54146 | 59.963 | 0.2 | |
| | 14 | 1 | 0 | 3 | 1.50688 | 61.486 | 6.5 | |
| | 15 | 2 | 1 | 2 | 1.45860 | 63.756 | 15.0 | |
| | 16 | 2 | 2 | 0 | 1.41125 | 66.163 | 10.2 | |
| | 17 | 3 | 1 | 0 | 1.35589 | 69.238 | 0.1 | |
| | 18 | 3 | 0 | 2 | 1.34387 | 69.947 | 1.6 | |
| | 19 | 2 | 0 | 3 | 1.32929 | 70.828 | 7.1 | |
| | 20 | 3 | 1 | 1 | 1.30385 | 72.426 | 7.7 | |
| | 21 | 4 | 0 | 0 | 1.22218 | 78.140 | 0.1 | |
| | 22 | 2 | 2 | 2 | 1.21336 | 78.818 | 2.9 | |
| | 23 | 2 | 1 | 3 | 1.20260 | 79.663 | 4.5 | |
| | 24 | 0 | 0 | 4 | 1.18800 | 80.842 | 1.7 | |
| | 25 | 4 | 0 | 1 | 1.18366 | 81.201 | 4.1 | |
| | 26 | 3 | 1 | 2 | 1.17763 | 81.704 | 4.8 | |
| | 27 | 1 | 0 | 4 | 1.15440 | 83.714 | 0.1 | |
| | 28 | 3 | 0 | 3 | 1.13583 | 85.404 | 0.1 | |
| | 29 | 3 | 2 | 0 | 1.12155 | 86.757 | 0.1 | |
| | 30 | 1 | 1 | 4 | 1.09496 | 89.416 | 4.4 | |
| | 31 | 3 | 2 | 1 | 1.09156 | 89.770 | 4.6 | |

7.1. – Simple quantitative evaluation using the RIR or I/Icor data

Example of Powder Diffraction File

<u>Stick Pattern</u>

CONCLUSION

Strengths of Powder X-ray Diffraction

- Non-destructive small amount of sample
- Relatively rapid
- Identification of compounds / phases not just elements
- Quantification of concentration of phases (sometimes)
- Classically for powders, but solids possible too
- Gives information regarding crystallinity, strain, crystallite size, and orientation

Limitations of Powder X-ray Diffraction

- Bulk technique generally unless a camera or microfocus source is used
- Not a "stand-alone" technique often need chemical data
- Complicated spectra multiphase materials identification / quantification can be difficult