Protocol
Mean Crystallite Size by X-Ray Diffraction (XRD)

1. Method

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. Line profile analysis is a diffraction technique used to obtain micro-structural information of the sample averaged over the diffraction volume.

In a powder diffractogram a polycrystalline material without any lattice strain and consisting of particle sizes larger than 500 nm, shows sharp lines. Imperfections in the structure of the crystallites constituting a sample, cause broadening of the diffraction line profiles. Large crystallites give rise to sharp peaks; as the crystallite size reduces, the peak width increases and the intensity decreases. Peak broadening can also originate from variations in lattice spacings, caused by lattice strain.

Several analysis methods exist to calculate crystallite sizes and lattice strain separately from diffraction line broadening:

- Approximate method
- Single Line method
- Warren Averbach method

We focus here on the single line method.

2. General recommendations for measuring X-Ray Diffractogram for this purpose

Always use the same instrument and same sample holder for carrying out all measurements.

3. Equipment

- Measurement device: Philips X-Pert, θ-θ configuration

  Wavelenght $Cu_{K\alpha 1,\alpha 2}$ (no monochromator) (more information from http://www-eu.analytical.philips.com)
- Circular sample holder, with an automatic charging system

4. Protocol

Preparation of the samples

In order to obtain accurate and comparable results, samples must be carefully and correctly prepared, mounted and aligned, prior to the measurements.

The ideal amount of powder is 400 [mg]. Put the powder in the sample holder ring, press it slightly with a glass slide, and remove surplus powder.

If there is not enough powder, an amorphous Si background can be used. Place the powder as much as possible in the centre.

A standard sample is always prepared in parallel with a series of samples. This standard is obtained by annealing the same powder at a high temperature (900 [°C]). A powder of LaB_6 can also be used. The broadening observed in this sample is then only attributed to the instrument (without any effect of the grain size or strain).

Operations

- Check that the instrument is ready (X-Ray generator: 40 [kV], 50 [mA], water flow to 300)
- If the X-Ray generator indicates 45 [kV], 20 [mA]

  Open X-Pert Data Collector, in the instrument control window, double-click on Instruments settings/X-Ray/Generator. Enter Tension: 40 [kV], Current: 50 [mA].
- Put the sample or a series of samples in the automatic sample charger, and close the window of the apparatus

Defining a measurement program

(a) The main program

- Open X-Pert Data Collector
- Select “File”, “Open program”, choose “Absolute scan”, and open the file associated to personal data: “First name”
- Choose “Spinner and changer” for the configuration, a scan axis Gonio, and a “Continuous” scan mode
- Choose the start angle [°], the end angle [°], and the time per step. The step size must be set to 0.0167113 [°]
- Close the window and save

(b) Sample series

- Open X-Pert Data Collector
- Select “File”, “Open program”, choose “Sample (changer) batch”, and open the file associated to personal data: “First name GB”
- Delete all the lines, corresponding to the former analysis
- Click on “Insert”, and browse the measurement program created before (Absolute scan, then “First name”)

  Select the position of the first sample: A1, name it in the line ID, then click OK
- Select the second line, then click on “Insert”.

  Change the position: A2, and name the second sample in the line ID
- Do the same for all the series
- When all the samples are added, click on “File name settings”. Click on “Use same folder”, and create a file where all the data of the series will be saved. Click on Ok twice. Close the window, and save

(c) Run the program

- Before characterising a series of samples, the peak position is first measured with Si (2θ = 28.43°), for evaluating the correction of the instrument
- Open X-Pert Data Collector
- Select “Measure”, then “Program”:
  - If there is only one sample: select “Absolute scan”, then “First name”
  - If there is a series of samples: select “Sample changer batch”, then “First name GB”

The measurement is starting after clicking on OK.

5. “Line Broadening” Data Treatment with Software X’Pert HighScore Plus

- Open X’Pert High Score Pus
- “File” menu, select “Open” and select one file (XRDML format)
- Select a two-theta range where there are at least 10 peaks of reasonable intensity (minimum 10% of highest intensity) with the cursor in the “Additional Graphics” window
- Go to the “Treatment” menu: select “determine background”
- For calculating line broadening: the definition of the background is very important
- A green line appears on the graph and it should overlap the red line at the level of the background
- In the box, click on “Accept” if you agree with the fitting. If you do not, modify the “Granularity” and “Bending factor” parameters
- Literature recommends a value of 20 for “Granularity” but we usually use 10. Most important it should be the same for all the samples to be compared between each other as this parameter could influence the mean crystallite size
- To check the effect of the modifications on the graph, it is possible to zoom using the left mouse button and travel across the graph to follow the line in the “Additional Graphics” window
- Go to the “Treatment” menu, select “search peaks”. In the box, click “search peaks”
- Check that each peak at the top of the graph represents a real peak in the measurement. If one is missing, modify “Minimum tip width” and “peak base width” so that more peaks can be included. However, the peak search tool usually works well without modifying those parameters
- Click “accept”
- A blue line appears, it shows the calculated diffractogram
- Go to the “Treatment” menu: select “Fit profile” and repeat 2-3 times
- If not satisfactory: go to the “Edit” menu and select “undo fit profile”
    - Go to the “Customize” menu, select “Document Setting” and tab: “Profile fitting”. Select “shape parameter” and click “apply” then “OK”
    - Then go to the “Treatment” menu again: select “Fit profile” and if necessary repeat 2-3 times
    - “Customize” menu, select “Document Setting” and the “Profile fitting” tab. Select “KA1/KA2 parameter” and click “apply” then “OK”
    - Repeat “Treatment” menu: select “Fit profile” and if necessary repeat 2-3 times
- Remark: When zooming on one peak, the fitting only applies to that peak
    - Start globally treating the diffratogram and then zoom in. A reasonable background line is needed on both sides of the peak (1/3, 1/3, 1/3)
    - Remark 2: if peaks overlap and show low intensity -> skip “fit profile” on these peaks

- Go to File/Save as Powder-Lotn°-XRD-Experimentn°-Operator.hpf

6. Presentation of the results, data storage and data treatment - Calculation of the mean crystallite size: Scherrer and Williamson-Hall method

Export the results

- In X'Pert High Score Plus, go to the "Reports" menu, select "Create Word report/Default". Save as Powder-Lotn°-XRD-Experimentn°-Operator.doc. The bookmarks of this report can be changed in "Reports/Edit report definition"
- Go to File/Save as and choose "General ASCII scan". Save as Powder-Lotn°-XRD-Experimentn°-Operator.txt

Data storage

- Copy the DOC report, the TXT and HPF files.
- Go to \\Ltppc40\powderfiles. Copy the folder *Powderfiles*. Paste it in your project folder, and change its name into Powder-Lotn°.
- Paste the TXT, HPF and DOC files respectively in the folders Project/Powder-Lotn°/CPS/Data and PDF.

Data treatment

- Go to \\Ltppc40\powderfiles. In the folder Project/Powder-Lotn°, open the Excel sheet "Powdersheet.xls"
- Click on the XRD button, and follow the instructions given in the Excel sheet to draw the XRD pattern

- Click on the *XRD_C* button, to access to **the calculation of the crystallite size**
- In parallel open Powder-Lotn°-XRD-Experimentn°-Operator.hpf
- Then select the "peak list" tab in the "List Pane" window. Go to the table, and with a right click, select "Delete all K Alpha2 peaks"
- With a new right click, select "Copy list"
- Paste it in the first page of the Excel sheet named "rawdata"
- Choose the peaks of interest in the page named "selected data" by their number and put them in the green cells (avoid doubled peaks, or peaks with low intensity)
- Make the same fitting for the standard sample (with the same position range [2Th]). Select the "peak list" tab in the "List Pane" window and with a right click, select "Delete all K Alpha2 peaks". With a new right click, select "Copy list"
- Paste it in the second page of the "XRD_size" Excel sheet named "Standard".
- The calculation is done in the page named "Calculation".
- In this page, enter Sample name as Powder-Lotn°-XRD-Experimentn°-Operator, and the date. Enter the wavelength of the X-Ray (generally copper K_α 1.54 Å)
- Choose the calculation mode: 1 – with a standard sample which is the same as your material, 2 – with a standard different from your material (use a mean value), or 3 – with a mean value of the width due to the equipment calculated elsewhere
- The Williamson-Hall plot is drawn automatically, as well as the calculations of the mean crystallite size and the strain of the powder. The formulas used are described in the page named "Calculation formulas". If the R^2 of the curve of tendency is very low, delete some points which are too far
- Also the crystallite size is calculated using the Scherrer equation in the dedicated cells. These values can be compared to the Williamson-Hall mean crystallite size.