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Quantitative phase analysis based on Rietveld structure refinement

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Table of contents

Acknowledgements ....

General introduction 1

Chapter1 : Rietveld method 2

1.1. Introduction: 3

1.2. Historic: 3

1.3. The Rietveld method: 4

1.4. Least-squares method: 6

1.4.1. Non-linear least-squares operation: 6

1.4.2. The problems in the least-squares: 9

1.4.3. Prototype of Rietveld method with least-square: 10

1.4.5. Figures of merit: 11

1.5. Understanding the pattern: 13

1.6. Introduction of $y_{i(calc)}$ parameter: 14

1.6.1. The background: 14

1.6.2. The reflection factor: 14

1.6.3. The Lorentz-Polarization factor Lk: 15

1.6.4. The Multiplicity factor: 16

1.6.5. Scale factor: 16

1.6.6. Structure factor [F_{hkl}]: 17

1.6.7. The absorption factor A: 17

1.6.8. The preferred orientation function Pk: 18

1.7. Conclusion: 19

Chapter2: Rietveld refinement using GSAS 20

2.1. INTRODUCTION: 21

2.2. Histories: 21

3. Definitions 21

3.1. X-ray diffraction: 21

3.2. Powder diffraction: 22

2.4. The evolution of the Rietveld refinement method: 23
2.4.1 Pre-rietveld refinement methods 23
2.4.2. Rietveld refinement: 23
2.5. Statistical and graphical measures of a refinement: 23
2.5.1. The R indices: 24
2.5.2. General Rietveld approach: 25
2.6. Rietveld refinement procedure: 27
2.7. Rietveld refinement with EXGPUI/GSAS: 27
2.7.1. Introduction: 27
2.7.2. EXPEDT: 27
2.7.3. GSAS: 28
A).GSAS structure: 28
B). GSAS interface: 28
C).GSAS features: 31
2.8. EXPGUI: 31
2.8.1. Crystal structure refinement using EXPGUI: 31
2.8.2. Crystal structure refinement of ZnO,Ca$F2, Al2O3$: 34
2.9. Conclusion: 44
Chapter3: Results and discussion
3.1. Introduction: 47
3.2. Application of Rietveld refinement on powder sample: 47
3.2.1. zinicite (ZnO) GSAS/EXPGUI refinement: 47
3.2.2. corindon ($Al2O3$) GSAS/EXGPUI refinement: 50
3.2.3. Fluorine ($CaF2$) GSAS/EXPGUI refinement: 53
3.2.4. ZnO,$Al2O3$, $CaF2$ refinement EXPGUI/GSAS: 57
3.3. Conclusion: 59
General conclusion: 61
Bibliography: 63

Table of figures

CHAPTER 01

Rietveld method

Figure1.1: example of rietveld refinement …………………………..…….……..…… 05

Figure1.2**:** example of a failed non-linear least squares technique in finding a best solution to Eq (2), ………………………………………..………..…………... 09

Figure1.3: represent from left to right a Debye ring and a pattern and how the peak intensity is founded……………………………………………….....………...... 13

Figure1.4: a Lorentz-polarization factor as a function of Bragg angle…………...16
Figure1.5: example of the absorbing experiment…………………….……..…...18
Figure 1.6: Schematic representation of the preferential orientation effect (2D)......19

CHAPTER02

Figure 1.1:x-ray diffractometer ………………………..………………………………… 22

Figure 1.2: X-ray powder diffraction pattern and Rietveld refinement profile of mixed stone……………………………………………………………………...……………....22

Figure1.3: A demonstration of the effect of the Rietveld fit on the background………….26

Figure1.4: peak shape……………………..…...……………………………………...… 26

Figure1.5: convolute with profile shape.. 26

Rietveld refinement with EXPGUI/GSAS

GSAS

Figure 1.6: pc-GSAS icon double click……………………………………..……. 28
Figuer1.7: start-up screen……………..…………….……………………….…..... 28
Figuer1.8: experiment name screen.………………………………….……….... 29
Figuer1.9: start-up screen after the experiment name……………………..…..... 29

Crystal structure refinement using EXPGUI

Figuer2.1: EXPGUI icon…………………………..……………..…………31
Figuer2.2: EXPGUI startup screen…………………………………………….…….. 32
Figuer2.3: select the D:/reffinement and specify refinement as the job name........... 32
Figuer2.4: select “create”……………………..………………………………… 33
Figuer2.5: chose a title and click “set”……………………………………..……….... 33

Figuer2.6: EXPGUI main window…………………………………………………………......33

Chapter3

Figure 1.1: plot of calculated and observed patterns with peak position of Zinicite. 47
Figure1.2: structure 2D of zinicite………………………………………..……. 49
Figure1.3: structure 3D of zinicite…………………………………………..….. 49
Fugure2.1: plot of calculated and observed patterns with peak position of corindo. 50
Figure2.2: structure 2D of corindon……………………………………………... 53
Figure2.3: structure 3D of corindon……………………………………………... 53
Figure3.1: plot of calculated and observed patterns with peak position of fluorine. 54
Figure3.2: structure 2D of fluorine………………………………………………… 55
Figure3.3: structure 3D of fluorine……………………………………………….... 56
Figure4.1: plot of calculated and observed pattern with peak position of mélange. 57
Figure4.2: structure 2D of the mélange …………………………………………… 59
Figure4.3: structure 3D of the mélange……………………………………………. 59

General introduction

General introduction:

The quantitative phase analysis is introduced by Hanawalt in 1938 and developed by Alexander and Klug in 1948; it helps in determining the multi-sample composite phases by linking each phase to its right component and the phase characterizes, and sorting it in the powder diffraction pattern.

Refining diffraction pattern with Rietveld method it is a technique described by Hugo Rietveld that gives the sample a visual shape or structure which facilitate the extracting of its crystalline materials characterization with the help of a program in massif calculation.

When an experiment for powder diffraction is realized extra information are counts in the result whether external or internal called the background it can affect the result of refinement or mislead it when its high so striving to cut it or lowering using some function to refine it is recommended.

With phase quantification detecting and calculating the quantity of a material in diffraction pattern is possible using the intensity peak with the scaling per phase after the quantitative phase analysis.

In the upcoming chapters we will discusses in:

- A brief understanding to the Rietveld method and how it works.
- General information about Rietveld refinement, GSAS program and how we use it for one phase and three phases.
- Results and discussion of the structure of the single phase and mixed

Chapter1 : Rietveld method

1.1. Introduction:

The Rietveld method proposed by **Hugo Rietveld** in 1960s, is a mean or a way to fit an approximate model of the structure and refine it to the shape and be more similar to the pattern giving by a x-ray powder diffraction or a neutron powder diffraction (in some case both are used) so the calculated structure from the model is closer in resemblance to the observed data of the powder diffraction patterns, this allow to get more perfect result to a single phase or a complexes one in the refined crystal structure since many data are lost during observing the diffraction patterns overlaps in crystallographic study. Using a complex minimizing procedure can close the distance of the two variable of intensity one observed $\mathbf{y_{i\,(obs)}}$ from the powder patterns and other calculated $\mathbf{y_{i\,(calc)}}$ from the structure by the numerical value function in each data point 'i' with eliminating or minimizing the error a more suitable pattern is created that allow to extract more accurate data and key properties of solid systems [1].

It all depend by determine the accuracy of a crystal structure model it is refined than fitted to a one dimension to suits the profile observed patterns [1].

1.2. Historic:

In the early days in the 1960s, the crystallography was already applying least-squares method to adjust structure parameters but some issue couldn't be handled where the experiments emphasis on single crystal diffraction and the X-ray diffraction powder method regarded as inferior result. In 1964 Hugo Rietveld start his career in Netherlands Energy Research Foundation (ECN), the research was based on neutron powder diffraction techniques noting the issues and ideas in his experiments with complex compound with low symmetry. Some ideas were represented in 1966, but the extra information steel be lost in sever overlap and due to large file and limitation in calculation, so some theories get frozen. After reporting the method to the seventh congress of the International Union of Crystallography "I.U.C" in Moscow the respond was very low to non-existent. Rietveld start publishing his works until 1969, it gets recognized fully and that open a way to a flourishing discussing and possibility of improving the method, where a total 172 were solved using Rietveld method. In 1977 a published work by Malmros and Thomas about application of X-ray

diffraction in Rietveld method that lead to more authors that contributed to the method improvement especially after Albinati and Willis article in 1982, and with the advancing technology in computer many adjusting program it is created to the point that even a normal person can refine a structure solution from a pattern with the right instructions [2].

1.3. The Rietveld method:

The Rietveld method minimizes the difference between observed and calculated patterns at each data point high in the diffraction pattern using a non-linear least squares algorithm [3]:

$$S_y = \sum_{i}^{n} \mathbf{W}_i \left(y_{i(obs)} + y_{i(calc)} \right)^2 \qquad \textbf{(1)}$$

Where $W_i = \frac{1}{y_{i(obs)}}$ and i = 0……n

$y_{i(obs)}$Is the observed intensity in the ith step of the pattern graph form the X-ray diffraction.

$y_{i(calc)}$ is the calculated intensity in the ith step of the crystal refined information characteristics.

W_i is the weight of the ith point in the observed intensity.

S_y is the quantity minimized in the non-linear least-squares method.

The calculated intensity $y_{i(calc)}$ are determinated by the sum of the contribution of the Background and all neighboring Bragg reflections, it is expressed mostly of nonlinear Analytic or non-analytic functions as:

$$y_{i(calc)} = S \sum_{k} L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + bkg_i \qquad \textbf{(2)}$$

This is a single i^th^ point calculation where the sum runs over all Bragg reflections. In general, there will be an outer sum runs all over crystalline phases p with Bragg peaks in the powder pattern while the inner sum runs over all Bragg reflections:

$$y_{i(calc)} = \sum_{j=1}^{n_{phases}} S_j \sum_{k=1}^{n_{peaks}} L_k \left|F_{k.j}\right|^2 \phi_j \left(2\theta_i - \theta_{k.j}\right) AP_{k.j} + bkg_i \qquad (3)$$

Where

S_j : The scale factor.

K represents the miller indices h, k, l. For a Bragg reflection.

L_k Contains the Lorentz; polarization; and multiplicity factors.

ϕ_j : The reflection (shape) profile function.

P_k : The preferred orientation functions.

A is an absorption factor.

F_k : The structure factor for the Kth Bragg reflection

bkg_j : The background intensity at the jth point.

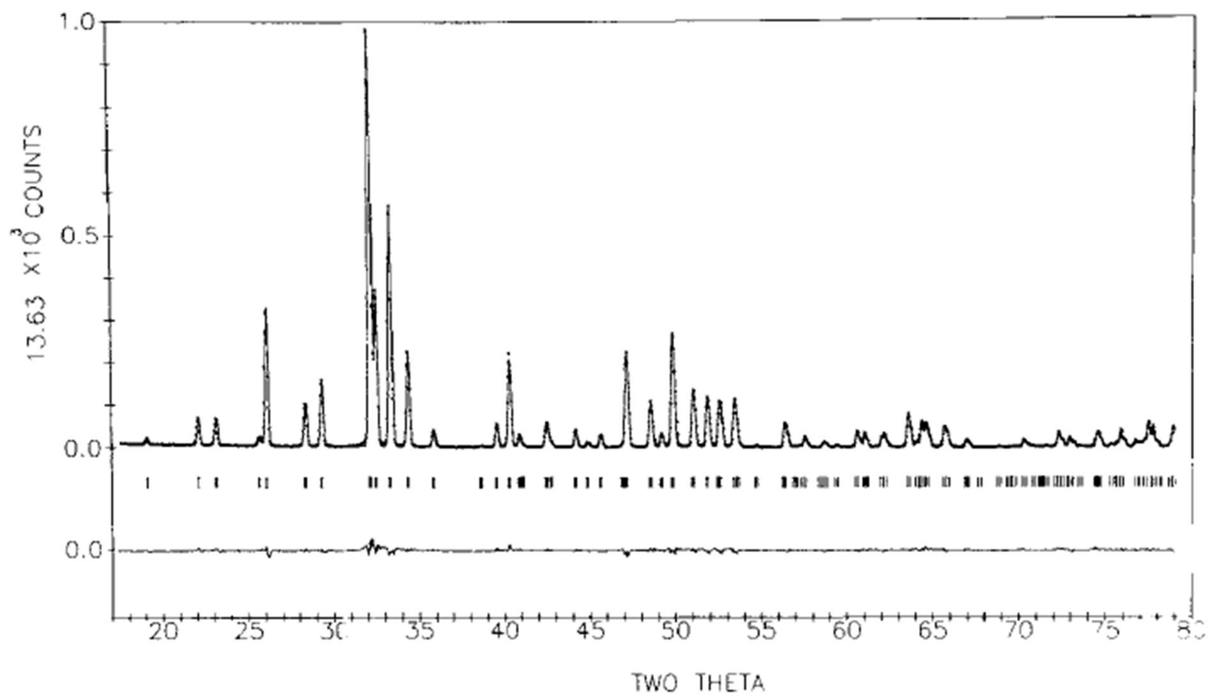


Figure1.1**:** example of Rietveld refinement plot [4]

This is how a good finished refinement plot looks like where the upper curve represents the intensity $y_{i(obs)}$ and $y_{i(calc)}$ almost matching each other usually colored line are used to distinguish between them with the peaks, the second vertical line is for Bragg reflection position and the last line represent the deference calculated between ($y_{i(obs)}$ - $y_{i(calc)}$).

1.4. Least-squares method:

1.4.1. Non-linear least-squares operation:

Many calculations are based on the non-liner lest squares like the Rietveld refinement since it is a minimization of the differences between the observed and calculated profiles.

Assumed the best solution of a system of n simultaneous equations with m unknown parameters (n >> m), with each equation is a non-linear function in respect to the unknowns.x_1, x_2... x_m. And the system is representing as [3]:

$$f_1(x_1, x_2, \dots, x_m) = y_i$$

$$f_2(x_1, x_2, \dots, x_m) = y_2$$

$$f_n(x_1, x_2, \dots, x_m) = y_n \dots (4)$$

The point is to convert each non-linear function to a linear function by the appropriate substitutions of variables thus reducing the problem to a linear case, which help in finding the best solution, note that the function is according to your choice or the situation.

The Taylor's series is an expansion of a real function about a point, in the case of one variable $f(x)$, the expansion in a point is $x = x'$ is giving as:

$$f(x) = f(x') + \Delta x f'(x') + \frac{\Delta x^2}{2!} f''(x') + \cdots + \frac{\Delta x^n}{n!} f^n(x') \qquad (5)$$

Where $\Delta x = (x - x')$ and x' is deferent from x.

This way we will modify or change our parameter or function according to the calculation, the goal when applying Taylor series that you find that you will return to the exact y form if it is correct.

We can obtain the solution of the least-squares to the equation (1) by applying the Taylor's series to every f in the equation, note that we only take the first partial derivation of the respective function knowing that it is the minimum when it's first derivation is zero in Taylor's series, and the different parameters $x_{1\ to\ m}$ is recognized as independent to each other so the solution to equation (1) will be:

$$\begin{aligned}
&\frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_1}\Delta x_1 + \dots + \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_m}\Delta x_m \cong y_1 - f_1(x'_1,\dots,x'_m) \\
&\frac{\partial f_2(x'_1,\dots,x'_m)}{\partial x_1}\Delta x_1 + \dots + \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_m}\Delta x_m \cong y_2 - f_2(x'_1,\dots,x'_m) \\
&\quad . \qquad \dots \qquad . \qquad .. \quad . \quad . \qquad (6) \\
&\frac{\partial f_n(x'_1,\dots,x'_m)}{\partial x_1}\Delta x_1 + \dots + \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_m}\Delta x_m \cong y_n - f_n(x'_1,\dots,x'_m)
\end{aligned}$$

Where: $y_n - f_n(x^0_1,\dots,x^0_m)$ is the residual symbolized by R_i it represents the error associated with the problem in the parameter of the function in each point,y_n is the actual data point and f_n is the choosing function in this calculation.

When the corresponding derivations exist and are finite, equation (2) is linear with respect to $\Delta x_1, \Delta x_2,\dots,\Delta x_m$ and a solution is obtained by applying conventional linear least squares technique as:

$$\Delta x = (A^T W A)^{-1}(A^T W y) \qquad (7)$$

Where:

$$\Delta x = \begin{pmatrix} x - x'_1 \\ x - x'_2 \\ \dots \\ x - x'_m \end{pmatrix} = \begin{pmatrix} \Delta x_1 \\ \Delta x_1 \\ \dots \\ \Delta x_1 \end{pmatrix}$$

$$A = \begin{pmatrix} \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_1} & \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_2} & \dots & \frac{\partial f_1(x'_1,\dots,x'_m)}{\partial x_m} \\ \frac{\partial f_2(x'_1,\dots,x'_m)}{\partial x_1} & \frac{\partial f_2(x'_1,\dots,x'_m)}{\partial x_2} & \dots & \frac{\partial f_2(x'_1,\dots,x'_m)}{\partial x_m} \\ \dots & \dots & \dots & \dots \\ \frac{\partial f_n(x'_1,\dots,x'_m)}{\partial x_1} & \frac{\partial f_n(x'_1,\dots,x'_m)}{\partial x_2} & \dots & \frac{\partial f_n(x'_1,\dots,x'_m)}{\partial x_m} \end{pmatrix}$$

$$y = \begin{pmatrix} y_1 - f_1(x'_1,\dots,x'_m) \\ y_2 - f_2(x'_1,\dots,x'_m) \\ \dots \\ y_n - f_n(x'_1,\dots,x'_m) \end{pmatrix}$$

$$W = \begin{pmatrix} w_1^2 & 0 & \dots & 0 \\ 0 & w_2^2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & w_n^2 \end{pmatrix}$$

W is a square matrix represent individual weights (w_i) for each available n data points, A^T is the transpose of A.

The refined parameters are component using the set of original x' that represents the initial approximation of the unknowns and the vector Δx obtained from least squares equation (3):

$$x = x' + \Delta x = \begin{pmatrix} x_1' + \Delta x_1 \\ x_2' + \Delta x_2 \\ \dots \\ x_m' + \Delta x_m \end{pmatrix} \qquad (8)$$

The standard deviations (uncertainty) for each refined parameter according to the least squares method are calculated from [3]:

$$\sigma(x_j) = \sqrt{\frac{(A^T W A)_{jj}^{-1} \sum_{i=1}^{n} w_i (y_i)^2}{n-m}}, \; j = 1, \dots, m \qquad (9)$$

Where:

- n is the number of equations in Eq (2).
- m is the number of unknown parameters in Eq (2).
- $(A^T WA)^{-1}_{jj}$ Is the corresponding diagonal element of the inverse normal equation matrix.
- w_i Is the corresponding weight.
- y_i Is the corresponding element of the vector y.

Note:

Since the Eq (2) is not exact, more cycle of least squares refinement are done to achieve a full convergence and during the second and following least squares cycles as the new set of parameters is obtained the previous step from Eq (4) is used as a the initial approximation for the new one.

1.4.2. The problems in the least-squares:

It is difficult to achieve a convergence because of iterative nature of non-linear least squares, especially when the initial approximation is far from correct or when the minimized function is poorly defined, it may diverge and unstable so to evade it numerical conditioning techniques is applied for improvement as explained in the figure below [3]:

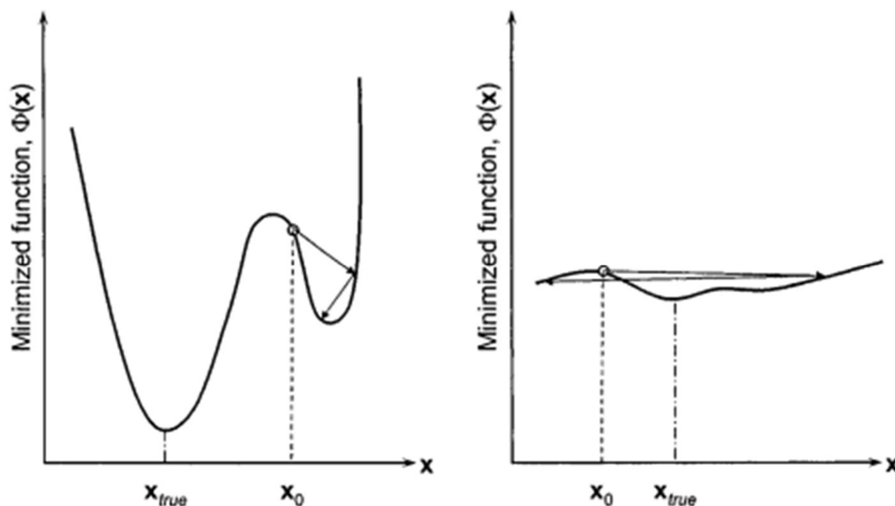


Figure1.2**:** example of a failed non-linear least squares technique in finding a best solution to Eq (2), the left-the initial approximation (x_0) is located near a false minimum; the right-the minimum is poorly defined [3]

To evade this problem a correlation coefficient is introduced in the form:

$$\rho_{ij} = (A^T WA)^{-1}_{ij} / \sqrt{(A^T WA)^{-1}_{ii} (A^T WA)^{-1}_{jj}} \quad (10)$$

The inverse of the matrix $(A^T WA)^{-1}$is used to evaluate the correlation coefficient (ρ_{ij}) among the pairs of variables$(x_i \; and \; x_j)$.

ρ_{ij} vary from 0 to 1, and the associated parameters show little to no correlation in the range from -0.5 to 0.5, when the coefficient is in unity the corresponding variables are fully (100%) correlated so one of them is eliminated from the refinement, it is useful when the figures of merit is detected the numerical worsen when the least-squares are unstable.

1.4.3. Prototype of Rietveld method with least-square:

In the case of Rietveld method, the function S_y that represents a nonlinear function of a minimized value in terms of various parameters (P_j). We say the function S_y has a minimum when the partial derivatives with respect to each of the parameters P_j are zero [1]:

$$\left(\frac{\partial S_y}{\partial P_j}\right) = \sum_{i=1}^{N} \left\{ 2w_i (y_{i(obs)} - y_{i(calc)}) \left(\frac{\partial y_i}{\partial P_j}\right) \right\} = 0 \quad (11)$$

Where (i=1…..N) is the number of observations

If there are M numbers of parameters P_j, then we will have M numbers of equation.

When you get a model that is close to the equation above but the parameters in your model differ from those of the true minimum by an amount ∂P_j, we use the Taylor series to calculate the value of the function:

$$f(x + \Delta x) = f(x) \frac{df(x)}{dx} + \frac{(\Delta x)^2}{2!} \frac{d^2 f(x)}{dx^2} + \frac{\Delta x^3}{3!} \frac{\Delta x^3 f(x)}{dx^3} + \cdots \quad (12)$$

As the difference Δx tends to δx tends to zero than the terms Δx^n in this expansion may be ignored for $n > 1$

If we applying it to the multi-parameter in the function $y_{i\,(calc)}$ it gives us:

$$y_{i(calc)} = y_i(P_1 \dots P_M) + \sum_{k=1}^{M} \delta P_k \left(\frac{\partial y_i}{\partial P_k}\right)_j \dots\dots (13)$$

Now we substitute equation (13) into equation (11) with rearranging the results in the jth normal equations:

$$\sum_{i=1}^{N}\sum_{k=1}^{M} W_i\, \delta P_k \left(\frac{\partial y_i}{\partial P_k}\right)_j \left(\frac{\partial y_i}{\partial P_j}\right)_k = \sum_{i=1}^{N}\left\{w_i\left(y_{i(obs)} - y_i(P_1 \dots P_M)\right)\left(\frac{\partial y_i}{\partial P_j}\right)_k\right\} \qquad (14)$$

When we visually realize it in a matrix it gives the form:

$$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & A & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}\begin{pmatrix} \cdot \\ S \\ \cdot \end{pmatrix} = \begin{pmatrix} \cdot \\ V \\ \cdot \end{pmatrix}$$

Where (A) is an (M × M) symmetric square matrix, S and V are the (M × 1) column matrices.

The column matrix (S) contains the shift δP_j as an addition to the parameters as part of the lest-squares refinement procedure.

In order to get the matrix (S) in is necessary to invert the square matrix (A) i.e:

$$S = A^{-1} \times V$$

The A is the sum of the products of the partial derivatives:

$$A(j,k) = \sum_{i=1}^{N} w_i \left(\frac{\partial y_i}{\partial P_k}\right)_j \left(\frac{\partial y_i}{\partial P_j}\right)_k \qquad (15)$$

While the elements of the matrix V are the observed data:

$$V(j) = \sum_{i=1}^{N}\left\{w_i\left(y_{i(obs)} - y_i(P_1 \dots P_M)\right)\left(\frac{\partial y_i}{\partial P_j}\right)_k\right\} \qquad (16)$$

1.4.5. Figures of merit:

In general, the residual or indices R-value is important in quantifying the quality of least-squares best fit by adjusting the parameters to a minimum, it is the result of subtract the calculated intensity from the observed intensity at each ith point, usually the fit

depend on the adequacy of the model and whether a global minimum rather than a local (false) minimum is reached, the less the R- value the better the fit in the pattern [3].

- **The pattern profile residual:**

$$R_p = \frac{\sum_{i=1}^{n} \left| y_{i(obs)} - y_{i(calc)} \right|}{\sum_{i=1}^{n} y_{i(obs)}} \times 100\%$$

Residual pattern is more affected by the signal-to-noise ratio in the background noise level and used as much as possible during fitting [3].

- **The weighted profile residual:**

$$R_{wp} = \left[\frac{\sum_{i=1}^{n} w_i \left(y_{i(obs)} - y_{i(calc)} \right)^2}{\sum_{i=1}^{n} w_i \left(y_{i(obs)} \right)^2} \right]^{1/2} \times 100\%$$

With $w_i = 1/\sigma^2$ and σ is the estimated standard deviation to consider experimental uncertainties, it depends on Brag scattering and the background it more value [3].

- **The Bragg residual:**

$$R_B = \frac{\sum_{j=1}^{m} \left| I_{j(obs)} - I_{j(calc)} \right|}{\sum_{j=1}^{m} I_{j(obs)}} \times 100\%$$

It is based on integrated intensities can judge the quality of the structure refinement and obtain crystal parameters and positions [3].

- **The expected profile residual:**

$$R_{exp} = \left[\frac{n - p}{\sum_{i=1}^{n} w_i \left(y_{i(obs)} \right)^2} \right]^{1/2} \times 100\%$$

It represents a possibility where R_{wp} reach a limit by pure statistics [3].

•The goodness of fit (chi- squared):

It is used to remove the entire dependency by normalizing the weight pattern residuals by an expected residual and must converge to a ratio of 1 [3].

$$\chi^2 = \frac{\sum_{i=1}^{n} w_i\left(y_{i(obs)} - y_{i(calc)}\right)^2}{n-p} = \left[\frac{R_{wp}}{R_{exp}}\right]^2$$

Where in order:

- n number of point measured in the experimental powder diffraction patterns.
- $y_{i(obs)}$ is observed intensity.
- $y_{i(calc)}$ is calculated intensity.
- w_i the weight of ith data point
- m The number of independent Bragg reflection.
- $I_{j(obs)}$The observed integrated intensity in the jth Brag peak.
- $I_{j(calc)}$ The calculated integrated intensity in the jth Brag peak.
- p The number of free lest-squares parameters.

1.5. Understanding the pattern:

It starts by radiating a sample of a single crystal or a quantity of crystallites grains (powder of crystals) similarly with a monochromatic incident beam and their random orientation appear and arranged in a spherical shape called Ewald's sphere with the cone axes at 4θ range in a 180° radius, the base of cone forms rings that are different in intensity and diameters called Debye rings which is considered evenly distributed allowing to take only a rectangle of it for measuring [5].

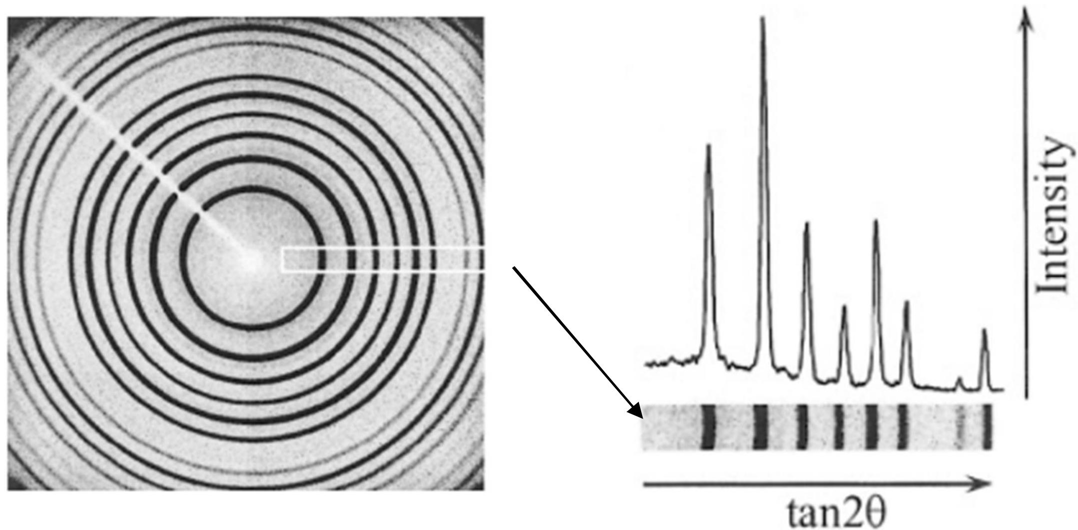


Figure1.3: represent from left to right a Debye ring and a pattern
And how the peak intensity is founded [3].

The displayed stable cones position in the Ewald's sphere makes the scattering intensity easy to introduced it as a one variable axis of (2θ), a Bragg angle 2θ variable in a plane of graph called a pattern or histogram, where it takes the shape of vertical line peaks or Gaussian peaks with the peak represent a miller index, in every material is subjected to many kinds of wavelength at a time and compare it with each other.

For a pattern his structure depends on position, intensity and multiple Bragg reflections shapes. From those, information is extracted concerning the crystal structure, the properties and the instrumental parameters it may be related to the pattern or be an error that need correction.

1.6. Introduction of $y_{i(calc)}$ parameter:

In the calculated intensity function many factors that enter in its calculation are extracted from any powder diffraction pattern that's composed of multiple Bragg peaks either have a central or secondary roles, other factors may participate in the function or be a part in it.

1.6.1. The background:

bkg_i is the background intensity at i[th] step, can be collected from operator-supplied in the background intensities table, the linear interpolation between operator-selected point in pattern or a specific back-ground function. The used function is a polynomial function in 2θ [4] [5]:

$$bkg(2\theta_i) = \sum_{n=0}^{N_b} a_n (2\theta_i)^n$$

Where: N_b the polynomial degree.

a_n It's the polynomial coefficients.

1.6.2. The reflection factor:

ϕ_jIs the reflection profile function, can approximates the effects of instrumental features like reflection-profile asymmetry and specimen characteristic like transparency, displacement, and broadening effect. There is different function [4].

This is a table of their function

(a) $\frac{C_0^{1/2}}{H_k \pi^{1/2}} e^{\left(\frac{-C_0(2\theta_i - 2\theta_k)^2}{H_k^2}\right)}$	Gaussien (G)

$$(b)\frac{C_1^{1/2}}{\pi H_k}\left(1/\left[1+C_1\frac{(2\theta_i-2\theta_k)^2}{H_k^2}\right]\right)$$ Lorentzian (L)

$$(c)\frac{C_2^{1/2}}{\pi H_k}\left(1/\left[1+C_1\frac{(2\theta_i-2\theta_k)^2}{H_k^2}\right]^2\right)$$ Mod 1 Lorentzian

$$(d)\frac{C_3^{1/2}}{\pi H_k}\left(1/\left[1+C_1\frac{(2\theta_i-2\theta_k)^2}{H_k^2}\right]^{3/2}\right)$$ Mod 2 Lorentzian

$$(e)\eta L+(1-\eta)G$$ pseudo-Voigt (pV)

With η as linear function of 2θ refinable variable

$$\eta = NA + NB*(2\theta)$$

$$(f)\frac{C_4}{H_k}\left[1+4*\left(2^{1/m}-1\right)\frac{(2\theta_i-2\theta_k)^2}{H_k^2}\right]^{-m}$$ Person VII

$$(g)TCHZ=\eta L+5(1-\eta)G$$ (Mod-TCH pV)

With:

H_k is the full width at half maximum (FWHM) of the Kth Bragg reflection with the refinable parameters.

$C_0 = 4\ln2$

$C_1 = 4$

$C_2 = 4(2^{1/2} - 1)$

$C_3 = 4(2^{2/3} - 1)$

$C_4 = \frac{2\sqrt{m}(2^{1/m}-1)^{1/2}}{\sqrt{(m-0.5)}\pi^{1/2}}$

1.6.3. The Lorentz-Polarization factor Lk:

The behavior change depends on instrument used (geometry, monochromatic (angel α), detector, beam size/sample volume and sample position (angular) and strongly relying on the Bragg angle. This factor has two different geometric effects and two components materialized the first from the Ewald’s sphere reciprocal lattice point and its finite thickness, the second from the Debye rings radii variable the function introduced [5][3][4] as:

$$L=\frac{1+cos^2 2\theta cos^2 2\theta_M}{cos\theta\ sin^2\theta}$$

The polarization factor comes from partial polarization of the electromagnetic wave after scattering, it two components are a parallel amplitude in the goniometric axis and a perpendicular amplitude in the same axis where $\mathbf{2}\theta_M$ is the Bragg angle reflection according to the instrument used.

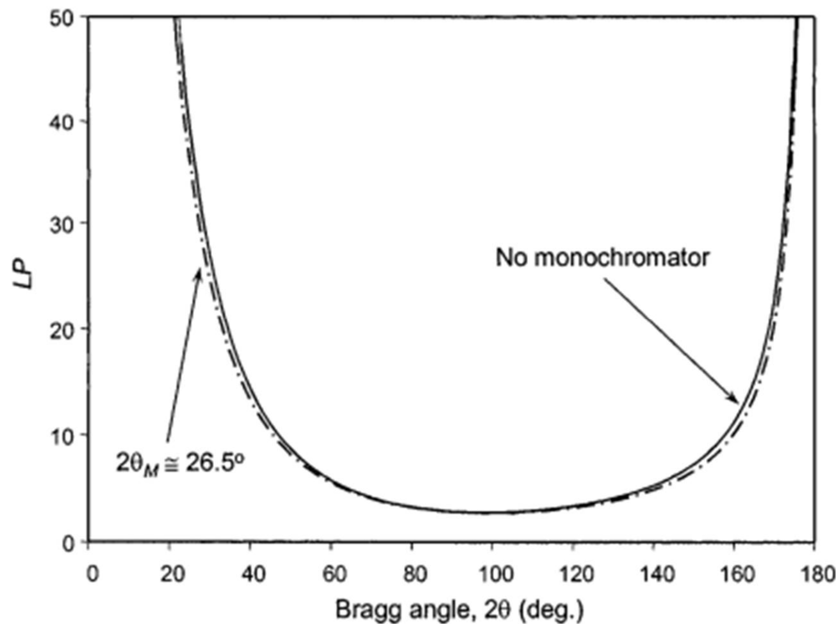


Figure 1.4: a Lorentz-polarization factor as a function of Bragg angle with two different line one with a monochromator and the other without it [3].

1.6.4. The Multiplicity factor:

It enters in the L_k, it is a function of lattice symmetry and a combination of Miller indices it shortens the repeated calculation of identical intensity in Bragg angles and used as a correction factor [5][3].

$$p_{hkl} = \mathbf{2} for\ h\mathbf{00},\mathbf{0}k\mathbf{0}\ and\ \mathbf{00}l$$
$$p_{hkl} = \mathbf{4}\ for\ hk\mathbf{0},\mathbf{0}kl\ and\ h0l$$
$$p_{hkl} = \mathbf{8}\ for\ hkl$$

Some of the multiple factors that used when calculating a Bragg peak.

1.6.5. Scale factor:

Scale factor is one of the variables in structure refinement and its correctness is critical in achieving the best agreement between the calculated and observed intensities, it is measuring the absolute value of the scattered intensity to find the difference between observed and calculated intensity by normalizing the two with respecting each other with the scale factor [3][6]:

$$\left(y_{i(calc)} = ky_{i(obs)}\right)$$

The scale factor here is k, and as long as all observed intensities are measured under nearly identical conditions the scale factor is a constant for each phase and is applicable to the entire diffraction pattern normally it equal 1, Many variable and constant in the other parameter enter in the scale factor in some condition.

1.6.6. Structure factor [F_{hkl}]:

This is an importing factor it is the square of the absolute value of the structure amplitude F_{hkl}, it includes multiple contributions from the unit cell and structural features in an atom in a general equation [4][5]:

$$\left|F_{k,j}\right|^2 = m_k \left|\sum_{n=1}^{N} f_n e^{-B_n \frac{sin^2\theta}{\lambda^2}} \left(e^{2\pi i(hx_n+ky_n+lz_n)}\right)\right|^2$$

With: N= number of atoms.

x_n , y_n , z_n coordination of the nth atom.

$f_n$is the Atomic Scattering factor.

(h k l) the Miller indices.

m_k the multiplicity of k reflection.

B_n is the temperature factor.

1.6.7. The absorption factor A:

It is considered as a correction factor, depending on the geometric and the method and the sample properties, the effect of absorbed calculated intensity in powder diffraction is imported for accuracy. in simple transition through a solid material is descripted as [3]:

$$A = \frac{I}{I_0}$$

With: I_0 the initial intensity, I is the transmitted intensity that depend on the solid thickness and his linear absorption coefficient μ $I = I_0 e^{-\mu x}$.

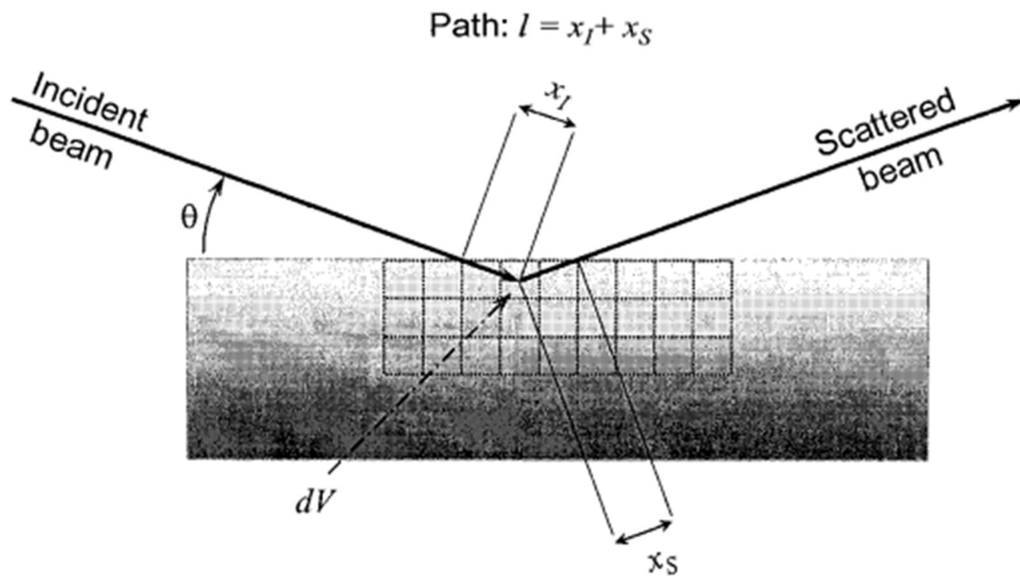


Figure 1.5: example of the absorbing experiment [3].

In the commonly used Bragg-Brentano where thick samples are used two case as fallowed

- The absorbed factor is constant $A = \frac{1}{2}\mu_{eff}$ so it is considered a part of the scalefactor when his coefficient is very high or the solid is thick enough, so the transmitted incident beam is negligible at any Bragg angle.

- The second case is the opposite of the first where the sample is thin or the coefficient is weaker so the beam is capable of penetrating through the simple, and we consider it a function of Bragg angle.

The same case for Debye-Scherrer geometry as the absorption is not constant. Some problem may occur in the calculation of absorbed factor like the contrast absorption.

1.6.8. The preferred orientation function Pk:

Powder diffraction is based on the perfect randomness of the orientations of the crystalline; experimentally it’s realizable if the structure has a spherical shape by putting needle like crystals or plate like crystals sample in a flat holder, we can see the crystals align themselves in one or more directions and this is what makes the intensity detected stronger or weaker in the different direction [3].

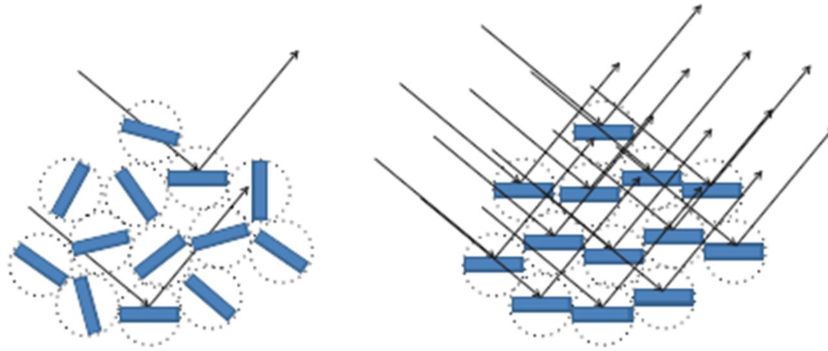


Figure 1.6: Schematic representation of the preferential orientation effect (2D).Left: Randomly oriented crystallites with proportional number of crystallites in the reflective state. Right: preferentially oriented crystallites with a disproportionately large number of crystallites in the reflective state [6].

The function used to calculate a preferred orientation and work as a corrector in the powder, it has many varieties one of them is the March-Dollase formula [4]:

$$P_{k,j} = \frac{1}{m_k}\sum_{n=1}^{m_k}\left(P_{MD}^{2}cos^{2}\alpha_n + \frac{sin^{2}\alpha_n}{P_{MD}}\right)^{-\frac{3}{2}}$$

With:

P_{MD} is a March-Dollase parameter.

m_k is a summation over all equivalent hkl reflections.

α_n Is the angle between the preferred orientation vector and the crystallographic plane hkl.

1.7. Conclusion:

The Rietveld method could be the most powerful refinement and optimization tool with its accurate technique in approaching the zero mark between the diffraction raw data and his theoretical calculated structure of the component but it all depend in finding the right model for it [5].

Its difficulty rises with the number of phases that mean a larger background and more correction to do from symmetries, geometry, direction, width…. to other instrument all need a step-to-step refining to decrease the value of R-indices with the help of a program.

Chapter2: different parameters influence on Rietveld refinement

2.1. INTRODUCTION:

The Rietveld refinement method was originally used for crystal structure analysis. However, this method is currently effective in quantitative phase analysis, with higher precision compared to traditional quantitative x-ray diffraction techniques. In the previous chapter, we try to know Parameters that affect Rietveld refinement through calculations and GSAS program.

2.2. Histories:

X-ray diffraction originates in 1912 when Max Von Laue and two of his colleagues have decided to perform an experiment using x-rays on crystals; they chose x-ray for this purpose because they have a wavelength similar to the inner atomic distances within crystal structures.

Powder diffraction was invented twice by peter Debye and Paul Scherrer in 1914 and by Albert Hull (General Electric) in 1917, Debye-Scherrer presented basically the complete theory underlying power diffraction patterns, to determine the unit cell dimensions, these two solved a number of structures (sodium chloride, diamond, graphite and iron) to obtain a patterns

Within a few years, many others, including the Braggs and Pauling, had exploited the powder method to study a wide range of materials, including metals, minerals, and simple organic solids.

In 1920 to the 1970 crystallographers presenting what the structure was and then showing that the diffraction reproduced it by the end of the 70s was single crystal diffraction, people were doing least squares refinement and structure derivate.

3. Definitions

3.1. X-ray diffraction:

Is the only laboratory technique that reveals structural information.

- Measure the average spacing between rows of atoms
- Determine the orientation of a single crystal
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline region [7]

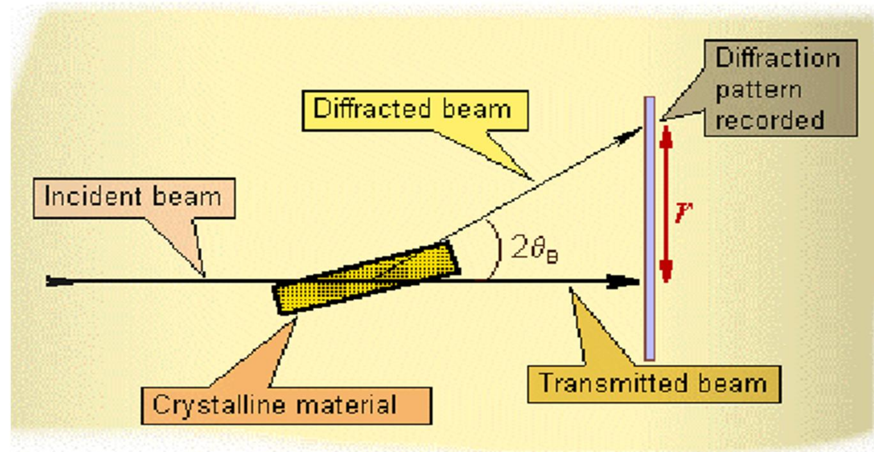


Figure 1.1:x-ray diffractometer [7]

Rietveld refinement using in x-ray diffraction to establish crystal structures

The figure 1.2 example to see XRD with rietveld refinement

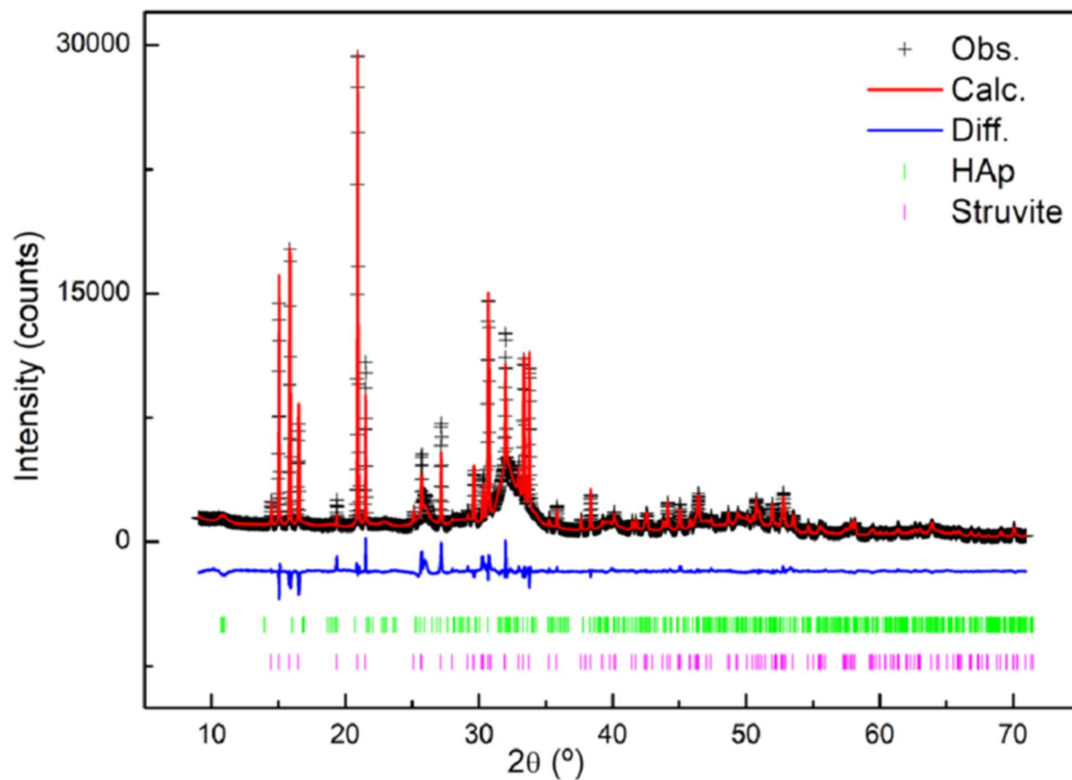


Figure 1.2:X-ray powder diffraction pattern and Rietveld refinement profile of mixed stone [8]

3.2. Powder diffraction:

Is one of the most powerful techniques for studying the atomic structure of real materials. [9].It can be used for phase or polymorph identification, quantitative analysis, determination of cellular parameters, and even full crystal structure analysis using the powerful Rietveld refinement method.

2.4. The evolution of the Rietveld refinement method:

2.4.1 Pre-rietveld refinement methods:

These methods began after the development of least squares crystallographic in 1960; it was developed through the increasing digital availability of digital computers .it used in single crystal data and also on powder data.

This method plays in important role in the quantitative structural characterization of high symmetry inorganic materials. [9]

2.4.2. Rietveld refinement:

In contrast to the previous method, which can only be applied to simple patterns, Rietveld refinement method is applied to complex patterns by obtaining patterns from materials of low symmetry by means of a curve fitting procedure.

And also, through the least square refinement reduces the difference between the observed and calculated profiles.

It utilized in x-ray data, neutron data and to analyses time-of-flight neutron powder data. [9]

2.5. Statistical and graphical measures of a refinement:

There is no single measure of the quality of Rietveld refinement. For best result Scientists tried to assess the differences between the observed and calculated data points in the pattern.so they use the Rietveld algorithm because it minimize the weighted sum of the differences between the observed and calculated profile points, the square root of the quantity minimized by the weighted profile factor (R_{wp}) is the best for direct statistical scale.[9]

$$R_{wp}^2 = \frac{\sum_i w(y_{oi} - y_{ci})}{\sum_i w y_{oi}^2} \quad \text{or}$$

$$R_p = \frac{\sum_i |y_{oi} - y_{ci}|}{\sum_i y_{oi}}$$

Some programs calculate both of $R_{wp}$and $R_p$for the full pattern and the back ground subtracted so, for shorten the accounts was used expected R-factor:

$$R_{exp}^2 = \frac{N-P}{\sum_i w_i y_i^2}$$ such as N is the number of data

P is the number of least square variable (parameter)

The R_{exp} is the minimum of R_{wp} value reachable using a certain number of refineable parameters.

A related and very useful concept is that of x^2 is a good measure on the quality of the rietveld refinement. If we have the perfect model, expected value $(y_{oi} - y_{ci})^2$ / σ^2 (y_{oi}) isone if σ is correct.as the average of these values:

$$x^2 = \frac{1}{N-P}\sum_i \frac{(y_{oi} - y_{ci})^2}{\sigma^2(y_{oi})}$$

The x^2 term is defined

$$x^2 = \frac{R_{wp}}{R_{exp}}$$

If x^2<1, that isσy_{oi} is invalid, usually due to an error in converting or scaling the data.

x^2Close to one does not guarantee that the model is correct; it just means that the error edominated by statistical effects.

If x^2> 1 at the end of the refinement, one (or more) three things:

(1) The model is reasonable, but σ is underestimated

(2) The model it contains systematic errors

(3) The model is incorrect. A high x^2 can occur when the data is very good

2.5.1. The **R** indices:

The R_{wp} factor is the most valuable factor. It's the absolute value of the intensity, but it depends of the background. When:

R_{wp} **< 1**: corresponds to an acceptable refinement, medium complex stage.

R_{wp} **< 0,15**: is a good value for a complex phase (monoclinic to triclinic)

R_{wp} **< 0.08**: is an acceptable value for a highly symmetric compound (cubic) with few peaks. [10]

When the background high the R_{wp} can be seen more clearly.

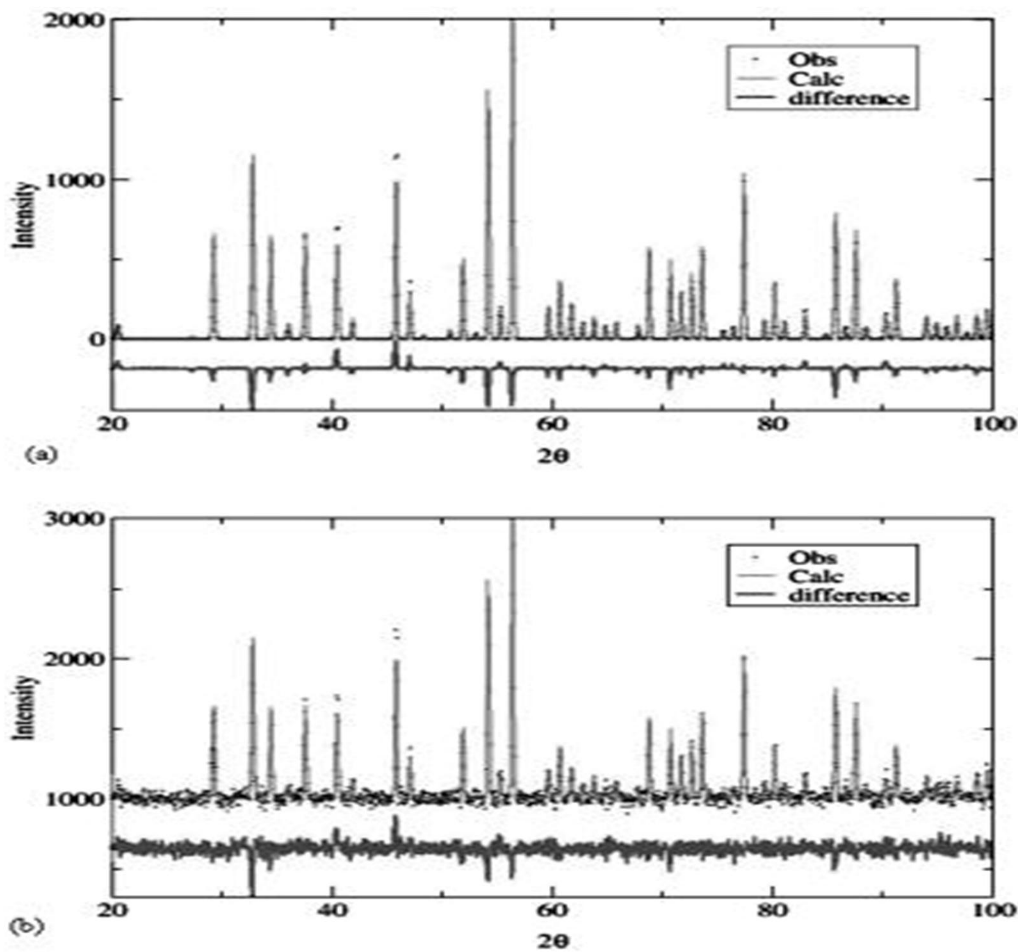


Figure1.3: A demonstration of the effect of the Rietveld fit on the background. Two simulated fits are shown, where the model deviates the same from the simulated data and where the Bragg intensities and counting times are equal. However, in (a) without background, R_{wp}= 23% and x^2= 2.54, while in (b) with significant background, R_{wp}= 3.5% and x^2= 1.31. [10]

2.5.2. General Rietveld approach:

- Calculate position (intensities): the first thing that happens in terms of when it's calculating a prediction is it's going to calculate the positions and intensities that are associated with diffraction from different families at peak

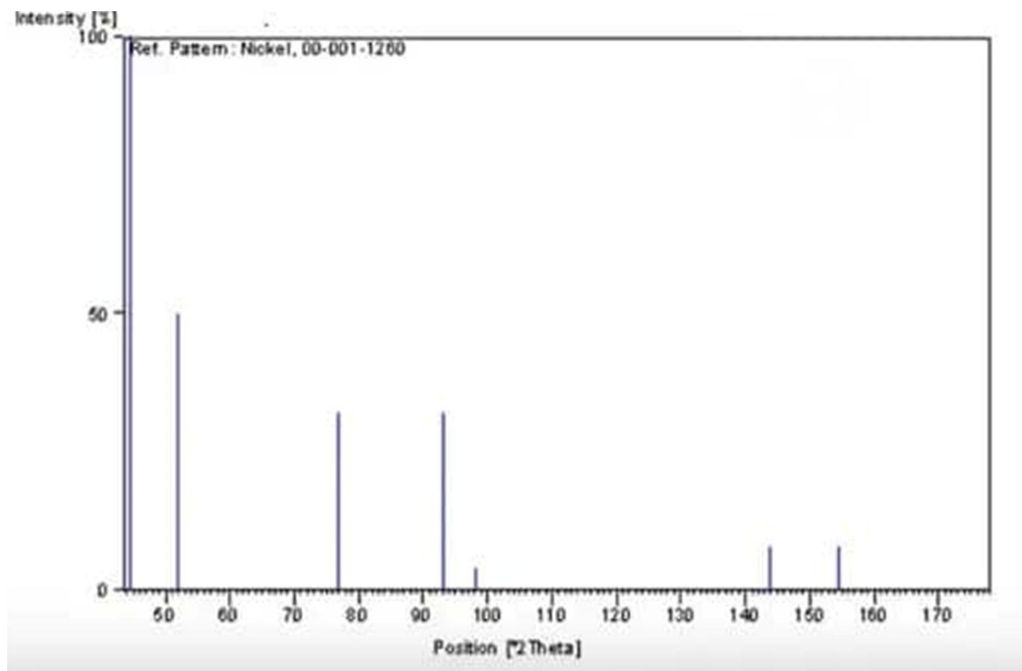


Figure1.4: peak shape

- Convolute with profile shapes: on a real diffraction system the peak is not a perfect delta function for get this wick by convoluting that intensity

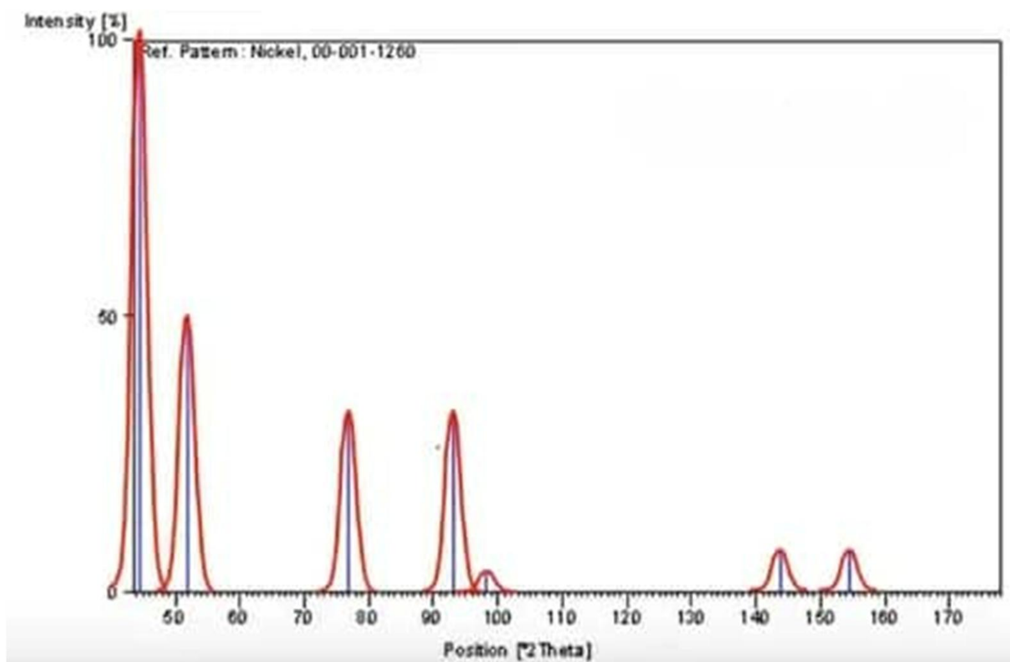


Figure 1.5: convolute with profile shape

- Generate background: the background is something that we can fit with a linear function
- Minimize the difference.

2.6. Rietveld refinement procedure:

To procedure Rietveld refinement we need:

- ❖ To install a program depending on what we need, there are several options:
  - ➢ Free programs like:
  - Full proff: it is used for Rietveld analysis (structure profile refinement of neutron), profile matching, time of flight neutron and neutron data analysis and the best option for magnetic materials… etc.
  - Maud: material analysis using diffraction use to fit diffraction, fluorescence and reflectivity data using X-ray, neutron, TOF or electrons.
  - Gsas : we use it in this chapter

From the free programs we find also: Rietan, Arit, Brass, DBWS, XRS-82, Topas academic and XND.

- ➢ Commercial programs: Topas and BGMN.
- ❖ Load or input phase into samples
- ❖ Manually adjust some parameters (cells, intensity, background)
- ❖ Optimize overall intensity and background
- ❖ Optimize top position
- ❖ Refine Peak Shape
- ❖ Refinement structure
- ❖ evaluation result [11]

2.7. Rietveld refinement with EXGPUI/GSAS:

2.7.1. Introduction:

The GSAS package contains about 50 programs, most of them require minimal or no user input. Only program in GSAS package that require a lot of user interaction known as EXPEDT. Also, the EXPGUI program provides another graphical interface –based mechanism view and edit GSAS experiment file.

2.7.2. EXPEDT:

The EXPEDT program operates through a series of single letters options, if you enter a question mark (?) EXPEDT outputs a short text description of each option. User provided information is saved in file named experiment (.EXP) file, the experiment file contains various information: e.g. atomic coordination, diffraction data file names, least squares and sum Fourier mapping options.

2.7.3. GSAS:

general structure analysis system was developed in the early 1980s by A.C. Larson and R.B. Von, Dreele the first version released in 1985 to address all things related to crystallographic optimization and subsequent structural analysis of all types of X-rays, neutron diffraction data, and the study of both powder and single crustal.

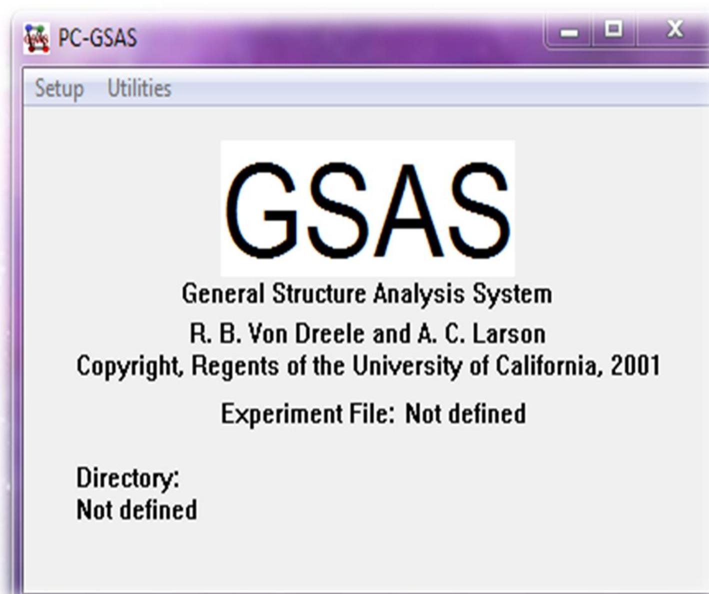
A).GSAS structure:

1. Multiple programs: each one has specific purpose (editing, powder preparation, least square ...etc.).
2. User interface (EXPEDT): continent control file complexity, edit control, multilevel menus, help listing and text interface
3. Common file structure consists of experiment name used throughout, extension
4. Graphics: found it in screen and hardcopy
5. EXPGI: graphical interface.

B). GSAS interface:

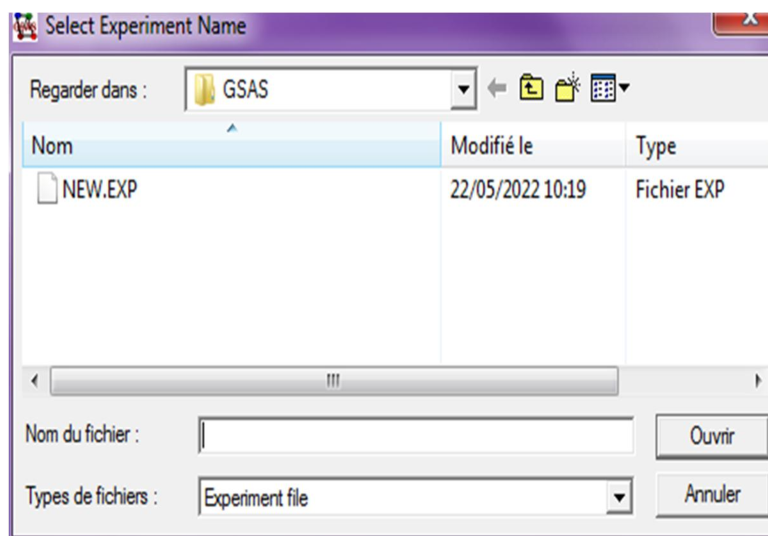
Pc-GSAS: for access to GSAS programs

Figuer1.6: pc-GSAS icon double click



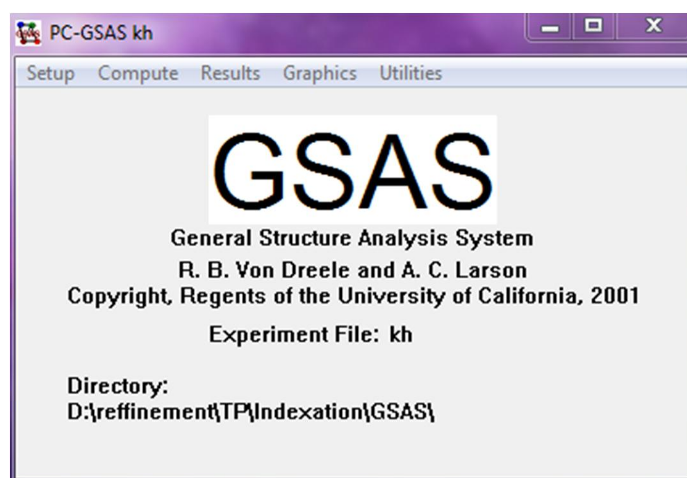
Figuer 1.7: Start- up screen

Select setup then “expname”, a screen appears to create a new file



Figuer1.8: experiment name screen

Enter a name for the file ‘test’ in the “ file name” section and press “open”, a question about creating this file will appear. After answering “yes” we got our named experiment.



Figuer1.9: startup screen after the experiment name

Selecting “setup” and then “EXPDT” from the drop –down menu, results in a question about the experiment when MS-DOS opens telling that the experiment file “test” does not exist in the existing directory.

```
D:\reffinement\TP\Indexation\GSAS>echo off
 Experiment - TEST - was not found in directory
 D:\reffinement\TP\Indexation\GSAS
```

To create a new file, we press “Y”, after the creation the file we enter the name “test”

```
 Do you wish to create it <Y/<N>>? >y
 The new experiment - TEST - has been created.
  Enter a title for this experiment
   >test
```

The main title shows all the information and the first menu

```
   >test

                    |-----------------------------------------|
                    |       Program EXPEDT Version Win32       |
                    | A menu driven routine to edit .EXP files |
                    | Distributed on Thu Apr 20 16:41:26 2006  |
                    |-----------------------------------------|

        |------------------------------------------------------------|
        |            Allen C. Larson and Robert B. Von Dreele        |
        |       Manuel Lujan, Jr. Neutron Scattering Center, MS-H805 |
        |       Los Alamos National Laboratory, Los Alamos, NM  87545 |
        |                                                            |
        | Copyright, 2000, The Regents of the University of California. |
        |------------------------------------------------------------|

 Experiment title:
          test
 EXPEDT data setup option <<?>,D,K,P,R,S,X> >
```

EXPEDT now states the type of calculation that can be illustrated and explained by pressing ‘ENTER’.

```
EXPEDT data setup options:
 <?> - Type this help listing
 D   - Distance/angle calculation set up
 K n - Delete all but the last n history records
 P   - Powder data preparation
 R   - Review data in the experiment file
 S   - Single crystal data preparation
 X   - Exit from EXPEDT
EXPEDT data setup option <<?>,D,K,P,R,S,X> >
```

We chose x for exit.

C).GSAS features:

The following sections describe some of the expected: [12]

- Reduce data from area detectors
- Data input
- Peak fitting
- Indexing
- Intensity extraction
- Structure solution
- Fourier maps
- Peak shape model
- PDF computation
- Refinement model
- Constraints
- Restraints
- Quantitative phase analysis
- Refinement minimize

2.8. EXPGUI:

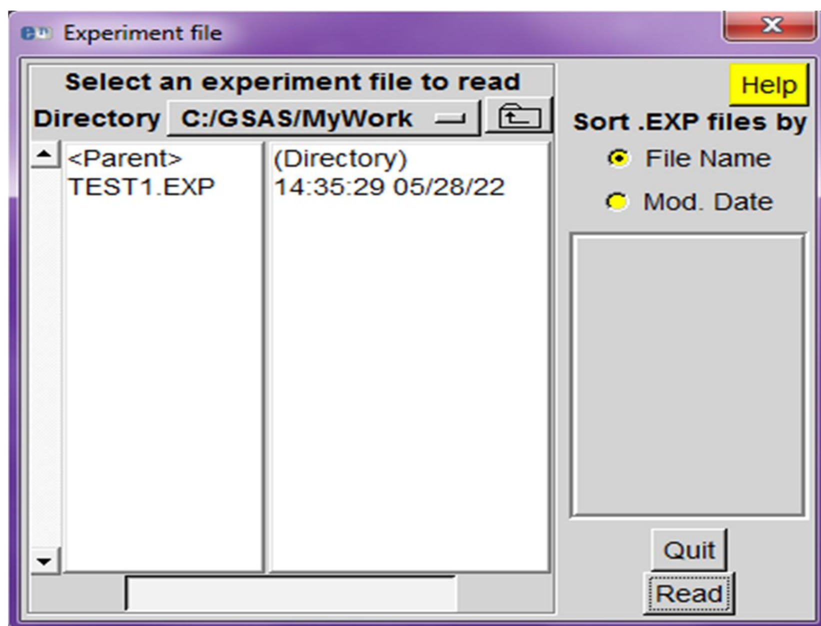
Later in 2001 EXGPUI was developed by B.H.Toby which is a graphical interface for the GSAS package .it can be used to modify the GSAS experimental file with graphical user interface (GUI) and used to invoke the program inside the GSAS. [13]

2.8.1. Crystal structure refinement using EXPGUI:

For this experience we use EXPGUI to specify most of the input needed. Before starting the EXPGUI and GSAS we create a new file called (refinement) on the D drive. In order to get started double click on the EXPGUI icon show in figure 5.

Figuer2.1: EXPGUI icon

Startup window appears (fig2.2)



Figur2.2: EXPGUI startup screen

We select the directory we created, write the name of the job at the bottom, and then click the Read button

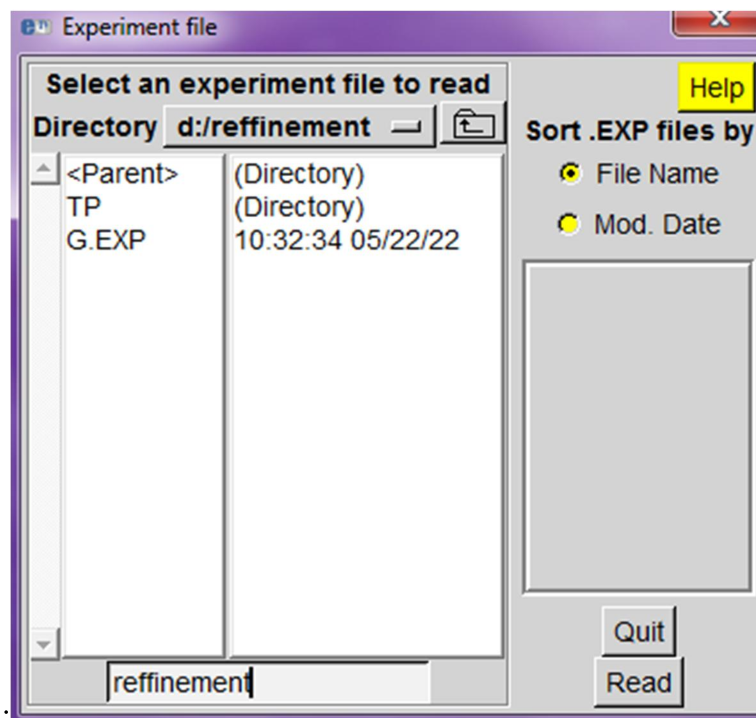


Figure2.3: select the D:/reffinement and specify refinement as the job name

It shows that the program cannot find the file and offers the option to select a different file or create a new file, press the “create” button (fig2.4)

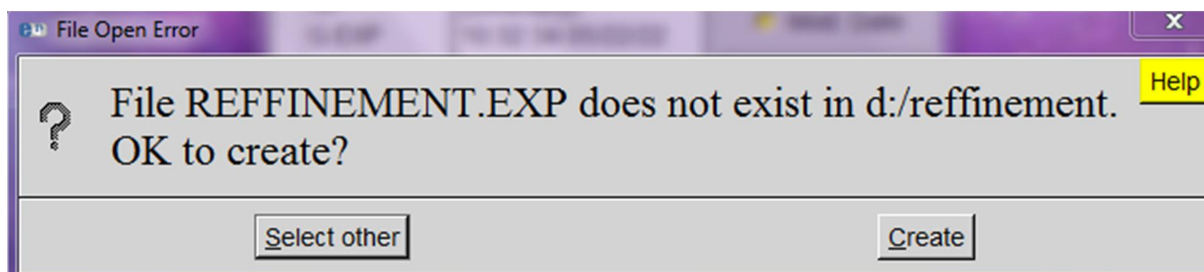


Figure2.4: select 'create'

Now we chose a title for the exercise e.g. (refin) (fig2.5)

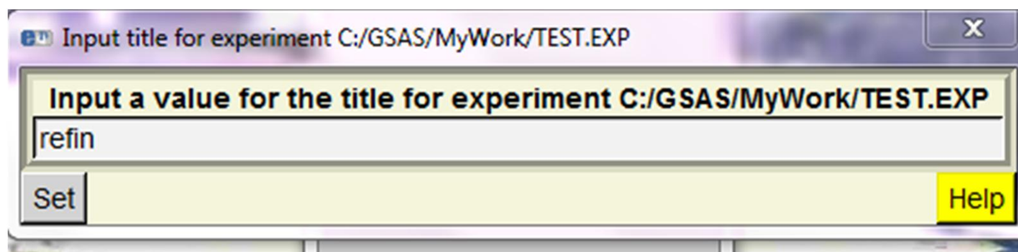


Figure2.5: chose a title and click 'set'

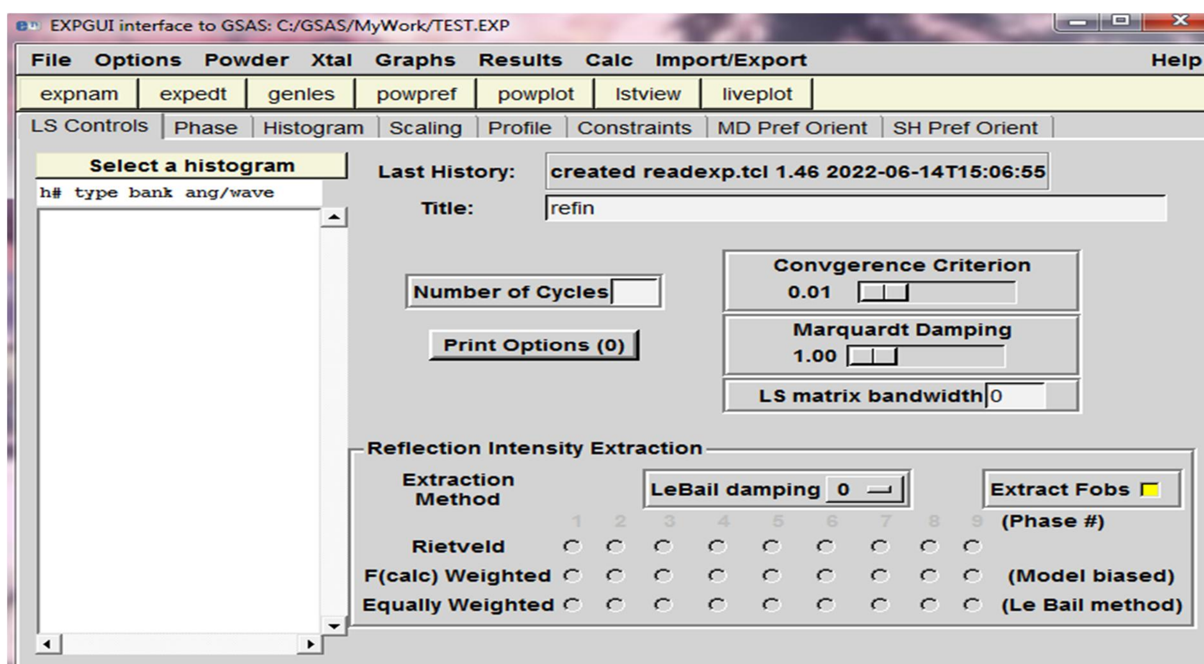


Figure2.6: EXPGUI main window

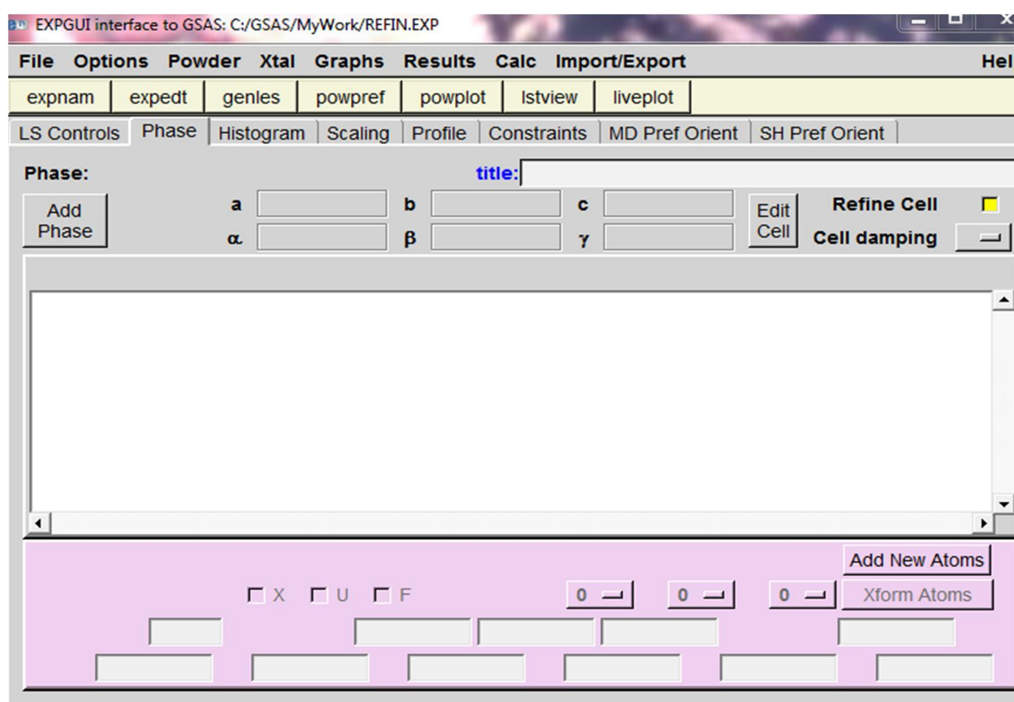
Now the program's main screen appears as an interface to enter most of the powder diffraction information (fig2.6) and it have also the option to refine single crystal data from x-rays constant-wavelength and time-of-flight neutron data.

2.8.2. Crystal structure refinement of ZnO, CaF_2 , Al_2O_3:

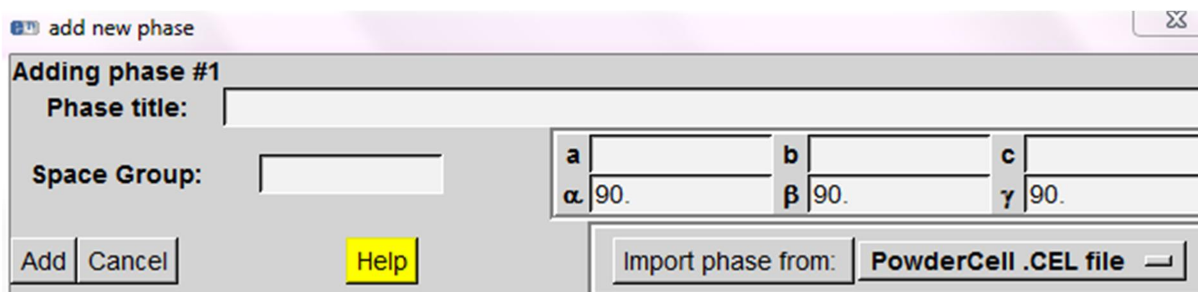
To conduct this expriment we need three file :

- **Cif (crystaligraphy information file**): is a standard format for storing crystal structure data .cif information has a specific structure or format that crystalography must follow in order to read the file.[14]
- **Raw data**:is a bunchof code and a set of information provided to the data provider by a specific data entity,raw data can be manually written down or typed,recorder or automaticly input by a machine.[15]
- **The instrument parameter file:** It is intended to describe the instrument and, in particular, to provide detailed information about the components of the instrument that strongly influence the signals observed in the experiment.

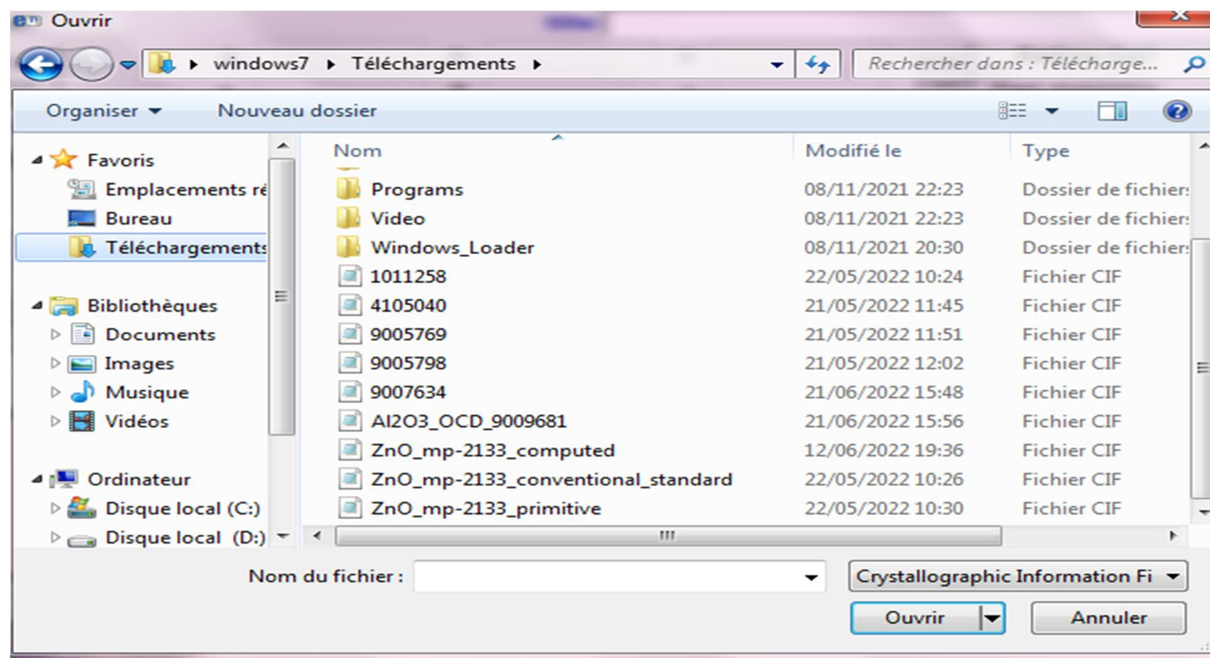
To enter information about crystallographic phase ,modify or select parameters crystallographic for optimization, the"Phase" panel must be selected by clicking on the "Phase" tab in the upper left corner of the EXPGUI window.



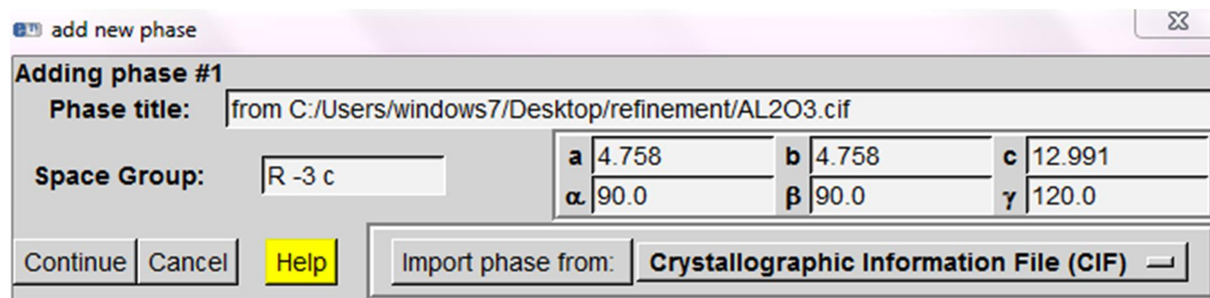
In the next step press "add phase" button, window appears



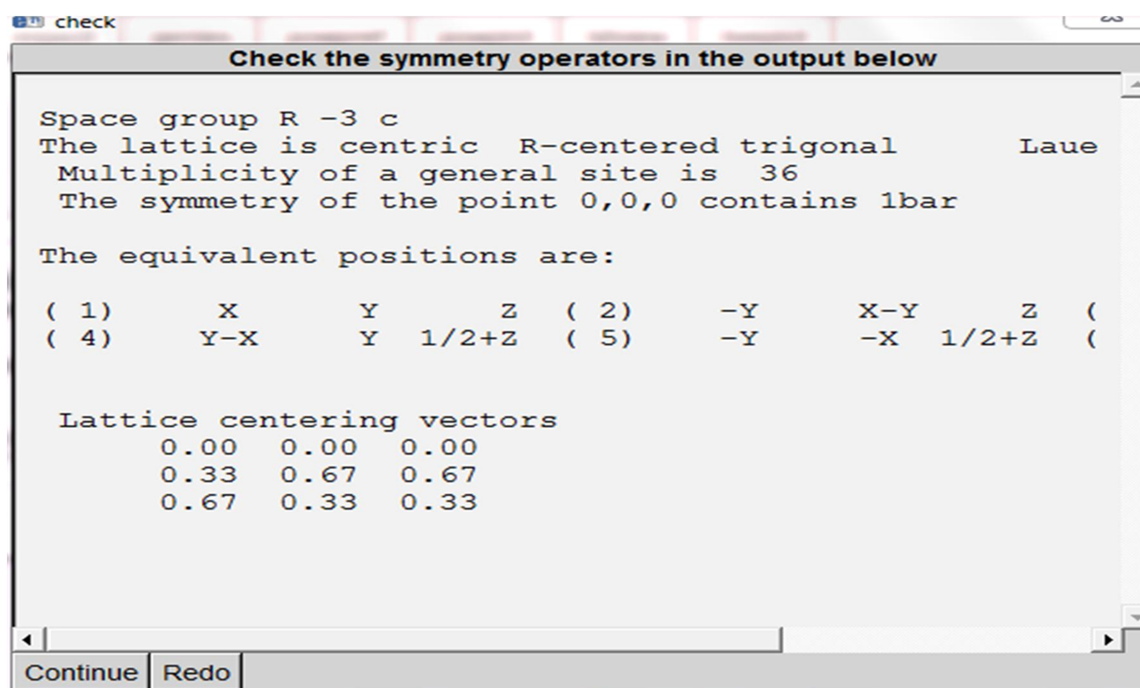
The "add new phase" window can use it for: information about the phase can be inserted directly into the boxes or the phase information can be read from a file. For this experiment we read the unit cell parameters, space group and atomic parameters from the "cif file", we select the crystallographic information file (cif) format from the options by clicking the file format button when the "import phase from" button is pressed.



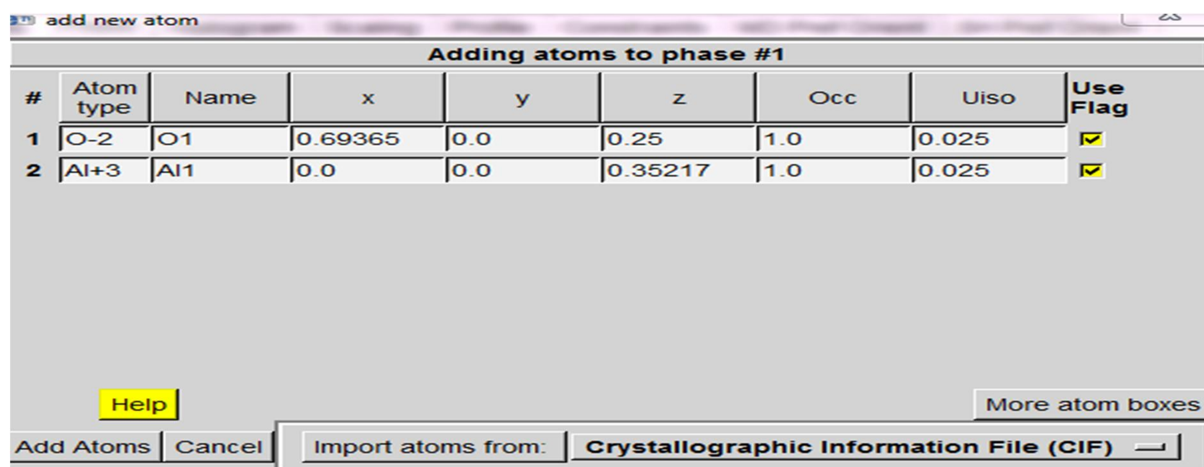
An "open file" window is created, in this window select the "cif file of Al_2O_3" and press "open" button.



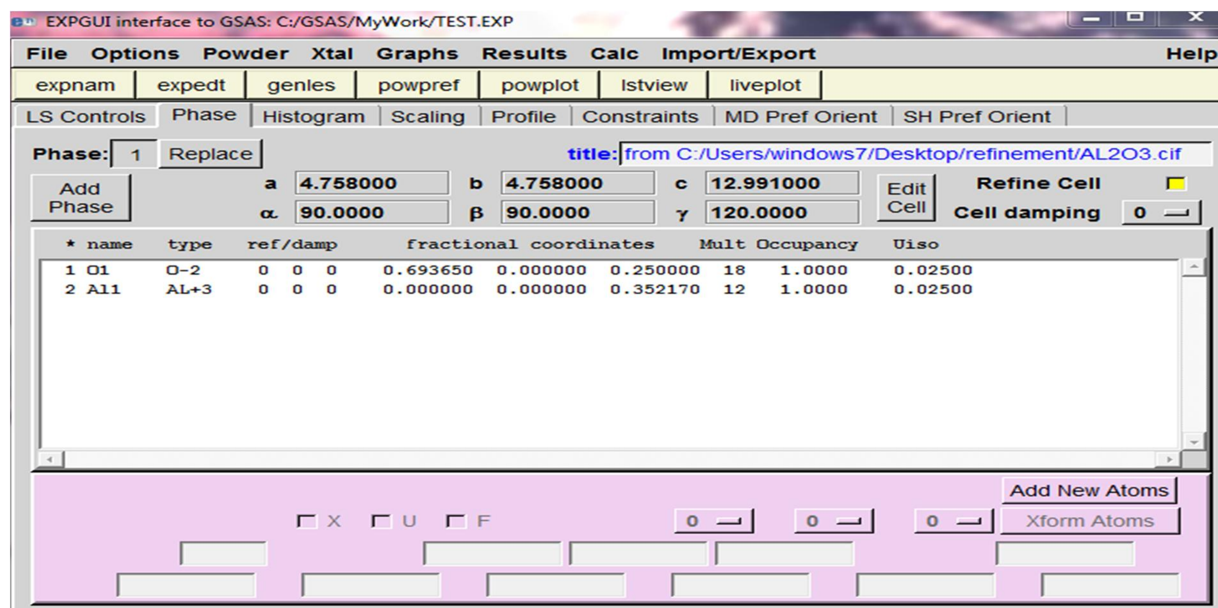
The cif is then read, if this input is acceptable press "continue". After pressing the "continue" button, a window like the one below will be created to help you confirm that the correct room group has been entered.



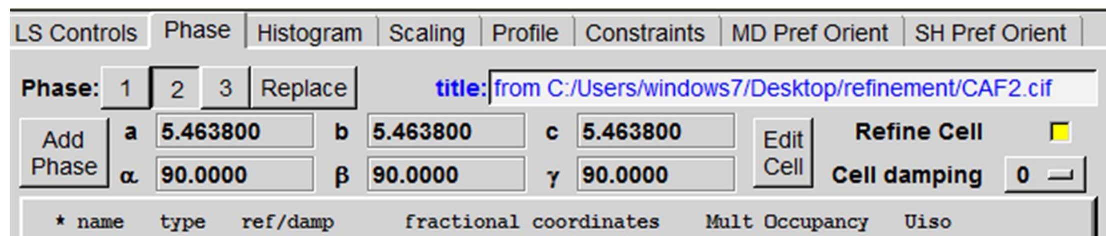
Since the symmetry is correct press "continue". The "add new atom" window open and enter the atom coordinates in the appropriate boxes as shown below.



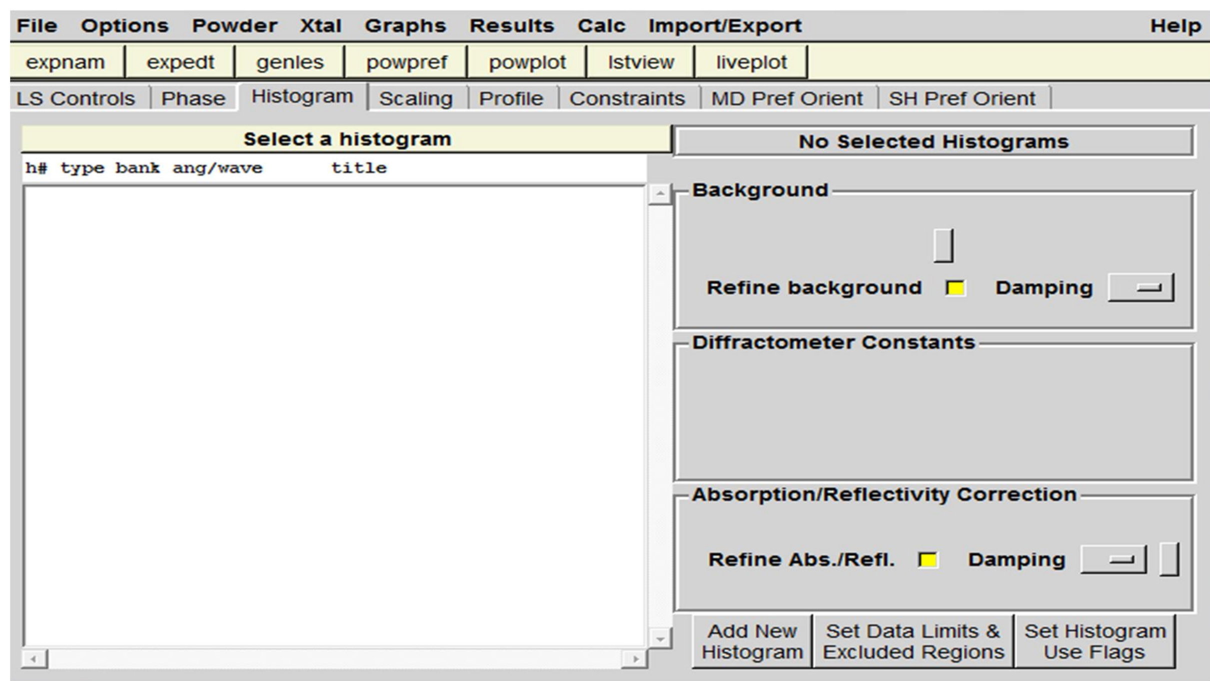
Click the "add atoms" button.



We do the same with (fluorite and zincite).



Now we chose histogram, the following screen will appear



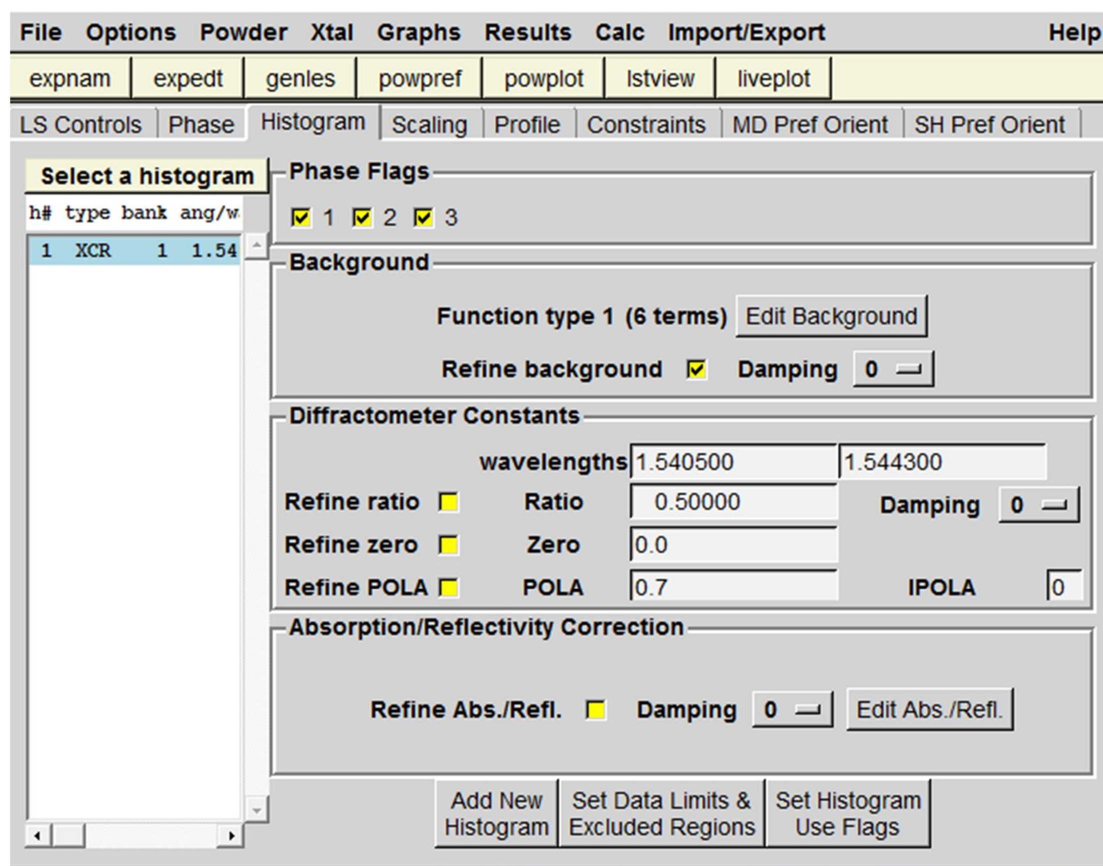
Pressing “add new histogram”, the “add new histogram” will shown

add new histogram
Adding a new histogram
Dummy Histogram
Data file:
Select File
Select bank
Instrument Parameter file:
Select File
Edit file
Select set
d-min
Q-max
TOF-min 2-Theta Max
Usable data limit:
Run RAWPLOT
Add
Cancel
Add multiple banks
Help

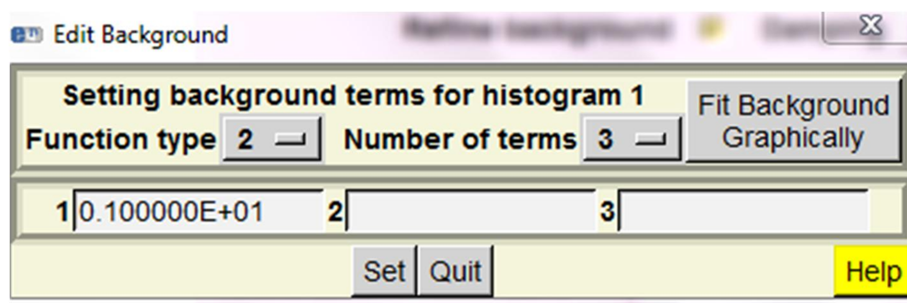
Notice: the GSAS program cannot read the data file so we convert it to (RAW, GSA or GSAS) and the instrument parameter file must be (INS or INST).

add new histogram
Adding a new histogram
Dummy Histogram
Data file: C:/Users/windows7/Desktop/7.gsas
Select File
Select bank 1
Instrument Parameter file: C:/Users/windows7/Desktop/poudre.prm
Select File
Edit file
Select set 1
CW X-ray
d-min
Q-max
TOF-min 2-Theta Max
Usable data limit: 150.0
Run RAWPLOT
Add
Cancel
Add multiple banks
Help

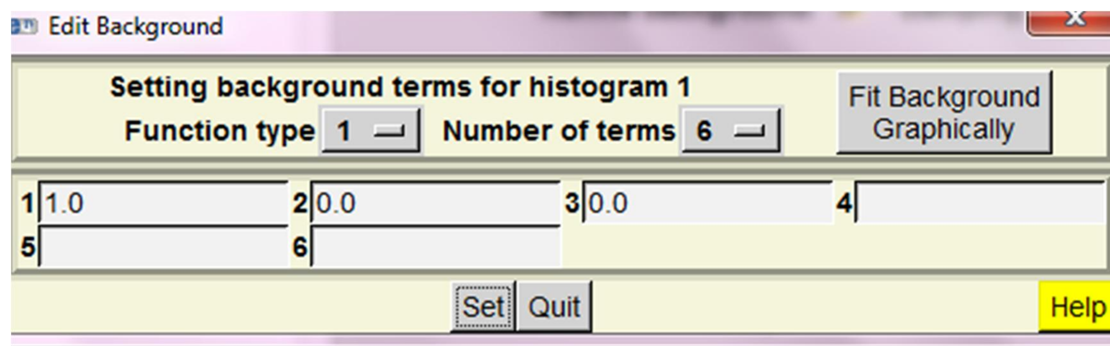
After selecting file press “add”. The following window appears



Press "Edit Background" to change the background function, the Edit Background window open.

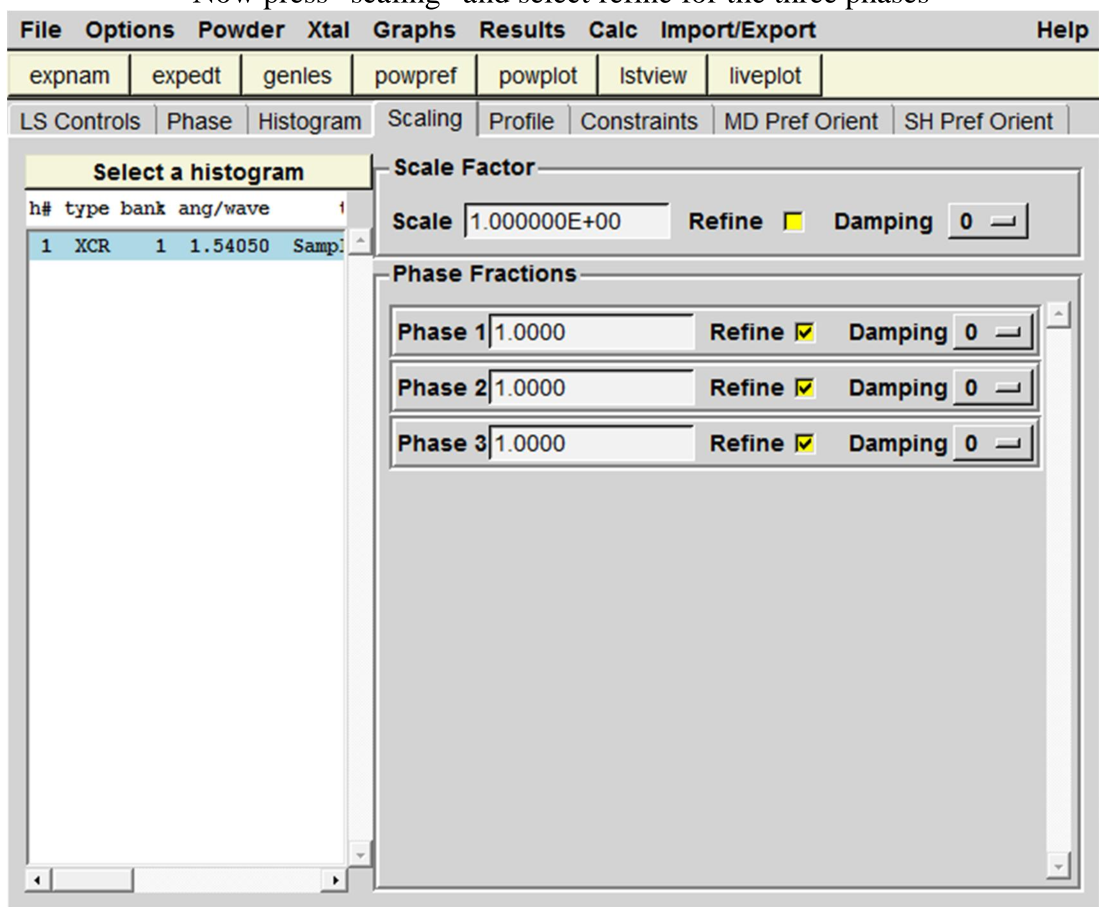


Both the function type and the number of items can be changed in this window, click to "function type" button. Menu offers a choice of function type appear, choose function type 1 "chebyschev function", also press the "number of terms" and change the number to "6".the "Edit background" become :

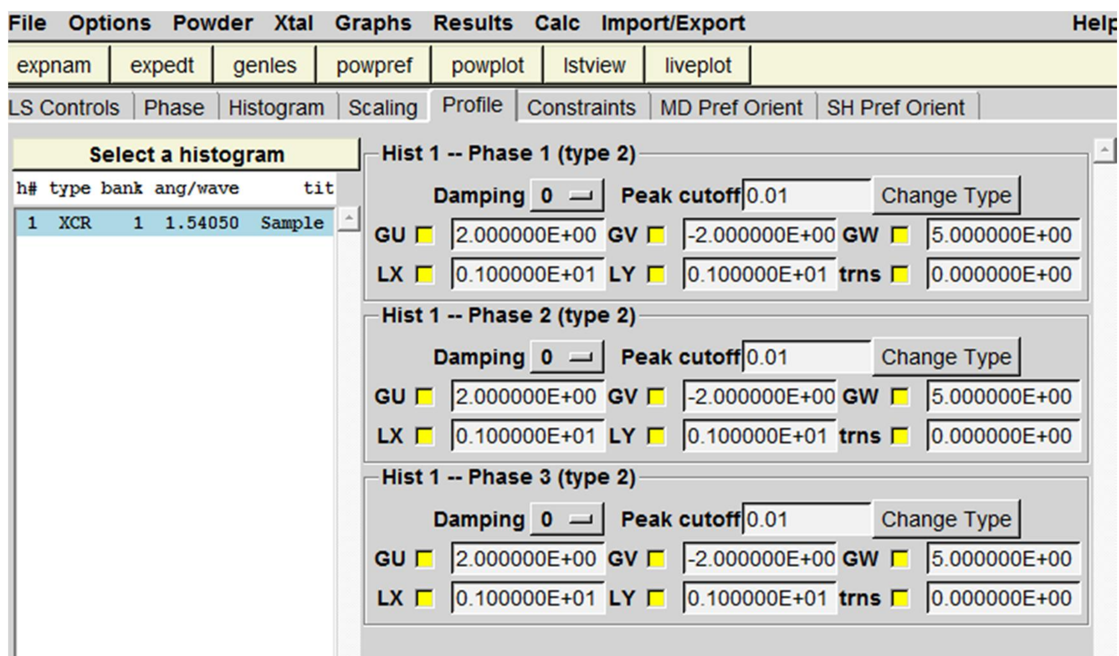


Press “set”.

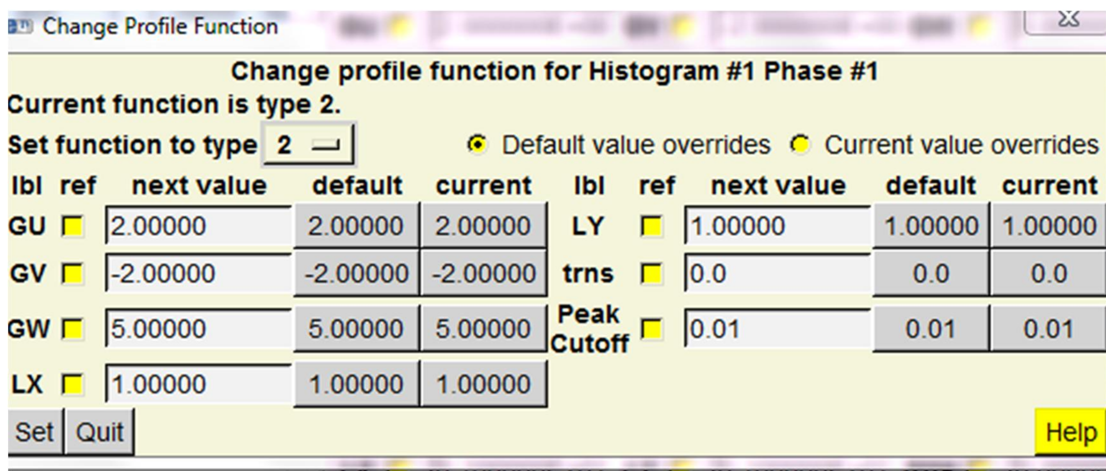
Now press “scaling” and select refine for the three phases



Select “profile” window will open



In the peak cutoff change the number to (0.001) then press “change type”



Change the number in set function type from (2) to(4).the “change profile function “window” be.

Change Profile Function

Change profile function for Histogram #1 Phase #1

Current function is type 2.

Set function to type 4 — (•) Default value overrides ( ) Current value overrides

lbl	ref	next value	default	current	lbl	ref	next value	default	current
GU		2.00000	2.00000	2.00000	S/L		0.01500	0.01500	
GV		-2.00000	-2.00000	-2.00000	H/L		0.01500	0.01500	
GW		5.00000	5.00000	5.00000	eta		0.75000	0.75000	
GP		0.0	0.0		S400		0.0	(none)	
LX		0.10000	0.10000	1.00000	S004		0.0	(none)	
ptec		0.0	0.0		S202		0.0	(none)	
trns		0.0	0.0	0.0	S301		0.0	(none)	
shft		0.0	0.0		Peak Cutoff		0.01	0.01	0.01
sfec		0.0	0.0						

Set Quit Help

Note: the boxes in this window represent (constant wavelength x-ray profile type 4). Do the same for the other two phases.

expnam | expedt | genles | powpref | powplot | lstview | liveplot

LS Controls | Phase | Histogram | Scaling | Profile | Constraints | MD Pref Orient | SH Pref Orient

Select a histogram

h#	type	bank	ang/wave	Sa
1	XCR	1	1.54050	Sa

Damping 0 — Peak cutoff 0.01000 — Change Type

GU	2.000000	GV	-2.000000	GW	5.000000
GP	0.00000000E+(	LX	0.100000	ptec	0.00000000E+(
trns	0.00000000E+(	shft	0.00000000E+(	sfec	0.00000000E+(
S/L	0.015000	H/L	0.015000	eta	0.750000
S400	0.00000000E+(	S004	0.00000000E+(	S202	0.00000000E+(
S301	0.00000000E+(				

Hist 1 -- Phase 2 (type 4)

Damping 0 — Peak cutoff 0.01000 — Change Type

GU	2.000000	GV	-2.000000	GW	5.000000
GP	0.00000000E+(	LX	0.100000	ptec	0.00000000E+(
trns	0.00000000E+(	shft	0.00000000E+(	sfec	0.00000000E+(
S/L	0.015000	H/L	0.015000	eta	0.750000
S400	0.00000000E+(	S220	0.00000000E+(		

Hist 1 -- Phase 3 (type 4)

Damping 0 — Peak cutoff 0.01000 — Change Type

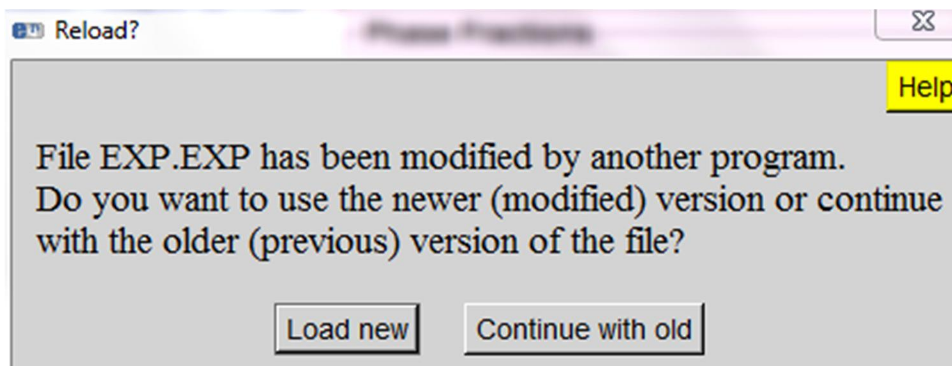
GU	2.000000	GV	-2.000000	GW	5.000000
GP	0.00000000E+(	LX	0.100000	ptec	0.00000000E+(
trns	0.00000000E+(	shft	0.00000000E+(	sfec	0.00000000E+(
S/L	0.015000	H/L	0.015000	eta	0.750000
S400	0.00000000E+(	S040	0.00000000E+(	S004	0.00000000E+(
S220	0.00000000E+(	S202	0.00000000E+(	S022	0.00000000E+(

For star running the program, first run powpref by pressing “powpref” button, that causes a window

C:\Windows\system32\cmd.exe - C:/gsas/expgui/gsastcl.bat C:\gsas\exe\powpref.exe EXP

```
C:\GSAS\MyWork>REM a batch file to a DOS command and pause

C:\GSAS\MyWork>if "C:\gsas" == "" set gsas=c:\gsas

C:\GSAS\MyWork>set PGPLOT_FONT=C:\gsas\pgl\grfont.dat

C:\GSAS\MyWork>set SYMOP=C:\gsas\data\symop.dat

C:\GSAS\MyWork>C:\gsas\exe\powpref.exe EXP
 Histogram no.   1 Bank no.  1 Lambda1,lambda2 =  1.54050 1.54430
 Title: Sample ID - Anode and Instrument
 Histogram is not ready to be used in least-squares
 Histogram needs to be processed by POWPREF
 Header on file:
 Sample ID - Anode and Instrument

STOP POWPREF terminated successfully statement executed

C:\GSAS\MyWork>pause
Appuyez sur une touche pour continuer...
```

Press “ENTER” key for continue. The “Reload” window will open press “load new”.



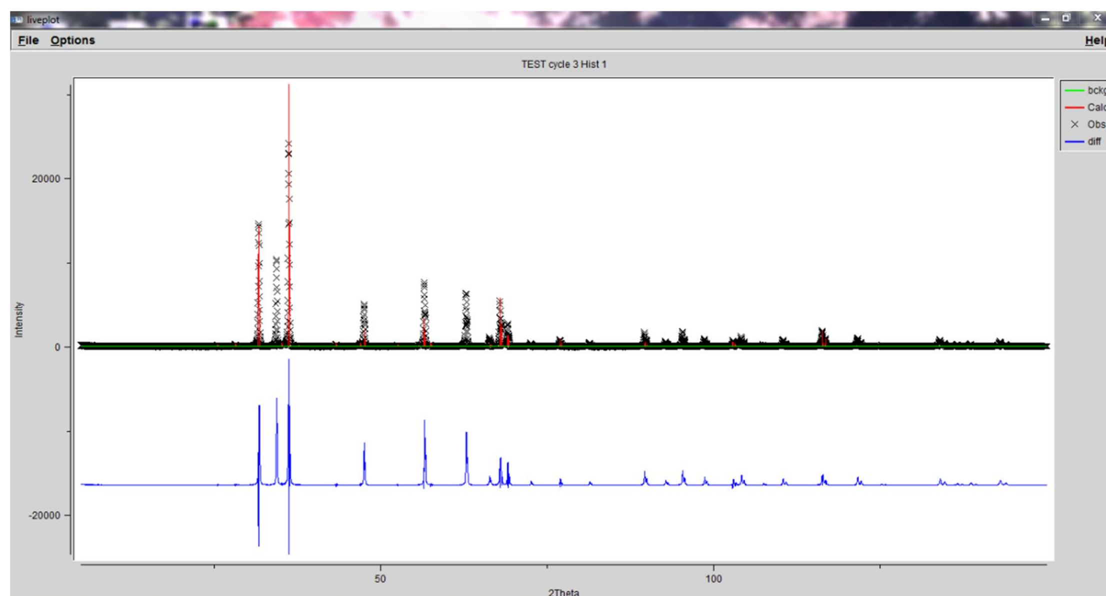
Now back to EXPGUI window and press “genles”.

C:\Windows\system32\cmd.exe - C:/gsas/expgui/gsastcl.bat C:\gsas\exe\genles.exe EXP

```
 CPU times for matrix build     2.39 sec; matrix inversion     0.00 sec
 Final variable sum((shift/esd)**2) for cycle   2:       1.#R Time:    2.39 sec

 Restraint data statistics:
 No restraints used

 Powder data statistics                Fitted          -Bknd           Average
              Bank Ndata Sum(w*d**2)  wRp      Rp     wRp      Rp      DWd  Integral

 Hstgm  1 PXC   1   7250 1.#QNAN     0.0000 9.9999 0.0000 9.9999   1.#QO   0.289
 Powder totals      7250 1.#QNAN     9.9999 9.9999 9.9999 9.9999   2.000
 Cycle   3 There were    7250 observations.
 Total before-cycle CHI**2 (offset/sig) = 1.#QNBE+00 ( 1.#QNBE+00)

 Reduced CHI**2 = 1.#QNB      for    18 variables

   18 Columns of the    18 Column matrix are 0.0

 CPU times for matrix build     2.42 sec; matrix inversion     0.02 sec
 Final variable sum((shift/esd)**2) for cycle   3:       1.#R Time:    2.43 sec
STOP GENLES terminated successfully statement executed

C:\GSAS\MyWork>pause
Appuyez sur une touche pour continuer...
```

Press “Enter” key.

For show the graph and examine the result press “liveplot”, “liveplot” window appear.



However, to see more details. "Zooming in" is done by clicking the mouse in the lower left and upper right corners of the area to be displayed. After the first mouse click, the box shown below will appear. After the second time, the plot is redrawn.

To see where the reflection is actually located. The display can be turned on by pressing the "1" key in the LIVEPLOT window (1 for phase 1, 2 for phase 2...).

Now change the constant wavelength, back ground function, atomic position…etc. press “geneles” after any change then “liveplot” for see if the plot change (more information in the next chapter).

2.9. Conclusion:

We conclude that the instrument parameters that effect on Rietveld refinement are:

- Constant wavelength x-ray profile (the Cagilloti terms u,v,w)
- Back ground function
- Atomic position (x,y,z)
- The scale factor
- Zero point of instrument

Chapter3: Results and discussion

3.1. Introduction:

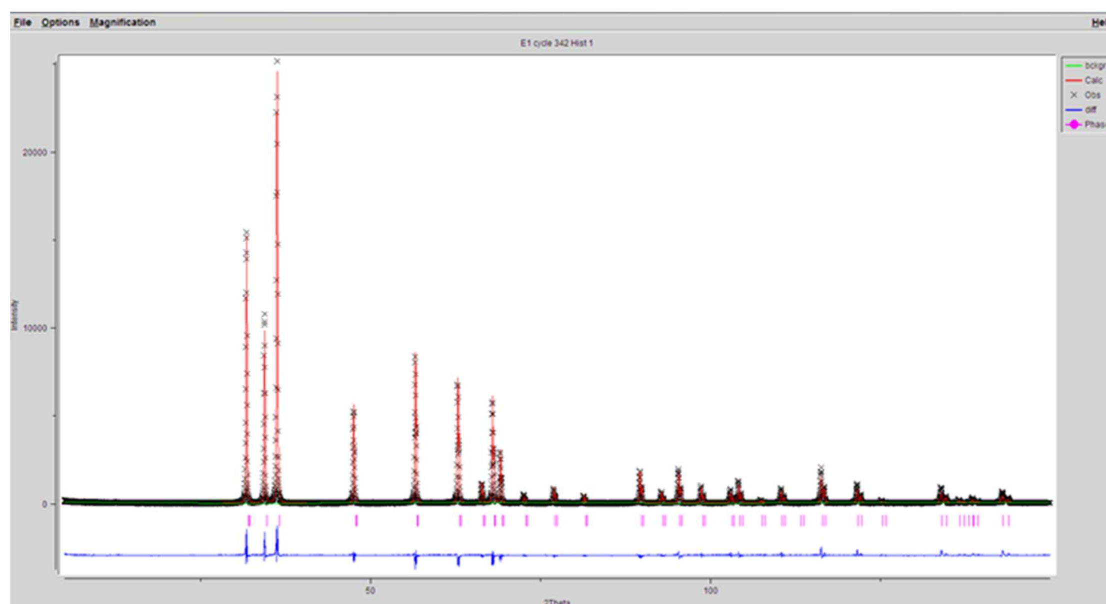
In this chapter we will see the results of previous chapter, and to explain more how we make the changes that led to the improvement of the plot for one single crystal and for the mélange of (ZnO, Al_2O_3, CaF_3).

3.2. Application of Rietveld refinement on powder sample:

After treating the three-powder simple (zinicite, corindon and fluorine) and the mélange of these powders, we follow these refinement steps to collect data to refine them.

3.2.1. Zinicite (ZnO) GSAS/EXPGUI refinement:

Step_1: changing the Background function.
Step_2: Refine scale factor and background.
Step_3: Refine scale factor and zero point.
Step_4: Refine scale factor and the unit cell parameters.
Step_5: Refine scale factor, unit cell parameters and the zero point.
Step_6: Refine scale factor and Gaussian widths terms at once (GU, GV and GW)
Step_7: Refine scale factor and profile shape parameters (LX then LY).
Step _8: refine scale factor and asymmetry parameter
Step_9: refine scale factor and Coordinates and overall Uiso
Step_10: Lx, GU and asymmetry parameter.
The resulting plot of observation and calculation pattern is as follow



Figuer1.1: plot of calculated and observed patterns with peak positions and difference plot of Zinicite

- **Structural information**:

a ,b	c	α ,β	μ	Space group
3.249	5.200	90.00	120.0	P6 3m

R_p	R_{wp}	CHI^2
0.1479	0.1869	5.523

- **Atom position**:

Atom/position	X	Y	Z	occ	uiso
Zn	0.3333	0.6667	0.0	1.0	0.025
O	0.3333	0.6667	0.3375	1.0	0.025

- **Gaussian width parameters:**

GU	GV	GW
0.0000E+00	0.022625E+02	-0.217307E+01

- **Laurantsian parameters:**

LX	LY
0.245451E+01	0.248831E+01

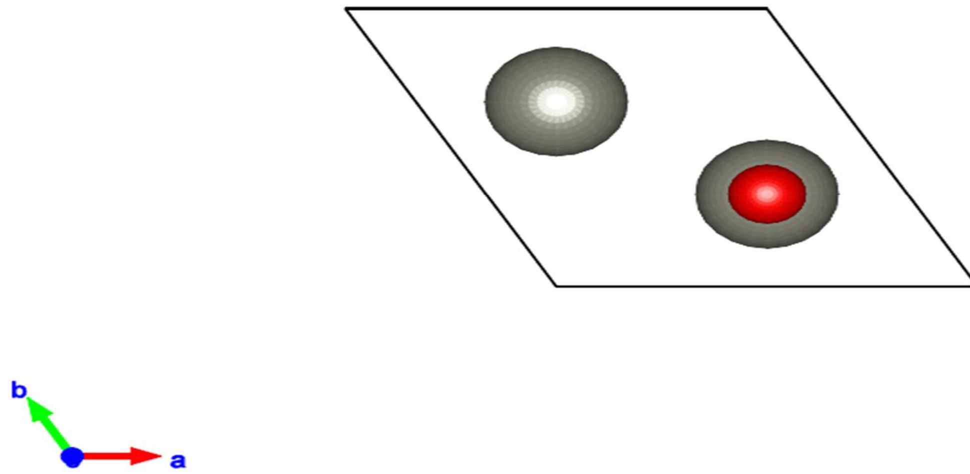


Figure 1.2: structure 2D of Zinicit

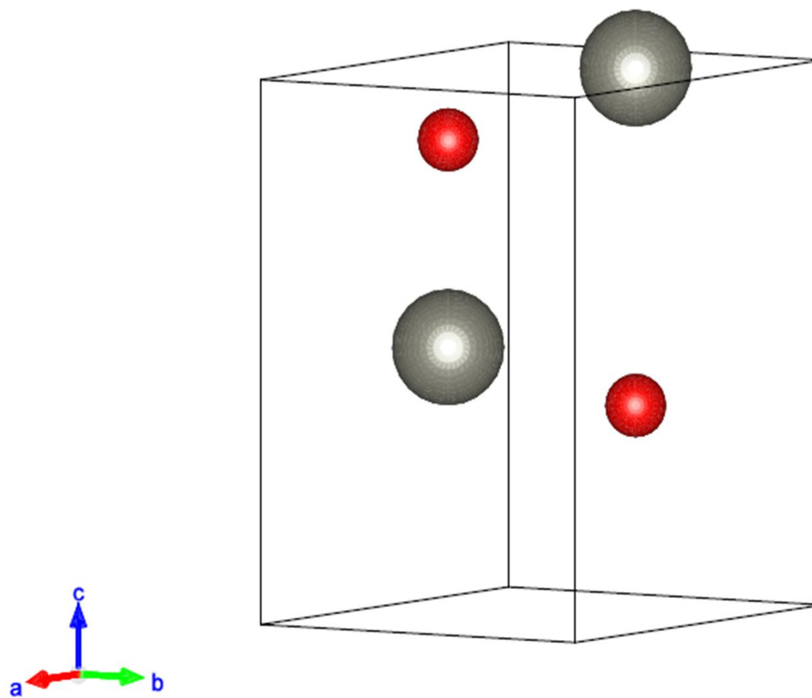


Figure 1.3: structure 3D of Zinicite

3.2.2. corindon (Al_2O_3) GSAS/EXGPUI refinement:

Step_1: changing the Background function
Step_2: Refine scale factor and background.
Step_3: Refine scale factor and zero point.
Step_4: Refine scale factor and profile shape parameters (LX then LY).
Step_5: Refine scale factor and Gaussian widths terms (GU then GV then GW)
Step _6: refine scale factor and asymmetry parameter.
Step_7: refine scale factor and Coordinates and overall Uiso.
Step_8: Refine scale factor and the March-Dollase Preferential Orientation.
Step_9: Refine scale factor and the unit cell parameters.
Step_10: Refine scale factor, unit cell parameters and the zero point.
Step_11: LX and GU
Step_12: LX and GV
Step_13: LX and GW
Step_14: LX and LY
Step_15: LX and GU and asymmetry parameter.
The resulting plot of observation and calculation pattern is as follow

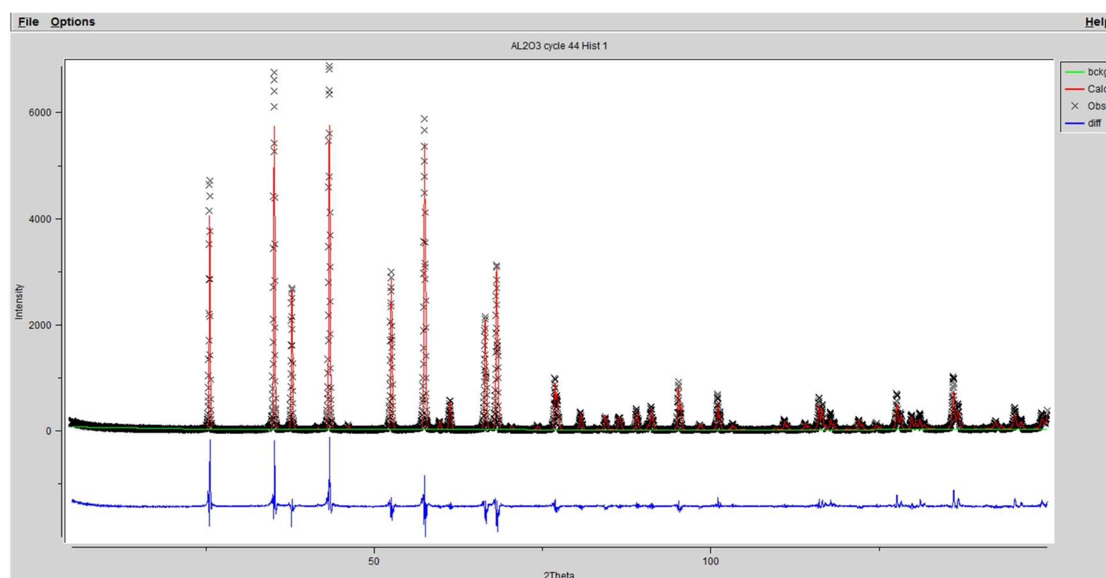


Figure 2.1: plot of calculate and observed patterns with peak position and difference plot of corindon.

- **Structure information**:

a,b	C	α ,β	μ	Space group
4.785	12.991	90.000	120.000	R-c3

- **Atom position:**

Atom/position	X	Y	Z	OCC	UISO
O	0.69365	0.00000	0.25000	1.00000	0.02500
AL	0.00000	0.00000	0.35217	1.00000	0.02500

- **Gaussian width parameters:**

GV	GW	GP
0.306676E+01	0.844971E+01	0.136201E+02

- **Laurantsian parameters:**

LX	LY
0.356612E+01	0.104442E+02

- **Asym:**

Asym	0.694229E+00

- **Agreement factors:**

R_p	R_{wp}	CHI^2
0.1317	0.1644	4.290

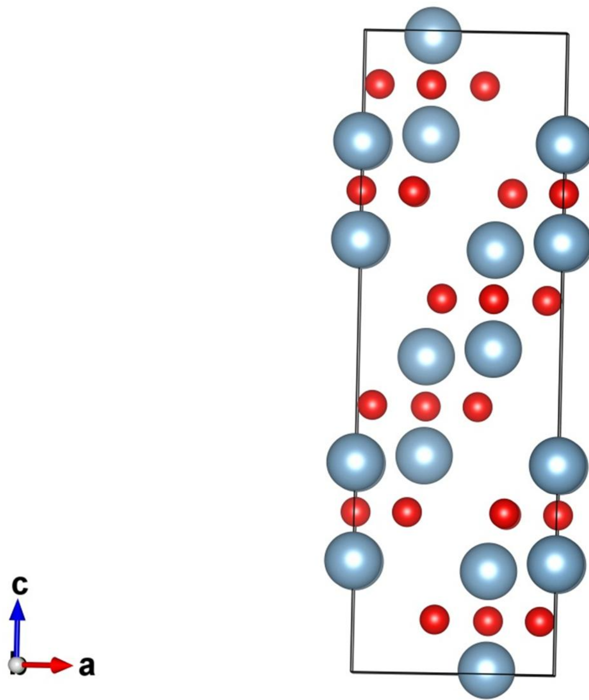


Figure 2.2: structure 2D of corindon

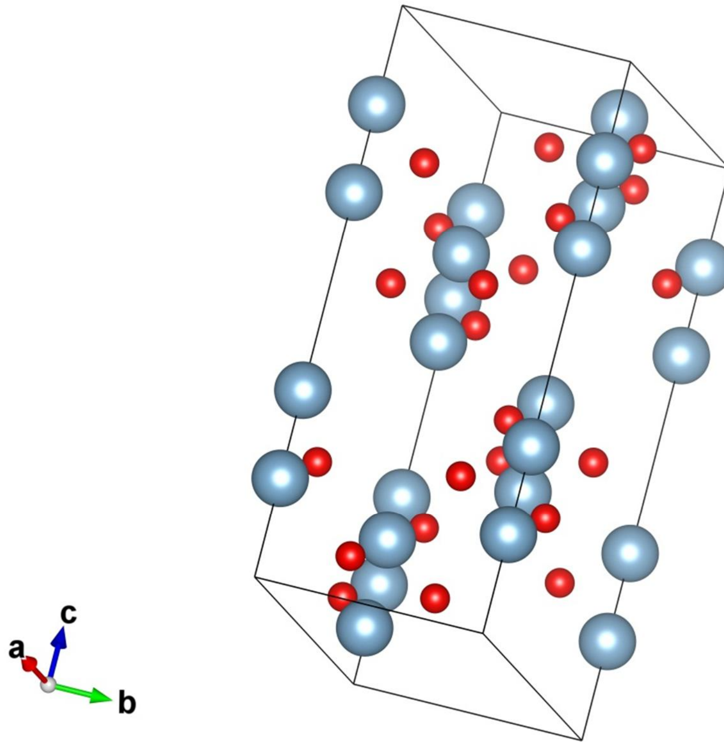
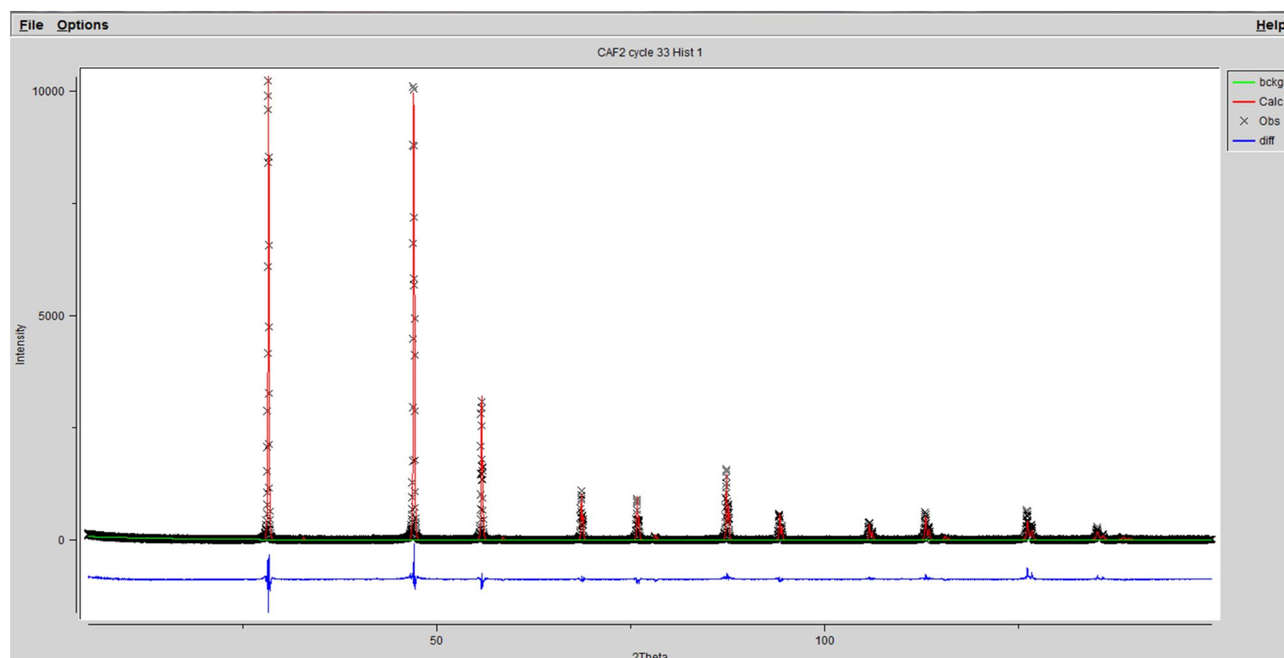


Figure 2.3: structure 3D of corindon

3.2.3. Fluorine (CaF_2) GSAS/EXPGUI refinement:

Step_1: changing the Background function
Step_2: Refine scale factor and background
Step_3: Refine scale factor and zero point
Step_4: Refine scale factor and profile shape parameters (LX then LY).
Step_5: Refine scale factor and Gaussian widths terms (GU then GV then GW)
Step _6: refine scale factor and asymmetry parameter
Step_7: refine scale factor and Coordinates and overall Uiso.
Step_8: Refine scale factor and the March-Dollase Preferential Orientation.
Step_9: Refine scale factor and the unit cell parameters.
Step_10: Refine scale factor, unit cell parameters and the zero point.
Step_11: LX and GU
Step_12: LX and GV
Step_13: LX and GW
Step_14: LX, LY and s/l

The resulting plot of observation and calculation pattern is as follow



Figuer3.1: plot of calculated and observed patterns with peak positions and difference plot of fluorine

- **Structural information**:

a,b,and c	α ,β and μ	System	Space group
5,462756	90,0000	Cubic	Fm-3m

- **Atomic position:**

Position / Atom	**X**	**Y**	**z**	**U**	**Occ**
Ca	0,000000	0,000000	0,000000	0,010	1,000
F_2	0,250000	0,250000	0,250000	0,013	1,000

- **Gaussian width parameters:**

GP	GV	GW
0,111920E+02	-0,220395E+02	0,732028E+01

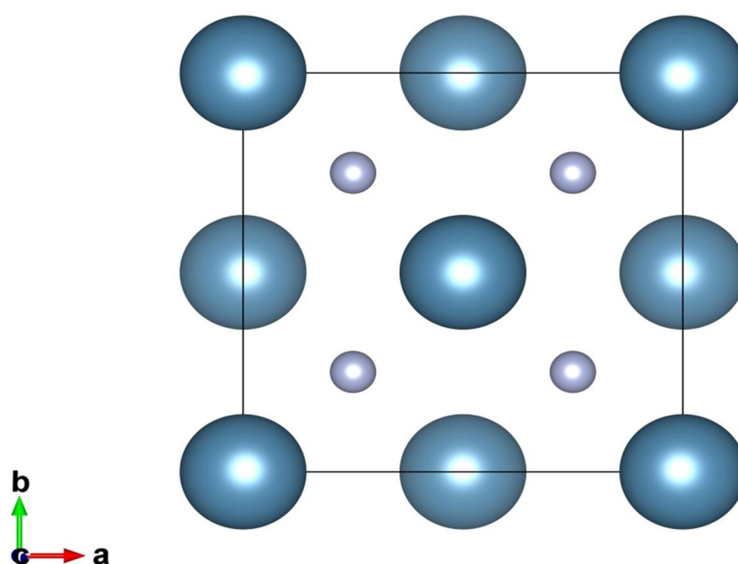
- **Laurantsian parameters:**

LX	LY
0,256638E+01	0,688266E+01

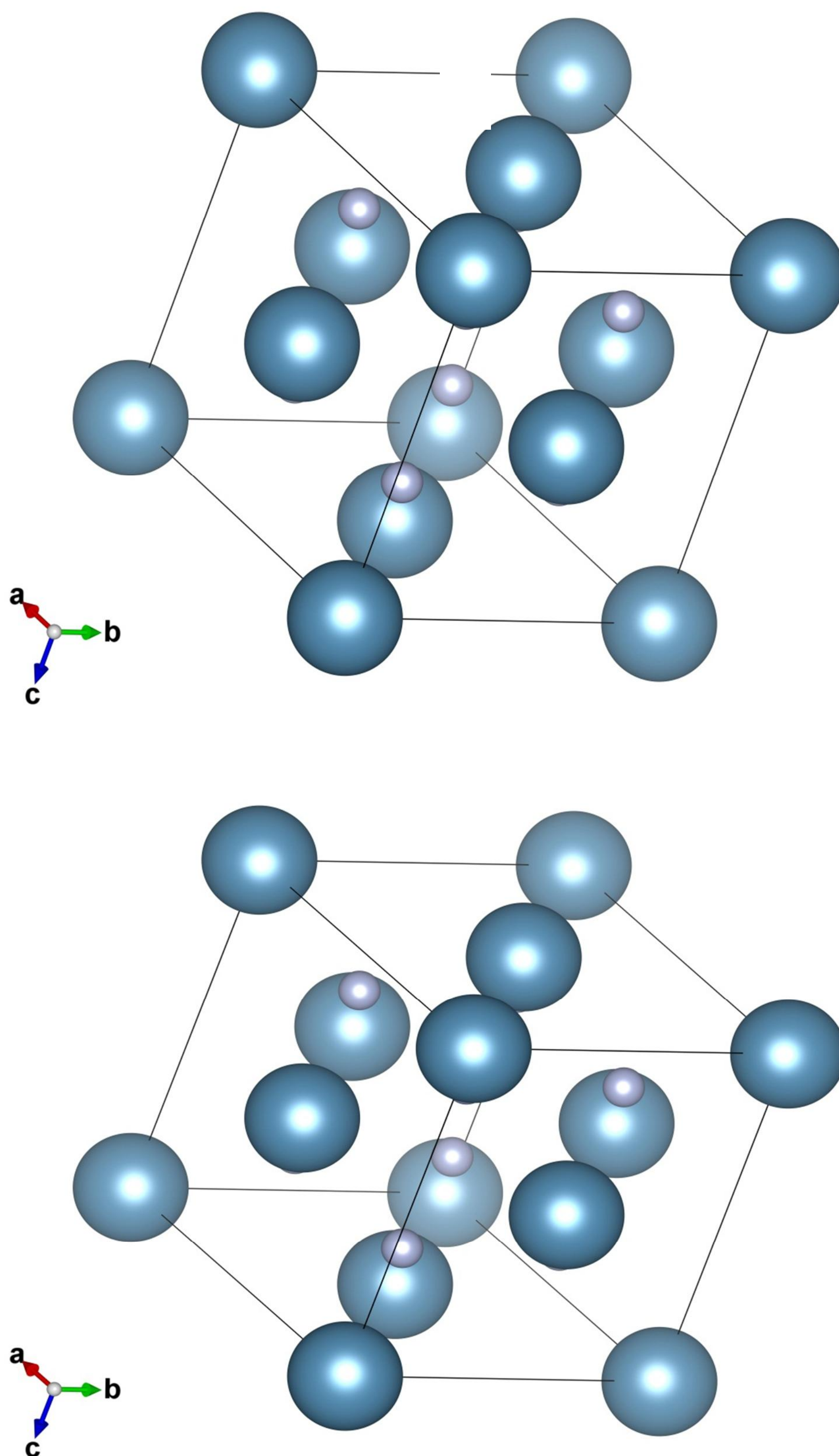
Axial divergence (S/L)	0,112149E-01

- **Agreement factors:**

R_p	R_{wp}	CHI^2
0,1369	0,2122	2,909



Figuer3.2: structural 2D of fluorine



Figuer3.3: structural 3D of fluorine

3.2.4. ZnO, Al_2O_3, CaF_2 refinement EXPGUI/GSAS:

Experimentally this mixture contains ZnO (92%) + Al_2O_3 (6%) + CaF_2 (1%) + impurity (1%). In order to estimate the quantification of each phase using Rietveld refinement we followed these steps:

Step_1: changing the Background function
Step_2: Refine scale factor and background.
Step_3: Refine scale factor, background and zero point.
Step_4: Refine scale factor and profile shape parameters (LX then LY).
Step_5: Refine scale factor and Gaussian widths terms (GU then GV then GW).
Step _6: refine scale factor and asymmetry parameter.
Step_7: refine scale factor and Coordinates and overall Uiso.
Step_8: Refine scale factor and the unit cell parameters.
Step_9: Refine scale factor, unit cell parameters and the zero point.
Step_10: LX and GU
Step_11: LX and LY
Step_12: LX and GU and asymmetry parameters

The resulting plot of observation and calculation pattern is as follow

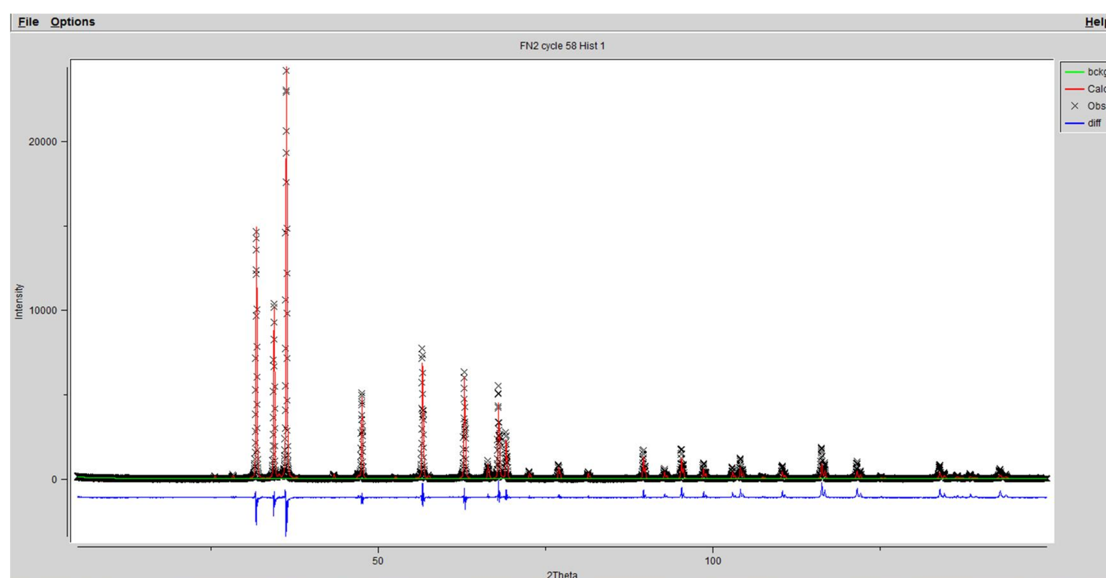


Figure 4.1: plot of calculated and observed patterns with peak position and difference plot of the mélange

- **Gaussian width parameters:**

GU	GV	GW
0.000000E+00	0.132604E+02	0.853435E+01
0.000000E+00	0.103077E+07	-0.270482E+07

- **Laurantsian parameters:**

LX	0.607058E+01
	0.107420E+05

- **Agreement factors:**

R_p	R_{wp}	CHI^2
0.1147	0.1570	5.722

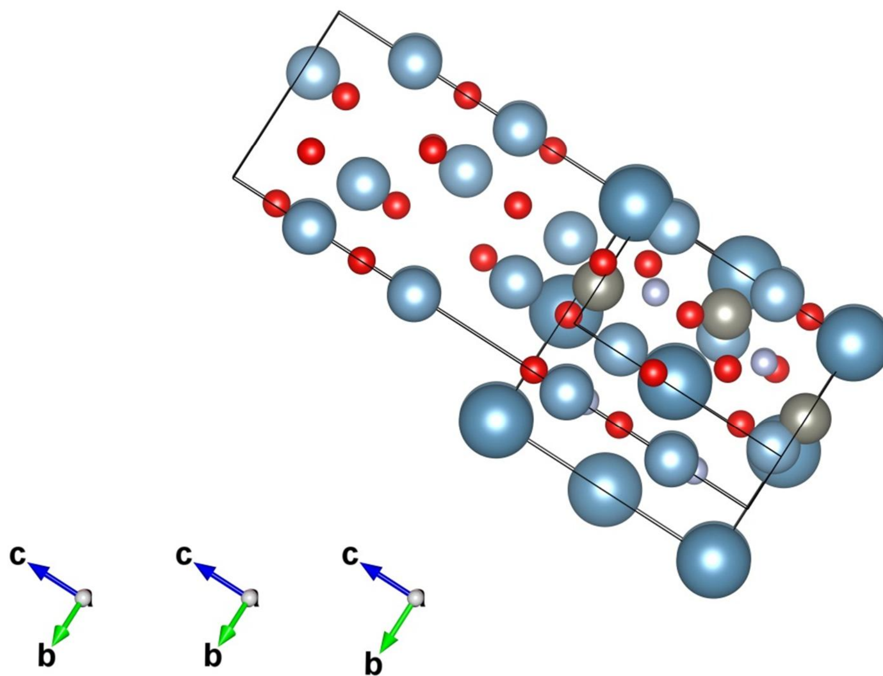


Figure 4.2: structure 2D of ZnO,Al_2O_3,CaF_2

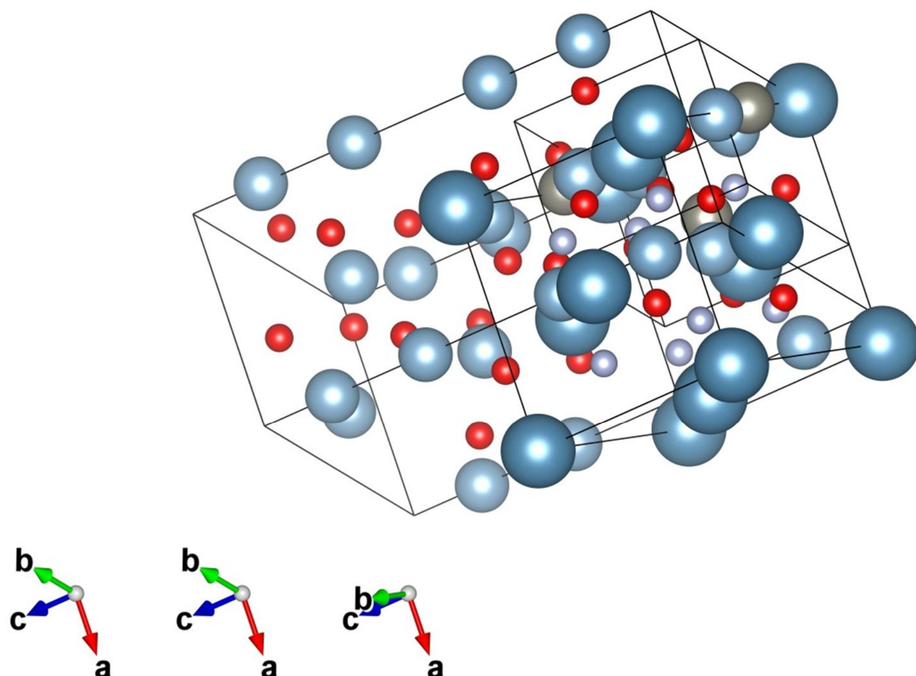


Figure 4.3: structure 3D of ZnO,Al_2O_3,CaF_2

The quantification of phases using Rietveld refinement is slightly different as comparation with experimental values where we found:

$$ZnO\ (96\%)\ +\ Al_2O_3\ (3\%)\ +\ CaF_2\ (1\%)$$

This different is due to the poor quality of experimental data of X-ray diffraction patterns.

3.3. Conclusion:

We conclude that Rietveld refinement use to improve the fit until it approaches the ideal value through the GSAS program by changing the parameters. In addition, it is very important to note that the refinement process need the high quality of XRD data.

General conclusion

General conclusion:

The Rietveld method circumvents the overlap problem by modeling the entire powder pattern using a series of parameters that can be refined to minimize the difference between the calculated and measured powder patterns, giving us enough information in a 1D data set to reconstruct the 3D structures.

In this work we getting a good result from refining a single or mixed phase using EXGPUI/GSAS program, it can be laborious with its difficulties that rise each time a phase is added, in this experiment we notice:

The presence of parameters that affect the results such as: the Gaussian parameters, the Lorentzian parameters and the asymmetry parameters.

For getting good plot, the value of x^2must be equal to or less than five.

Bibliography

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