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The Rietveld Method: Theory and Applications

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ABSTRACT

The method of refinement of crystal structure from one dimensional powder diffraction pattern was first proposed by H. M. Rietveld in the year 1967. Rietveld proposed that it is possible to extract much more information from the digitized (step scanned) powder diffraction pattern using the computer codes available by fitting the entire diffraction data. The powder diffraction pattern was then considered to be inferior compared to the single crystal diffraction data which was used for the calculation of the crystal structure. The integrated intensity was the smallest unit of measurement. But the individual raw intensity at a particular value of 2θ for a constant wavelength diffraction set up carries much more information than that was previous thought. This is how the birth of Rietveld method took place and it rapidly gained momentum and acceptability to the materials scientists for crystal structure refinement where it is not always possible to crystallize new and exotic materials into good single crystals.

Increasing complexity in the field of Materials Science, Crystallographic problems forces one to rethink the existing domains and earmarks the area of future developments in the Rietveld's method. Improved modeling will lead to physically significant characterizations of anisotropic microstructure, as well as crystal structure details. Finally in the computational area more faster and efficient algorithms will certainly lead to the improvement of the method. Numerous computer software are available now-a-days some free others commercial to perform the Rietveld refinements. Thus it is fast becoming a global phenomenon started way back in 1969.

KEYWORDS : Powder Diffraction, Crystal Structure Refinement, Whole Pattern Fitting.

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1. INTRODUCTION

It was von Laue who first suggested in 1912 that x-rays could be used as a tool for investigating the structure of crystal. A crystal diffracts the x-ray beam in an analogous fashion as ordinary light is diffracted by a grating. Since then the powder diffraction (a powder is an assembly of very small single crystals) method has been used to study crystal structures. Although used as a mere qualitative tool, structures of crystals having higher symmetry had been solved primarily using trial-and-error methods. Till the mid-sixties the powder method was regarded to be inferior particularly for *structure refinement*. The logic is simple. The three dimensional intensity data obtained from a single crystal is compressed into a single dimension in the powder method, resulting in serious peak overlap. The problem is worse for complex low symmetry systems. The need was to unscramble the complex diffraction pattern. One obvious solution was to improve the resolution of the pattern. Synchrotron x-rays and time-of-flight neutron methods provided partial answer by reducing dramatically the peak overlap, and the problem of partially resolved peaks (a major source of ambiguity in obtaining integrated intensity information) was tackled by fitting the groups of overlapping intensities to Gaussian function by H. M. Rietveld and this is how the birth of Rietveld method took place at the Seventh Congress of the IUCr in Moscow in 1966 [1,2]. Since then there was no turning back. It is the Rietveld method which made it possible to *determine* the structure of high T_c superconductor $YBa_2Cu_3O_{7-x}$ [3] unambiguously where the single crystal structure determination failed. It is the power of the Rietveld method supplemented by the latest computational techniques which made it possible the *refinement* of 181 parameters ‘simultaneously’ with X-ray data on ZSM-5 Zeolite [4]. Many more examples can be found in the literature.

2. WHAT IS RIETVELD’S METHOD?

Basically in Rietveld method of analyzing the powder diffraction data, the crystal structure is refined by fitting the entire diffraction pattern to a calculated pattern. One obvious question may arise- ’why one should take recourse to powder diffraction at all when single crystals are available?’ The answer is simple as possible - ‘the general lack of adequate specimens for single crystal method’. Let us for example take the case of YBCO superconductor. The results obtained from the single crystal diffraction from all over the world were not in consensus. In the words of Rietveld himself - ‘even in those cases where it is possible to grow large single crystals, these may suffer from such effects such as extinction making a proper interpretation of the diffracted intensities unreliable’.

It was during his assignment in mid-sixties at the Neutron Diffraction Group at the Netherlands Energy Research Foundation (then the Reactor Centrum Nederland) at Petten, work on Uranium compounds was conducted. The use of Neutron diffraction technique was essential for the accurate determination of the position of the position of Oxygen atoms in the presence of Uranium atom. As good quality single crystals were not available powder diffraction technique was mandatory. The least squares method of adjusting structure parameters to minimize the differences between the observed and the calculated structure factors was already well established in crystallography. It was a small step from there. In the pre-computer period the idea of considering the individual intensities y_i constituting a step-scanned diffraction peak as data was unrealistic. Single crystal diffractionists used the integrated intensities as the smallest data element for handling complex structures. Rietveld recognized that if the full power of the computers could be exploited the individual step intensities could be used instead of integrated intensities, with the assumption that the intensity at the i^{th} step is the summation of the intensities from the peaks constituting the pattern along with the background. The calculated pattern is simulated using the structural parameters (structure factor, unit cell parameters etc.) along with a Gaussian spreading function. Rest is the usual non-linear least squares algorithm of minimizing the difference between the observed and the calculated pattern.

A conference on ‘Diffraction Profile Analysis’ sponsored by the International Union of Crystallography was held at Cracow, Poland in August 1978. It was suggested that the phrase ‘Rietveld Method’ should used in preference to other phrases such as ‘Profile Analysis’ or ‘Profile Fitting Structure Refinement’. It ended the era of confusion between Rietveld method (which deals with the entire diffraction pattern at one shot) and the analysis of the profiles of the individual diffraction lines (for example Warren 1969) [5]. The principal goal of the Rietveld Method is to refine crystal structure, not profiles. Although recently many applications has been made to deal simultaneously with these two aspects and often both structural and microstructural information are available. A distinction at this point seems necessary between Profile Fitting/Pattern Decomposition and Rietveld Method. In the first method decomposition of the powder pattern into individual Bragg components is achieved without any structural model. The peak positions are unconstrained and are refined during the fitting cycle. In the Pawley method [6] better known as whole pattern decomposition lattice parameter constrains the peak position, whereas in Rietveld method a structural model is required, which constrains both the peak area and the peak position. While Profile Fitting /Whole pattern Powder Decomposition is suitable for microstructural analysis (crystallite size and microstrains), the Rietveld Method is most suitable for structure refinement. However, it is possible to incorporate the essence of Parrish (individual profile fitting based on convolution scheme) method [7] into the Rietveld method by first determining the convolution product W*G (W is due to radiation source and G is due to the instrument geometry) with the help of a suitable standard and then further convoluting with it the symmetric sample dependent function (S). An analytic profile shape is required in each step. The whole thing (W*G)*S thus represents the model of the intensity spreading function recorded in the reciprocal space. The structural model is then used to determine the actual intensity at each step. The whole thing thus becomes the calculated model which is finally matched with the experimental pattern in a least squares sense to calculate something sensible from it.

The Rietveld method was first applied to Neutron diffraction patterns. Rietveld's original code of structure refinement (written in ALGOL and later modified with FORTRAN IV) was based on Neutron diffraction at fixed wavelength. A wavelength of 2.6Å was chosen with a monochromator of Cu crystal with its <111> plane in reflecting position. Pyrolitic graphite was used to suppress the second order contributions. A continuous neutron source was used from a steady-state reactor. The peak shape which is a convolution of various factors like the mosaicity of the monochromator crystal, slit geometry and finally the crystallinity of the sample was assumed to be Gaussian with small asymmetry at very low and high scattering angles. Later the Time-of-Flight technique was developed with the main application for structural studies at high pressure (ToF technique is a constant scattering angle technique where the detector is placed at a particular angle and the time-of-flight of the neutron beam is recorded) ToF technique was further developed using pulsed neutron sources produced by spallation and here the Rietveld method was confronted with the biggest challenge of modeling the profile shape. The peak shapes in case of this high-resolution ToF neutron data is highly asymmetric due to different response in the leading and trailing edge of the pulse. Although previous results of neutron diffraction based on Gaussian peak shapes resulted in good refinements, ToF technique using pulsed neutron sources required urgently better profile modeling based on convolution relation involving several Gaussian functions. With increasing demand for modeling anisotropic line broadening from the sample the situation becomes more complex. Rietveld in his 1969 paper proposed that the technique could be used for x-ray diffraction as well and it was in 1977 first RR technique was employed to X-ray data [8]. The dream of a well behaved Gaussian peak shape was over. X-ray line shapes are neither pure Gaussian nor Lorentzian. Furthermore the axial divergence of the slit system makes the profiles asymmetric. The best way is thus to ascribe a Voigtian shape to X-ray diffraction line or more simply a Pseudo-Voigt function (Pearson VII is another choice). We will in the later sections deal with the mathematical formulations involved in Rietveld method and its recent developments.

3. THE RIETVELD METHOD: CORE MATHEMATICS AND BASIC FORMULATION

The core mathematics involved in a Rietveld Refinement program is basically a non-linear least squares method. The procedure leads to a set of normal equations involving derivatives of all of the calculated intensities with respect to the adjustable parameters and are solved by the inversion of the normal matrix.

In the Rietveld method the quantity which is minimized in the non –linear least squares procedure is the residual. It is defined as

$$S = \sum w_i \ (y_i - y_{ci})^2 \qquad \text{------- (1)}$$

where y_i is the observed or gross intensity (actually measured in terms of the number of x-ray photons detected) at any point i of the observed powder pattern and y_{ci} is the theoretical intensity . The weight, w_i, is expressed as, $w_i=y_i^{-1}$

The theoretical intensity y_{ci} has contribution from Bragg reflections, diffraction optics and instrumental factors. To simulate the theoretical diffraction pattern the Rietveld method requires two basic starting models: a structural model based on the approximate atomic positions in the lattice and a non-structural model, which takes care of the instrumental features and specimen features such as aberration due to absorption, specimen displacement, crystallite size and microstrain effects etc. The structural model helps to determine the total intensity of Bragg reflection along with their positions and the non structural model gives a description of individual profile in terms of an analytical of other differentiable functions (Psuedo-Voigt, Pearson VII, Gaussian, Lorentzian and modified Lorentzian functions are widely used).

Using the structural and non-structural models the intensity at any arbitrary point i is calculated as:

$$y_{ci} = S \sum_K L_K |F_K|^2 \Phi(2\theta_i - 2\theta_K)\, P_K A + y_{bi} \qquad \text{-------- (2)}$$

where S is the overall scale factor,

K represents miller Indices, hkl for a Bragg reflection,

L_K contains Lorentz polarization and multiplicative factor,

Φ_K is a diffraction profile function which approximate the effect of both instrumental features and specimen features such as aberration due to absorption, specimen displacement, crystallite size and microstrain effects etc.,

P_K is preferred orientation function,

F_K is structure factor for K^{th} Bragg reflection,

y_{bi} is background intensity at i^{th} point.

The simulated pattern is obtained by adding up the calculated intensities y_{ci}, at each step. The contribution at each step includes all the reflections in the corresponding diffraction pattern and also from different phases constituting the pattern. This calculated intensity is fitted to the observed pattern.

The Bragg reflections contained in the summation expressed in eqn. 2 at each point of the powder pattern are determined from the possible reflections at $2\theta_i$. Let us now examine in detail the terms involved in equation 2.

3.1 *Structure Factor*

The amplitude of X-ray scattered by a crystal is determined by the arrangement of atoms in the diffracting planes. The atoms in the unit cell scatters strongly in certain directions and weakly in others. The structure factor F_K contains the structural information. F_K gives the result of scattering from all of the atoms in the unit cell to form a diffraction peak from a set of (hkl) planes. It is given by

$$F_k = \sum_j g_j f_j \exp\left(2\pi i\left[hx_j + ky_j + lz_j\right)\exp\left[-\frac{B_j Sin^2\theta}{\lambda^2}\right] \qquad \text{-------(3)}$$

where

f_j is the atomic scattering factor of j th atom ,

g_j is the atomic occupancy factor,

x_i,y_i and z_i are the fractional atomic coordinates,

and B_j the temperature factor .

The position and intensity of peaks in a diffraction pattern are determined by the crystal structure and the Bragg's Law $n\lambda = 2d_{hkl}\sin\theta$. Bragg's law calculates the angle where constructive interference from X-rays scattered by parallel planes of atoms will produce a diffraction peak. In most diffract meters, the X-ray wavelength is fixed and consequently a diffraction peak is produced at a specific angle 2θ. The lattice parameters of the unit cell are used to calculate d_{hkl} .

3.2 *Background*

The background intensity y_{bi} at the i^{th} step may be obtained by any of the following three method (1) a specified background function, usually a polynomial (2) linear interpolation between user-selected points in the pattern or (3) a user-supplied function. For a simple pattern where most peaks are resolved to the baseline, all methods tend to work well. For complex patterns with a high degree of overlap, however, the majority of the peaks are not resolved to the baseline, so the estimation of the background is difficult. However, the polynomial functions usually used for this purpose are largely or entirely empirical. Synchrotron sources due to its excellent signal-to-noise ratio, the background in a synchrotron experiment tends to be more sensitive to structural disorder and fluctuations than that in a laboratory X-ray experiment. For constant-wavelength neutron source the prime contributor to the background is incoherent scattering from the sample container and from the sample itself. The background apart from the phenomenological approach stated above may also be based on physical reality such as amorphous component and thermal diffuse scattering.

3.3 *Diffraction Line Profile*

The diffraction profile Φ_k is a combination of two effects [5]. The first is the instrumental effect which includes the instrument geometry, optics, slit systems etc. and the other includes sample related effects collectively called the microstructure. This includes crystallite size, microstrain, certain defects etc. The two effects hence forth described as g-profile (instrumental) and f-profile (microstructure) appears as a convolution and the resultant x-ray diffraction pattern is described by the following convolution product

$$h = f * g \qquad \text{------ (4)}$$

and the diffraction profile Φ_K is physically expressed as

$$\Phi_K = \int f(x - x')g(x')dx' \qquad \text{------- (5}$$

where x' is expressed in 2θ. Thus it becomes clear from the structure of above equation that if sample microstructure is taken into account in a rigorous sense the calculated intensity is extremely complicated to calculate.

3.3.1 Instrumental Contribution

The instrumental contribution is generally classified into two types. One arises out of the slit geometry and the other due to spectral distribution of the X-ray emission profile

(1) Spectral distribution (W)

The inherent spectral profile of the $K_{\alpha1}$ line from a Cu target sealed X-ray tube has a breadth of 0.518×10^{-3}Å [9] and is approximately Cauchy and not completely symmetric. Usually due to the presence of $K_{\alpha2}$ and other satellite components $K_{\alpha3,4}$ additional smearing takes place. The spectral dispersion varies as tanθ and it can dominate the diffraction line profiles at high angles.

(2) Instrumental contribution (G) [10]

These are non-spectral contribution

a) The x-ray source image in a sealed tube system can be approximated with a symmetric Gaussian curve with a FWHM of 0.02° at a take-off angle of 3°.

b) The flat specimen used in most experimental set-up introduces a cotθ dependence on the line breadth and produces a small asymmetry in the profile. It is particularly noticeable at low diffraction angles where the irradiated length of the sample is large.

c) Axial divergence of the incident beam follows an approximately cotθ dependence at low angles and causes substantial asymmetry in the profile.

The other slit systems also produce additional small broadening in the diffraction profile. A sum total of all these effects are generally referred to as instrumental contribution.

The different contributing factors to the profile shape function discussed in the previous section forms the basis of the appropriate choice of the profile shape function. Unlike the case of neutron diffraction where the profile shapes are nearly Gaussian and symmetric (except for T-O-F neutron data), the better resolution of the x-ray powder diffractometer indicates that more individual contribution to the line shape are likely to be observed experimentally. Further depending on the nature of the specimen (i.e. the degree of lattice imperfections), the asymmetry in the line profile (arising out of instrumental contribution as well as specific specimen effects like twin faults and compositional inhomogeneity) and the variation of the line shape with diffraction angle (at low angle the instrument controls the line shape whereas at high angle spectral distribution is more prominent) fitting of X-ray diffraction lines is difficult.

Early X-ray Rietveld studies and Integral breadth methods discarded the assumption of simple profile shape functions like the Gaussian or Cauchy (Lorentzian) for X-ray line profiles and established that tunable functions like Voigt, pseudo-Voigt and the Pearson VII functions are likely to be the better choice for X-ray line profiles [11]. All the functions described above fits only the symmetric part of the profile. To include line profile asymmetry other additional functions are to be used. The demanding need for a more flexible single function to model asymmetric X-ray lines gave rise to the split-type functions like Split pseudo Voigt, Split Pearson VII, having different widths and asymmetries for different halves of the profiles. Table 1 gives a list of functions generally used in Rietveld refinement.

Regardless of the type of peak-shape function selected, the range of the peak (i.e. when it no longer contributes to peak intensity) must be established. This truncation effect renders all the functions assumed to be finite which may lead to truncation errors. As a rule of thumb, a peak can be considered to be down to background level when the intensity is less than 0.1±1.0% of the peak maximum. The appropriate percentage depends upon the peak shape. If the tails of the peaks are long (indicative of a Lorentzian character), a wider range will be required than for peaks with more Gaussian character. The range needed depends upon the FWHM of the peak. It is usually expressed as an integral number of FWHM values. Typically, the value ranges from 10 to 20 times the FWHM depending upon the Lorentzian character of the peak.

There are two approaches to determine the instrumental contribution g

(a) Measuring it with a standard specimen like NIST SRM’s, or

(b) Fundamental Parameter or Ray Tracing approach.

Both these method are now being used in several computer programs for Rietveld refinement.

One important aspect of Rietveld analysis is to determine the angular dependence of the profile shape parameters. In the original Rietveld program, the dependence of the FWHM (full-width-at-half-maximum,) H of the reflection profiles was modelled as the Caglioti equation [12]

$$H = [U\, tan^2\theta + V\, tan\theta + W]^{1/2} \qquad ----- \qquad (6)$$

This formula worked satisfactorily for the initial developed medium (or less) resolution powder diffractometers where the instrumental function was predominantly Gaussian. Even with the x-ray diffractometers operating on sealed-off x-ray tube and rotating anode, whose instrumental profiles are neither Gaussian nor symmetric, Caglioti function was widely used for the lack of anything better.

An essential step in applying Rietveld method on data from modern diffractomenters is to examine the variation of FWHM (or integral breadth) with 2θ or d^* and to compare this with the resolution curve of the instrument used. If the two curves are identical, indicating that sample effects are negligible, then Caglioti formula can be used to model breadth variation. If the curves differ, but the scatter for the sample curve is not greater than that would be expected from counting statistics or there is no marked 'anisotropy', on the average, then also one can model the breadth of the profile with Caglioti formula, but this time U, V and W should be treated as refinable parameters. But if the sample curve exhibits a scatter which is 2θ or d^* dependent, then the nature of 'anisotropic' breadth variation must be ascertained and the dependence of breadth on hkl has to be modelled with special care.

A more suitable formulation applicable to x-ray method is to use the Modified TCH pseudo-Voigt function where the Gaussian and Lorentzian contributions have different dependence on diffraction angle θ [13]. (see Table 1)

Table No. 1: Profile Shape Functions used in Rietveld Refinement

S.No	Profile shape	Analytical formula
1	Gaussian	$G=\frac{\sqrt{C_0}}{\Gamma_k\sqrt{\pi}}\exp\left[-\frac{C_0}{\Gamma_k^2}(2\theta_i-2\theta_k)^2\right];\quad C_0=4\ln 2$
2	Lorentzian	$L=\frac{2\sqrt{C_0}}{\pi\Gamma_k}\frac{1}{1+\frac{C_0}{\Gamma_k^2}(2\theta_i-2\theta_k)^2};\quad C_0=4$
3	Pseudo-Voigt	$pV=\eta L+(1-\eta)G$ $\eta=\eta_0+X*(2\theta)$
4	Pearson VII	$P_{VII}=\frac{C_0}{\Gamma_k}\left[1+\frac{4\left(\sqrt[m]{2}-1\right)}{\Gamma_k^2}(2\theta_i-2\theta_k)^2\right]^{-m};\quad C_0=\frac{2\sqrt{m}\left(\sqrt[m]{2}-1\right)^{\frac{1}{2}}}{\sqrt{\pi(m-0.5)}}$ $m=m_0+100\frac{X}{2\theta}+1000\frac{Y}{(2\theta)^2}$
5	Voigt	$V=I_V(0)\frac{\beta}{\beta_G}\mathrm{Re}\{erf[\frac{x\sqrt{\pi}}{\beta_G}+ik]\}$
6	Assymetric pseudo-Voigt	$pV_{asym}(2\theta)=[pV*A](2\theta)\ A(2\theta)=\exp\left[-a_s\lvert 2\theta-2\theta_0\rvert\tan(2\theta_0)\right]$
7	Split PearsonVII	$pV_{split}(x)=\frac{(1+A)[\eta_h+(1-\eta_h)(\pi\ln 2)^{1/2}]}{\eta_l+(1+\eta_l)(\pi\ln 2)^{1/2}+A[\eta_l+(1-\eta_h)(\pi\ln 2)^{1/2}]}$ $\mathrm{X}\left\{\eta_l\frac{2}{\pi W}\left[1+\left(\frac{1+A}{A}\right)^2\left(\frac{\Delta}{W}\right)^2\right]+(1-\eta_l)(2/W)\left(\frac{\ln 2}{\pi}\right)^{1/2}\exp\left[-\left(\frac{1+A}{A}\right)^2\ln 2\left(\frac{\Delta}{W}\right)^2\right]\right\}$

3.3.2 Sample Contribution

Apart from the inherent width (or Darwin width) produced by a perfect crystal, there are two principal physical sample effects which contribute to the broadening of the f profile. Scherrer (1918) [14] pointed out that if crystallite size is less than 1 μm then the integral breadth varies as

$$\beta=\frac{\lambda}{\tau}\mathrm{Cos}\theta \qquad \text{------- (7)}$$

where λ is the X-ray wavelength and τ is the crystallite size.

Microstrains also broaden the f profile according to the relation (Stokes and Wilson 1944) [15]

$$\beta=k\varepsilon\tan\theta \qquad \text{-------- (8)}$$

where ε is the microstrain and k is a constant whose value depends on the definition of microstrain used.

In general, sample induced line broadening includes contributions which are independent of 2θ or d*, known as 'size effect'. The other contribution which depends on 2θ or d* is known as 'strain' effect collectively.

There have been various attempts to make allowance for smoothly varying (isotropic) microstructural effects in Rietveld programs. David and Matthewman [16] modelled experimental line profile by means of a Voigt function and assigned the 'Lorentzian' and 'Gaussian' components to the 'size' effects and the instrumental broadening respectively. A different approach was adopted by Howard and Snyder in the program SHADOW,[17] who convoluted a Lorentzian simple line profiles, assumed to be due to 'crystallite size' and/or 'microstrains', with experimentally determined instrumental profiles, to match the observed data. The simultaneous presence of isotropic 'size' and 'strain' effects was considered by Thompson, Cox and Hastings [13]. They used a psuedo-Voigt function to model the overall line broadening and assigned the Lorentzian components of the psuedo-Voigt functions to 'size' effects and Gaussian components to the combined 'strain' and instrumental contributions. All the above models are phenomenological in nature and lacks physical basis as has been shown by later authors that both size and strain breadths may contain Gaussian and Lorentzian components [18].

An early attempt to model anisotropic line broadening in the Rietveld method was made by Greaves [19], who assumed that the crystallites had the form of platelets with thickness H and infinitely large lateral dimensions. In this case the contribution to the integral breadth of reflection from plates parallel to the surface, in the reciprocal unit, is simply $1/H$. In order to allow for the direction dependence of microstrain, some assumptions must be made regarding the stress distribution. If this is assumed to be statistically isotropic, then the anisotropy of the elastic constants leads to an hkl dependence of strain. Thompson, Reilly and Hastings [13], expressed microstrain as a function of hkl indices and refined appropriate strain parameters based on elastic compliances. Simultaneous anisotropic ‘size’ and ‘strain’broadening was incorporated in the Rietveld method by Le Bail [20] and Lartigue, Le Bail & Percheron-Guegan [21]. The hkl dependent nature of these quantities was modelled by means of ellipsoids and size Fourier series was employed to represent the line profiles. The number of microstructural parameters to be refined was restricted by adopting Lorentzian function for ‘size’ contributions and an intermediate Lorentz-Gauss function for ‘strain broadening. In a similar approach Lutterotti and Scardi [22] first included crystallite size and microstrain as refinable parameters, in the place of usual angular variation line-profile width Caglioti parameters.

3.3.3 Two-stage Approach

The approaches discussed above is purely phenomenological and do not have any apriori basis. The primary reason for modelling crystal-imperfection and instrumental effect in the Rietveld method is to provide an accurate description of line-profile breadths and shapes, and therefore of the associated intensities, and, ideally, of the displacement of peaks from their true Bragg positions.

Peak shifts arise from instrumental aberrations, from specimen transparency and displacement, from imperfections (e.g 'mistakes' and non-stoichiometry) and from homogeneous (macro) strain. Owing to the possible complexity of microstructural features, and the fact in general the nature of any imperfection present is not known apriori, accurate modelling of line profiles for use in a Rietveld analysis can be very difficult to achieve. Therefore a two-stage approach is recommended.

In the first stage the position, intensity, breadth and some shape parameter (e.g. Lorentzian/Gaussian fraction or Pearson VII parameter) of individual lines are obtained by pattern decomposition [23-26], for which no structural information is required. From these parameters the dependence of breadth and shape as the function of position and direction in reciprocal space (2θ or d^* and hkl dependence) can be determined for all peaks. These parameters can then be predicted for reflections not found by pattern decomposition, owing to too severe overlap or too low intensity. If desired, the results of pattern decomposition can be interpreted in terms of microstructural properties. Also, the pattern can be indexed, if the unit cell is not already known, and the precise cell dimension can be obtained after the line positions have been corrected for systematic errors. The latter are not necessarily obtained from Rietveld program with the same accuracy, since refinement of cell dimension along with other parameters merely absorbs peak shifts due to any instrumental aberration for which no allowance has been made and shifts due to lattice imperfections. If the cell parameters are known, a special constrained pattern-decomposition method can be applied. Another advantage of using pattern-decomposition is that intensities of unambiguously indexed Bragg reflections can be used in ab-initio structure determination.

In the second stage, (semi)empirical relationship describing the behavior of breadth, shape and perhaps position of lines as a function of 2θ (or d^*) and hkl are used in the Rietveld refinement. After the line-profile parameters are obtained by means of pattern-decomposition, the variation of breadth and shape parameters with 2θ or d^* is examined. This is an essential preliminary step in all applications of the Rietveld method. By comparing the breadth variation with the resolution curve of the instrument used, the significance of any sample broadening is immediately apparent. Also, from the scatter of the plot, it can be ascertained whether the broadening is 'isotropic' or 'anisotropic'. If practicable, it is clearly desirable at this stage to reduce crystal imperfection broadening by suitable treatment of the specimen, such as annealing, for example. In any event, the breadth versus 2θ or d^* plot can provide a basis for subsequent modelling of line breadth in the refinement of the structure.

On the basis of the above following cases may arise.

(a) Isotropic case

If the breadth and shape parameters vary smoothly, with a scatter attributable solely to counting statistics, then microstructural effect is either negligible or their contribution is 'isotropic'.

By fitting suitable functions (e.g. psuedo-Voigt) to these curves, an empirical description of the breadth (FWHM for psuedo-Voigt) and shape (η for psuedo-Voigt) can be incorporated in the Rietveld method. The nature of the functions used in the isotropic case is unimportant, provided that residual systematic errors after fitting are negligible.

(b) Anisotropic case

If the scatter in the breadth (FWHM) versus 2θ or d^* plot is clearly greater than that would be expected on statistical ground, hkl (lattice direction) dependence is indicated. There are then various ways of modelling breadth and shape parameters in the anisotropic case.

(i) The simplest, which may be acceptable if the 'anisotropy' is not too severe, is to obtain the average curves and proceed as in the 'isotropic' case. If the widths lie on two or more curves which correlate with particular family of hkl, then each can be modelled separately, with provision for the lattice-direction dependence. Such selective broadening is typical of layer structures with stacking faults.

(ii) For a more rigorous treatment of anisotropic broadening, the breadth variation needs to be examined in detail. Firstly after correction for instrumental effect the order-independent and order-dependent contributions to the line profiles are separated, to ascertain if only one or both are appreciable.

If the order-dependent broadening is negligible, the lattice direction dependence of breadth can be deduced by assuming that on average domains have particular shapes. From a least squares comparison of the observed values of the domain size and those calculated for the selected shape and orientation of domains with respect to the crystallographic axes, the breadth can be predicted for all reflections.

A similar approach can be adopted for the 'strain only' case, where the assumption of an ellipsoid may suffice to describe the lattice direction dependence of the (mean strain) strain component considered. Alternatively, for a give state of stress, an expression for the (mean strain) strain component considered can be derived containing terms depending on hkl, elastic compliances and stress components. The number of these terms depends on the crystal symmetry. Then the non-hkl dependent parameters in either of the expression of the 'strain' components can be determined be (least-squares) fitting.

If both 'size' and 'strain' broadening are present, the above approaches can be adopted for both the order-independent and order-dependent contributions and β^h (or $(\beta^*)^h$) for each reflection used in the refinement can be obtained from a successive 'convolution' of all component concerned.

3.4 The Lorentz Polarisation Factor

Another factor which affects the intensity at a particular value of 2θ is the Lorentz-Polarisation factor [10]. It is dependent on the instrument geometry used for data collection. The condition for obtaining diffraction is that a reciprocal lattice point is on the Ewald circle. The total intensity we record when a reciprocal lattice point passes the circle will be proportional to the time it takes to cross it. At a given angular velocity ω, a reciprocal lattice point with a long reciprocal lattice vector will move faster than one with a short. Thus a reciprocal lattice point has to travel a certain distance to ensure that all the diffracted intensity from a particular reflection is captured. The correction factor is referred to as the Lorentz factor. For Bragg-Brentano geometry the factor is

$$L(2\theta) = (1/\sin 2\theta \cos\theta) \qquad \text{-------- (9)}$$

Apart from the Lorentz factor there is another factor which is known as the Polarisation factor which arises due to the fact that the incident X-ray is unpolarised whereas the scattered one is polarized. The combined Lorentz-Polarisation correction term is given as

$$LP = \frac{1+cos^2 2\alpha\, cos^2 2\theta}{sin^2\theta\; cos\theta} \qquad \text{---------(10)}$$

3.5 Preferred Orientation

By preferred orientation it is meant that the crystallites tend to arrange themselves according to their habit. Flat crystallites tend to be stacked. A proper powder diffraction pattern requires a random crystallite orientation. Any preferred orientation will show up as an incorrect intensity distribution, but the peak positions will remain the same. The problem can be reduced by careful sample preparation, for reflection geometry side-loading or back-loading is preferred. If preferred orientation cannot be eliminated by sample preparation alone suitable corrections must be applied during Rietveld refinement. The two mostly used models are 1) Rietveld –Toraya model [1,2] and 2) March-Dollase model [27]

$$P_H = G_2 + (1 - G_2)\exp(G_1\, \alpha_H^2) \qquad \text{----------- (11)}$$

$$P_H = \left[(G_1 \cos\alpha_H)^2 + \frac{sin^2\,\alpha_H}{G_1}\right]^{-\frac{3}{2}} \qquad \text{----------- (12)}$$

3.6 Criterion of Fit

The beauty of the Rietveld method lies in that it allows simultaneous adjustments of structural parameters, profile parameters, unit cell, background etc.

In the non linear least squares minimization process derivatives of the calculated intensities with respect to each adjustable parameter is taken and subsequently equated to zero. It gives us a set of normal equations. From the normal equations we may write **Mx**=**V** where **M** is an p x p matrix, p being the number of refined parameters with elements $M_{kl} = \sum w_i(\delta y_{ci}/\delta p_k)(\delta y_{ci}/\delta p_l)$. The summation is performed over all observations. **x** is a p-dimensional vector with the parameters shifts, Δp_k, as its elements. **V** is also a p-dimensional vector with elements $V_k = \sum w_i(y_{ci}-y_i)(\delta y_{ci}/\delta p_k)$. By inverting the matrix **M** and multiplying with **V** gives the solution to the parameter shifts $\mathbf{x}=\mathbf{M}^{-1}\mathbf{V}$. The solution thus gives us the parameter shifts relative to the starting parameters. After applying the shifts to the original parameters, the procedure is repeated until convergence is reached.

Thus it is clear that as the number of adjustable parameters increase the size of the normal matrix also increases and subsequently the computer time. Moreover the starting model should be accurate otherwise the parameter values will diverge. This is in essence true for any non-linear least squares algorithm. The refinement process runs till the residuals are minimized and a 'best fit' is achieved. However, the criterion of 'best fit' is closely linked with the accuracy of the starting model. The most important fact is that a 'global minima' should be reached (model inaccuracy may lead to false 'local minima'). Normally two kinds of errors occur, the counting statistical error and model error (which is a systematic error). The residuals R_{bragg} and $R_{structure\text{-}factor}$ are model dependent whereas $R_{profile}$ or $R_{weighted\text{-}profile}$ or R_{exp} depends on the profile model used and are affected by counting statistics [28]. Another important measure is the 'estimated standard deviation'-which is of course a measure of precision not accuracy of the model involved. It is important to note that some systematic errors (like preferred orientation, anisotropic line broadening, bad crystal statistics and other specimen errors) [29-31] are not considered in the e.s.d's but still large inadequacies may project them as random errors and the Rietveld refinement can largely be wrong.

3.6.1 R-Factors

As a visual guidance the difference plot is probably the best way of judging the progression of a Rietveld refinement. The reliability of the fit of the calculated pattern to the observed data can also be given numerically. This is usually done in terms of agreement indices or R values. There are several reliability factors. The most important is the R_{wp}.

The weighted-profile R value, R_{wp}, is defined as

$$R_{wp} = [\frac{\sum_i w_i (y_i - y_{ci})^2}{\sum_i w_i y_i^2}]^{\frac{1}{2}} \qquad \text{--------(13)}$$

where y_i is the observed intensity at step i, y_{ci} the calculated intensity, and w_i the weight. The expression in the numerator is the value that is minimized during a Rietveld refinement. The quantity y_i includes the background contribution. The high background will automatically produce a low R_{wp} value, because a significant part of the intensity is accounted for by the background function. Thus, the comparison of R_{wp} values from different kinds of powder diffraction experiments can be extremely misleading. For example, R_{wp} for neutron TOF data are often quite small (e.g. a few %), while those for laboratory X-ray data are larger (e.g. 10%). Ideally, the final R_{wp} should approach the statistically expected R value, R_{exp} defined as,

$$R_{\exp} = [\frac{N - P}{\sum_i w_i y_i^2}]^{\frac{1}{2}} \qquad \text{---------- (14)}$$

where N is the number of observations and P the number of parameters. The index R_{exp} gives an indication of the quality of the data or counting statistica. The ratio between the two, R_{wp}/R_{exp} is called the goodness-of-fit or GoF. The GoF should ideally approach 1. If the data have been over a sufficient time (if the noise is less) R_{exp} will be very small and GoF will be much larger than 1. Conversely, if the data have been collected too quickly (a noisy pattern), R_{exp} will be large and GoF could be less than 1.

The approximate error magnitudes can be calculated from the 'estimated standard deviation' of the refined parameters. In least squares refinement esd's are computed as

$$\sigma_i \sigma_i = [\frac{m_{ii} S}{N - P}]^{1/2} \qquad \text{------- (15)}$$

where m_{ii} are diagonal elements of the inverse matrix of the equation coefficients. The esd's are used as convergence criterion of the minimization process.

4. REFINEMENT GUIDELINES

4.1 Data Collection Strategy

It is essential to collect a good quality data prior to any refinement. The points that should be considered prior to data collection are the geometry of the diffractometer, the quality of the instrument alignment and calibration. For usual Bragg-Brentano geometries, it is important that the incident beam be kept on the sample at all angles to ensure a constant-volume condition. This is achieved by automatic divergence slits. For good counting statistics throughout an Xray powder diffraction pattern, more time should be spent on data collection at high angles where the intensities are lower. There should be at least five steps across the top of each peak (i.e. step size = FWHM/5, where FWHM is the full width at half-maximum), the time per step should approximately compensate for the gradual decline in intensity with 2θ. Another problem is that of sample transparency. The assumption for reflection geometry is that the sample is `infinitely thick' (i.e. the X-ray beam is totally absorbed by the sample).

4.2 Computer Programs

Several programs on Rietveld method have been written. Some programs are freely available whereas others are commercial. One of the earliest programme is DBWS [32]. Other robust programme includes GSAS [33], FULLPROF [34], RIETAN etc. These programs are available free of cost and can be downloaded from the corresponding sites. It has been shown that more information can be obtained on microstructure of the samples by introducing line broadening analysis into Rietveld method. The program MAUD [35] is very robust in this regard. It can be applied with ease for Structure Refinement as well as Microstructural Refinement.

For all the programs there is a common list of parameters. They are described as given below.

The general parameters which affect each phase are

Background parameters;

Intensity, position and width of the amorphous halos (if present);

Three parameters for peak width (U,V,W), the gaussianity of psuedo-Voigt function and parameters for asymmetry. All these parameters are fixed once a standard (Si standard) profile has been refined;

Sample displacement, absorption, transparency, beam divergence, These parameters are necessary to model some frequent errors influencing peak position;

The phase specific parameters for each phase are

Scale factor;

Lattice parameters;

Atomic positions and displacements;

Atomic occupation number;

Temperature factor (isotropic and anisotropic);

Preferred orientation parameters (March-Dollase, harmonic trexture, WIMV)

Crystallite sizes and microstrains along different crystallographic directions and their average values;

Intrinsic and extrinsic stacking faults and twin fault probabilities;

Antiphase boundary.

Prior to any fitting an input parameter file containing approximate values of the above parameters should be prepared. Once the parameter file is created and experimental data is loaded and the calculated XRD spectrum corresponding to the structure described by input parameters is synthesized.

To refine the microstructure, i.e. crystallite size and microstrain, the pattern of the instrumental standard must be refined first. This procedure is necessary to define the instrumental peak width, shape and asymmetry as a function of 2θ. However, if broadening effect is negligible, crystallite size and microstrain can be set zero so that the program can run using the usual Caglioti formula as other Rietveld refinement routines do. But if there is broadening we use various models to describe the trend of the profile width considering crystallite size and microstrain anisotropy. There are option for refinement of stacking and twin fault probabilities and texture, if needed in some programs.

The program generates an output file containing for each phase, volume or weight percentage, cell parameters, list of reflections including 'd' values, Miller indices, multiplicities, structure factors, intensities, crystallite sizes, microstrains and textures. The output files also contain the values of stacking and twin fault probabilities of the sample as a whole, if applicable. The quality of fitting can be checked from the quality factor GoF displayed after any iteration.

The basic features of some of the programs are described

Some of the most important features of applicability of FullProf [34] are summarised below:

- X-ray diffraction data: laboratory and synchrotron sources.
- Neutron diffraction data: Constant Wavelength (CW) and Time of Flight (TOF).
- One or two wavelengths (eventually with different profile parameters).
- The scattering variable may be 2θ in degrees, TOF in microseconds and Energy in KeV.
- Background: fixed, refinable, adaptable, or with Fourier filtering.
- Choice of peak shape for each phase: Gaussian, Lorentzian, modified Lorentzians, pseudo-Voigt, Pearson-VII, Thompson-Cox-Hastings (TCH) pseudo-Voigt, numerical, split pseudo-Voigt, convolution of a double exponential with a TCH pseudo-Voigt for TOF.
- Multi-phase (up to 16 phases).
- Preferred orientation: two functions available.
- Absorption correction for a different geometries. Micro-absorption correction for Bragg-Brentano set-up.
- Choice between three weighting schemes: standard least squares, maximum likelihood and unit weights.
- Choice between automatic generation of hkl and/or symmetry operators and file given by user.

- Magnetic structure refinement (crystallographic and spherical representation of the magnetic moments). Two methods: describing the magnetic structure in the magnetic unit cell of making use of the propagation vectors using the crystallographic cell. This second method is necessary for incommensurate magnetic structures.
- Automatic generation of reflections for an incommensurate structure with up to 24 propagation vectors. Refinement of propagation vectors in reciprocal lattice units.
- hkl-dependence of FWHM for strain and size effects.
- hkl-dependence of the position shifts of Bragg reflections for special kind of defects.
- Profile Matching. The full profile can be adjusted without prior knowledge of the structure (needs only good starting cell and profile parameters).
- Quantitative analysis without need of structure factor calculations.
- Chemical (distances and angles) and magnetic (magnetic moments) slack constraints. They can be generated automatically by the program.
- The instrumental resolution function (Voigt function) may be supplied in a file. A microstructural analysis is then performed.
- Form factor refinement of complex objects (plastic crystals).
- Structural or magnetic model could be supplied by an external subroutine for special purposes (rigid body TLS is the default, polymers, small angle scattering of amphifilic crystals, description of incommensurate structures in real direct space, etc).
- Single crystal data or integrated intensities can be used as observations (alone or in combination with a powder profile).
- Neutron (or X-rays) powder patterns can be mixed with integrated intensities of X-rays (or neutron) from single crystal or powder data.
- Full Multi-pattern capabilities. The user may mix several powder diffraction patterns (eventually heterogeneous: X-rays, TOF neutrons, etc.) with total control of the weighting scheme.
- Montecarlo/Simulated Annealing algorithms have been introduced to search the starting parameters of a structural problem using integrated intensity data.

Another very robust program is MAUD [35] which stands for Material Analysis Using Diffraction. It is a general diffraction/reflectivity analysis program mainly based on the Rietveld method. The main features of MAUD are

- Written in Java can run on Windows, MacOSX, Linux, Unix (needs Java VM 1.7 or later).
- Easy to use, every action is controlled by a GUI.

- Works with X-ray, synchrotron, Neutron, TOF and electrons.
- Developed for Rietveld analysis, simultaneous multi spectra and different instruments/techniques supported.
- Ab-initio structure solution integration, from peak finding, indexing to solving
- Different optimization algorithms available (Least Squares, Evolutionary, Simulated Annealing, Metadynamics, Simplex, Lamarckian…).
- Le Bail fitting.
- Quantitative phase analysis wizard.
- Microstructure analysis (size-strain, anisotropy, planar defects, turbostratic disorder and distributions included).
- Texture and residual stress analysis using part or full spectra.
- MEEM and superflip algorithm for Electron Density Maps and fitting.
- Thin film and multilayer aware; film thickness and absorption models.
- Reflectivity fitting by different models, from Parratt (Matrix) to Discrete Born Approximation.
- Fluorescence full pattern fitting based on crystal structure models (XRF and GIXRF full quantification).
- Works with TEM diffraction images and electron scattering.
- Several datafile input formats.
- Works with images from 2D detectors (image plates, CCDs, flat or curved), integration and calibration included.
- CIF compliance for input/output; import structures from databases.

5. SUMMARY AND CONCLUSION

In spite of the tremendous success of the method there seems to be one or two points which puts a question mark on the reliability of the method. The first conflict arises between the two classes of refinement parameters. The structural parameters depend on the integrated intensities of the profile parameters which depend primarily on the peak shapes and hence on the intensities at each step. Simultaneous refinement of both classes of parameters thus leads to open criticism as done by Cooper et al. [36] According to Cooper et al. Rietveld Method should be replaced by a two-stage procedure-profile parameters are refined in the first stage and the structural parameters in the second. In spite of this theoretical limitation, Rietveld Method appears to give reliable results for the structural parameters and reasonable estimates of the corresponding standard deviations. Another limitation which may be more serious is the anisotropic line broadening for imperfect crystalline materials arising out of the crystallite size and non-uniform microstrain effects. As a consequence the profile parameters do not vary smoothly with the diffraction vector. Most of the Rietveld Refinement programs which incorporates size-strain analysis is based Voigt specimen broadened profile and isotropic size strain behaviour and the Rietveld method thus need to be replaced by a two-stage procedure as suggested earlier. Incorporation of direction dependent broadening effect in the Rietveld method can thus provide a better insight into the structural parameters extracted from it.

The increasing complexity in the field of Materials Science, Crystallographic problems forces one to rethink the existing domains and earmarks the area of future developments in the Rietveld's method. It was shown by various workers that precision in the data is rarely a limiting factor in the precision of the structural results. The domain of the applicability of Rietveld method is increasing day by day. The main focus of Structure refinement in 1969 has now smeared out to a host of applications. Apart from the usual studies on "dead" samples - the field of standard powder crystallography, studies on "real" materials -non-equilibrium systems undergoing physical and/or chemical changes is gaining thrust. In brief Rietveld method is opening up the field of real-time crystallography. Another important area is the *ab-initio technique* for solving structures from powder data. Recent advances in both instrumentation and computational methods have brought us to the point where the powder method can easily compete with the single-crystal methods. Improved modeling on the instrumental front will certainly lead to physically significant characterizations of anisotropic crystallite-size and micro-strain, as well as crystal structure details. Finally in the computational area more faster and efficient algorithms will certainly lead to the improvement of the method.

Numerous computer software are available now-a-days some free others commercial to perform the Rietveld refinements. Thus it is fast becoming a global phenomenon started way back in 1969. The citation index of Rietveld's original method is increasing day-by-day. Finally a point of warning to the users as given by Prince, 'Estimated standard deviations are a measure of precision not accuracy'. So be aware of wrong models!

6. REFERENCES

General Reading

Young RA (Ed). The Rietveld Method. Oxford University Press: Washington DC; 1996.

Specific References

1. Rietveld HM. The crystal structure of some alkaline earth metal uranates of the type M_3UO_6. Acta Cryst. 1966; 20: 508-513.

2. Rietveld HM. A profile refinement method for nuclear and magnetic structures. J. Appl. Cryst. 1969; 2: 65-71.
3. Von Dreele RB, Larson AC. LANSCE Newsletter No. 4, Winter, Los Alamos National Laboratory, Los Alamos; 1988.
4. Baerlocher Ch. Proc. of the 6th International Zeolite Conf. Butterworth Scientific; 1984.
5. Warren BE. X-ray Diffraction. Reading MA. Addison-Wesley: New York; 1969.
6. Pawley GS. Unit-cell refinement from powder diffraction scans. J. Appl. Cryst. 1981; 14(6): 357-361.
7. Huang TC, Parrish W. Accurate and rapid reduction of experimental x-ray data. Appl. Phys. Lett. 1975; 27(3): 123-124.
8. Malmros G, Thomas JO. Least-squares structure refinement based on profile analysis of powder film intensity data measured on an automatic microdensitometer. J. Appl. Cryst. 1977; 10(1): 7-11.
9. Edwards HJ, Langford JI. A comparison between the variances of the Cu K_α and Fe K_α spectral distributions. J. Appl. Cryst. 1971; 4: 43-50.
10. Klug HP, Alexander LE. X-ray Diffraction Procedures. Wiley: New York; 1974.
11. Young RA, Wiles DB. Profile shape functions in Rietveld refinements. J. Appl. Cryst. 1982; 15: 430-438.
12. Caglioti G, Paoletti A, Ricci FP. Choice of collimators for a crystal spectrometer for neutron diffraction. Nucl. Instrum. 1958; 3 (4): 223-228.
13. Thompson P, Cox DE, Hastings JB. Rietveld refinement of Debye-Scherrer synchrotron X-ray data from $A1_2O_3$. J. Appl. Cryst. 1987; 20: 79–83.
14. Scherrer P. Determination of the internal structure and size of colloid particles by X-rays. Nachr. Ges. Wis. Gottingen. 1918; 2: 98-100.
15. Stokes AR, Wilson AJC. The diffraction of X rays by distorted crystal aggregates - I. Proc. Phys. Soc. 1944; 56(3): 174-181.
16. David WIF, Matthewan JC. Profile refinement of powder diffraction patterns using the Voigt function. J. Appl. Cryst. 1985; 18: 461-466.
17. Howard SA, Snyder RL. Mat. Sci. Res.; Symp. on Advances in Mat. Res. 1985; 19: 57-71.
18. Balzar D. Profile fitting of X-ray diffraction lines and Fourier analysis of broadening. J. Appl. Cryst. 1992; 25(5): 559-570.
19. Greaves C. Rietveld analysis of powder neutron diffraction data displaying anisotropic crystallite size broadening. J. Appl. Cryst. 1985; 18: 48-50.

20. Le Bail A. Global Analyze of Diffraction Spectra of Badly Crystallized Materials. Proc.10th Colloque Rayons X, Siemens, Grenoble, 1985; 45.
21. Lartigue C, Le Bail A, Percheron-Guegan A. A new study of the structure of $LaNi_5D_{6.7}$ using a modified Rietveld method for the refinement of neutron powder diffraction data. J. Les. Com. Met. 1987; 129: 65-76.
22. Lutterotti L, Scardi P. Simultaneous structure and size-strain refinement by Rietveld method. J. Appl. Cryst. 1990; 23(4): 246-252.
23. Taupin D. Automatic Peak Determination in X-ray Powder Patterns. J. Appl. Cryst. 1973; 6(4): 266-273.
24. Parrish W, Huang TC, Ayers GL. Profile fitting: A powerful method of computer X-ray instrumentation and analysis. Trans. Am. Cryst. Assoc. 1976; 12: 55-73.
25. Langford JI, Louer D, Sonneveld EJ, Visser JW. Application of Total Pattern Fitting to a Study of Crystallite Size and Strain in Zinc Oxide Powder. Powder Diffrac. 1986; 1(3): 211-221.
26. Toraya H. Whole-powder-pattern fitting without reference to a structural model: application to X-ray powder diffraction data. J. Appl. Cryst. 1986; 19(6): 440-447.
27. Dollase WA. Correction of intensities for preferred orientation in powder diffractometry: application of the March model. J. Appl. Cryst. 1986; 19: 267-272.
28. Young RA, Wiles DB. Profile shape functions in Rietveld refinements. J. Appl. Cryst. 1982; 15(4): 430-438.
29. Jorgensen JD, Beno MA, Hinks DG, Soderholm L, Volin KJ, Hitterman RL. Oxygen ordering and the orthorhombic-to-tetragonal phase transition in $YBa_2Cu_3O_{7-x}$. Phys. Rev. B. 1987; 36(7): 3608-3616.
30. Young RA, Sakthivel A. Bimodal distributions of profile-broadening effects in Rietveld refinement. J. Appl. Cryst. 1988; 21: 416-425.
31. De Boer GB, Sakthivel A, Cagle JR, Young RA. Determination of the antimony substitution site in calcium fluorapatite from powder X-ray diffraction data. Acta. Cryst. B. 1991; 47(5): 683-692.
32. Wiles DB, Young RA. A new computer program for Rietveld analysis of X-ray powder diffraction patterns. J. Appl. Cryst. 1981; 14: 149-151.
33. Larson AC, von Dreele RB. General Structure Analysis System (GSAS). Los Alamos National Laboratory Report; 2001.
34. Rodriguez- Carvajal J. Reference Guide for the computer program Fullprof. Laboratorie Leo Brillouin (CEA-CNRS): France; 1996.

35. Lutterotti L, Matthies S, Wenk HR. MAUD: a friendly Java program for Material Analysis Using Diffraction. IUCr. Newsl. CPD. 1999; 21: 14-15.
36. Cooper MJ, Rouse KD, Sakata M. An alternative to the Rietveld profile refinement method. Zeit. Kristall. 1981; 157(1-2): 101-117.