

# An Overview on Powder X-Ray Diffraction and Its Current Applications

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## Abstract

*Industries and research centres are continuously developing novel materials with light weight, higher strength and which can retain their properties at environmental temperatures. The cited properties mainly depend upon micro-structure and chemical composition of materials. Many research works focused to characterize the materials by different experiment techniques. Among them powder x-ray diffraction (XRD) is a most prominent, non-destructive technique used for investigation, characterization, and quality control of crystalline materials. Numerous fundamental XRD techniques and software packages are available for analyzing the crystal structure, crystallite size, degrees of crystallinity and other structural parameters of materials. In this work the brief description of XRD techniques employed in quantitative analysis and its current applications have been discussed.*

**Keywords:** XRD, crystal structures, crystallite size, degrees of crystallinity, quantitative analysis

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## INTRODUCTION

The micro-structure and chemical composition of crystalline materials are characterized by different experiment techniques such as scanning electron microscope (SEM), transmission electron microscope (TEM), dynamic light scattering (DLS), photon correlation spectroscopy (PCS), scanning probe microscope (SPM), neutron diffraction (ND), electron backscatter diffraction (EBSD), x-ray diffraction (XRD) and selected area electron diffraction (SAED). Powder x-ray diffraction is one of the primary analytical techniques employed in characterizing the crystalline, amorphous and thin film materials. XRD is a unique technique applicable in determining the crystal structure, crystalline phases, crystalline orientation and other structural properties such as crystallite size, lattice parameters, strain, stress, energy density, epitaxy, phase composition, preferred orientation, order-disorder transformation and thermal expansion. It can be also used to measure the thickness of thin films, multi-layers as well as to determine the atomic arrangement of solid materials [1].

In XRD analysis the powder sample is placed on a sample holder where a collimated x-ray

beam of known wavelength  $\lambda$  is illuminated. A scattered beam of similar wavelength of incident beam is diffracted at angle  $2\theta$  with respect to the lattice planes based on Bragg's law [2]. Bragg's law determines the relationship between the wavelength of x-ray ( $\lambda$ ), distance between the lattice planes ( $d$ ) and diffracted angle ( $\theta$ ) as described in the Eq. (1):  
$$n\lambda = 2d \sin\theta \quad (1)$$
Where;  $n$  is an integer which represents the order of reflections,

The XRD machine generates only intensity plot as a function of  $2\theta$ , identification of material is based on Bragg's law and miller indices ( $h k l$ ). Diffraction patterns recorded by XRD machine is like a "fingerprint" of crystalline materials, where it can be compared with standard patterns for identification of unknown materials. According to BCC research the global market for spectroscopy equipments were valued at \$8.5 billion in 2012 and is expected to grow at compound annual growth rate (CAGR) of 11.7% from 2012 to 2017 [3]. X-ray diffraction is one of the prominent spectrometry used for characterization of crystalline materials. The market of spectrometry is dominated in North America followed by Europe, Asia and rest of

the world. The global x-ray diffraction analytical market has been dominated by many companies such as Brucker AXS, PANalytic B.V, Thermo Fisher Scientifics, Rigaku, AMETEK etc., [4]. Besides, increasing investigation in the fields of solid state chemistry, material science, forensic science, pharmaceuticals and environmental science the demand for XRDs are growing further for research and development of advanced materials. In current scenario many software packages are developed on the basis of XRD techniques with ICDD database for profile fitting of diffraction data. The main objective of this work is to investigate the powder XRD techniques for identification and quantification of materials and its current applications.

### BRIEF DESCRIPTION OF TECHNIQUES AND SOFTWARE PACKAGES FOR QUANTITATIVE ANALYSIS OF SAMPLE

XRD analysis techniques and software packages are used for full-profile fitting of measured diffraction pattern with observed diffraction pattern. Numerous fundamental mathematical functions and softwares are employed in quantitative analysis of crystalline materials. Quantitative analysis usually involves determination of phase composition, lattice parameters, crystallite size and degree of crystallinity etc., of bulk, nano and thin film materials [5–6]. Among the available techniques for quantitative analysis of materials are the Scherrer's equation, Williamson-hall method, Rietveld refinement method, pseudo-Voigt function, Warren-Averbach analysis, direct comparison method, absorption-diffraction method and internal standard method [7–13]. In this present work three such techniques are explained in brief as follows:

#### Scherrer's Equation

The Scherrer's equation is used to estimate the nano-crystallite size more accurately using XRD. This equation was published by Scherrer in 1918 for calculation of the crystallite size of nano crystalline bulk materials as described in Eq. (2):

$$D = \frac{K \times \lambda}{\beta \times \cos\theta} \quad (2)$$

Where;  $D$  is the crystallite size,  $\lambda$  is the wavelength of x-ray beam,  $\theta$  is the diffraction angle,  $\beta$  (in radian) is the peak width (full

width at half maximum or integral breadth (IB)) after correcting with instrument broadening ( $\beta_{hkl}$ ) and  $K$  is the Scherrer's constant (0.9). According to Uvarov,  $K$  value depends upon the type of definition of peak's width, the crystallite size distribution, the crystalline shape and the indexes of diffraction line [7].  $K$  value actually varies from 0.62 and 2.08, in absence of crystalline shape information, it is accepted to use  $K$  as 0.89–1. The first definition of peak's breadth used in Scherrer's equation is the full width at half height of diffraction peak. The second definition of peak's width is an integral breadth, which is measured as the ratio of total area of diffraction peak by the maximum peak intensity of particular diffraction peak. Ahmad described that  $K=1$  when an integral breadth definition is used for calculation of crystallite size [8].

#### Williamson-Hall Analysis

Williamson-Hall (W-H) analysis is an X-ray peak broadening analysis and a simplified integral breadth method used to calculate the crystallite size and lattice strain of crystalline materials. The physical parameters such as strain, stress and energy density of crystalline materials are calculated by using the W-H analysis models, viz., uniform deformation model (UDM), uniform deformation stress model (UDSM) and uniform deformation energy density model (UDEDM) as represented in Eq. (3)–(5).

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta \quad (3)$$

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4 \frac{\sin\theta \sigma}{E_{hkl}} \quad (4)$$

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D} + 4 \sin\theta \left( \frac{2u}{E_{hkl}} \right)^{1/2} \quad (5)$$

Where;  $\varepsilon$  is the lattice strain,  $\sigma$  is the lattice stress,  $E_{hkl}$  is the Young's modulus in the perpendicular direction to the set of crystal lattice planes (hkl) and  $u$  is the energy density (energy per unit volume). According to Mote, the crystallite size obtained from UDM, UDSM and UDEDM are in good agreement with the values obtained by Scherrer's equation and TEM analysis [9].

#### Rietveld Refinement Analysis

The Rietveld refinement analysis is a full-profile fitting approach employed in

refinement of crystal structures using XRD [11–13]. This method is based on least-squares refinement fit between step-scan data of calculated XRD pattern and observed XRD pattern, the refinement procedure is continued until the best fit is obtained. The least-squares fitting method leads to minimal residual quantity  $S_y$  described in Eq. (6):

$$S_y = \sum_i W_i (y_{oi} - y_{ci})^2 \quad (6)$$

Where;  $y_{oi}$  = observed intensity at  $i^{\text{th}}$  step,  $y_{ci}$  = calculated intensity at  $i^{\text{th}}$  step and  $W_i = 1/y_{ci}$ .

The calculated profile of diffraction pattern can be described by Eq. (7):

$$y_{ci} = S \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) O_k A + y_{bi} \quad (7)$$

Where;  $S$  is the scale factor,  $K$  is the miller indices (hkl) of diffracted peaks,  $L_k$  contains the polarization, Lorentz and multiplicity factors,  $\phi$  is the reflection profile function,  $O_k$  is the preferred orientation function,  $A$  is the absorption factor,  $F_k$  is the structure factor for the  $K^{\text{th}}$  Bragg reflection and  $y_{bi}$  is the background intensity at  $i^{\text{th}}$  step.

The fitting quality of diffraction pattern can be estimated by using  $R_{wp}$  factor that is measured by the following Eq. (8):

$$R_{wp} = \frac{\sum_{i=1,n} w_i |y_{oi} - y_{ci}|^2}{\sum_{i=1,n} w_i y_{oi}^2} \quad (8)$$

According to AL-Dhahir, the Rietveld refinement has numerous advantages compared with other x-ray diffraction method such as having better accuracy, no need of additional internal standards/pure-phase standards for the Rietveld method analysis [12].

### Computer-Based Expert Systems

The peak indexing and refinement of crystal structures of diffraction data are carried out using the commercial/freeware software packages such as International centre for diffraction data (ICDD) in the name of PDF 4+, EVA, PCW, TOPAS, Win-XRD, Crystal Diffract, X'Pert High Score, DAJUST\_Software, MAUD, FullProfSuite, MATCH Software and Reflex Plus software package etc. The ICDD is a non-profit scientific institute dedicated in collecting, editing, publishing and distributing powder diffraction data in the name of PDF (powder diffraction file) for quantitative analysis of

solid state materials. Today about 291,440 inorganic, 34,212 mineral and 370,844 inorganic standard diffraction patterns have been collected and stored in PDF database by ICDD. The above mentioned software packages allows the application of the Rietveld refinement method, pseudo-Voigt functions and fundamental parameters approach (FPA) for full-profile fitting of diffraction data. It also makes use of Williamson-Hall method and the Scherrer's equation for the calculation of crystallite size.

## CURRENT APPLICATIONS OF POWDER X-RAY DIFFRACTION

Most recent applications of powder x-ray diffraction are as follows [13]:

### Mineralogy

Powder XRD is a primary technique used by mineralogist and geologist to identify minerals - in museums, mineral and mining industries etc., According to Post, powder XRD is a non-destructive techniques used for quantitative analysis of birnessite, a manganese oxide with layer structure present in many soils [14].

### Space Exploration

Bish described that recently NASA sent a miniaturized XRD instrument to the MARS planet named as CheMin, which is employed in analyzing the soils and rocks on Mars surface and it has sent a diffraction data which unravels that the sample contains clay minerals and amorphous materials [15].

### Energy Storage Materials

Powder XRD and the Rietveld refinement methods are used in investigating MOF74 sorbents which is an efficient solid storage and capture materials [16].

### Pharmaceuticals

Powder x-ray diffraction is a prominent technique used in the field of pharmaceuticals in analysis and discovery of drugs. XRD played a major role in discovery of Atomoxetine drug used for the treatment of attention deficit hyperactivity disorder (ADHD) [17].

### Construction

Powder XRD is used to examine the cement-phases, atomic structures for optimal use in

construction. XRD allows for analyzing and monitoring the composition of cement during production [18].

### Superconductors

Powder XRD is used to characterize the purity in the synthesis of superconducting materials. Many new superconductors such as Hg-based superconductor materials are developed by the application of XRD and Rietveld refinement. According to Antipov, power XRD is used in refinement of  $\text{Bi}_2 \text{Sr}_2 \text{Eu}_{1.3} \text{Ce}_{0.7} \text{Cu}_2 \text{O}_{10.17}$  structure [19].

### Nano-Composites

Using XRD, researchers can follow the process involved in manufacturing of nanocomposites, determine composition of nanocomponents and can predict the performance of nanocomposites in different environmental conditions. XRD is used to determine the interlayer distance and intercalation or exfoliation in lattice structure. For example, XRD is applicable in quantitative analysis of graphite oxide based nanocomposites [20].

### Art, Archaeology and Cultural Heritage

Powder x-ray diffraction plays a key in the analysis of art and museum objects. Corbeil found the x-ray diffraction is most applicable technique in the study of art and museum objects [21].

### Forensic Science

Powder XRD is a non-contact; non-destructive versatile techniques used in the field of forensic science to qualitatively and quantitatively analyze the organic, inorganic and metallic materials. A major example of its value is in the analysis and identification of street narcotics seizures, adulterants, drugs etc. [22].

### Polymers

Powder diffraction is a very sensitive method used in the fields of polymers to determine the crystalline structure, degrees of crystallinity, molecular weight, packing density and chemical composition. Fawcett described that XRD is used in characterizing the cellulose materials and to study the changes at molecular level for production or quality control of polymer materials [23].

## CONCLUSION

Powder x-ray diffraction is a most significant characterization tool applicable in quick analysis of single crystal, polycrystalline and amorphous materials. The diffracted pattern recorded by XRD machine is like a fingerprint of atomic structures used for identification and characterization of material. Many software packages and XRD techniques are available for quantitative analysis of materials.

XRD finds many applications in the fields of solid state chemistry and material science in development of advanced materials, it can also be ideal with *in-situ* studies. Thus, x-ray diffraction is a powerful technique used to examine physico-chemical properties of unknown materials. However, XRD techniques need to be developed for analysis of mixed-layer clay minerals and pure amorphous materials.

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