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### **X-ray Diffraction for Characterization of Nanomaterials**

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#### **ABSTRACT:**

The purpose of this paper to give an idea about X-ray diffraction techniques that is used for characterization of nanomaterials. X-ray diffraction techniques are a very powerful characterization tool to study, non-destructively, the crystallographic structure, chemical composition and physical properties of materials and thin films etc. It should also be used to measure various structural properties of these crystalline phases such as strain, grain size, phase composition, and defect structure. XRD is also used to determine the thickness of thin films, as well as the atomic arrangements in amorphous materials such as polymers. This review reports the importance of X-ray diffraction technique for the characterization of nano bmaterials.

**KEYWORDS:** X-Ray diffraction, Nanomaterials, crystalline solid

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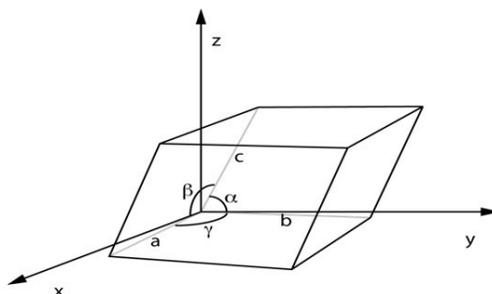
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## INTRODUCTION

We know solid matters are of two types: amorphous and crystalline. In an amorphous solid the atoms are arranged in an irregular way (e.g glass). But in a crystalline solid the atoms are arranged in a regular way and there is a smallest volume element (called unit cell) that, by repetition in three dimensions, can describe the crystal. The dimensions of this unit cell can be described by three axes namely:  $a$ ,  $b$  and  $c$  and the angles between the axis are  $\alpha$ ,  $\beta$  and  $\gamma$ . A schematic diagram of the unit cell is given in Figure 1.



**Figure 1: A unit cell from a 3D lattice**

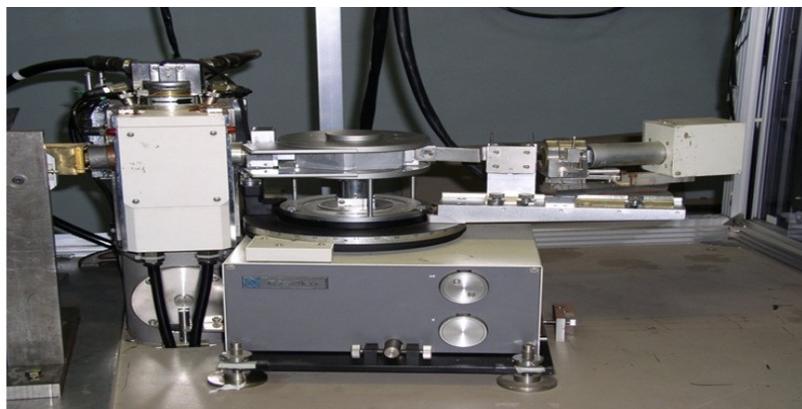
About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. Today about 893,400+ inorganic and organic single components, crystalline phases and diffraction patterns have been collected and stored on magnetic or optical media as standards. International Center Diffraction Data (ICDD) or formerly known as (JCPDS) Joint Committee on Powder Diffraction Standards is the organization that maintains the data base of inorganic and organic spectra's. The data base is available from the Diffraction equipment manufacturers or from ICDD direct. The set number is incremented every calendar year and the sequence number starts from 1 for every year. The yearly release of the data base is available in September of each year.

There are several methods available for characterization for nanomaterials such as electron microscopy, the various scanning microscopy methods, IR-, UV-, or FTIR-spectroscopy, NMR, EPR, or MS. But X-ray diffraction and scattering are considered important due to two essential reasons- (i) X-ray diffraction is virtually non-destructive and (ii) X-ray photons with a wavelength in the nm range are the ideal sensor for the nanocosmos. X-ray diffraction offers a number of different dedicated methods to investigate nano- structures-(i) X-ray Reflectometry (XRR) determines layer thickness, roughness, and density (ii) High-Resolution X-ray Diffraction (HRXRD) helps to verify layer thickness, roughness, chemical composition, lattice spacing and mismatches, relaxation, etc. (iii) X-ray diffuse scattering to determine lateral and transversal

correlations, distortions, density, and porosity (iv) in-plane grazing incidence diffraction (IP-GID) to study lateral correlations of thinnest organic and inorganic layers, and depth profiling (v) Small Angle X-ray Scattering (SAXS) in transmission or grazing incidence SAXS (GI-SAXS) in reflection to determine the size, the shape, the distribution, orientation, and correlation of Nanoparticles(NPs) present in solids or solutions.

## **PRINCIPLE AND BACKGROUND**

X-ray diffraction (XRD) is a powerful method for the study of nanomaterials. The wavelength of X-rays is on the atomic scale ( $0.1 \text{ \AA}$  to  $100 \text{ \AA}$ ), so X-ray diffraction (XRD) is a primary tool for finding structure of nanomaterials. XRD offers unparalleled accuracy in the measurement of atomic spacing and for determining strain states in thin films. Intensities measured with XRD can provide quantitative and accurate information on the atomic arrangements at interfaces. With lab-based equipment, surface sensitivities down to a thickness of  $\sim 50 \text{ \AA}$  are achievable. XRD is non contact and non-destructive, which makes it ideal for in situ studies. Nanomaterials have a characteristic microstructure length comparable with the critical length scales of physical phenomena, giving them unique mechanical, optical and electronic properties. X-ray diffractograms of nanomaterials provide a wealth of information - from phase composition to crystallite size, from lattice strain to crystallographic orientation. The main use of powder diffraction is to identify components in a sample by a search/match procedure. The areas under the peak are related to the amount of each phase present in the sample. The powder diffraction method is ideally suited for characterization and identification of polycrystalline phases.



**Figure 2 : X-ray Diffract meter with rotating anode X-ray Generator**

A powder XRD instrumentation consists of four main components-(i) X-ray source (ii) specimen stage (iii) receiving optics and (iv) X-ray detector as shown in figure 2. The source and detector with its associated optics lie on the circumference of a focusing circle and the sample stage at the center of the circle. X-ray diffractions are explained with the help of Bragg's law. With this law

it is possible to make accurate quantifications of experimental results in the determination of crystal structures. The angle between the plane of the specimen and the X-ray source is  $\theta$ , known as Bragg's angle and the angle between the projection of X-ray and the detector is  $2\theta$ . For the XRD analysis, fine powder samples were mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites. When a beam of X-ray is incident on the sample, X-rays are scattered by the atoms present in the sample. If the scattered beams are in phase, these interfere constructively and one gets the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as 'reflecting planes'.

## THEORETICAL ANALYSIS OF XRD

The basic features of an X-ray diffractometer are shown in figure 3 where  $2\theta$  (diffraction angle) is the angle between the incident and diffracted X-rays. A typical diffraction spectrum is a plot of reflected intensities versus the detected angle  $2\theta$ . The  $2\theta$  values of the peak depend on the wavelength of the anode material of the X-ray tube. By choosing the right anode and energy of accelerated electrons, a known wavelength and therefore a known energy of X-rays will be generated. Copper X-ray tubes are most commonly used for X-ray diffraction of inorganic materials. For practical applications of X-ray diffraction, we typically want to use x-rays of a single wavelength, i.e. monochromatic radiation to improve experimental results. In general,  $K_\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ) is used for analytical work while all other radiation ( $K_\beta$ , etc.) are removed by means of a nickel filter.

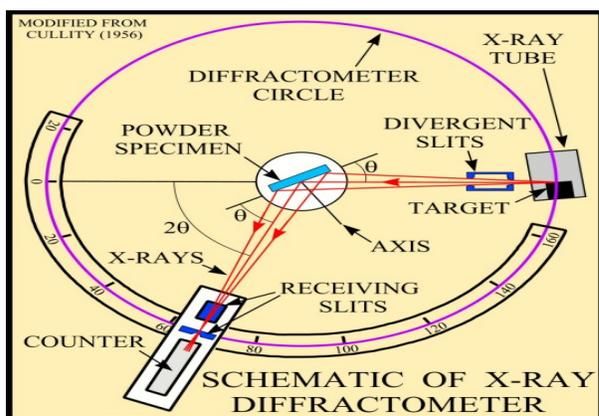


Figure 3: Basic features of X ray diffract meter

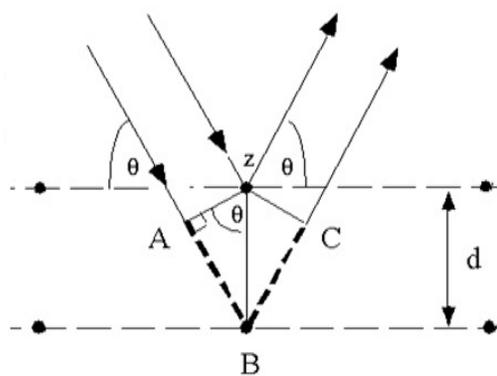


Figure 4: Bragg's Law

The angle between the transmitted and diffracted beams will always be equal to  $2\theta$ . This angle is readily obtained in experimental situations and the results of X-ray diffraction are therefore given in terms of  $2\theta$ . It is however very important to remember that the angle that is used in the Bragg's equation must correspond to the angle between the incident radiation and the diffracting plane, i.e.  $\theta$ .<sup>1</sup>

In case of first order diffraction,  $n=1$ , and knowing  $\theta$  and  $\lambda$ , one can calculate the interplanar spacing  $d$ -value for a particular plane. Fig.5 shows the information we can get from an idealized diffraction pattern. The first step of X-ray diffraction pattern involves the indexing of XRD peaks. The indexing means assigning the correct Miller indices to each peak of the diffraction pattern. There are three main methods for indexing a diffraction pattern- (i) comparing the measured XRD pattern with the standard data base (JCPDS-cards) (ii) analytical methods (iii) graphical methods. The intensity of the diffraction signal is usually plotted against the diffraction angle  $2\theta$  [indegree], but  $d$  [nm] or  $1/d$  [nm<sup>-1</sup>] may also be used.

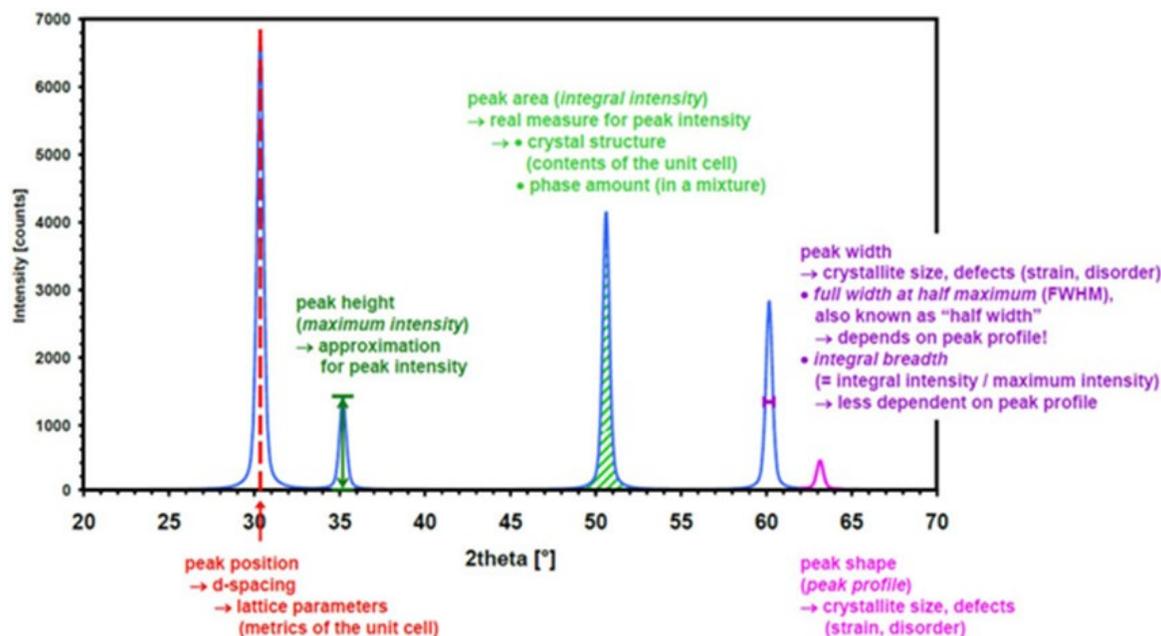


Figure 5: Information content of an idealized diffraction pattern

P. Scherrer' showed that, when parallel monochromatic radiation falls on a random oriented mass of crystals, the diffracted beam is broadened when the particle size is small. Thus the line broadening can be a measure of the average size of the crystallites by using the Scherrer formula.<sup>2</sup>

$$D_v = K \lambda / \beta \cos\theta \quad (2)$$

Where;  $D_v$  is the average particle size,  $\lambda$  is wave length of the radiation and  $\beta$  is the FWHM (full width at half maximum) of the reflection peak that has the same maximum intensity in the diffraction pattern (integral breadth of the peak located at angle  $\theta$ ).

$K$  is the Scherrer constant. The Scherrer constant ( $K$ ) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9.<sup>3</sup> The size obtained from the Scherrer formula yields the apparent or average particle-size for a material. Powders of materials are generally aggregates of smaller particles, and thus consist of a distribution of particle sizes.

The Debye Scherrer equation has some limitations. The value of the constant K used in the equation changes with the shape of the particles. It does not take into account the existence of a distribution of sizes and the presence of defects in the crystalline lattice. Therefore, the calculation of diameter of grain from FWHM of the peak can over estimate the real value since the larger grains give strong contribution to the intensity, while the smaller grains the base of the peak. Moreover, the presence of defects in a significant amount causes an additional enlargement of the diffraction line. These problems can be overcome by measuring the particle size by TEM and SEM.

Heat treatment causes particles to anneal and form larger grains, thereby increasing the degree of crystalline of the sample. This effect is often seen as increased peak intensity in the diffraction data. Heat treatment of samples provides an opportunity to compare diffraction patterns of nanoparticles and bulk materials, thereby seeing how the shape and intensity of peaks change between samples of various particle sizes.<sup>4</sup>

There are some important differences between the diffraction patterns of nano and bulk materials. Nano materials have small particle size and this causes the lines in their diffraction peak to broaden. The broadening of the peak is due to a small number of crystal planes. This broadening in turn causes a loss of intensity in the signal of their diffraction patterns. Bulk materials, on the other hand, have sharp, narrow and high-intensity peaks.

## **APPLICATIONS**

**Particle identification:** The most common use of powder (polycrystalline) diffraction is chemical analysis. This can include phase identification (search/match), investigation of high/low temperature phases, solid solutions and determinations of unit cell parameters of new materials. Each different crystalline solid has a unique X-ray diffraction pattern which acts like a “fingerprint”. Phases with same chemical composition have different XRD pattern

### **Polymer crystallinity:**

Polymers are partly crystalline and partly amorphous. The crystalline parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo). The ratio between these intensities can be used to calculate the amount of crystalline in the material.

### **Residual stress:**

The deformation per unit length is called strain. Residual stress is the stress that remains in the material after the external force that caused the stress has been removed. Stress is defined as force per unit area. Positive values indicate tensile (expansion) stress; negative values indicate a compressive state. The residual stress can be introduced by any mechanical, chemical or thermal process, e.g. machining, plating and welding. The principals of stress analysis by the X-ray diffraction is based on measuring angular lattice strain distributions. Here we choose a reflection at

high  $2\theta$  and measure the change in the d-spacing with different orientations of the sample. Using Hooke's law the stress can be calculated from the strain distribution.<sup>5</sup>

### **Texture analysis:**

The determination of the preferred orientation of the crystallites in polycrystalline aggregates is referred to as texture analysis. The preferred orientation is described in terms of pole figures. The most common representation of the pole figures is stereographic or equal area projections. The intensity of a given reflection (h,k,l) is proportional to the number of h, k, l planes in reflecting condition (Bragg's law). Hence, the pole figure gives the probability of finding a given crystal-plane- normal as function of the specimen orientation. If the crystallites in the sample have a random orientation the recorded intensity will be uniform.

### **CONCLUSIONS**

XRD is the main method for crystallographic characterization for bulk, nano and thin film materials. The diffraction patterns observed in XRD is like a finger print of the crystal structure. It is a powerful and rapid technique for identification of an unknown material. It provides an unambiguous phase determination. It requires minimal sample preparation. XRD units are widely available. The Data interpretation is relatively straight forward and easy to understand. This is a very good method to identify homogeneous and single phase material.

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