

# X-ray diffraction: a powerful method of characterizing nanomaterials

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## Abstract

X-ray diffraction techniques are a very useful characterization tool to study, non-destructively, the crystallographic structure, chemical composition and physical properties of materials and thin films. It can 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 paper reports the importance of X-ray diffraction technique for the characterization of nanomaterials.

**Keywords:** X-Ray diffraction, Nanomaterials, crystal

## INTRODUCTION

Solid matter consists out of two types of material: amorphous and crystalline. In an amorphous sample the atoms are arranged in a random way, glasses are an example of amorphous materials. In a crystalline sample the atoms are arranged in a regular or ordered pattern and there is a smallest volume element that, by repetition in three dimensions, can describe the crystal. This smallest volume element is called a unit cell. 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.

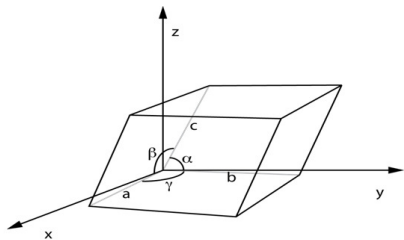


Fig 1. A unit cell from a three dimensional lattice

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 50,000 inorganic and 25,000 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 data base format consists of a set number and a sequence number. 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.

Besides methods such as electron microscopy, the various scanning microscopy methods, IR-, UV-, or FTIR-spectroscopy,

NMR, EPR, or MS, X-ray diffraction and scattering are considered important due to two essential reasons: X-ray diffraction is virtually non-destructive, and 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: X-ray Reflectometry (XRR) determines layer thickness, roughness, and density; High-Resolution X-ray Diffraction (HRXRD) helps to verify layer thickness, roughness, chemical composition, lattice spacing and mismatches, relaxation, etc.; X-ray diffuse scattering to determine lateral and transversal correlations, distortions, density, and porosity; in-plane grazing incidence diffraction (IP-GID) to study lateral correlations of thinnest organic and inorganic layers, and depth profiling; 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 nano-particles present in solids or solutions.

## Background

X-ray diffraction (XRD) is a powerful method for the study of nanomaterials (materials with structural features of at least one dimension in the range of 1-100 nm). The wavelength of X-rays is on the atomic scale, so X-ray diffraction (XRD) is a primary tool for probing structure of nano-materials. XRD offers unparalleled accuracy in the measurement of atomic spacing and is the technique of choice for determining strain states in thin films. The intensities measured with XRD can provide quantitative, 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, but synchrotron radiation allows the characterization of much thinner films and for many materials, monoatomic layers can be analyzed.

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. Furthermore, the areas under the peak are related to the amount of each phase present in the sample. In 1919 A.W.Hull gave a paper titled, "A New Method of Chemical Analysis". Here he pointed out that "... every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others. "The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases.

## Experimental Arrangements

In X-ray diffraction work we normally distinguish between single crystal and polycrystalline or powder applications. The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. Powder diffraction is mainly used for various solid materials, e.g. asbestos, quartz. In powder or polycrystalline diffraction it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample down to particles of about 0.002 mm to 0.005 mm cross section. The ideal sample is homogeneous and the crystallites are randomly distributed. The sample is pressed into a sample holder so that we have a smooth flat surface.

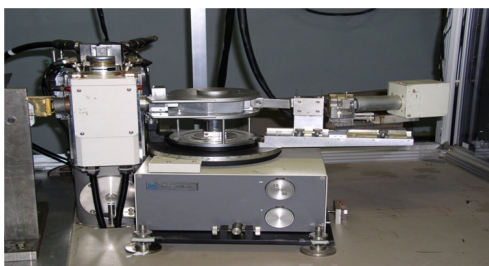


Fig 2. X-ray Diffractometer with rotating anode X-ray Generator

A typical powder XRD instrumentation consist of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector as shown in fig.2. The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the center of the circle. Bragg's law is the basis of XRD analysis. 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 each atom 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 Principles

Figure 3 shows the basic features of an X-ray diffractometer,

in which the diffraction angle  $2\theta$  is the angle between the incident and diffracted X-rays. A typical diffraction spectrum consists of 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 is used for analytical work while all other radiation (K $\beta$ , etc.) are removed by means of a nickel filter.

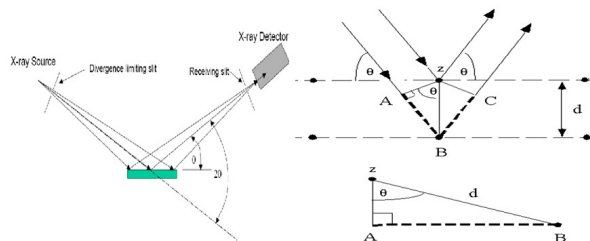


Fig 3. Basic features of an X-ray diffractometer

Fig 4. Bragg's law

The lattice planes in the simple crystal in Figure 4 are separated by a distance  $d$ . The Bragg's law relates the wavelength ( $\lambda$ ) of the reflected X-ray, the spacing between the atomic planes ( $d$ ) and the angle of diffraction ( $\theta$ ) as follows:

$$2d \sin \theta = n \lambda \quad (1)$$

The angle between the transmitted and diffracted beams will always be equal to  $2\theta$ . This angle can be obtained readily 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.  $\theta$  [1].

For the 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  $2\theta$  [ $^\circ$ ], but  $d$  [nm] or  $1/d$  [nm $^{-1}$ ] may also be used. The most common wavelength used in XRD is 1.54  $\text{Å}$  (Cu K $\alpha$ ).

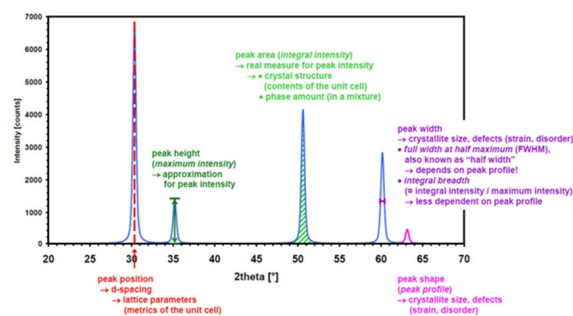


Fig 5. Information content of an idealized diffraction pattern

The line broadening can be a measure of the average size of the crystallites by using the Scherrer formula (2).

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

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 [3]. 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 few limitations. The value of the constant 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 crystallinity 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 [4].

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 contrary, have sharp, narrow and high-intensity peaks.

## APPLICATIONS

The most traditional use of XRD is:

**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 patterns

**Polymer crystallinity:** A polymer can be considered partly crystalline and partly amorphous. The crystalline domains act as a reinforcing grid (like the iron framework in concrete), and improves the performance over a wide range of temperature. However, too much crystallinity causes brittleness. 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 crystallinity in the material.

**Residual stress:** 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 deformation per unit length is called strain. 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. That is, 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.

**Texture analysis:** The determination of the preferred orientation of the crystallites in polycrystalline aggregates is referred to as texture analysis, and the term texture is used as a broad synonym for preferred crystallographic orientation in the polycrystalline material, normally a single phase. The preferred orientation is usually described in terms of polefigures. The most common representation of the polefigures 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 polefigure 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 pattern is like a finger print of the crystal structure. It is a powerful and rapid technique for identification of an unknown material. In most cases, it provides an unambiguous phase determination. It requires minimal sample preparation. XRD units are widely available. The Data interpretation is relatively straight forward. It is a very good method to identify homogeneous and single phase material.

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