

# X- RAY DIFFRACTION

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**Abstract:** For determining the behaviour of material, the most important concept that we have to understand is its structure. Here, we have discussed how we calculate the dimensions of unit cell through which we have easily understand the internal structure of crystals. X-rd diffraction method is mostly used for analysing the crystals. Out of various method of X-rd, here we have explained only an easy and reliable powder method and factors which generally affect the peak of X-rd. Effect of stress, strain and temperature on peaks position and intensity.

## I. INTRODUCTION

The internal structure of the crystal i.e. the arrangement of the molecule and atoms inside the crystal can be enquired by X-ray diffraction. When we pass X-rays through the crystal they generally formed an interference pattern that can be express on the film and used to examined the structure inside the crystal. X-rays diffraction method is readily available and powerful and one of most important tool of solid state chemistry for determining atomic arrangement in crystal. When X-ray beam fall on the crystal, scattered radiation is produced by all the atoms present in the crystal. These scattered waves are spread out spherically and the interference effect is observed. The intensity of the scattered radiation usually shows a maxima and minima in different direction. This important concept was firstly given by Van Laue in 1912 and later tested by Friedrich and Knipping. Such type of study is possible only because of the fact that both intensities of diffracted beam and their direction are directly related to the arrangement of atoms inside the crystal. Therefore the intensity measurement and direction would give us the reliable information of the crystal.

In XRD Where X-rays are the electromagnetic waves of short wavelength of about  $1\text{\AA}$  to  $10\text{\AA}$  and it is an ordinary light having a very high energy, as we know energy of e.m waves are directly proportional to the frequency that's why frequency of X-rays are also greater. X-rays have more energy and penetrating power than light waves . Having high energy , X-rays can pass through the objects easily that ordinary light waves can't . These rays travel with the speed of light in straight lines. Wavelength of X-rays is 1000 times shorter than ordinary light. Now, Diffraction is being defined as the bending of X-rays around the corners of an obstacle. All the longitudinal & transverses waves & sound waves show diffraction.

Condition for diffraction of waves:

- 1.) Size of aperture and size of the obstacle should be comparable to the wavelength of wave for diffraction to occur.
- 2.) In diffraction grating we should use 'n' number of slits.
- 3.) Gratings are used for optical light  $4000\text{\AA}$  -  $7000\text{\AA}$  i.e. ( $0.4\mu\text{m}$  –  $0.7\mu\text{m}$ ).
- 4.) Grating can't diffract X-rays because X-rays have very small wavelength and such a fine grating is not available.
- 5.) If we incident some X-rays on crystal then it will be diffracted from atomic planes because crystal is made up by placing atomic planes.
- 6.) By one plane  $10^{-3}$ -  $10^{-5\text{th}}$  part of X-ray is diffracted so to diffract X-ray, we need  $10^3$ -  $10^5$  planes.

## II. Crystal Structure

A crystal structure is obtained simply by connecting the network of lattice points in space.

“Basis is the assembly of atoms, ions or molecules which when repeated in three dimensions generates a crystal structure.

Crystal Structure = Space lattice + Basis

There are five Bravais lattice types in 2-D, i.e., oblique, square, hexagonal, primitive rectangular and centred rectangular.

### III. Importance of Index system

To enquire the internal structure of crystals, we have to specify planes and its direction. For this purpose Miller devised a system which is known as Miller indices. The indices determined by the following rule:

- Firstly, determine the intercepts on the axes in terms of the lattice constants  $a_1$ ,  $a_2$ ,  $a_3$ . The axes should be primitive or non-primitive cell.
- Secondly, Take the reciprocals of these three intercepts and then reduce these three integers to the same ratio, generally with the integer which is smallest. The results should be enclosed in parentheses (h k l), is known as the index of the plane.
- Suppose the plane intercepts the A, B, C axes at 4A, 1B, 1C. The reciprocals of above three numbers are,  $\frac{1}{4}, \frac{1}{1}, 1$ . The smallest three integers having the same ratio are (114).
- If a plane is parallel to a coordinate axis then the intercept of the plane is infinity and hence index is zero.

### IV. X-Ray Diffraction

X-ray provide the answer of most common question that can ask of a material is simply ‘What is it?’.

X-ray diffraction method is primarily used to identify phase of crystalline material and provides knowledge of unit cell dimension. The unknown material should be finely ground, homogeneous in nature. Each crystalline material gives a unique pattern; the same crystal always show the same kind of pattern and in a mixture

of crystalline material each crystalline produce its unique pattern which is independent from each other.

In a common way we can understand that, X-ray pattern of any crystal is like a fingerprint of that crystal.

XRD laboratory based technique is commonly used for determining the atomic structure and dimensions of unit cell. When X-rays interact with the crystalline material, rays get diffracted in to different directions. A crystallographer provide a 3D picture of electrons density inside the crystal, by calculating the angles and measuring intensity of diffracted rays. By analyzing the electrons density, we can easily determine the average position of atoms inside the crystal as well as the type of chemical bonds, their disorder and numerous other information about the crystal. Because the wavelength of X-rays is of the same order as that of atomic nuclei in solids, e.g. 4Å (bond are roughly 1.5 – 2.5Å). It is like a waves fit nicely and snugly between the atoms and “fill” the crystal and thereby give us the information about “cavities” inside the crystal and thus by reciprocal analysis, we can determine where the “rigid” stuff of atoms.

### V. Diffraction of Waves by Crystals

#### BRAGG LAW

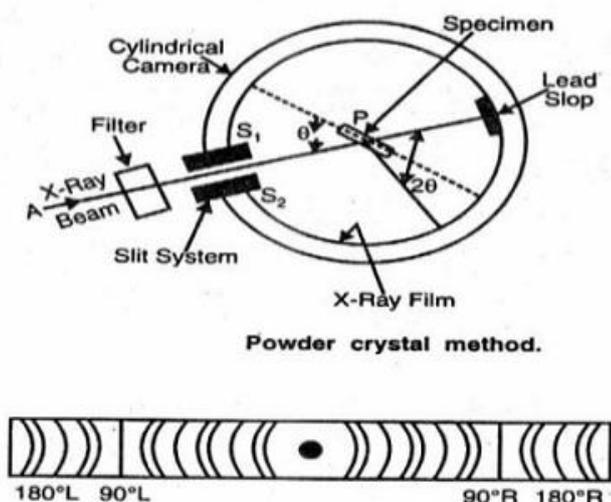
W.L. Bragg explained the concept of the diffraction of beam from a crystal in a simple way. Suppose the waves are incident on the atomic planes and it gets reflected from the parallel planes in the crystal, entire planes within the crystal reflect only a small part of radiation. When constructively reflections from parallel planes of atoms interfere then diffracted beam are obtained. Radiation are constructively interfere from consecutive planes, when the path difference is an integral multiple of wavelength ( $\lambda$ ),

$$2d\sin\theta = n\lambda$$

This is called Bragg’s law, which can be satisfied only for wavelength  $\lambda \leq 2d$ .

## VI. POWDER METHOD

This method is mainly used for those substances which cannot be obtained in the form of perfect crystals. In this method atoms of individual crystallites are randomly oriented in different directions. This method was given by Debye and Scherrer. In experimental arrangement, a cylindrical camera is fitted with photographic film and powdered form of sample should be considered in this method. This powdered sample should be placed in a movable mount at the center of the camera as shown below.



Whenever the collimated beam of monochromatic X-rays strikes on the powdered sample which consists of large number of small crystals. Always there will be possibility that some of the crystals are oriented in such way that they satisfy Bragg's equation. The diffracted rays will form a cone which is concentric with original beam and form a semi-vertical angle  $2\theta$ , where  $\theta$  is the Bragg's angle. It had been observed that whenever the rays are diffracted through small angles, we get arcs around the central spot on the film. When the rays are diffracted through  $90^\circ$ , the cones become flat and a straight line is observed. At  $180^\circ$ , the curvature is reversed and it is nearly circular in shape. Mostly, powder method will be preferred as compared to other methods, because in this each phase of crystals get diffracted by x-ray beam and produce a unique diffraction pattern.

### A. Peak Profile Analysis in X-ray Diffraction

Now we analyse the x-ray diffraction pattern of crystal, that we have observed from any of the

above method. When we plot a graph between intensity(counts) and Bragg's angle( $2\theta$ ).

The information that we gathered are as follows:

a) Peak position: It gives us knowledge about d-spacing between planes of crystal and determine the lattice parameters.

$$\text{For cubic crystal (a=b=c), } d = \frac{a}{\sqrt{(h^2+k^2+l^2)}}$$

Where d is interplaning distance,

a,b,c are lattice parameters of plane (h,k,l).

b) Peak height (=max. intensity): It give us approximate knowledge about peak intensity.

c) Peak area(=integral intensity): It helps in determining the crystal structure (contents of unit cell), amount of phase present in crystal(in a phase mixture) and it is a real measure of peak intensity.

d) Peak width : It helps in determining the crystallite size, defects(strain,disorder) by knowing full width at half maxima(FWHM). using scherre's formula which is given by:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where 'D' is crystalline size.

' $\lambda$ ' is wavelength of x-ray beam incident on crystal.

'k' is constant i.e. 0.92 .

' $\beta$ ' is full width at half maxima(FWHM).

' $\theta$ ' is Bragg's angle.

### B. Factors which effects the peak profile:

Sometimes when we plot peaks, a shift and broadening in peaks has been observed. This shift and broadening in peak give us information about the forces acting on the crystal, if there is any impurity in the crystal or not.

Following are the factors which effects peak profile:

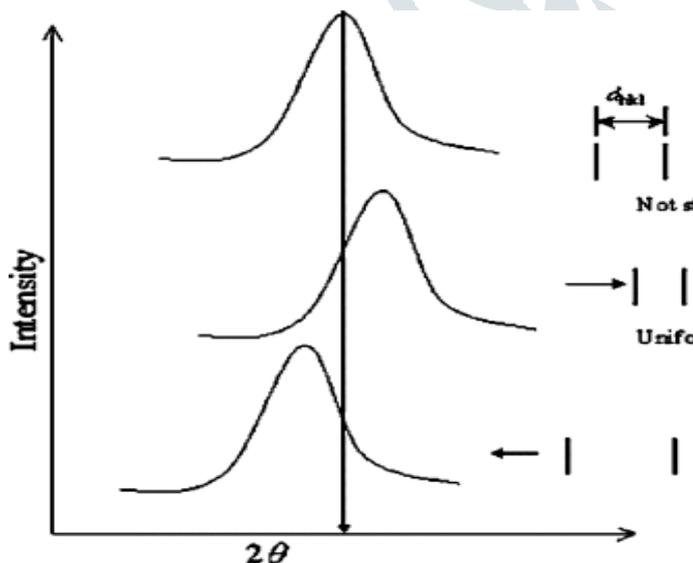
- instrumental error
- sample error ( like in x-ray powder diffraction method, sample is not in purely powder form)
- Stress: When we apply a stress on a body then internally a force of reaction comes in to play to resist body for undergoing further deformation and tending to restore the body to its original condition. The restoring or the recovering force per unit area set up inside the body is called stresses.
- By hooke's law, Stress  $\propto$  Strain
- Strain is defined as response of any system to an applied stress.

$$\text{Stress} = \frac{\text{force}}{\text{Area}}$$

Two types of stresses can be identified:

- Microstress : vary from one grain to another or from one part of the grain to another part, on a macroscopic scale.
- Macrostress : the stress may be quit uniform over large distances.

### C. Lattice strain effects on peaks position and widths :



From the above graph we can determine the effect of stress (strain) on crystals.

- First peak is for the pure crystal when there is no external force is applied.

- Second peak is for the crystal on which external force (i.e. strain) is applied and the crystal gets uniform compression (i.e. inter-planar distance decreases) which causes shift in peak towards right hand side.
- Third peak is for the crystal on which external force (i.e. strain) is applied and the crystal gets uniform expansion (i.e. inter-planar distance increases) which causes shift in peak towards left hand side.
- Doping (impurities in crystal)
- Peak broadening is the cause of applying non- uniform strain to the crystal etc.

### D. Effect of temperature on XRD pattern

- Consider a normal (300K) and modified (350K) sample. Maxima of both the sample are same i.e. they are lying on same value of  $2\theta_B$  there is no stretching and no compression because in stretching and compression there is change in  $\theta_B$ . This is the effect of temperature.
- The atoms of any solid can be considered as harmonic oscillators, because atoms vibrate at their equilibrium position.

$$F \propto x$$

$$U \propto x^2$$

This simple harmonic motion is valid only when temperature is not high. Because at high temperature vibrations are large and bond will break.

So, simple harmonic motion is considered as there is no thermal expansion.

- Due to vibration (no thermal expansion), inter-planer spacing is not changing. if  $d_{hkl}$  values is not changing then peak is fix.
- At high temperature, intensity of of peak decreases.
- On increasing temperature line spacing i.e. distance between two peaks decreases.
- At high temperature number of peaks increases.

**VII. Usefulness of X-ray Diffraction**

- To determine the interspacing between the layers and the rows of atom of crystal.
- To investigate the crystal structure of unidentified material.
- To determine the orientation of single crystal.
- Used for evaluating internal stress on the small crystalline region in crystal.
- Moreover, we can explore the size and shape of crystal also.

