Chhatrapati Shahu Ji Maharaj University
(Formerly Kanpur University)

Pre -Ph.D. Course Work 2021

Department of Physics

Topic: Experimental Tools and Techniques

Lecture 1: Principle and Applications of Powder X-Ray Diffractometer

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Outlines

1. Introduction to X-Rays
2. Principle of X-Ray Diffraction
3. Bragg’s Law
4. X-ray Diffractometer
5. Types of X-Ray radiation
6. X-Ray Diffraction Methods
7. Applications of Powder X-Ray Diffraction

Experimental tools and Techniques

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1	**Principle and Application of Powder X-Ray Diffractometer**	**Lecture 1**
2	SEM and Energy Dispersive X-Ray Analysis	Lecture 2
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5	Spectrometer (IR and UV Visible) FT-IR Spectrometer	Lecture 5

Introduction

1.X-rays were discovered in 1895 by the German physicist Wilhelm Conrad Röntgen.

2.Electromagnetic radiation described as having packets of energy, or photons. The energy of the photon is related to its frequency by the following formula: $E = h\nu$ $(E = hc/\lambda)$

3.Electromagnetic radiation can be expressed in terms of energy, wavelength, or frequency.

The entire range (electromagnetic spectrum) is given by radio waves, microwaves, infrared radiation, visible light, ultra-violet radiation, X-rays, gamma rays in the increasing order of frequency and decreasing order of wavelength. The type of radiation and their frequency and wavelength ranges are as follows:

Type of Radiation	**Frequency Range (Hz)**	**Wavelength Range**
gamma-rays	$10^{20} – 10^{24}$	$< 10^{-12}$ m
x-rays	$10^{17} – 10^{20}$	1 nm – 1 pm
ultraviolet	$10^{15} – 10^{17}$	400 nm – 1 nm
visible	$4 – 7.5*10^{14}$	750 nm – 400 nm
near-infrared	$1*10^{14} – 4*10^{14}$	2.5 μm – 750 nm
infrared	$10^{13} – 10^{14}$	25 μm – 2.5 μm
microwaves	$3*10^{11} – 10^{13}$	1 mm – 25 μm
radio waves	$< 3*10^{11}$	> 1 mm

X-Ray Diffraction

X-rays are electromagnetic radiation with wavelengths between 1 pm to 1 nm. The wavelength of X-rays is on an atomic level and is much smaller than that of visible light (400 nm to 750 nm).

Since X-rays have a smaller wavelength than visible light, they have higher energy and are more penetrative. Its ability to penetrate matter, however, is dependent on density of the matter. Therefore, X-rays are useful in exploring structures of atoms.

X-Ray Crystallography is a technique used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. This forms a pattern, this type of pattern is called the X-ray **diffraction p**attern

Interference

X-ray diffraction, a phenomenon in which the atoms of a crystal, by virtue of their uniform spacing, cause an interference pattern of the waves present in an incident beam of X rays. The atomic planes of the crystal act on the X rays in exactly the same manner as does a uniformly ruled grating on a beam of light.

Because X-rays are bundles of separate waves, each wave can interact with on another either constructively or destructively. The interaction between waves is called interference. If waves are in phase meaning that each of their crests and troughs occur exactly at the same time, then the waves will stack together to produce a resultant wave that has a higher amplitude and results in the constructive interference.

If they waves are out of phase, then destructive interference occurs and the amplitude of the resultant wave will be reduced. If waves are exactly out of phase by a multiple of n/(2*lambda) then there will be complete destructive interference and the resultant wave has no amplitude, meaning that it is completed destroyed.

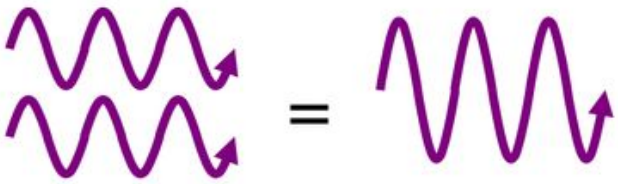
Principle of X-Ray Diffraction

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. The phenomenon is called X-ray diffraction. And scattering of X-rays by the atoms of a crystal that produces an interference effect so that the diffraction pattern gives information on the structure of the crystal or the identity of a crystalline substance.

So X-ray diffraction is based on constructive interference of monochromatic **x-rays** and a **crystalline sample.** Or X-rays are relatively short-wavelength EM radiation and can exhibit wave characteristics such as interference when interacting with correspondingly small objects.

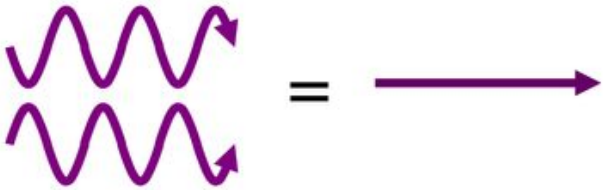
Constructive vs. destructive interference; Coherent vs. incoherent interference

Waves that combine **in phase** add up to relatively high irradiance.



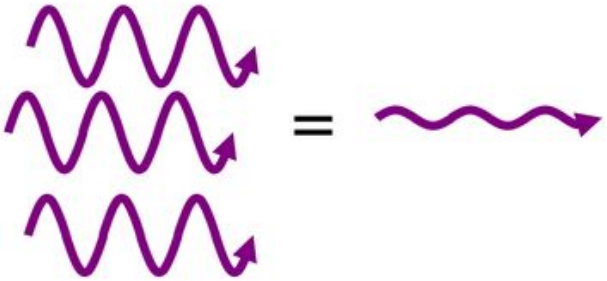
Constructive interference (**coherent**)

Waves that combine **180° out of phase** cancel out and yield zero irradiance.



Destructive interference (**coherent**)

Waves that combine with **many different random phases** nearly cancel out and yield very low irradiance.



Incoherent addition

Bragg’s Law

Bragg's law is **a special case of diffraction**, which determines the angles of coherent and incoherent scattering from a crystal lattice. When X-rays are incident on a particular atom, they make an electronic cloud move like an electromagnetic wave.

When the X-ray is incident onto a crystal surface, its angle of incidence, θ, will reflect with the same angle of scattering, θ. And, when the path difference, d is equal to a whole number, n, of wavelength, constructive interference will occur.

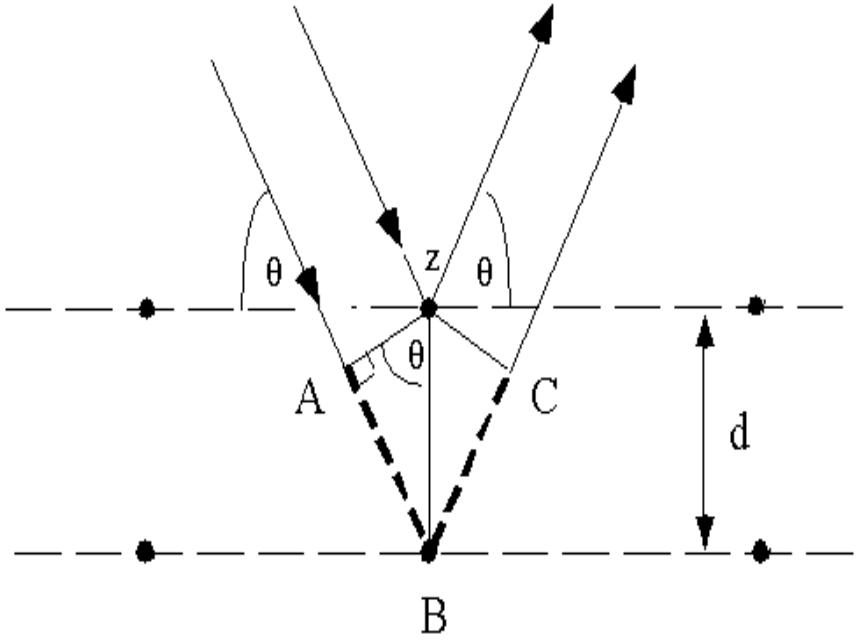
Bragg's Law can easily be derived by considering the conditions necessary to make the phases of the beams coincide when the incident angle equals to reflecting angle.

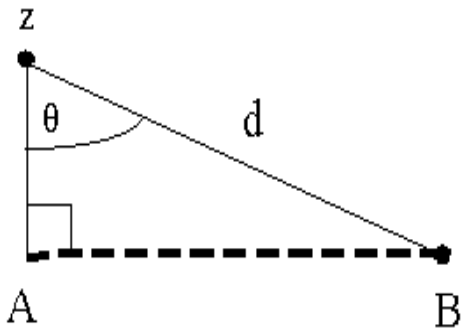
The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z.

The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance
AB + BC if the two beams are to continue traveling adjacent and parallel.

This extra distance must be an integral (n) multiple of the wavelength ( ) for the phases of the two beams to be the same:

$n\lambda$ = AB +BC----------(1)





Recognizing d as the hypotenuse of the right triangle ABZ, we can use trigonometry to relate d and to the distance (AB + BC).

The distance AB is opposite θ So,

AB = d sin θ----------(2)

Because AB = BC eq. (1) becomes,

nλ = 2AB ----------(3)

Substituting eq. (2) in eq. (3) we have,

nλ = 2 d sin θ ----------(4)

So the principle is that when a beam of X-rays of wavelength λ enters a crystal, the maximum intensity of the reflected ray occurs when sin θ = nλ/2d, where θ is the complement of the angle of incidence, n is a whole number, and d is the distance between layers of atoms.

Deriving Bragg's Law - $n\lambda = 2d\sin\theta$

Constructive interference occurs only when

$n\lambda = AB + BC$

$AB = BC$

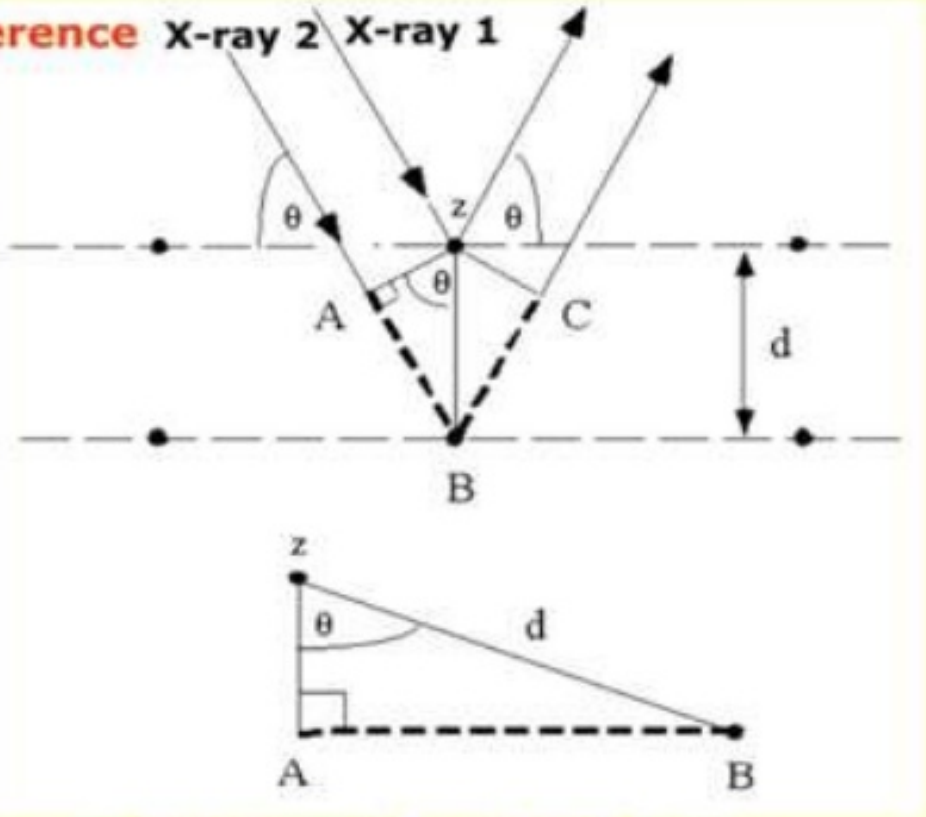
$n\lambda = 2AB$

$\sin\theta = AB/d$

$AB = d\sin\theta$

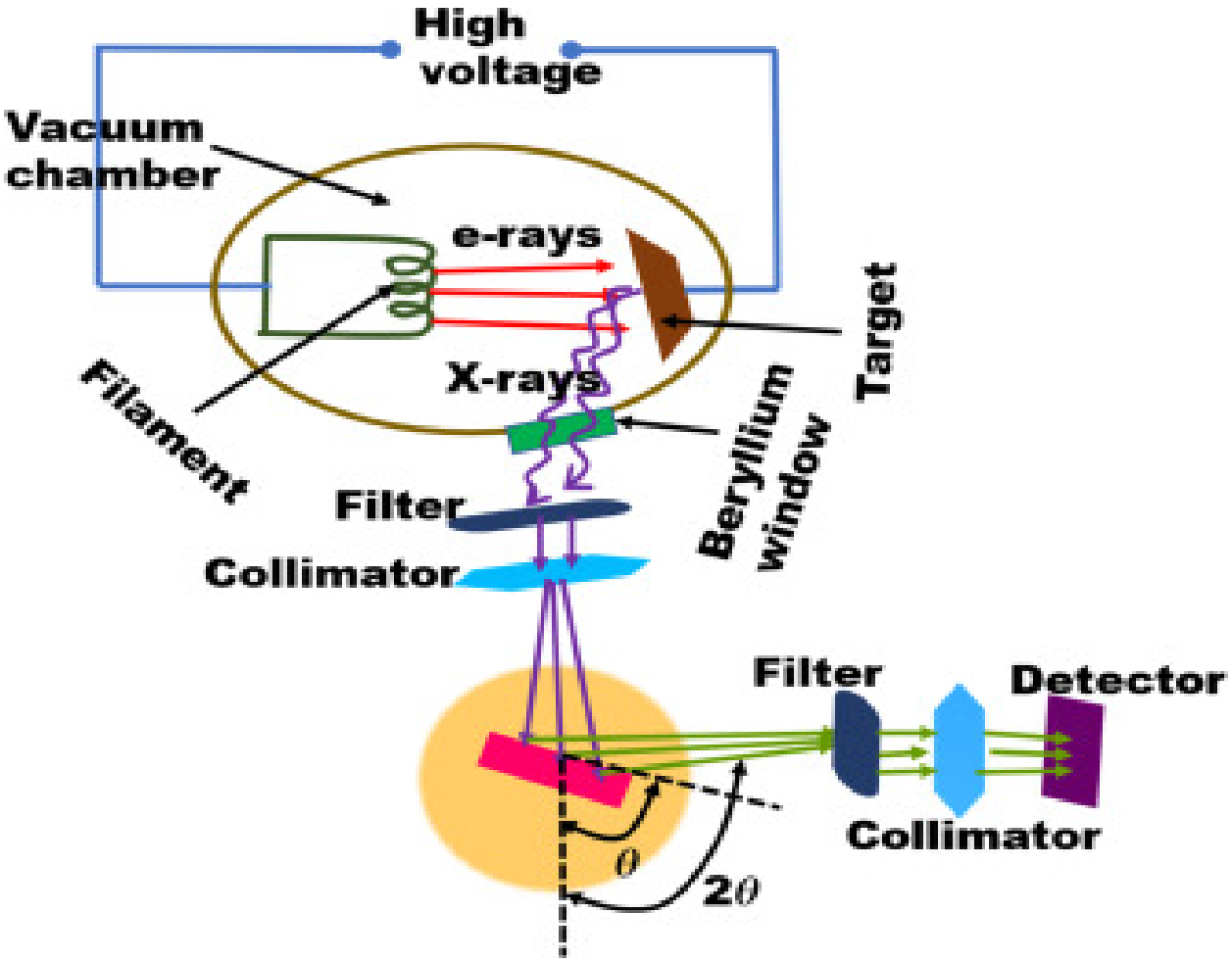
$n\lambda = 2d\sin\theta$

$\lambda = 2d_{hkl}\sin\theta_{hkl}$



n – integer, called the order of diffraction

X-ray Diffractometer



Working of X-ray Diffractometer

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-Rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target (tungsten) by applying a voltage, and bombarding the target material with electrons.

When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced.

These spectra consist of several components, the most common being K_{α} and K_{β}. K_{α} consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr).

Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used.

Copper is the most common target material for single-crystal diffraction, with CuK_{α} radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The dominant effect that occurs when an incident beam of monochromatic X-rays interacts with a target material is scattering of those X-rays from atoms within the target material.

In materials with regular structure (i.e. crystalline), the scattered X-rays undergo constructive and destructive interference. This is the process of diffraction. The diffraction of X-rays by crystals is described by Bragg's Law,

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

The directions of possible diffractions depend on the size and shape of the unit cell of the material. The intensities of the diffracted waves depend on the kind and arrangement of atoms in the crystal structure.

However, most materials are not single crystals, but are composed of many tiny crystallites in all possible orientations called a polycrystalline aggregate or powder.

When a powder with randomly oriented crystallites is placed in an X-ray beam, the beam will see all possible interatomic planes. If the experimental angle is systematically changed, all possible diffraction peaks from the powder will be detected.

X-rays are generated via interactions of the accelerated electrons with electrons of tungsten nuclei within the tube anode. There are two types of X-ray generated: characteristic radiation and bremsstrahlung radiation. Electrons traveling from the filament (cathode) to the target (anode) convert a small percentage (1%) of their kinetic energy into x-ray photons by the formation of bremsstrahlung and characteristic radiation.

BREMSSTRAHLUNG RADIATION

Bremsstrahlung interactions, the primary source of x-ray photons from an x-ray tube, are produced by the sudden stopping, breaking or slowing of high-speed electrons at the target. When the electrons from the filament strike the tungsten target, x-ray photons are created if they either hit a target nucleus directly (rare) or their path takes them close to the nucleus.

If a high speed electron hits the nucleus of a target atom, all its kinetic energy is transformed into a single x-ray photon. (Total absorption has occurred). Thus, the energy of the resultant photon (keV) is numerically equal to the energy of the electron. This in turn is equal to the kilovoltage applied across the x-ray tube at the instant of its passage.

CHARACTERISTIC RADIATION

Characteristic radiation occurs when an electron from the filament displaces an electron from an inner-shell of the tungsten target atom, thereby ionizing the atom.

When this happens, another electron in an outer-shell of the tungsten atom is quickly attracted into the void in the deficient inner-shell.

When the displaced electron is replaced by the outer-shell electron, a photon is emitted with an energy equivalent to the difference in the two orbital binding energies.

X-Ray Diffraction Methods

There are three diffraction methods by which we can obtain the information about crystal structures:

- Laue Diffraction method
- Rotating crystal Diffraction method
- Powder Diffraction method

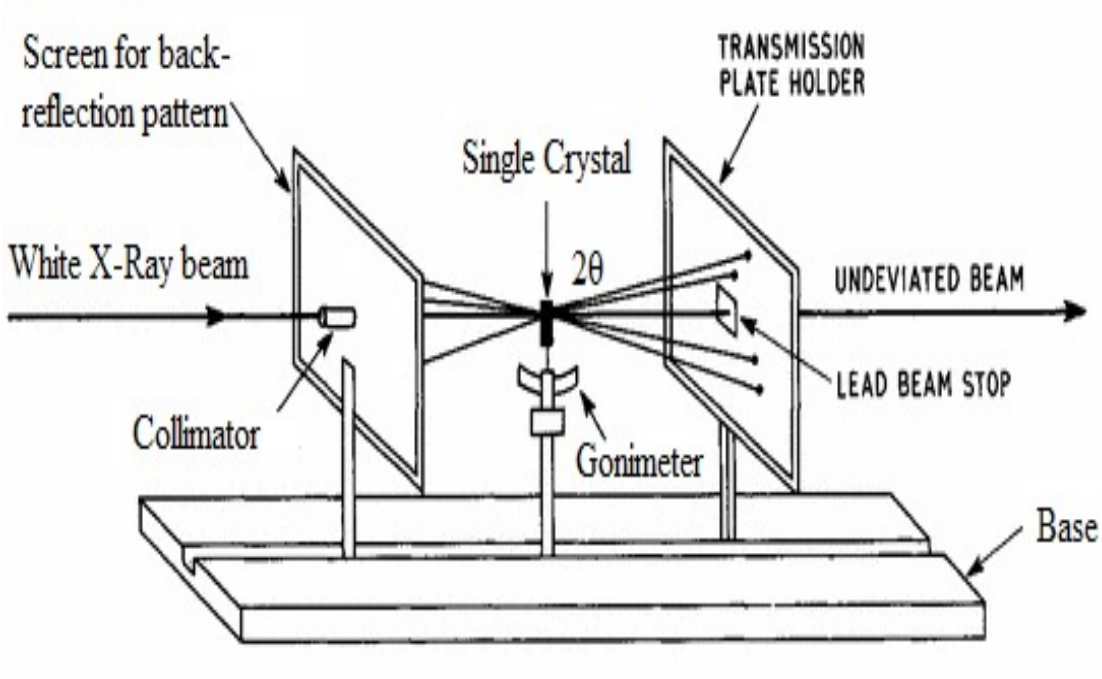
Laue Diffraction method

The Laue method is a single crystal diffraction method. The discovery of the phenomenon of crystal diffraction was obtained for the first time by the Laue method.

The method requires a polychromatic beam, i.e. the full spectrum of x-ray wavelengths. The single crystal placed in the polychromatic beam diffracts in many different directions.

The resulting Laue diffraction pattern depends on the orientation of the crystal. Thus the Laue method is ideal to detect the orientation of a single crystal, i.e. to find the directions of the translation vectors of the unit cell.

Laue Diffraction method



Laue Diffraction method

A single crystal is mounted on a rotating table which enables the crystal to be rotated through certain known angles and maintained stationary with respect to a beam of X-rays of different wavelengths.

The crystal selects out and diffracts those discrete values of λ, for which crystal planes exist, of spacing d and glancing angle θ satisfying Bragg's equation:

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

A narrow, parallel beam is collimated on the crystal. Photographic films are placed either to receive the transmitted or reflected beams.

The resultant pattern consists of a series of sharp well defined spots. These are indicative of a perfect crystal structure, whereas broken, extended spots indicate lattice distortion and imperfections in the crystal.

Laue Diffraction method

- Single crystal placed on a three-axis goniometer in front of narrow beam of x-rays

- X-rays are not monochromatic

- 2θ and d remain fixed for each set of planes (only λ is varied)

- Each set diffracts that particular λ which satisfies the Bragg equation for it

- Each diffracted beam has a different λ

- Incident beam passes through photographic film, hits the crystal, and is back-reflected towards the film

Rotating crystal Diffraction method

In the rotating crystal method, a single crystal is mounted with an axis normal to a monochromatic x-ray beam.

A cylindrical film is placed around it and the crystal is rotated about the chosen axis. As the crystal rotates, sets of lattice planes will at some point make the correct Bragg angle for the monochromatic incident beam, and at that point a diffracted beam will be formed.

Lattice constant of the crystal can be determined by means of this method; for a given wavelength if the angle θ at which a reflection occurs d hkl known, is can be determined.

The reflected beams are located on the surface of imaginary cones. By recording the diffraction patterns (both angles and intensities) for various crystal orientations; one can determine the shape and size of unit cell as well as arrangement of atoms inside the cell.

Powder Diffraction method

➢It is a scientific technique using X-Ray , neutron, or electron diffraction on powder or microcrystalline samples for structural characterization of materials. An instrument dedicated to performing such powder measurements is called a **powder diffractometer.**

➢Powder diffraction stands in contrast to single crystal diffraction techniques, which work best with a single, well-ordered crystal. If a powdered specimen is used, instead of a single crystal, then there is no need to rotate the specimen, because there will always be some crystals at an orientation for which diffraction is permitted. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample. This method is useful for samples that are difficult to obtain in single crystal.

➢The powder method is used to determine the value of the lattice parameters accurately. Lattice parameters are the magnitudes of the unit vectors a, b and c which define the unit cell for the crystal. For every set of crystal planes, by chance, one or more crystals will be in the correct orientation to give the correct Bragg angle to satisfy Bragg's equation. Every crystal plane is thus capable of diffraction. Each diffraction line is made up of a large number of small spots, each from a separate crystal

Powder Diffraction method

A diffractometer produces waves at a known frequency, which is determined by their source. The source is often x-rays, because they are the only kind of energy with the correct frequency for inter-atomic-scale diffraction. However, electrons and neutrons are also common sources, with their frequency determined by their de Broglie wavelength.

When these waves reach the sample, the atoms of the sample act just like a diffraction grating, producing bright spots at particular angles. By measuring the angle where these bright spots occur, the spacing of the diffraction grating can be determined by Bragg's law Because the sample itself is the diffraction grating, this spacing is the atomic spacing .

Powder Diffraction method

The distinction between powder and single crystal diffraction is the degree of texturing in the sample. Single crystals have maximal texturing, and are said to be anisotropic

In contrast, in powder diffraction, every possible crystalline orientation is represented equally in a powdered sample, the isotropic case. PXRD operates under the assumption that the sample is randomly arranged.

Therefore, a statistically significant number of each plane of the crystal structure will be in the proper orientation to diffract the X-rays. Therefore, each plane will be represented in the signal. In practice, it is sometimes necessary to rotate the sample orientation to eliminate the effects of texturing and achieve true randomness.

Laue method	**Rotating crystal method**	**Powder method**
Orientation Single crystal	Lattice constant Single crystal	Lattice parameter Polycrystal
Polychromatic beam Fixed angle	Monochromatic beam Variable angle	Monochromatic beam Variable angle

Applications of PXRD

Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles.

The atoms in a crystal are periodically arranged thus diffract light. The wavelength of X-ray are similar to the distance between atoms, Powder X-ray Diffraction (PXRD) techniques uses this principle to elucidate the crystalline nature of materials.

The scattering of X-rays from atoms produce a diffraction pattern that contains information about the atomic arrangement in crystal.

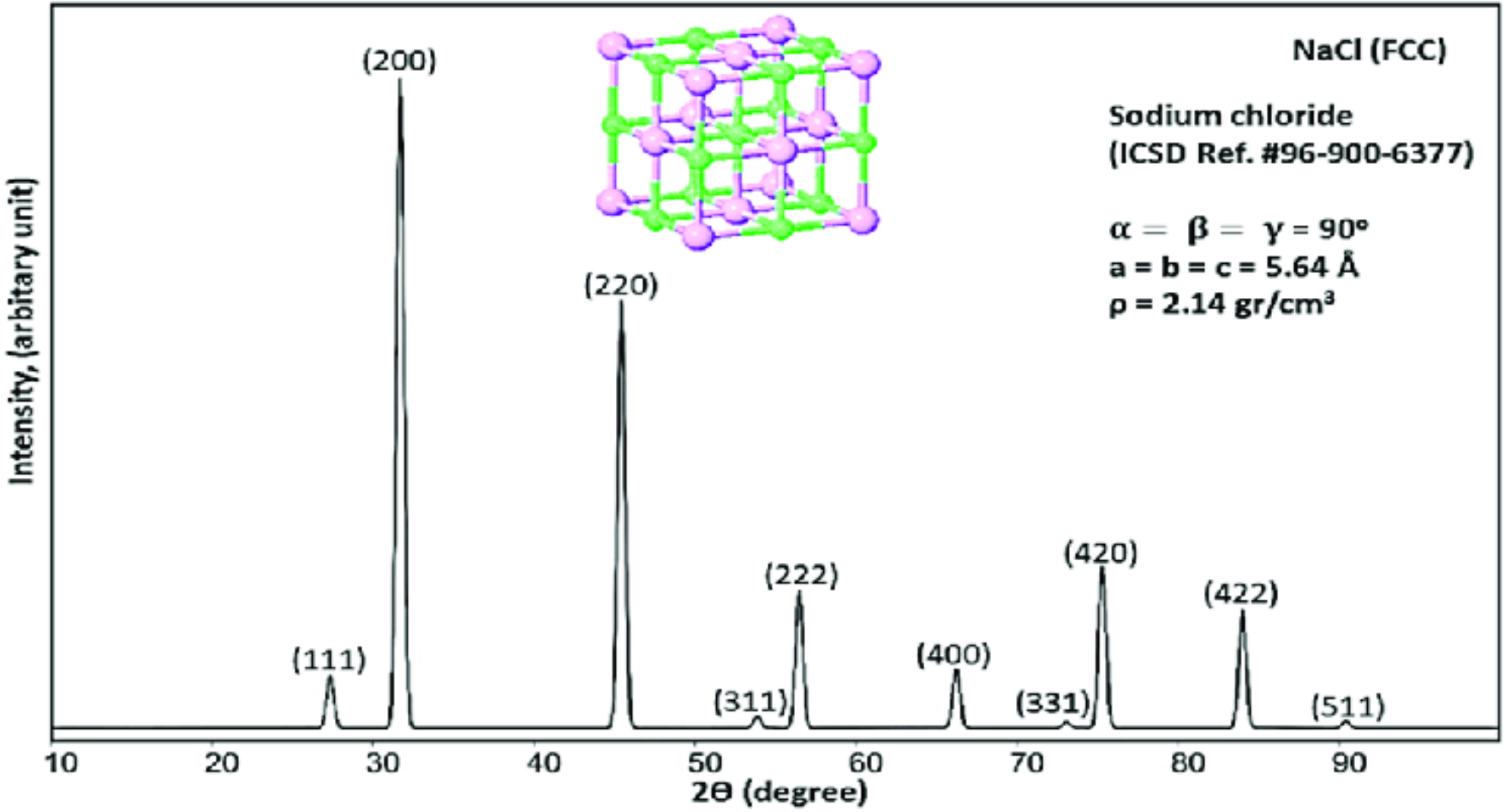
Amorphous materials like glass do not have periodic array with long-range order so; they do not produce any significant peak in diffraction pattern

Crystal structure and Lattice parameters using PXRD

X-ray diffraction provides ample information about the lattice parameters. The position of a diffraction peak is determined by the size and shape of unit cell of the crystalline phase. Peak represents a lattice plane and therefore can be characterized by Miller index.

If the symmetry is high as in case of cubic or hexagonal, it is not difficult to identify the peak index for an unknown phase. This is very useful in solid-state chemistry to identifying new materials. Once a pattern gets indexed, it serves as reference for new entitie

XRD Graph


NaCl (FCC)
Sodium chloride
(ICSD Ref. #96-900-6377)
α = β = γ = 90°
a = b = c = 5.64 Å
ρ = 2.14 gr/cm³
(200)
(220)
(111)
(311)
(222)
(400)
(331)
(420)
(422)
(511)
Intensity, (arbitary unit)
10
20
30
40
50
60
70
80
90
2θ (degree)

Polymorph study

PXRD is helpful in identification and characterization of polymorph (**Polymorphism** describes the existence of a solid material in more than one form or crystal structure). , monitoring the stability, method development and validation for identification and quantification of drugs in Pharmaceutical Industries.

The part of the X-ray that is not scattered simply passes through the next layer of atoms, where again part of the X-ray is scattered and part of it passes through to the next layer. This causes an overall diffraction pattern, similar to how a grating diffracts a beam of light. In order for an X-ray to diffract, the sample must be crystalline and the spacing between atom layers must be close to the radiation wavelength.

Polymorph study

If beams diffracted by two different layers are in phase, constructive interference occurs and the diffraction pattern shows a peak. However, if they are out of phase, destructive interference occurs appear and no peak is observed. Diffraction peaks only occur if it follows Bragg's Law.

Since, a highly regular structure is needed for diffraction to occur, only crystalline solids diffract, the PXRD of amorphous materials do not depict any significant peak in diffraction pattern

Crystallinity study by PXRD

The XRD analysis of crystalline compounds gives a diffraction pattern consisting of a well-defined, narrow, sharp and significant peak while amorphous materials do not give clear peaks rather the pattern has noise signals, smeared peak or it can have some short order bumps.

Many polymers depict semi-crystalline behavior and produce halo pattern. Powder XRD can be used to determine the **crystallinityy** by comparing the integrated intensity of the background pattern to that of the sharp peaks.

Particle Size and Crystallite Size

The term particle size and crystallite size refer to two distinct properties in a material. Particles comprise of several small **crystallite**.

Crystallite size is the fundamental property of materials. Properties of nanomaterials depend on crystals size and not particle size.

PXRD can measure millions of crystals and accurately determine the size distribution of nanomaterials.

Phase Transition

Some crystals exhibits several phase transitions such as $BaTiO_3$. With temperature variation these different phases occurs. At this point new diffraction peaks will appear or old ones disappear according to the symmetry of the new phase.

These phases have different symmetry. So diiferent phases with correspond to different crystal structure can be identified. In such cases the **symmetry** may change because the existing structure is distorted rather than replaced by a completely different one.

Summary

X-Ray Diffraction is a technique used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. This forms a pattern, this type of pattern is called the X-ray **diffraction p**attern

When the X-ray is incident onto a crystal surface, its angle of incidence, θ, will reflect with the same angle of scattering, θ. And, when the path difference, d is equal to a whole number, n, of wavelength, constructive interference will occur.

X-Ray diffraction methods along with Several Applications of Powder X-Ray Diffraction were explored.

References

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2. Elements of X-Ray Diffraction , Second Edition by B.D. Cullity.