

**Indus University**

**IISHLS**

Department of Chemistry

**M.Sc. Analytical Chemistry**

Semester: 3<sup>rd</sup>

**Name of Subject: Qualitative Spectroscopic Techniques**

Subject Code: MCH0321

**Unit-4- X- ray Diffraction**

## ❖ Introduction:

- X-ray diffraction is a tool for the investigation of the fine structure of matter.
- This technique had its beginnings in von Laue's discovery in 1912 that crystals diffract x-rays, the manner of the diffraction revealing the structure of the crystal.
- At first, x-ray diffraction was used only for the determination of crystal structure. Later on, however, other uses were developed, and today the method is applied, not only to structure determination, but to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibria and the measurement of particle size, to the determination of the orientation of one crystal or the ensemble of orientations in a polycrystalline aggregate.
- X-rays were discovered in 1895 by the German physicist Roentgen and were so named because their nature was unknown at the time. Unlike ordinary light, these rays were invisible, but they traveled in straight lines and affected photographic film in the same way as light.
- On the other hand, they were much more penetrating than light and could easily pass through the human body, wood, quite thick pieces of metal, and other "opaque" objects.
- X-ray Diffraction in crystal was discovered by **Max Von Laue**. The wavelength range is 0.01 to about 10 nm.
- X-rays are short wavelength of electromagnetic radiation produced by the **deceleration of high energy electrons or by electronic transition of electrons in the inner orbital of atoms.**
- The penetrating power of X rays depends on energy also, there are two types of X-ray can be produced .

## 1. Hard X-rays

- Have high frequency and more energy.

## 2. Soft X-rays

- Have less penetrating and have low energy

→ X-ray diffraction (XRD) is a non-contact and non-destructive technique used to understand **the crystalline phase, different polymeric forms and the structural properties of materials.**

→ The XRD pattern of a pure substance is therefore like a **FINGERPRINT** of that substance.

→ XRD technique is based on the **scattering of X-ray by crystals.**

→ XRD technique is very important as it give the following information...

**Measure the average spacing between layers of the rows of atoms**

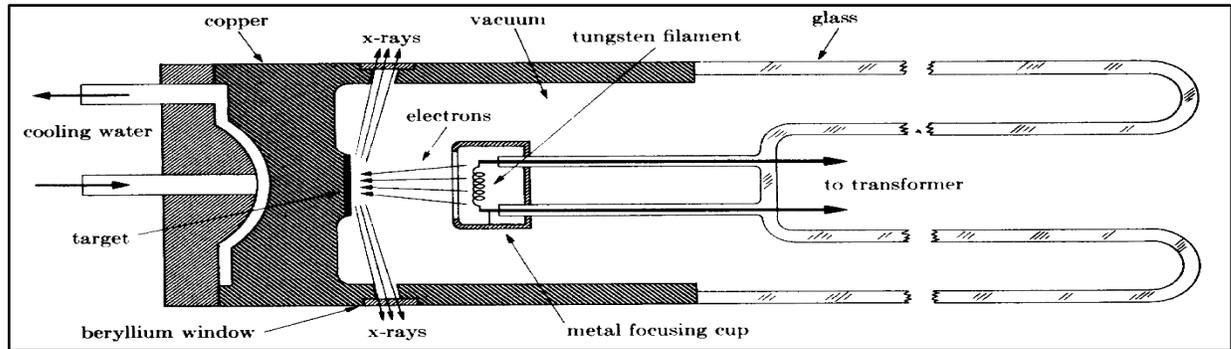
**Determine the orientation of a single crystal**

**Find the crystal structure of unknown material**

**Measure the size, shape and internal stress of small crystalline region.**

**To determine the phase composition of the crystal**

## ❖ Generation of X-Rays



**Fig. Schematic of filament X-ray tube**

→ We have seen that x-rays are produced whenever high-speed electrons collide with a metal target. Any x-ray tube must therefore contain

**A source of electrons**

**A high accelerating voltage**

**A metal target**

**Vacuum: to control the number and speed of the accelerated electrons independently.**

**Pyrex glass: connecting wires same coefficient of linear expansion as glass.**

**Negative terminal of the x-ray tube is called cathode or filament. Along with filament 2 other elements: connecting wires and focusing cup**  
**Filament made of tungsten wire 0.2 mm diameter coiled to form a vertical spiral 0.2 cm diameter and 1 cm length**

➤ **Some basic terms**

✓ **Cathode**

**Filament**

- Made of thin (0.2 mm) tungsten wire because tungsten:
  - has a high atomic number (A 184, Z 74)
  - is a good thermionic emitter (good at emitting electrons)
  - can be manufactured into a thin wire
  - has a very high melting temperature (3422°C)
- The size of the filament relates to the size of the focal spot. Some cathodes have two filaments for broad and fine focusing

✓ **Focusing cup**

- Made of molybdenum as:
  - high melting point
  - poor thermionic emitter so electrons aren't released to interfere with electron beam from filament
- Negatively charged to focus the electrons towards the anode and stop spatial spreading

✓ **Anode**

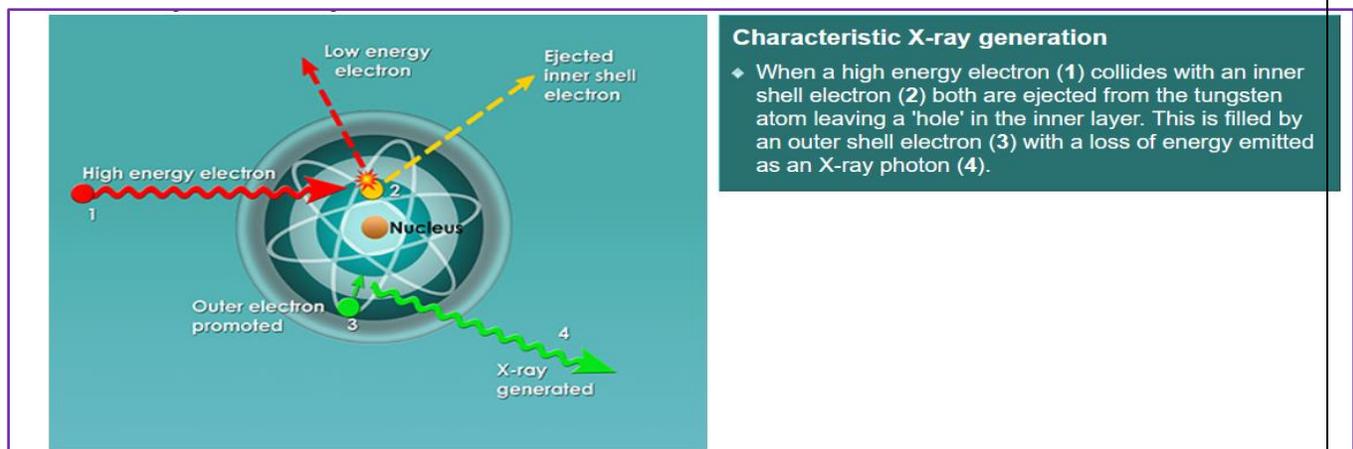
- Target made of tungsten for same reasons as for filament
- Rhenium added to tungsten to prevent cracking of anode at high temperatures and usage
- Set into an anode disk of molybdenum with stem
- Positively charged to attract electrons
- Set at angle to direct x-ray photon beam down towards patient. Usual angle is 5° - 15°

✓ **Definitions**

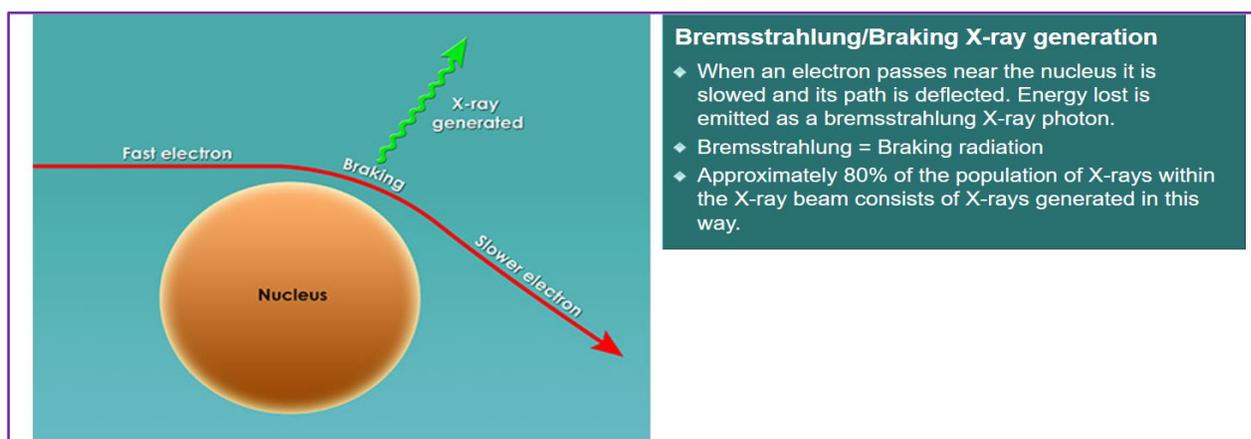
- **Target, focus, focal point, focal spot:** where electrons hit the anode
- **Actual focal spot:** physical area of the focal track that is impacted
- **Focal track:** portion of the anode the electrons bombard. On a rotating anode this is a circular path
- **Effective focal spot:** the area of the focal spot that is projected out of a tube

- A current is passed through the tungsten filament and heats it up.
- As it is heated up the increased energy enables electrons to be released from the filament through **thermionic emission**(i.e. Emission of electrons resulting from the absorption of thermal energy).
- Electron cloud surrounding the filament produced by thermionic emission is termed “**Edison effect**”
- The electrons are attracted towards the positively charged anode and hit the tungsten target with a maximum energy determined by the tube potential (voltage).
- As the electrons bombard the target they interact via Bremsstrahlung and characteristic interactions which result in the conversion of energy into heat (99%) and x-ray photons (1%).
- The x-ray photons are released in a beam with a range of energies (**x-ray spectrum**) out of the window of the tube and form the basis for x-ray image formation.
- Since most of the kinetic energy of the electrons is converted into heat in the target, the latter must be water-cooled to prevent its melting.
- All x-ray tubes contain two electrodes, **an anode** (the metal target) maintained, with few exceptions, **at ground potential**, and a **cathode**, maintained at a **high negative potential**, normally of the order of 30,000 to 50,000 volts for diffraction work.
- X-ray tubes may be divided into two basic types, according to the way in which electrons are provided: **filament tubes**, in which the source of electrons is a hot filament, and **gas tubes**, in which electrons are produced by the ionization of a small quantity of gas in the tube.
- **Filament tubes** : They consist of an evacuated glass envelope which insulates the anode at one end from the cathode at the other, the cathode being a tungsten filament and the anode a water-cooled block of copper containing the desired target metal as a small insert at one end.
- One lead of the high-voltage transformer is connected to the filament and the other to ground, the target being grounded by its own cooling water connection.
- The filament is heated by a filament current of about 3 amp and emits electrons which are rapidly drawn to the target by the high voltage across the tube.

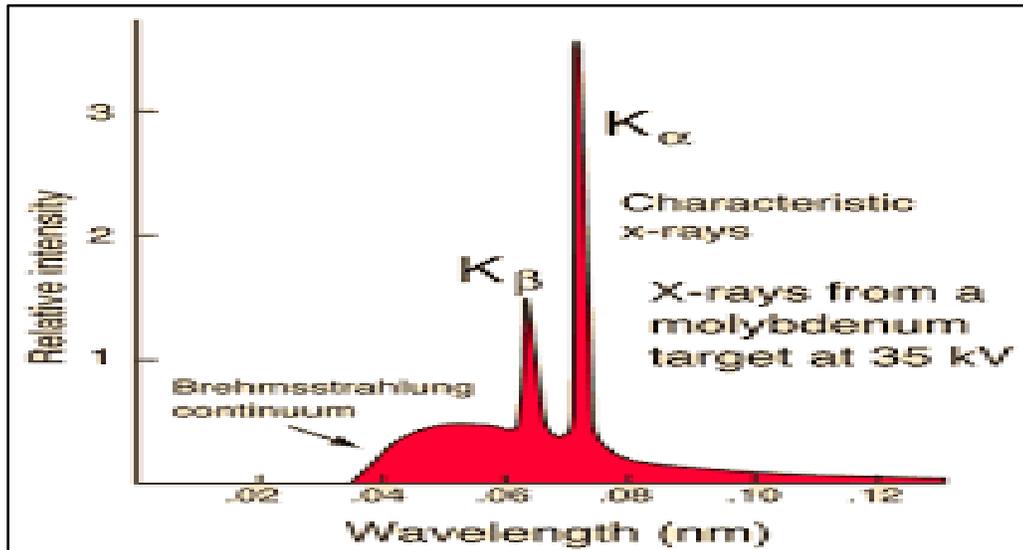
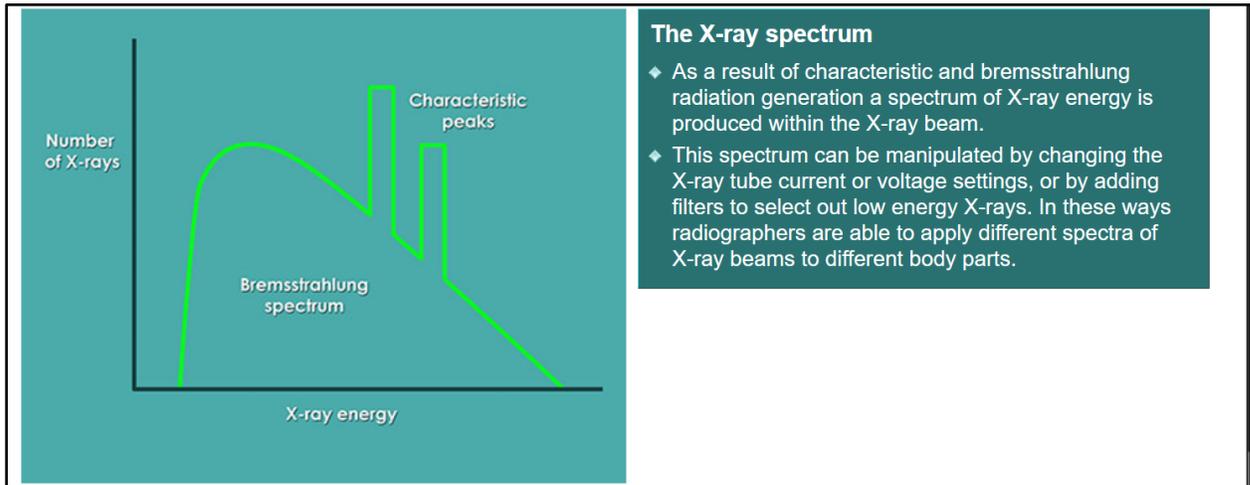
- Surrounding the filament is a small metal cup maintained at the same high (negative) voltage as the filament: it therefore repels the electrons and tends to focus them into a narrow region of the target, called the focal spot.
- X-rays are emitted from the focal spot in all directions and escape from the tube through two or more windows in the tube housing. Since these windows must be vacuum tight and yet highly transparent to x-rays, they are usually made of beryllium, aluminum, or mica.
- 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.



**Fig. Characteristic radiation**



**Fig. Bremsstrahlung X-ray generation**



**Fig. Characteristic Spectrum of X ray**

- When high velocity electrons will strike the metal target then it will produce x-rays.
- The continuous spectrum is caused by the rapid deceleration of electrons by the target metal, the origin of the characteristic spectrum lies in the atoms of the target material itself.
- To understand this phenomenon , it is enough to consider an atom as consisting of a central nucleus surrounded by electrons lying in various shell.

- If one of the electrons bombarding the target has sufficient kinetic energy , it can knock an electron out of the K shell leaving an atom in an excited high energy state.
- One of the outer electrons immediately falls into the vacancy in the K shell , emitting energy in the process and the atom is once again in its normal energy state.
- The energy emitted is in the form of radiation of definite wavelength and is in fact characteristic of K radiation.
- The K shell vacancy may be filled by an electron from any of the outer shell, thus giving rise to a series of K lines.  $K\alpha$  and  $K\beta$

### ❖ **Basic Principle of X- ray Diffraction:**

- Wavelength of x-ray is 0.01 to 10 nm.
- For analytical purpose , the wavelength of x-ray is 0.07 to 0.2 nm.

#### **[A] X-ray Diffraction**

- This method is based on the scattering of x-rays by crystals.
- By using this method, analyst can easily identify the crystal structure of any solid compound with high degree of specificity and accuracy.
- XRD is highly important method as compared to other x- ray spectroscopy.

#### **[B] X-ray Absorption**

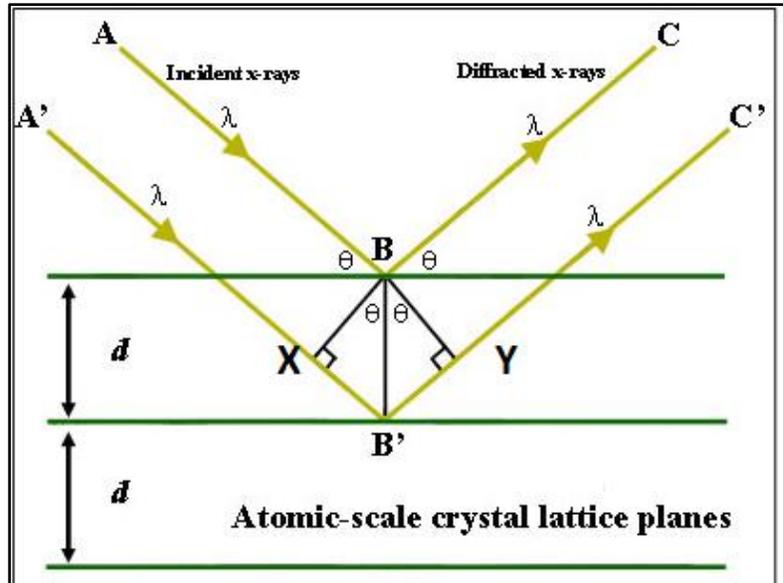
- This is similar to absorption method in other region of electromagnetic spectra like UV visible, IR spectroscopy.
- It gives the information about the absorbing material.
- In this method a beam of x-ray is passed through the sample and the fraction of x-ray photons absorbed is considered to be a measure of the concentration of the sample.
- This method is least used as compared to other methods.
- It is used only to detect **imperfection in the internal structure , elemental analysis , thickness measurement.**

### [C] X-ray Fluorescence (Emission)

- In this method, x-rays are generated within the sample and by measuring the wavelength and intensity of the generated x-rays.
- Analyst can perform qualitative as well as quantitative analysis.

### ❖ The Bragg's Law for X-ray Diffraction

- Bragg pointed out that the unlike reflection of ordinary light, reflection of X-ray can take place only at a certain angle which are determined by the wavelength of x-ray and distance between the plane of in the crystal.
- Two geometrical facts are worth remembering:
  - (1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar.
  - (2) The angle between the diffracted beam and the transmitted beam is always  $2\theta$ . This is known as the diffraction angle, and it is this angle, rather than  $\theta$ , which is usually measured experimentally.
- As previously stated, diffraction in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This requirement follows from the Bragg law.
- Suppose a beam of x-ray falls on the crystal at glancing angle (tangential angle)  $\theta$ , then some of these rays will be reflected from the upper plate at same angle  $\theta$ .
- While some of these rays will be absorbed and get reflected from the successive layer.



**Fig. The Bragg's Law**

∴ So, here angle will be  $\angle XBY = \theta$  &  $\angle YBB' = \theta$

∴  $AB = A'X$  &  $CB = C'Y$

∴ Path difference =  $XB' + B'Y$

→ Path difference is defined as an integral multiple of wavelength =  $n \lambda$

∴  $n \lambda = XB' + B'Y$

→ Now for  $\Delta XBB'$  ;

$$\therefore \sin \theta = \frac{XB'}{BB'}$$

∴  $XB' = BB' \sin \theta$

$$\therefore XB' = d \sin \theta$$

Now for  $\Delta YBB'$  ;

$$\therefore \sin \theta = \frac{YB'}{BB'}$$

∴  $YB' = BB' \sin \theta$

$$\therefore YB' = d \sin \theta$$

$$\therefore n \lambda = XB' + B'Y$$

$$\therefore n \lambda = d \sin \theta + d \sin \theta$$

$$\therefore \mathbf{n \lambda = 2d \sin \theta}$$

Where  $n$  = Order of diffraction

$\lambda$  = wavelength

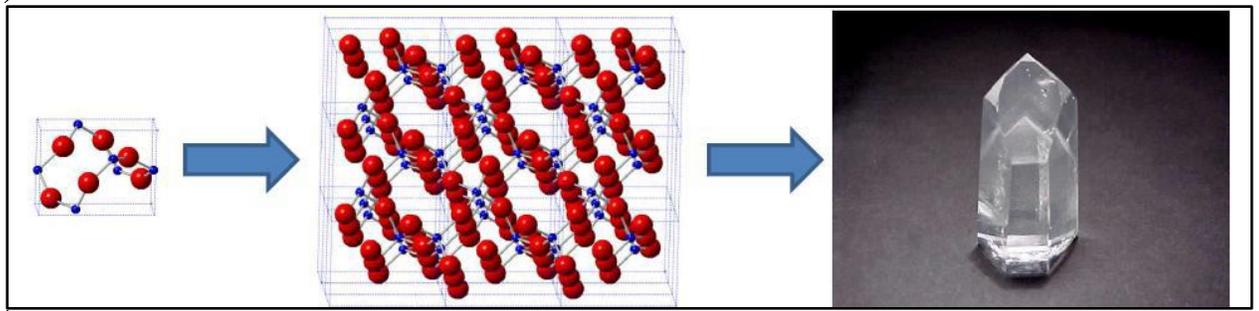
$d$  = Interplanar distance

$\theta$  = Glancing angle

### ❖ Single Crystal X ray Diffraction

**What is a crystal?**

- Atoms (molecules) pack together in a regular pattern to form a crystal.
- The unit cell is the basic repeating unit that defines the crystal structure.
- The unit cell contains the symmetry elements required to uniquely define the crystal structure.
- The unit cell might contain more than one molecule: For example, the quartz unit cell contains 3 complete molecules of  $\text{SiO}_2$ .
- The crystal system describes the shape of the unit cell.
- The lattice parameters describe the size of the unit cell.
- The unit cell repeats in all dimensions to fill space and produce the macroscopic grains or crystals of the material.



**Fig. Basic of Crystal structure**

- The crystal structure describes the atomic arrangement of a material.
- The crystal structure determines the position and intensity of the diffraction peaks in an X-ray scattering pattern.
- Interatomic distances determine the positions of the diffraction peaks.
- The atom types and positions determine the diffraction peak intensities.
- Diffraction peak widths and shapes are mostly a function of instrument and microstructural parameters.
  
- To understand the atomic arrangement in the single crystal, single crystal X-ray diffraction has been used to determine the crystal structure. When X-ray interacts with the crystal, it will diffract into directions. The angles and intensities of these diffracted X-rays will be measured to produce a 3D image of the density of electron, which reflect the average positions of atoms in the crystal.
- Further the length of chemical bonds between atoms, bond strength, their disorder, and defects can be determined. The samples can be ranged from minerals, alloys, vitamins, drugs to proteins.
- When a crystal is mounted on a goniometer of the X-ray diffractometer, it will gradually rotate. The electrons will be excited with X-rays, producing a diffraction pattern (also known as reflection) according to the regularly spatial arrangement. The 2D images will be collected due to the different rotations.

Further these 2D images will be converted into a 3D model of the density of electrons by the mathematical method of Fourier transforms.

→ The X-ray diffraction is known as a rapid, nondestructive analysis of multicomponent mixtures without the need for extensive sample preparation. This method has the ability to quickly analyze unknown materials and perform materials characterization in the fields of metallurgy, mineralogy, forensic science, archeology, condensed matter physics, and the biological and pharmaceutical sciences. Using X-ray diffraction, series information can be obtained, such as the phase identification, crystallinity, lattice parameters, expansion tensors and bulk modulus, crystal structure refinement and determination, size and strain broadening, and periodically arranged clusters.

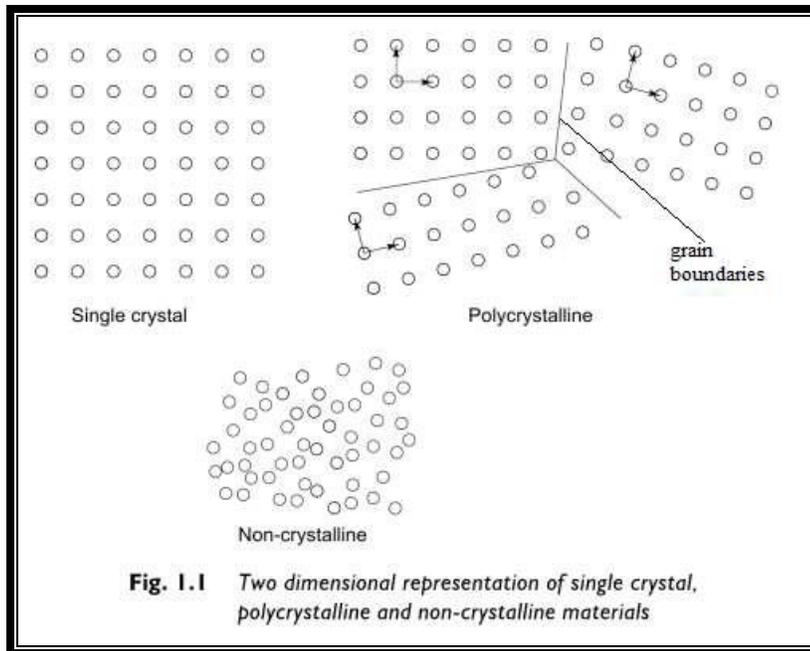
➤ **What is meant by Crystallography and why to study the structure of crystalline solids?**

→ Crystallography is the experimental science of determining the arrangement of atoms in the crystalline solids. The properties of some materials are directly related to their crystal structures.

→ For example, pure and undeformed magnesium and beryllium, having one crystal structure, are much more brittle (i.e., fracture at lower degrees of deformation) than pure and undeformed metals such as gold and silver that have yet another crystal structure.

→ Furthermore, significant property differences exist between crystalline and non-crystalline materials having the same composition. For example, non-crystalline ceramics and polymers normally are optically transparent; the same materials in crystalline (or semi-crystalline) form tend to be opaque or, at best, translucent.

- An important reason to have an understanding of interatomic bonding in solids is that, in some instances, the type of bond allows us to explain a material's properties. For example, consider carbon, which may exist as both graphite and diamond. Whereas graphite is relatively soft and has a “greasy” feel to it, diamond is the hardest known material. This dramatic disparity in properties is directly attributable to a type of interatomic bonding found in graphite that does not exist in diamond.
- Thus, by studying the crystal structure and bonding nature of different materials, we can investigate the reasons for the similar or dissimilar nature of the selected materials in terms of different properties or different parameters.
- The crystal structure and symmetry of a material play a vital role in determining many of its physical properties, such as cleavage, electronic band structure, and optical transparency, etc.
- Based on the atomic arrangement in a substance, solids can be broadly classified as either **crystalline or non-crystalline**.
- In a crystalline solid, all the atoms are arranged in a periodic manner in all three dimensions whereas in a non-crystalline solid the atomic arrangement is random or nonperiodic in nature.
- A crystalline solid can either be a single crystalline or a polycrystalline. In the case of single crystal, the entire solid consists of only one crystal and hence, periodic arrangement of atoms continues throughout the entire material.
- A polycrystalline material is an aggregate of many small crystals separated by well-defined grain boundaries and hence periodic arrangement of atoms is limited to small regions of the material called as grain boundaries.



### Fig. Two-dimensional representation of single crystal, polycrystalline and non-crystalline material

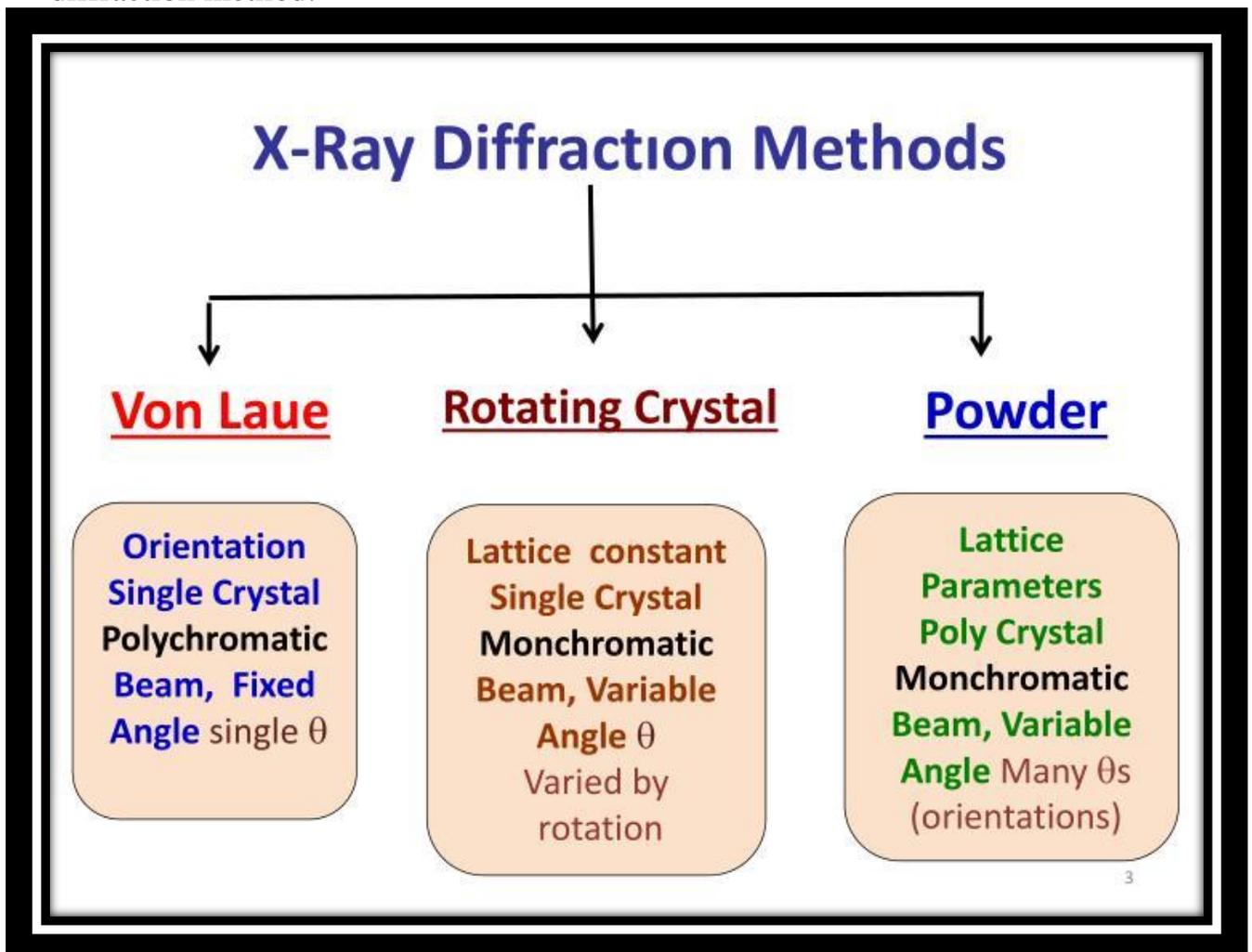
→ The non-crystalline substances are also called as amorphous substances materials. Single crystalline materials exhibit long range as well as short range periodicities while long range periodicity is absent in case of poly-crystalline materials and non-crystalline materials.

**Table 1.1 Distinction between crystalline and amorphous solids**

Crystalline Solids	Amorphous Solids
1. The atoms or molecules of the crystalline solids are periodic in space.	1. The atoms or molecules of the amorphous solids are not periodic in space.
2. Some crystalline solids are anisotropic i.e., the magnitude of physical properties [such as refractive index, electrical conductivity, thermal conductivity, etc.] are different along different directions of the crystal.	2. Amorphous solids are isotropic i.e., the magnitude of the physical properties are same along all directions of the solid.
3. Crystalline solids have sharp melting points.	3. Amorphous solids do not possess sharp melting points.
4. Breaks are observed in the cooling curve of a crystalline solid.	4. Breaks are not observed in the cooling curve.
5. A crystal breaks along certain crystallographic planes.	5. When an amorphous solid breaks, the broken surface is irregular because it has no crystal planes.

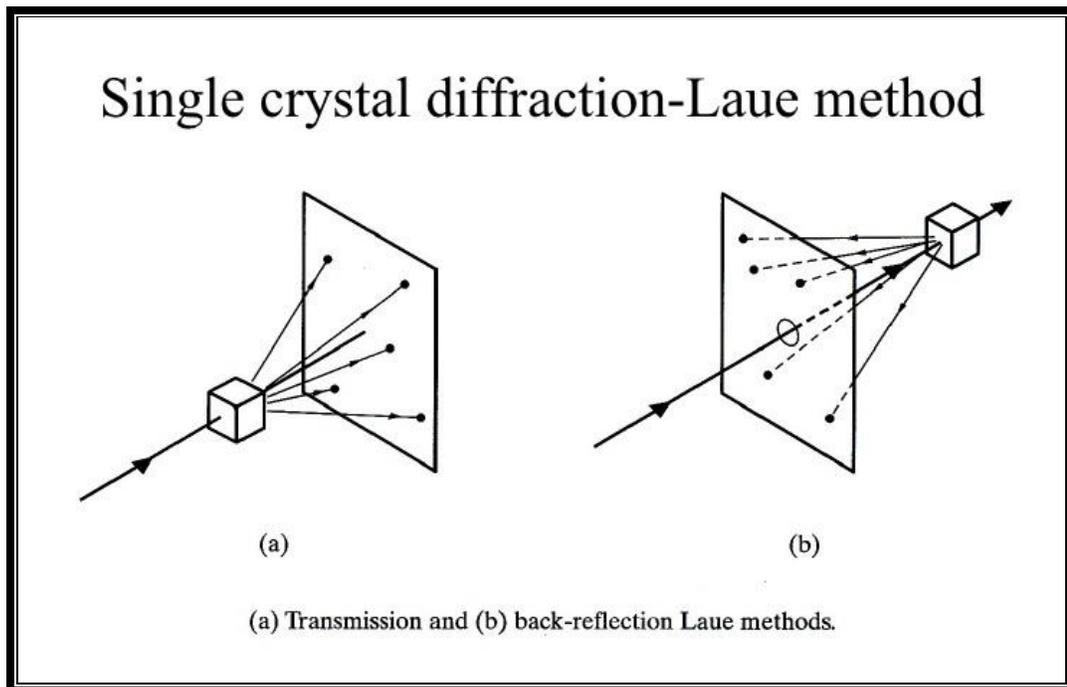
## ➤ X-ray Diffraction method

- Diffraction can occur whenever the Bragg law  $n\lambda = 2d \sin\theta$ , is satisfied. This equation puts very important condition on  $\lambda$  and  $\theta$  for any given crystal.
- With monochromatic radiation, an arbitrary setting of a single crystal in a beam of x-ray will not in general produce any diffracted beams.
- Someway of satisfying the Bragg law must be devised, and this can be done by continuously varying either  $\lambda$  or  $\theta$  during the experiments.
- The way in which these quantities are varied distinguish the three main diffraction methods.



Method	$\lambda$	$\theta$	Applicable for
Laue method	Variable	Fixed	Single Crystal
Rotating Crystal method	Fixed	Variable (in Part)	Single crystal
Powder method	Fixed	Variable	Crystalline or polycrystalline powder

❖ Von Laue method



→ The Laue method was the first diffraction method ever used. This method is used to study the orientation of crystal and to verify crystal symmetry.

- The Bragg angle  $\theta$  is therefore fixed for every set of planes in the crystal, and each set picks out and diffracts that particular wavelength which satisfies the Bragg law for the particular values of  $d$  and involved.
- Each diffracted beam thus has a different wavelength.
- A small crystal (sample) is placed in the path of a narrow beam of X-rays from a tungsten target at about 60 KV.
- The x ray beam will pass through a pinhole collimator to get the sharp x-rays.
- These sharp beams of x ray will go towards the sample to be examined.
- These sharp x rays beam will pass through a crystal and gives

**(1) Transmitted rays**

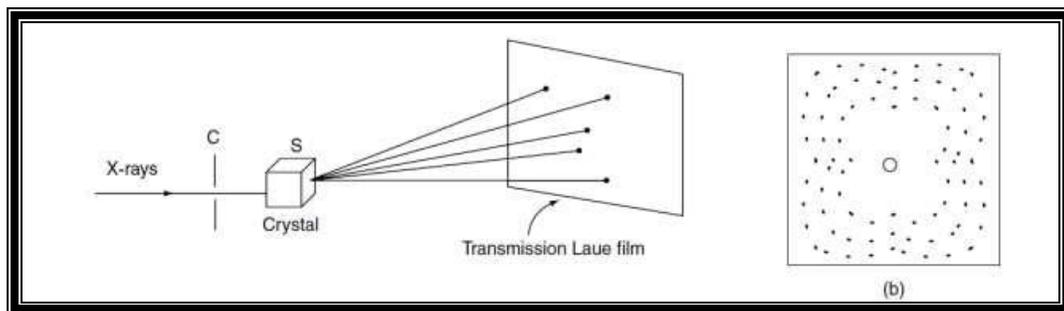
**(2) Diffracted rays (Transmission Laue method)**

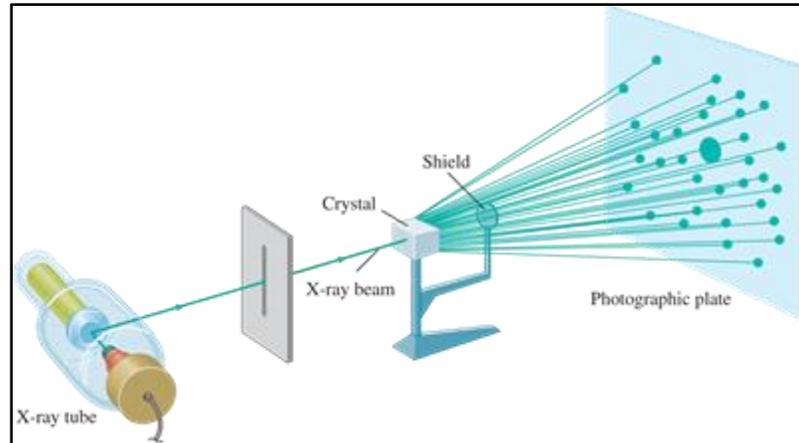
**(3) Reflected rays (Back reflection Laue method)**

- There are two variations of the Laue method, depending on the relative positions of source, crystal, and film (See the figure).

**• Transmission Laue Method**

- The film is flat and placed perpendicular to the incident beam. **The film in the transmission Laue method (the original Laue method) is placed behind the crystal so as to record the beams diffracted in the forward direction.**



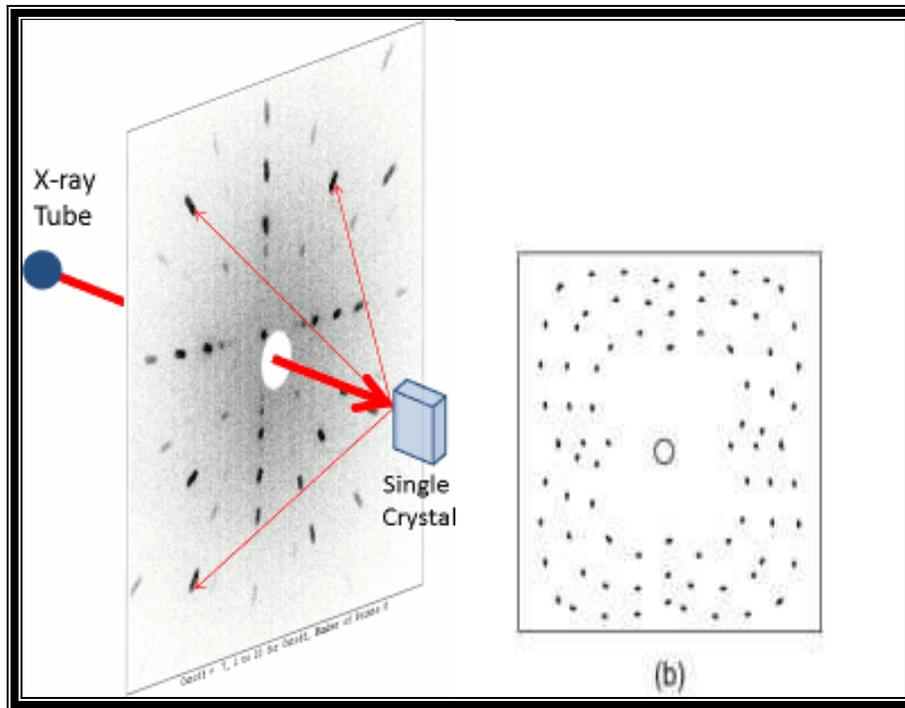


**Fig. Transmission Laue Method and Laue Pattern**

- This method is so called because the diffracted beams are partially transmitted through the crystal.
- Value of  $\theta$  is calculated and relative spacing between the planes are estimated.

- **Back-reflection Laue method**

- It is used for large and thick specimen, where the diffraction is difficult to get.
- In the back-reflection Laue method the film is placed between the crystal and the x-ray source, the incident beam passing through a hole in the film, and the beams diffracted in a backward direction are recorded.



**(a) Back Reflection Laue Method**

**(b) Laue Pattern**

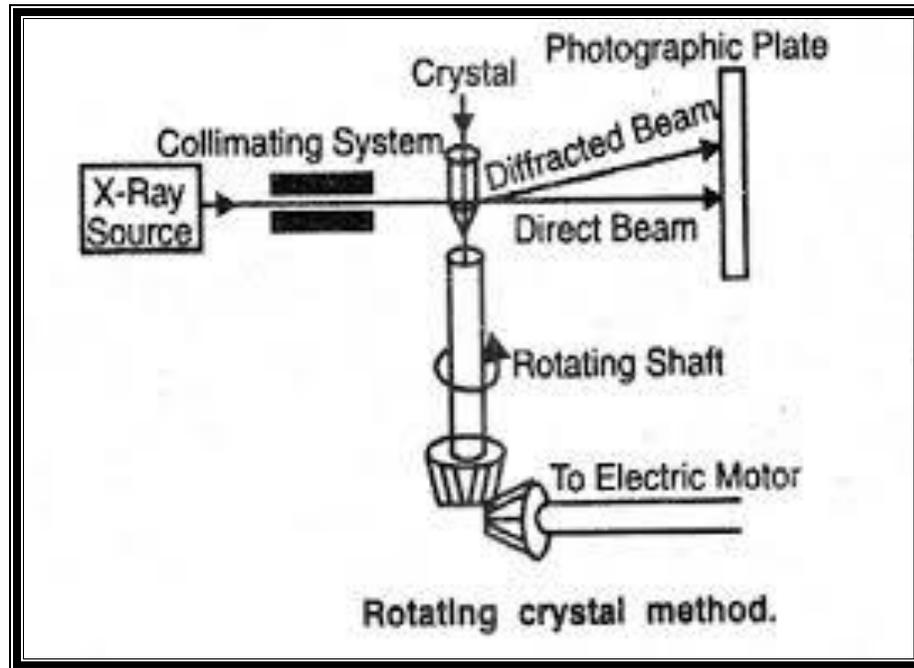
→ In either method, the diffracted beams form an array of spots on the film as shown in Fig. for a cubic crystal. This array of spots is commonly called a pattern, more specifically, **Laue pattern**, but the term is not used in any strict sense and does not imply any periodic arrangement of the spots.

→ Disadvantage of Back reflection method are

**(1) A big crystal is required**

**(2) It is used to orient solid state experiments and to determine the single crystal symmetry.**

## ❖ Rotating crystal method



**Fig. Rotating crystal method**

- X-ray is generated in the x-ray tube and x-ray beam is made monochromatic.
- Monochromatic radiation will fall on the crystal mounted on a shaft which can be rotated at uniform angular rate.
- Shaft will rotate the crystal at slow rate.
- This causes the set of planes to come successively into their reflecting position.
- Whenever it follows Bragg's equation, in that condition reflection and diffraction occurs.
- Each plane will produce a spot on the photographic film present in the camera.
- Photographic film will be fixed perpendicular to the incident x-ray beam inside the cylindrical camera.
- There are two methods available for photography.

### **(a) Complete rotation method**

- Series of complete revolution takes place.
- Each plane in the crystal diffracts x-ray four times during rotations.
- These four beams are distributed in the form of rectangular pattern.

### **(b) Oscillation method**

- Crystal is oscillated through an angle of  $15^{\circ}$  to  $20^{\circ}$ .
- The photographic film is also moved accordingly. This method is used to detect the size of unit cell in the crystal.

## **❖ Powder diffraction method**

- X-ray powder method is usually carried for polycrystalline materials.
- The powder method of x-ray diffraction was devised independently in 1916 by Debye and Scherrer in Germany and in 1917 by Hull in the United States.
- Basically, this method involves the diffraction of monochromatic x-rays by a powder specimen. In this connection, "monochromatic" usually means the strong K characteristic component of the general radiation.
- x-ray tube operated above the K excitation potential of the target material. "Powder" can mean either an actual, physical powder held together with a suitable binder or any specimen in polycrystalline form.
- The method is thus eminently suited for metallurgical work, since single crystals are not always available to the metallurgist and such materials as polycrystalline wire, sheet, rod, etc., may be examined nondestructively without any special preparation.
- There are three main powder methods in use, differentiated by the relative position of the specimen and film:

→ (1) **Debye-Scherrer method**. The film is placed on the surface of a cylinder and the specimen on the axis of the cylinder.

→ (2) **Focusing method**. The film, specimen, and x-ray source are all placed on the surface of a cylinder.

→ (3) **Pinhole method**. The film is flat, perpendicular to the incident x-ray beam, and located at any convenient distance from the specimen.

→ In all these methods, the diffracted beams lie on the surfaces of cones whose axes lie along the incident beam or its extension; each cone of rays is diffracted from a particular set of lattice planes.

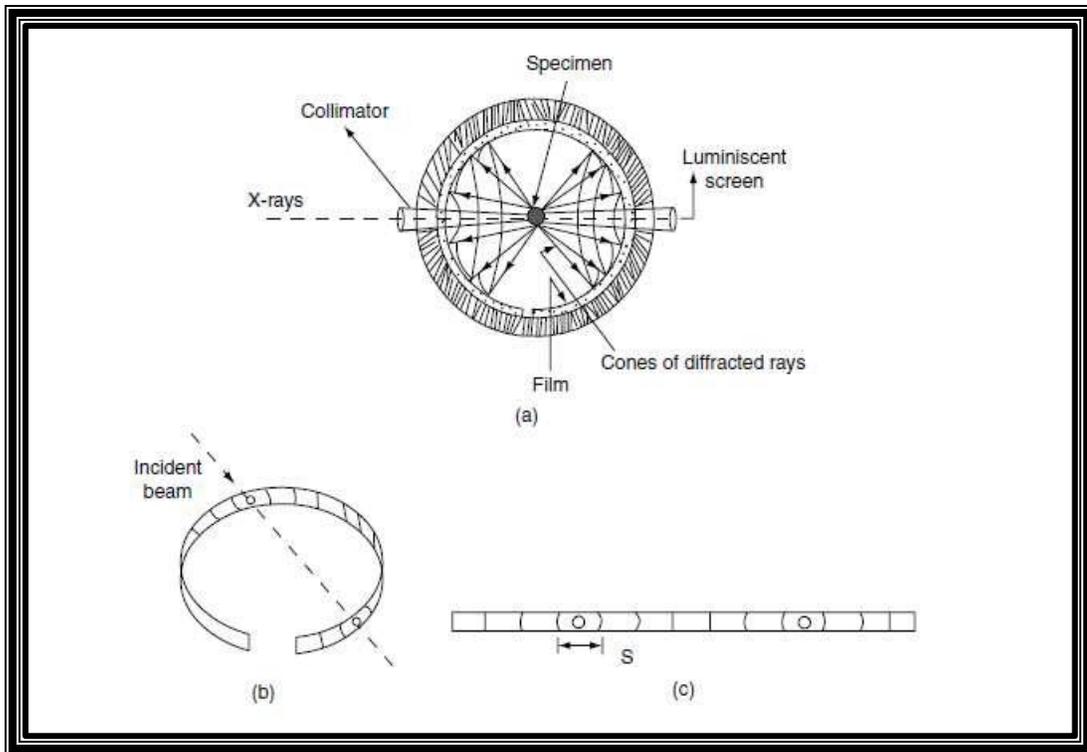
→ In the Debye-Scherrer and focusing methods, only a narrow strip of film is used and the recorded diffraction pattern consists of short lines formed by the intersections of the cones of radiation with the film.

→ In the pinhole method, the whole cone intersects the film to form a circular diffraction ring.

→ The powder photograph is obtained in the following way.

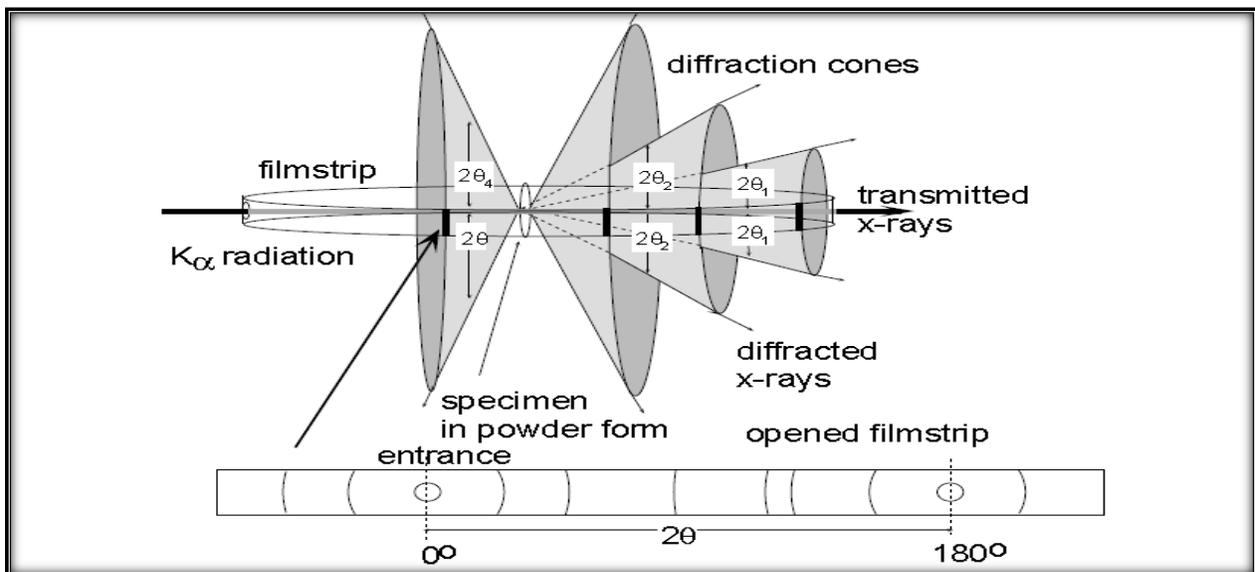
### ➤ **Debye-Scherrer powder diffraction method**

→ The given polycrystalline material is grinding to fine powder and this powder can be taken either in a capillary tube made up of non-diffracting material or is just struck on a hair with small quantity of binding material and fixed at the center of cylindrical Debye-Scherrer camera as shown in Fig.

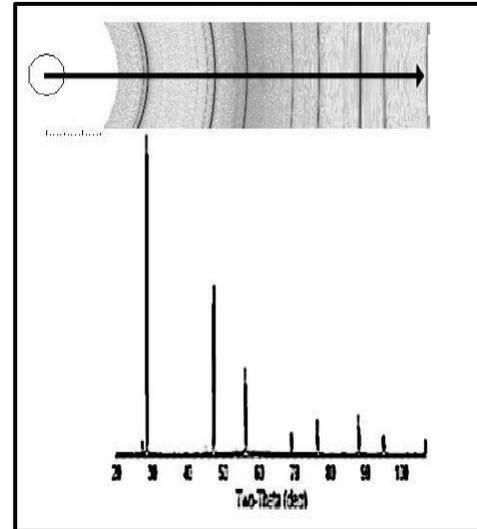
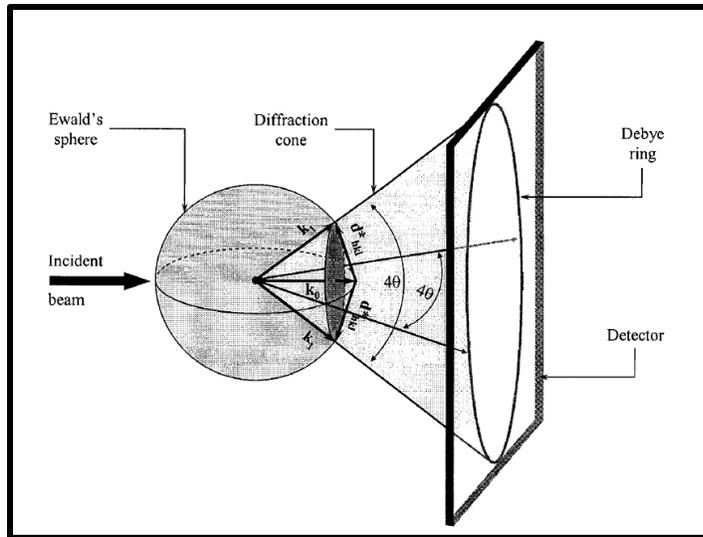


**Figure: Powder diffraction method**

- (a) Debye -Scherrer cylindrical camera
- (b) Film mounted in camera
- (c) Film on stretch-out



**Fig. Debye-Scherrer powder diffraction setup and analysis**



**Fig. Cross-section and pattern of powder diffraction method**

- A stripe of X-ray photographic film is arranged along the inner periphery of the camera.
- A beam of monochromatic X-rays is passed through the collimator to obtain a narrow fine beam of X-rays.
- This beam falls on the polycrystalline specimen and gets diffracted.
- The specimen contains very large number of small crystallites oriented in random directions.
- So, all possible diffraction planes will be available for Bragg reflection to take place.
- Such reflections will take place from many sets of parallel planes lying at different angles to the incident X-ray beam.
- Also, each set of planes gives not only first-order reflections but also of higher orders as well. Since all orientations are equally likely, the reflected rays will form a **cone** whose axis lies along the direction of the incident beam and whose

semi-vertical angle is equal to twice the glancing angle ( $\theta$ ), for that particular set of planes.

- For each set of planes and for each order, there will be such a cone of reflected X-rays. Their intersections with a photographic film set with its plane normal to the incident beam, form a series of concentric circular rings.
- In this case, a part of the reflected cone is recorded on the film and it is a pair of curves, the resulting pattern is shown in Fig.(c).
- Diameter of these rings or corresponding curves is recorded on the film, and using this the glancing angle and interplanar spacing of the crystalline substance can be determined. Figure (b) shows the film mounted in the camera and the X-ray powder pattern obtained.
- The film on spread-out is shown in Fig (c). The distance between any two corresponding curves on the film is indicated by the symbol  $S$ .
- In case of cylindrical camera, the diffraction angle  $\theta$  is proportional to  $S$ . Then,

$$\theta = \frac{S}{4R}$$

where  $R$  is representing the radius of the camera.

$S$  is the distance between any two corresponding curves on the film

If  $S_1, S_2, S_3, \dots$  etc. are the distance between symmetrical lines on the stretched film, then,

$$\theta_1 = \frac{S_1}{4R}, \theta_2 = \frac{S_2}{4R}, \theta_3 = \frac{S_3}{4R} \dots\dots$$

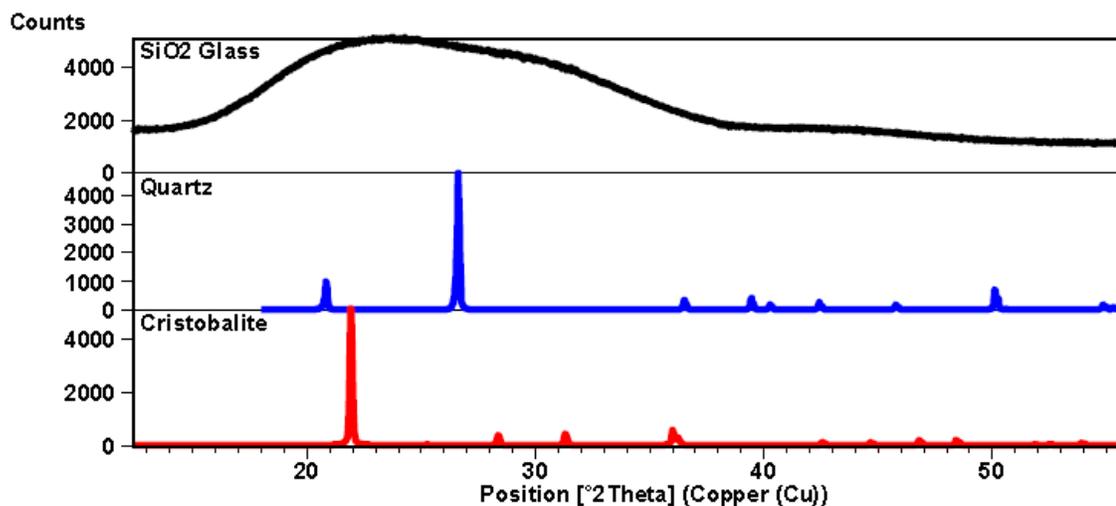
Using these values of  $\theta_n$  in Bragg's equation  $n\lambda = 2d \sin \theta_n$

Where  $n = 1, 2, 3, \dots$  = order of diffraction

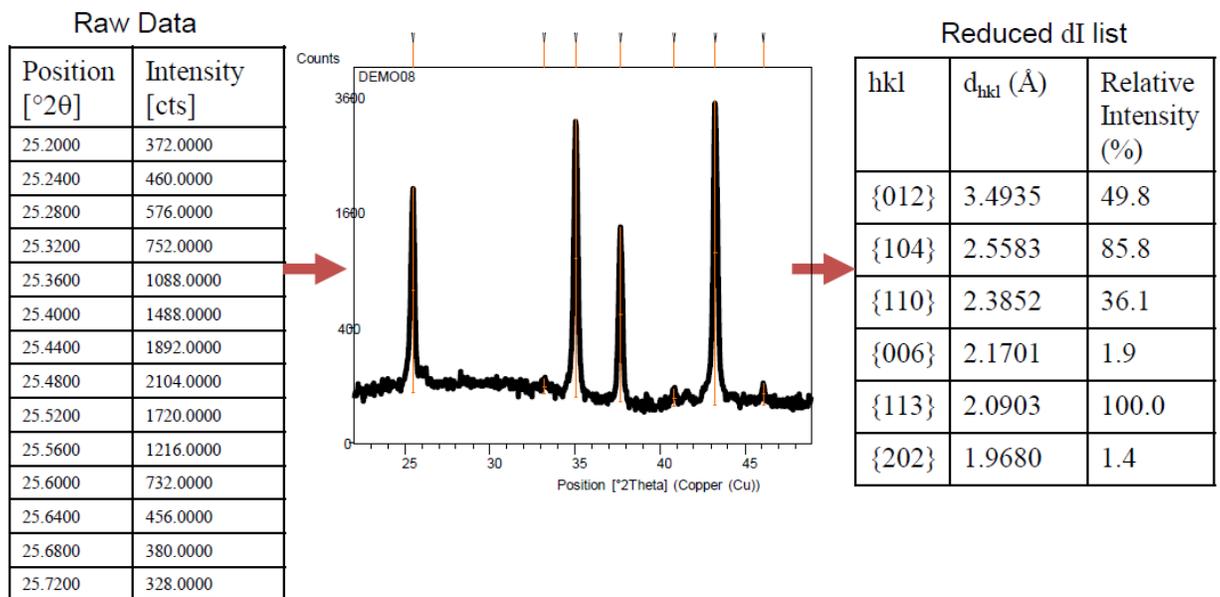
$d$  = Interplanar spacing

$\theta_n$  = Angle of diffraction for  $n$ th order.

- Each diffraction peak is actually a Debye diffraction cone produced by the tens of thousands of randomly oriented crystallites in an ideal sample. A cone along the sphere corresponds to a single Bragg angle  $2\theta$
- The linear diffraction pattern is formed as the detector scans along an arc that intersects each Debye cone at a single point
- Only a small fraction of scattered X-rays are observed by the detector.
  
- In a Debye–Scherrer arrangement, after exposing a powder of a crystalline material to monochromatic X-rays, the developed film strip will exhibit diffraction patterns such as indicated in fig. 12. Each diffraction peak (dark line) on the film strip corresponds to constructive interference at planes of a particular interplanar spacing  $[d_{(hkl)}]$ . The problem now consists of “indexing” the individual lines – i.e., determining the Miller indices (hkl) for the diffraction lines:
- X-rays scatter from atoms in a material and therefore contain information about the atomic arrangement



- The three X-ray scattering patterns above were produced by three chemically identical forms SiO<sub>2</sub>
- Crystalline materials like quartz and Cristobalite produce X-ray diffraction patterns –Quartz and Cristobalite have two different crystal structures –The Si and O atoms are arranged differently, but both have long-range atomic order – The difference in their crystal structure is reflected in their different diffraction patterns.
- Diffraction patterns are collected as absolute intensity vs 2θ, but are best reported as relative intensity vs d<sub>hkl</sub>.
- Example :



→ The peak position as 2θ depends on instrumental characteristics such as wavelength.

- **The peak position as d<sub>hkl</sub> is an intrinsic, instrument-independent, material property.**
- **Bragg's Law is used to convert observed 2θ positions to d<sub>hkl</sub>.**
- **The absolute intensity, i.e. the number of X rays observed in a given peak, can vary due to instrumental and experimental parameters.**

- **The relative intensities of the diffraction peaks should be instrument independent.**
- **To calculate relative intensity, divide the absolute intensity of every peak by the absolute intensity of the most intense peak, and then convert to a percentage.**
- **The most intense peak of a phase is therefore always called the “100% peak”.**
- **Peak areas are much more reliable than peak heights as a measure of intensity.**

→ **The wavelength of X rays are similar to the distance between atoms in a crystal. Therefore, we use X-ray scattering to study atomic structure.**

→ **The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal.**

→ The amorphous glass does not have long-range atomic order and therefore produces only broad scattering features

→ Amorphous materials **like glass do not have a periodic array** with long-range order, so they **do not produce a diffraction pattern**. Their X-ray scattering pattern features broad, poorly defined amorphous **‘humps’**.

### **❖ Analytical Information**

- **Phase Composition of a Sample**

→ Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities

- **Unit cell lattice parameters and Bravais lattice symmetry**

→ Index peak positions

→ Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.

- **Residual Strain (macrostrain)**
- **Crystal Structure**

→ By Rietveld refinement of the entire diffraction pattern

- **Epitaxy/Texture/Orientation**
- **Crystallite Size and Microstrain**

→ Indicated by peak broadening

→ Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

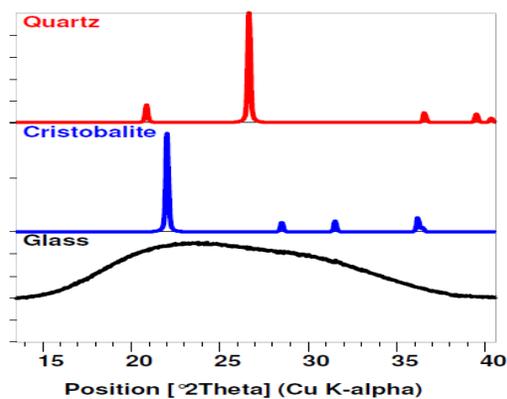
### ➤ Phase Identification

→ The diffraction pattern for every phase is as unique as your fingerprint

→ Phases with the same chemical composition can have drastically different diffraction patterns.

→ Use the position and relative intensity of a series of peaks to match experimental data to the reference patterns in the database

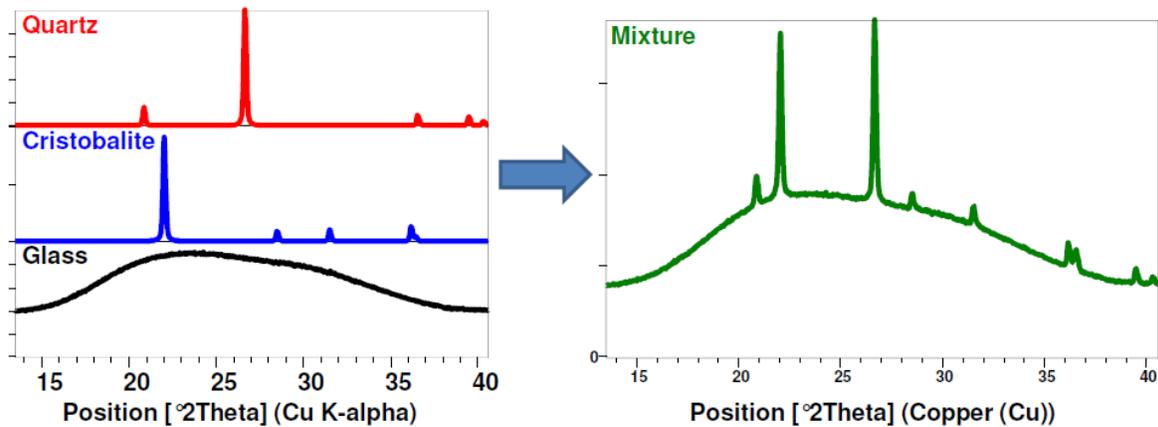
### Each “phase” produces a unique diffraction pattern



- A phase is a specific chemistry and atomic arrangement.
- Quartz, cristobalite, and glass are all different phases of SiO<sub>2</sub>
  - They are chemically identical, but the atoms are arranged differently.
  - As shown, the X-ray diffraction pattern is distinct for each different phase.
  - Amorphous materials, like glass, do not produce sharp diffraction peaks.

The X-ray diffraction pattern is a fingerprint that lets you figure out what is in your sample.

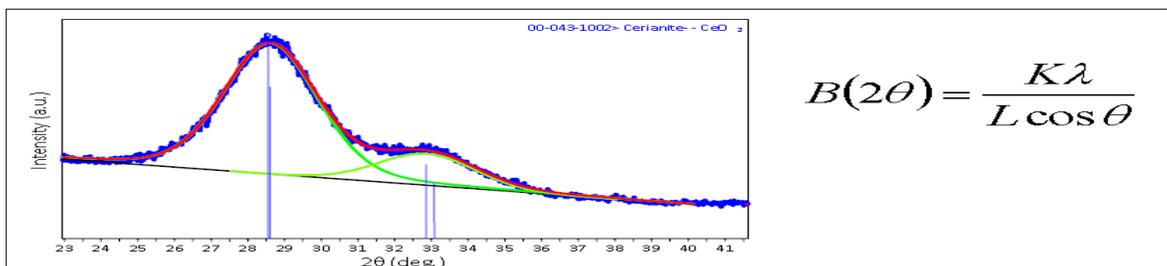
The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



### ➤ Unit Cell Lattice Parameter Refinement

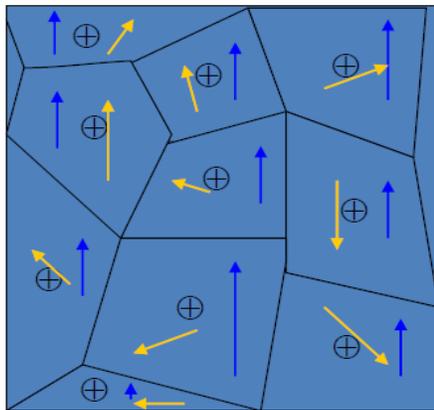
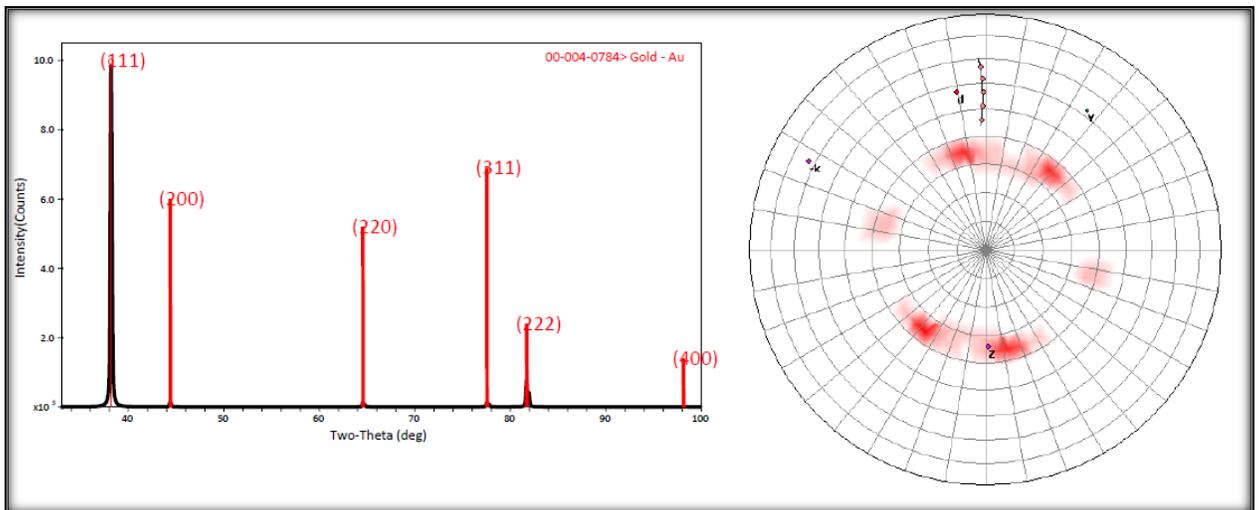
- By accurately measuring peak positions over a long range of  $2\theta$ , you can determine the unit cell lattice parameters of the phases in your sample
- Alloying, substitutional doping, temperature and pressure, etc can create changes in lattice parameters that you may want to quantify
- Use many peaks over a long range of  $2\theta$  so that you can identify and correct for systematic errors such as specimen displacement and zero shift
- Measure peak positions with a peak search algorithm or profile fitting
- Profile fitting is more accurate but more time consuming than numerically refining the lattice parameters

### ➤ Crystallite Size and Microstrain



- Crystallites smaller than ~120nm create broadening of diffraction peaks
  - This peak broadening can be used to quantify the average crystallite size of nanoparticles using the **Scherrer equation**
  - Must know the contribution of peak width from the instrument by using a calibration curve
- Microstrain may also create peak broadening
  - Analyzing the peak widths over a long range of 2theta using a Williamson-Hull plot can let you separate microstrain and crystallite size

➤ Preferred Orientation (texture)



Also, if the direction  $[u_1v_1w_1]$  is parallel for all regions, the structure is like a single crystal  
 However, the direction  $[u_1v_1w_1]$  is not aligned for all regions, the structure is like a mosaic structure, also called as **Mosaic Texture**

⊕  $[uvw]$  i.e. perpendicular to the surface of all grains is parallel to a direction  $[uvw]$

→ Preferred orientation of crystallites can create a systematic variation in diffraction peak intensities

- Can qualitatively analyze using a 1D diffraction pattern
- A pole figure maps the intensity of a single peak as a function of tilt and rotation of the sample
- This can be used to quantify the texture

### ➤ **Analytical Information: Qualitative and Quantitative Analysis**

→ A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances.

→ This fact is the basis for the diffraction method of chemical analysis.

→ **Qualitative analysis** for a particular substance is accomplished by identification of the pattern of that substance.

→ **Quantitative analysis** is also possible, because the intensities of the diffraction lines due to one constituent of a mixture depend on the proportion of that constituent in the specimen.

### ❖ **Qualitative analysis**

→ The particular advantage of diffraction analysis is that it discloses the presence of a substance as that substance actually exists in the sample, and not in terms of its constituent chemical elements.

→ For example, if a sample contains the compound  $A_xB_y$ , the diffraction method will disclose the presence of  $A_xB_y$  as such, whereas ordinary chemical analysis would show only the presence of elements A and B. Furthermore, if the sample contained both  $A_xB_y$  and  $A_xB_{2y}$ , both of these compounds would be disclosed by

the diffraction method, but chemical analysis would again indicate only the presence of A and B.\*

- The powder pattern of a substance is characteristic of that substance and forms a sort of fingerprint by which the substance may be identified.
- If we had on hand a collection of diffraction patterns for a great many substances, we could identify an unknown by preparing its diffraction pattern and then locating in our file of known patterns one which matched the pattern of the unknown exactly.
- The collection of known patterns has to be fairly large, if it is to be at all useful, and then pattern-by-pattern comparison in order to find a matching one becomes out of the question.
- What is needed is a system of classifying the known patterns so that the one which matches the unknown can be located quickly. Such a system was devised by Hanawalt in 1936. Any one powder pattern is characterized by a set of line positions  $2\theta$  and a set of relative line intensities  $I$ .
- But the angular positions of the lines depend on the wavelength used, and a more fundamental quantity is the spacing  $d$  of the lattice planes forming each line.
- Hanawalt therefore decided to describe each pattern by listing the  $d$  and  $I$  values of its diffraction lines, and to arrange the known patterns in decreasing values of  $d$  for the strongest line in the pattern.
- This arrangement made possible a search procedure which would quickly locate the desired pattern. In addition, the problem of solving the pattern was avoided and the method could be used even when the crystal structure of the substance concerned was unknown.
- Identification of a phase or phases in a specimen by comparison with “standard” patterns” (i.e., data collected or calculated by someone else), and relative

estimation of proportions of different phases in multiphase specimens by comparing peak intensities attributed to the identified phases.

### • Hanawalt Method:

- The Hanawalt Manual, lists standard phases from the file, along with their eight most intense d-spacings and intensities.
- The d value of the strongest line on the pattern is used to determine which group is to be consulted in the manual. If the other six lines of one of these standards patterns match lines of similar relative intensity in the unknown pattern, the standard selected is most likely a match for the unknown.
- To be more certain, the data for the full pattern are then compared with the unknown pattern; any lines from the unknown that do not match lines of the standard may indicate the presence of a second phase and that the unknown pattern did not come from a single phase.

→ After the experimental values of d and  $I/I_1$  are tabulated, the unknown can be identified by the following procedure :

- 1) **Locate the proper  $d_1$  group in the numerical index.**
- 2) **Read down the second column of d values to find the closest match to  $d_2$ . (In comparing experimental and tabulated d values, always allow for the possibility that either set of values may be in error by 0.01Å.)**
- 3) **After the closest match has been found for  $d_1$ ,  $d_2$ , and  $d_3$ , compare their relative intensities with the tabulated values.**

4) When good agreement has been found for the three strongest lines listed in the index, locate the proper data card in the file, and compare the  $d$  and  $I/I_1$  values of all the observed lines with those tabulated. When full agreement is obtained, identification is complete.

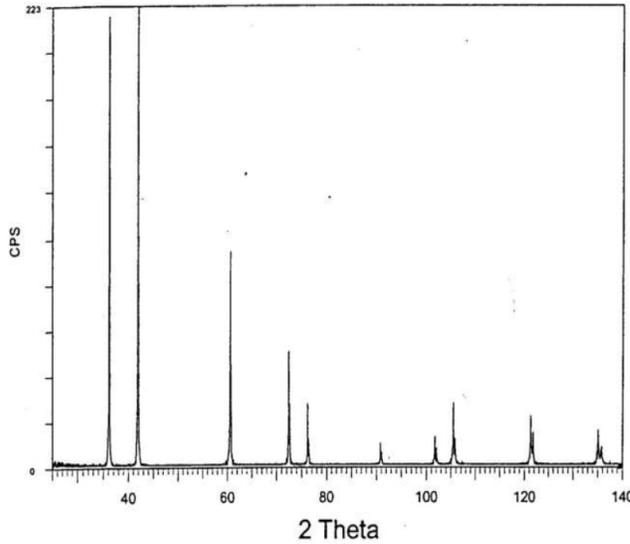


Fig 2. X-ray diffraction pattern of the unknown material

Peak number	$2\theta$ (°)	$d$ (Å)	$I/I_1$
1	35.84	2.503	85
2	41.73	2.163	100
3	60.47	1.530	55
4	72.37	1.305	32
5	76.02	1.251	18
6	90.75	1.082	11
7	101.71	0.993	13
8	105.48	0.968	25

Table 1. Experimental Data for Identifying an Unknown Sample

- **TiC** is the unknown specimen

Strongest reflections				PSC	Chemical formula	PDF#				
2.18 <sub>x</sub>	2.50 <sub>x</sub>	2.49 <sub>5</sub>	2.27 <sub>5</sub>	2.19 <sub>5</sub>	1.68 <sub>5</sub>	1.44 <sub>5</sub>	1.30 <sub>5</sub>	oP12.50	C <sub>20</sub> Cr <sub>25</sub> V <sub>55</sub>	18-401
2.18 <sub>x</sub>	2.50 <sub>4</sub>	1.53 <sub>4</sub>	1.56 <sub>3</sub>	2.60 <sub>2</sub>	2.59 <sub>2</sub>	1.31 <sub>2</sub>	1.30 <sub>2</sub>	hR8	NaFe <sub>2</sub> O <sub>3</sub>	32-1066
2.17 <sub>x</sub>	2.50 <sub>7</sub>	2.44 <sub>6</sub>	3.30 <sub>3</sub>	3.12 <sub>3</sub>	1.56 <sub>3</sub>	2.63 <sub>2</sub>	3.81 <sub>1</sub>	hP*	Ga <sub>3</sub> Ta <sub>5</sub> O <sub>x</sub>	33-750
2.17 <sub>8</sub>	2.50 <sub>x</sub>	1.53 <sub>4</sub>	1.31 <sub>4</sub>	1.25 <sub>3</sub>	0.00 <sub>1</sub>	0.00 <sub>1</sub>	0.00 <sub>1</sub>	cF8	TaN	32-1283
2.16 <sub>8</sub>	2.50 <sub>x</sub>	3.40 <sub>8</sub>	2.33 <sub>8</sub>	2.11 <sub>8</sub>	1.74 <sub>8</sub>	1.53 <sub>8</sub>	2.74 <sub>5</sub>	oP20	LaCrOS <sub>2</sub>	31-659
2.16 <sub>8</sub>	2.50 <sub>x</sub>	2.19 <sub>x</sub>	1.38 <sub>5</sub>	1.25 <sub>5</sub>	1.93 <sub>1</sub>	2.32 <sub>1</sub>	2.27 <sub>1</sub>		(Al <sub>25</sub> Fe <sub>25</sub> Nb <sub>50</sub> )	23-1008
2.16 <sub>x</sub>	2.50 <sub>8</sub>	1.53 <sub>6</sub>	1.30 <sub>3</sub>	0.97 <sub>3</sub>	0.88 <sub>3</sub>	1.25 <sub>2</sub>	0.83 <sub>2</sub>	cF8	TiC	32-1383
2.15 <sub>x</sub>	2.50 <sub>5</sub>	2.28 <sub>5</sub>	1.32 <sub>x</sub>	1.23 <sub>7</sub>	1.29 <sub>6</sub>	1.89 <sub>5</sub>	1.36 <sub>5</sub>	cF116	(Re <sub>0.65</sub> Fe <sub>0.35</sub> ) <sub>23</sub> B <sub>6</sub>	19-619
2.15 <sub>8</sub>	2.50 <sub>x</sub>	2.20 <sub>x</sub>	1.45 <sub>5</sub>	1.38 <sub>5</sub>	1.25 <sub>5</sub>	2.03 <sub>2</sub>	1.93 <sub>2</sub>		μ'-Al <sub>23</sub> Co <sub>23</sub> Ta <sub>54</sub>	23-1007

An entry of 0.00<sub>1</sub> indicates that either there were no additional reflections present in the pattern or they were not indexed. The subscript 1 is included only for computer purposes, it has no physical meaning.

[Hanawalt Method]

- **Practical difficulties.** In theory, the Hanawalt method should lead to the positive identification of any substance whose diffraction pattern is included in the card file.
- In practice, various difficulties arise, and these are usually **due either to errors in the diffraction pattern of the unknown or to errors in the card file.**
- Errors of the first kind, those affecting the observed positions and intensities of the diffraction lines, have been discussed in various parts of this book and need not be reexamined here.
- There is, however, one point that deserves some emphasis and that concerns the diffractometer. **It must be remembered that the absorption factor for this instrument is independent of the angle  $2\theta$ , whereas, in a Debye-Scherrer camera, absorption decreases line intensity more at small than at large angles; the result is that the low angle lines of most substances appear stronger, relative to medium- or high-angle lines, on a diffractometer chart than on a Debye-Scherrer photograph.**
- This fact should be kept in mind whenever a diffractometer pattern is compared with one of the standard patterns in the ASTM file, because practically all of the latter were obtained with a Debye-Scherrer camera.
- On the other hand, **it should not be concluded that successful use of the Hanawalt method requires relative intensity measurements of extremely high accuracy. It is enough, in most cases, to be able to list the lines in the correct order of decreasing intensity.**
- Errors in the card file itself are generally more serious, since they may go undetected by the investigator and lead to mistaken identifications.

- Even a casual examination of the ASTM alphabetical index will disclose numerous examples of substances represented in the file by two or more cards, often with major differences in the three strongest lines listed.
- Work is now in progress at the National Bureau of Standards to resolve such ambiguities, correct other kinds of errors, and obtain new standard patterns.
- The results of this work, which is all done with the diffractometer, are published from time to time in NBS Circular 539, "Standard X-Ray Diffraction Powder Patterns, and incorporated in card form in the most recently issued sections of the ASTM file.
- Whenever any doubt exists in the investigator's mind as to the validity of a particular identification, he should prepare his own standard pattern. Thus, if the unknown has been tentatively identified as substance X, the pattern of pure X should be prepared under exactly the same experimental conditions used for the pattern of the unknown.
- Comparison of the two patterns will furnish positive proof, or disproof, of identity. The Hanawalt method fails completely, of course, when the unknown is a substance not listed in the card file, or when the unknown is a mixture and the component to be identified is not present in sufficient quantity to yield a good diffraction pattern.

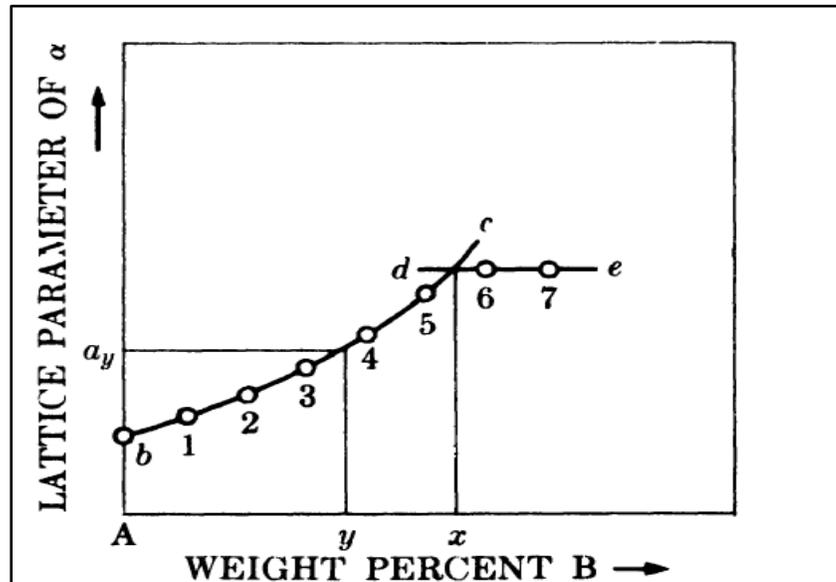
### ❖ **Quantitative Analysis**

- The determination of amounts of different phases in multi-phase samples.
- Determination of particular characteristics of single phases including precise determination of crystal structure or crystallite size and shape.
- All quantitative analysis requires precise and accurate determination of the diffraction pattern for a sample both in terms of peak positions and intensities

→ Many factors prevent the direct comparison of concentration with peak intensity. The basic factor is the different x-ray absorption properties of the substances in the sample.

→ The most common methods of Quantitative Analysis are:

- **Chemical analysis by parameter measurement.**



**Fig. Parameter v/s Composition Curve**

→ The lattice parameter of a binary solid solution of B in A depends only on the percentage of B in the alloy, as long as the solution is unsaturated.

→ This fact can be made the basis for chemical analysis by parameter measurement. All that is needed is a parameter vs. composition curve, such as curve be of Fig. , which can be established by measuring the lattice parameter of a series of previously analyzed alloys.

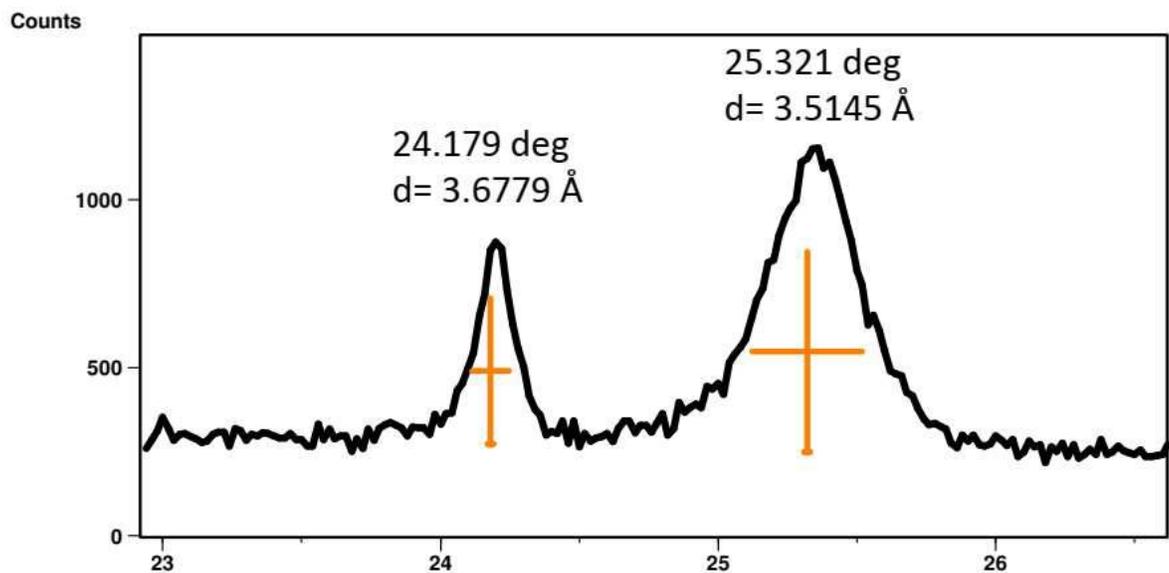
→ This method has been used in **diffusion studies to measure the change in concentration of a solution with distance from the original interface.**

→ Its accuracy depends entirely on the slope of the **parameter-composition curve.**

- In alpha brasses, which can contain from to about 40 percent zinc in copper, an accuracy of 1 percent zinc can be achieved without difficulty.
- **This method is applicable only to binary alloys.** In ternary solid solutions, for example, the percentages of two components can be independently varied. The result is that two ternary solutions of quite different compositions can have the same lattice parameter.

### ▪ Lattice Parameter Method

- Applicable **for continuous solid-solutions**
- Accurate method of **determining the chemical compositions by lattice parameters**
- Determine **composition of single phase, not amounts**
- **Determination of unit cell dimensions**



- **To calculate unit cell lattice parameters from the diffraction peak positions**

- Convert the observed peak positions,  $2\theta$ , into  $d_{hkl}$  values using Bragg's Law:

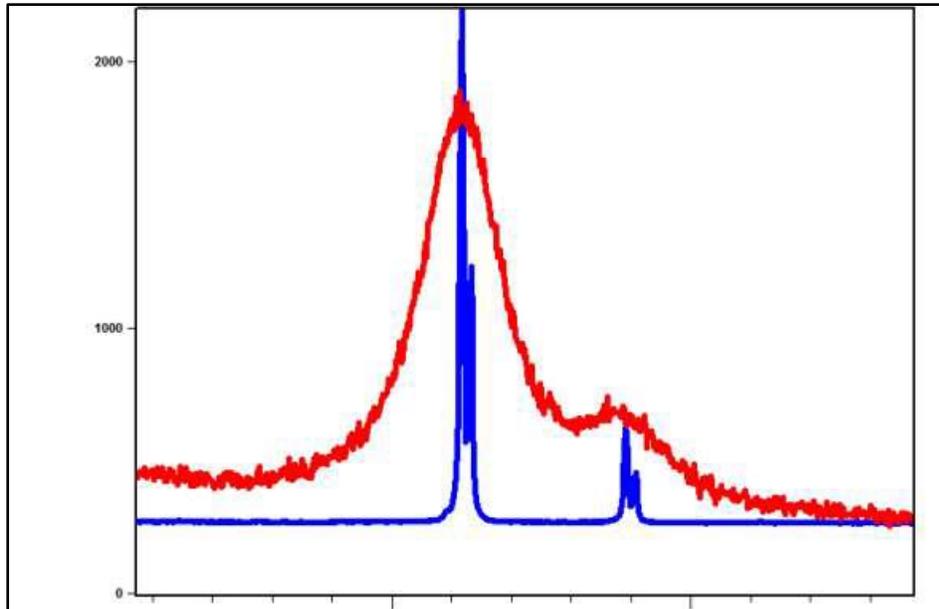
$$d_{hkl} = \frac{\lambda}{2 \sin \theta}$$

- Determine the Miller indices (hkl) of the diffraction peaks from the published reference pattern
  - If you do not have access to a reference pattern that identifies (hkl) then you will need to index the pattern to determine the (hkl)
- Use the  $d^2$  equation to calculate the lattice parameters
  - Most analysis programs contain an unit cell refinement algorithm for numerically solving the lattice parameters
  - These programs can also calculate and correct for peak position error due to specimen displacement.

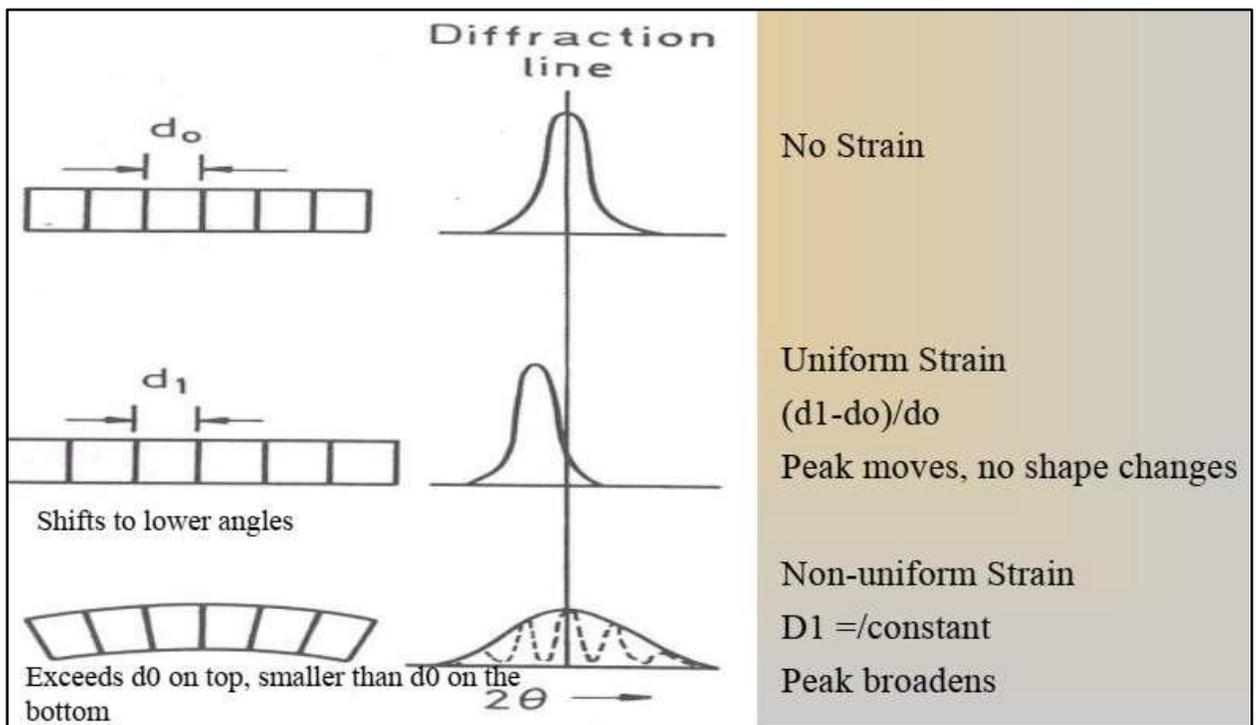
$$d_{hkl}^2 = h^2 a^2 + k^2 b^2 + l^2 c^2 + 2hka^* b^* \cos \gamma^* + 2hla^* c^* \cos \beta^* + 2klb^* c^* \cos \alpha^*$$

#### → Microstructural Information

- Peak Broadening:
- Smaller crystallite size in nano-crystalline materials
- More stacking faults, microstrain and other defects in crystal
- An inhomogeneous composition in a solid solution



These patterns show the difference between **bulk ceria (blue)** and **nanocrystalline ceria (red)**



### ▪ The Absorption Method

→ Requires the **measurement of intensity from a diffraction peak in the mixture** and **from a pure standard of material**.

$$\frac{I}{I_{\text{pure}}} = \frac{(\mu/\rho)}{(\mu/\rho)_m} X$$

#### Diffraction Equation for The Absorption Diffraction Method

- $I_{\text{pure}}$  is the intensity of a peak from a pure phase
- $I$  is the intensity of the same peak of the phase in mixture
- $X$  is the weight fraction of the phase in the mixture
- $(\mu/\rho)$  is the mass-absorption coefficient of the phase
- $(\mu/\rho)_m$  is the mass-absorption coefficient of the entire sample

→ The mass-absorption coefficient of the sample and the phase under analysis must be known (International Tables for X-Ray Crystallography)

→ The accuracy of this technique depends strongly on consistent sample preparation and on appropriate pure standards

### ▪ The Method of Standard Additions

→ Also known as the **Spiking Method** or **The Doping Method**

→ The peak intensity is first measured of the phase of interest then again measuring the intensity after adding a small amount of this phase.

→ Useful when only one phase is to be quantified.

$$C_0 = \frac{I_1 C_1}{I_2 - I_1}$$

#### Equation for The Method of Standard Additions

- $I_1$  is the intensity of a diffraction line from the sample
- $I_2$  is the intensity of the same line after it has been spiked
- $C_0$  is the concentration of the phase of interest
- $C_1$  is the amount of phase added to spike the sample

## ▪ **The Rietveld Method**

→ The Rietveld method refines user-selected parameters to **minimize the difference between an experimental pattern (observed data) and a model based on the hypothesized crystal structure and instrumental parameters (calculated pattern)**

→ Can **refine information about a single crystal structure**

- Confirm/disprove a hypothetical crystal structure
- Refine lattice parameters
- Refine atomic positions, fractional occupancy, and thermal parameter

→ **Refine information about a single sample**

- Preferred orientation

→ **Refine information about a multiphase sample**

- Determine the relative amounts of each phase

## ❖ Applications in Pharmaceutical Industry and in Forensic Science

### ❖ Pharmaceutical Industries

- X-ray diffraction (XRD) can be used to unambiguously characterize the composition of pharmaceuticals. An XRD-pattern is a direct result of the crystal structures, which are present in the pharmaceutical under study. As such, the parameters typically associated with crystal structure can be simply accessed. For example, once an active drug has been isolated, an indexed X-ray powder diffraction pattern is required to analyse the crystal structure, secure a patent and protect the company's investment.
- For multi-component formulations, the actual percentages of the active ingredients in the final dosage form can be accurately analysed in situ, along with the percentage of any amorphous packing ingredients used.
- XRD is the key technique for solid-state drug analysis, benefiting all stages of drug development, testing and production.

### ❖ Forensic science

- XRD is used mainly in contact trace analysis. Examples of contact traces are paint flakes, hair, glass fragments, stains of any description and loose powdered materials. Identification and comparison of trace quantities of material can help in the conviction or exoneration of a person suspected of involvement in a crime.

→ [X-ray diffraction](#) or XRD is one such technique which is nondestructive and the sample requires minimum sample preparation prior to analysis. The only requirement is that the sample should be homogeneous in nature so as to provide uniform analysis results even if a small portion is analysed from a bulk quantity. Samples commonly received for forensic testing commonly include:

- Building materials such as cement, concrete, steel rods, bricks,etc
- Drugs of abuse and other banned substances
- Residues from site of arson such as kerosene oil, gasoline or cotton lints
- Explosive residues and splinters from sites
- Accident scene samples such as blood spots, paint chips,etc
- Assault samples such as torn garments, broken glass,cosmetic marks etc.
- Theft and robbery site samples which include gunshot residues, tools, murder weapons, forged documents, blood residues,etc.

→ The samples can be analysed by XRD if it exhibits a degree of crystallinity even if the remaining content is amorphous. The technique helps establish the presence or absence of a particular material through comparison against a reference XRD data base. The present article discusses some of the [XRD applications](#) of common samples picked up from scene of crime.