X-Ray Diffraction

Phase identification of crystalline materials

XRD

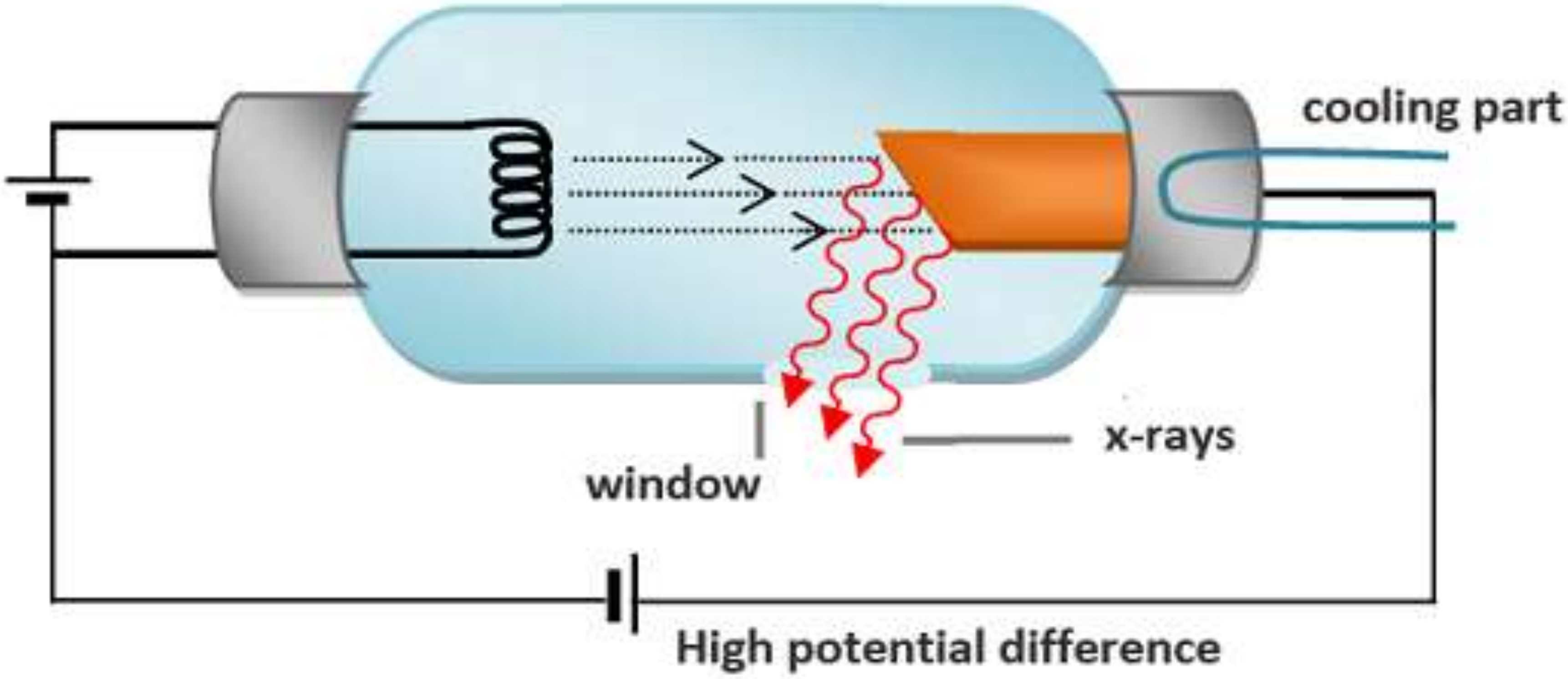
- **X-ray diffraction analysis is a technique used in materials science to determine the crystallographic structure of a material**
- **XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material**

- **X-rays are electromagnetic waves having wavelength in the range of 0.1-100 A° and energies in the range of 120 eV to 120 keV**
- **X-rays up to about 10 keV (1-100 A° wavelength) are classified as "soft" X-rays, and from about 10 to 120 keV (0.1-1 A°) as "hard" X-rays, due to their penetrating abilities**
- **The X-rays when interact with matter resulted into Fluorescence, Ionization or Diffraction**

Production of x-rays

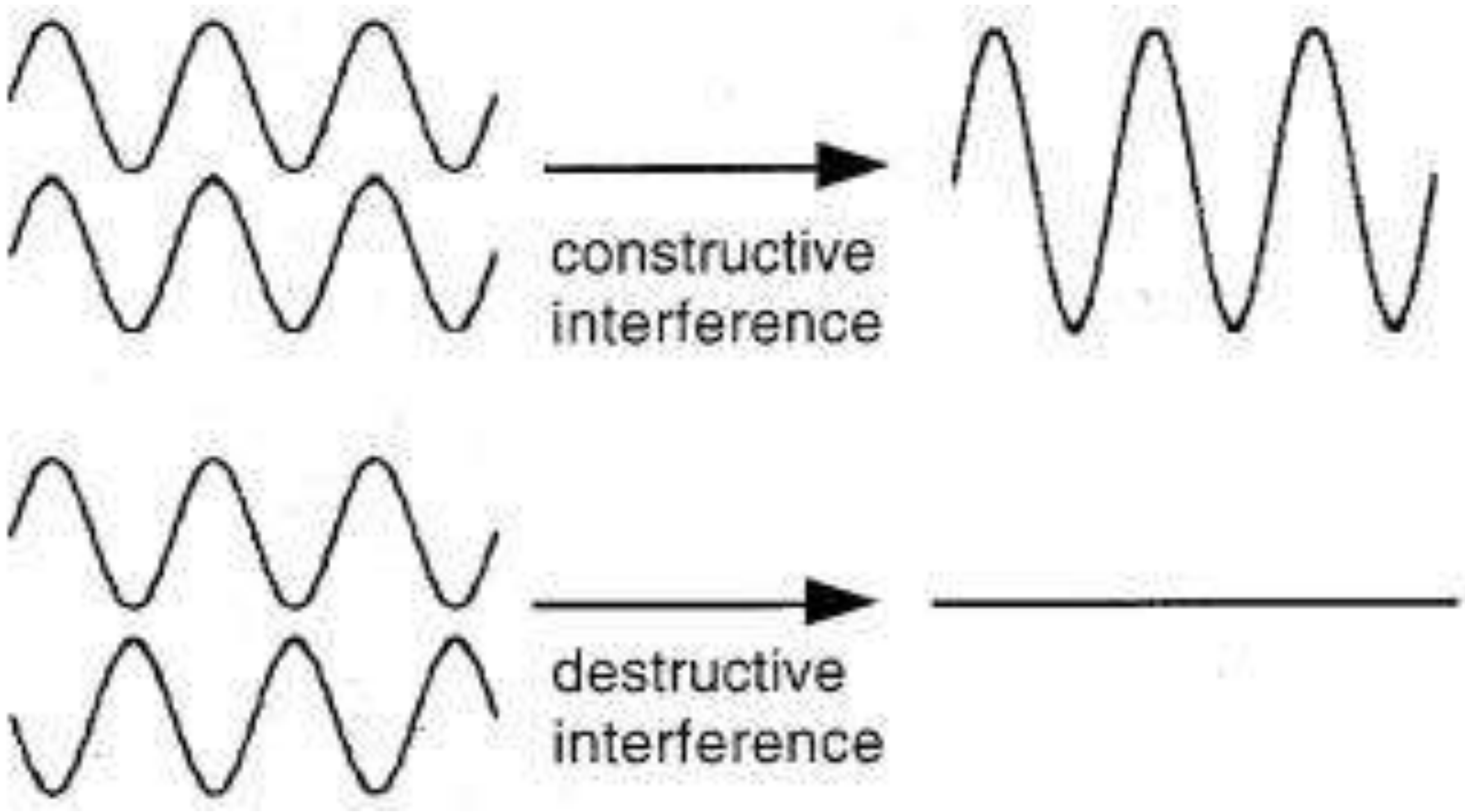
- A beam of electrons is generated from the hot tungsten filament are accelerated towards the anode with a high potential difference between the cathode and anode (Target)
- Anode is mainly Cu, Mo, Al and Mg
- After striking the anode the electrons generate the X-rays
- Monochromatic source is preferred, the X-ray beam actually consists of several characteristic X-ray lines

Cathode Ray Tube



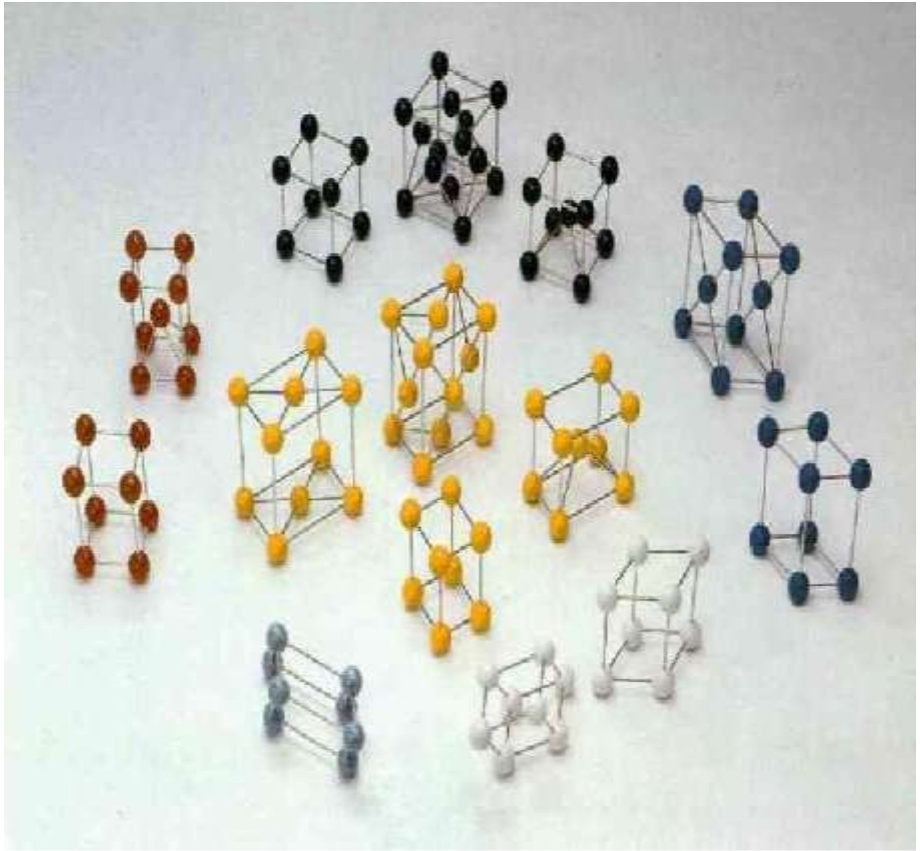
What is X-ray diffraction

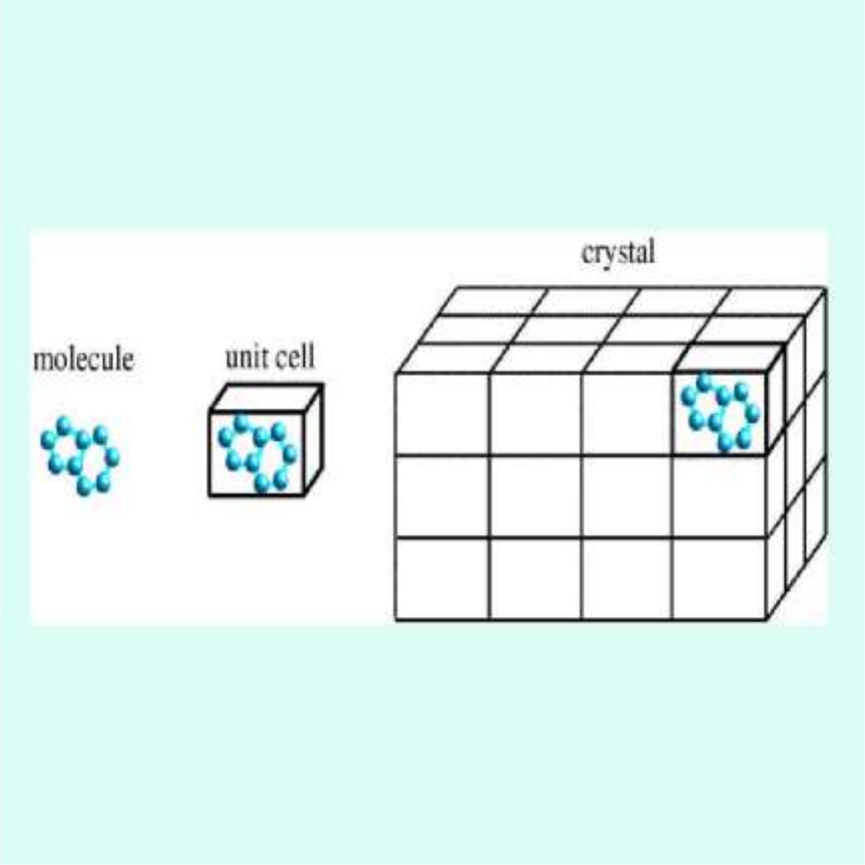
- The x-rays when pass through the crystals "bouncing" off of the atoms in the structure, and changing the direction of the beam at some different angle, theta, from the original beam
- Some of these diffracted beams cancel each other out, but if the beams have similar wavelengths, then constructive interference occurs
- Due to Constructive interference a new beam with a higher amplitude is generated


constructive
interference
destructive
interference

Principle

- Crystals are regular arrays of atoms, whilst X-rays can be considered as waves of electromagnetic radiation
- Crystal atoms scatter incident X-rays, primarily through interaction with the atoms' electrons
- This phenomenon is known as elastic scattering; the electron is known as the scatterer
- A regular array of scatterers produces a regular array of spherical waves
- In the majority of directions, these waves cancel each other out through destructive interference, however, they add constructively in a few specific directions,




molecule
unit cell
crystal

Bragg's Law

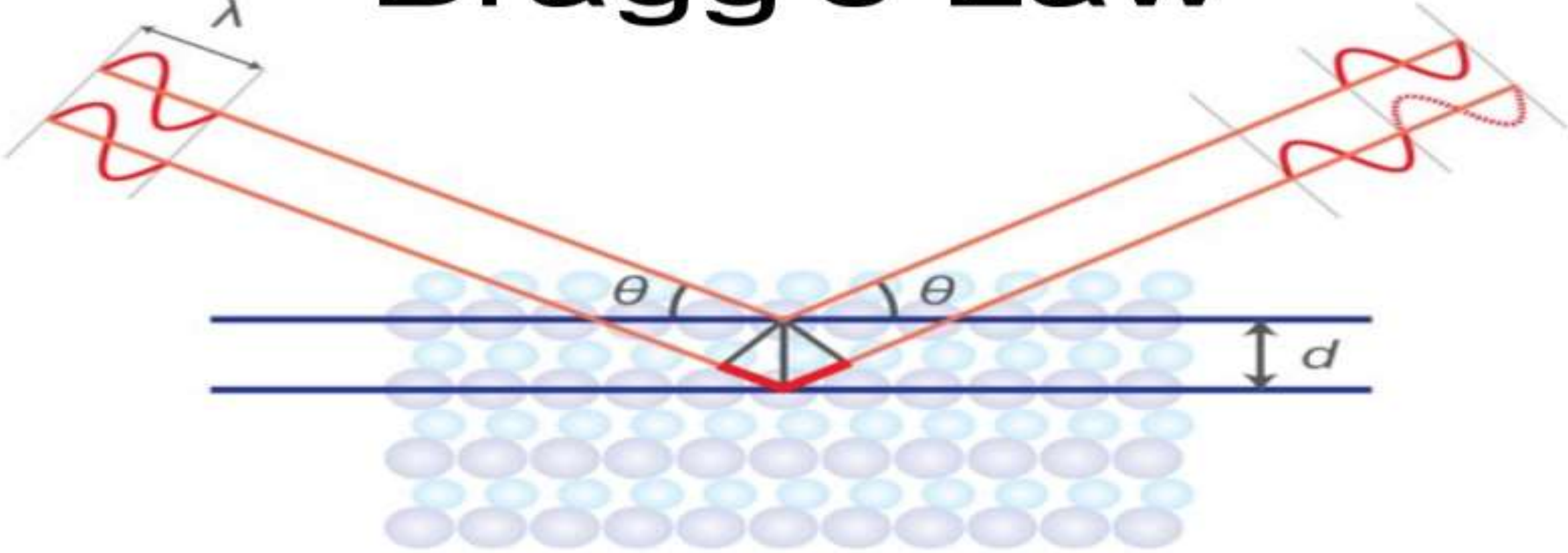
- The cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (theta)
- The variable d is the distance between atomic layers in a crystal, and the variable lambda is the wavelength of the incident X-ray beam; n is an integer

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

- The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond

- **This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample**
- **These diffracted X-rays are then detected, processed and counted**
- **By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material**
- **Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings**
- **Typically, this is achieved by comparison of d-spacings with standard reference patterns**

Bragg's Law

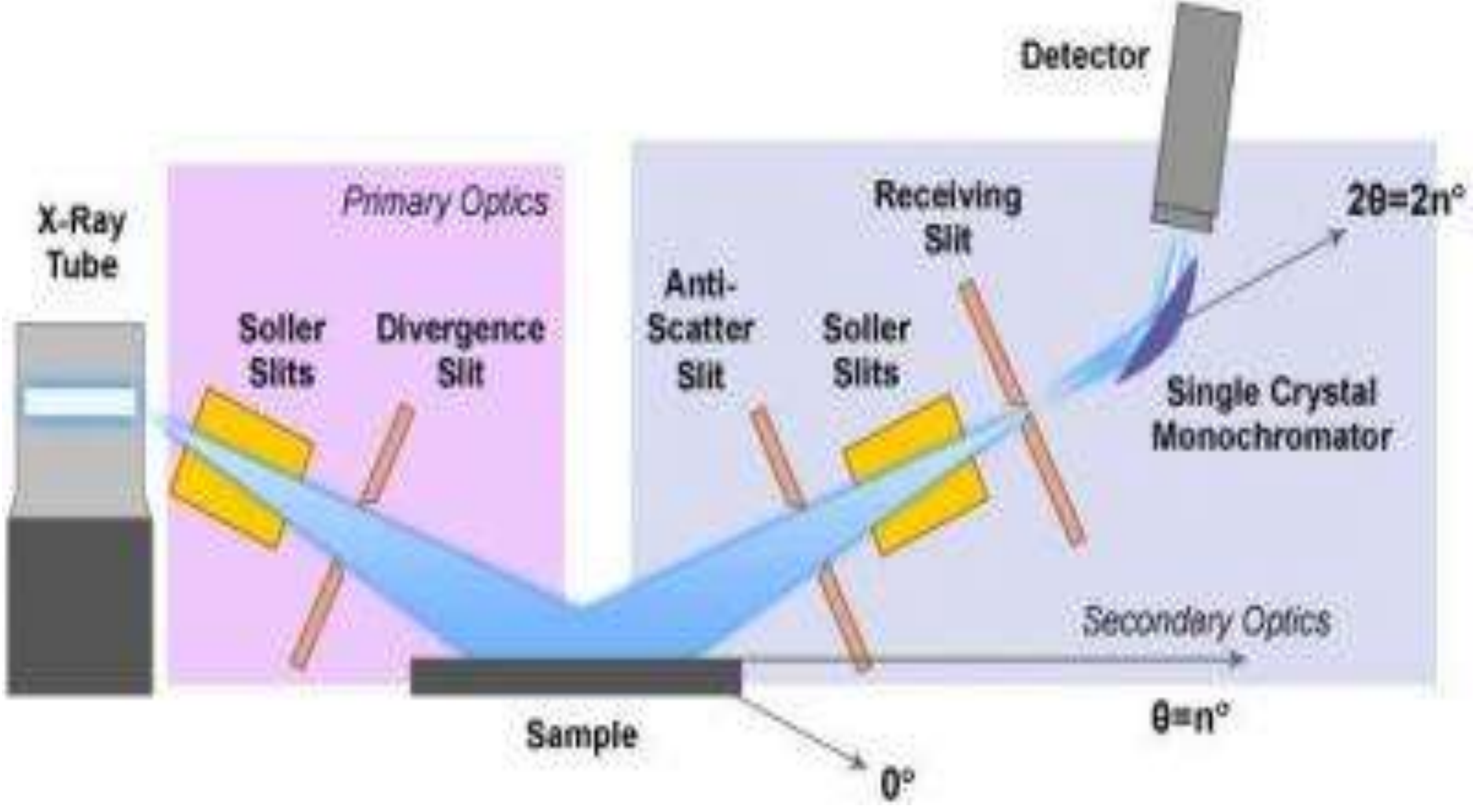


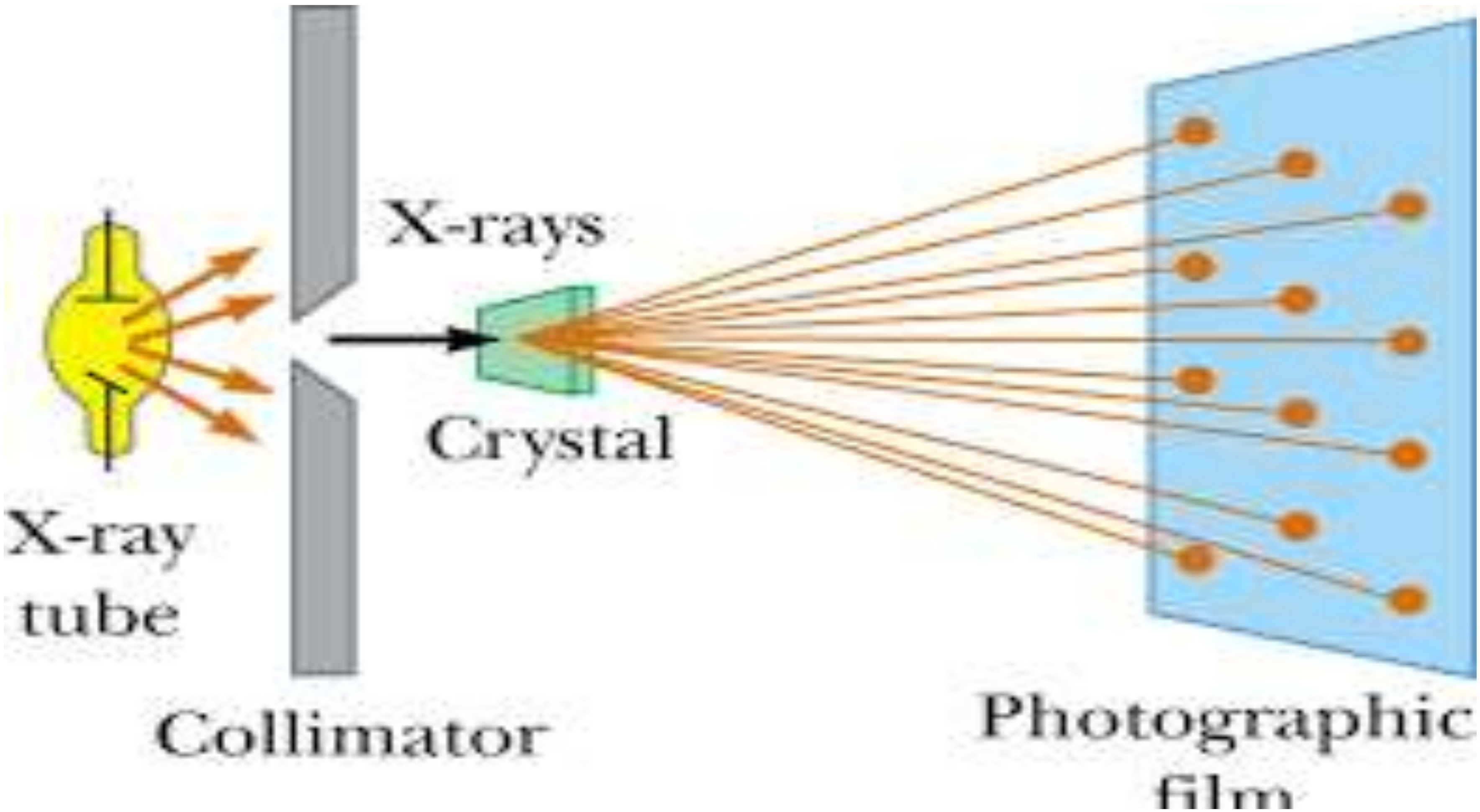
$$n\lambda = 2d\cdot\sin\theta$$

- **The specific directions appear as spots on the diffraction pattern called reflections**
- **Consequently, X-ray diffraction patterns result from electromagnetic waves impinging on a regular array of scatterers**
- **X-rays are used to produce the diffraction pattern because their wavelength, λ, is often the same order of magnitude as the spacing, *d*, between the crystal planes (1-100 angstroms)**

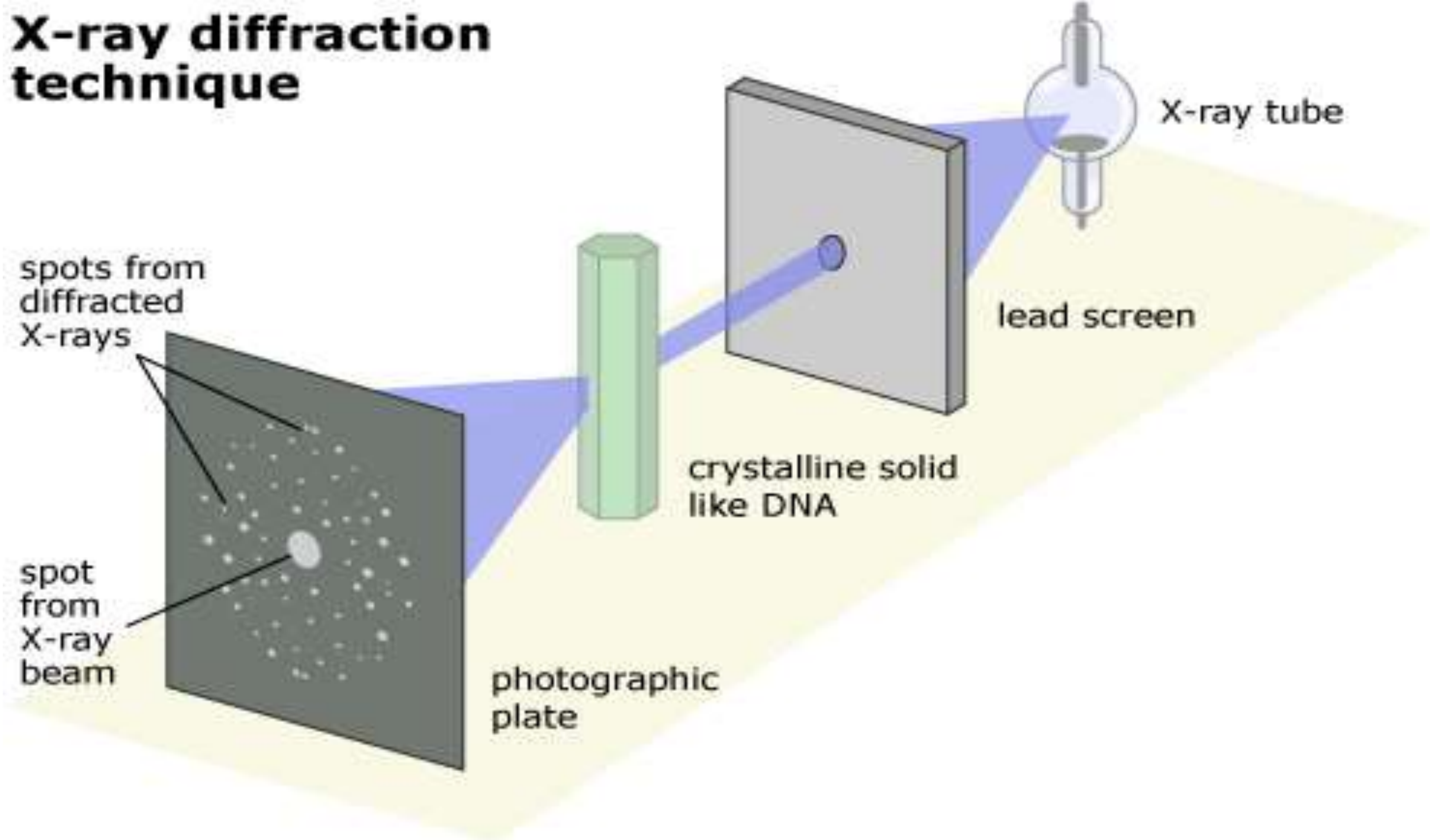
Essential Parts

- X-ray Tube: The source of X rays
- Incident-beam optics: Condition the X-ray beam before it hits the sample
- The goniometer: The platform that holds and moves the sample, and detector
- The sample & sample holder
- Receiving-side optics: Condition the X-ray beam after it has encountered the sample
- Detector: Count the number of X rays scattered by the sample

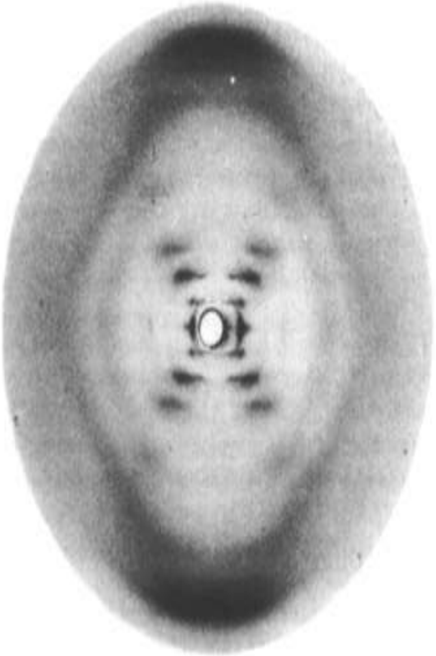

Detector
X-Ray Tube
Primary Optics
Receiving Slit
2θ=2n°
Anti-Scatter Slit
Soller Slits
Divergence Slit
Soller Slits
Single Crystal Monochromator
Secondary Optics
Sample
θ=n°
0°


X-rays
X-ray
tube
Crystal
Collimator
Photographic
film

X-ray diffraction technique



A Typical XRD Machine



Crystallographic Analysis of DNA

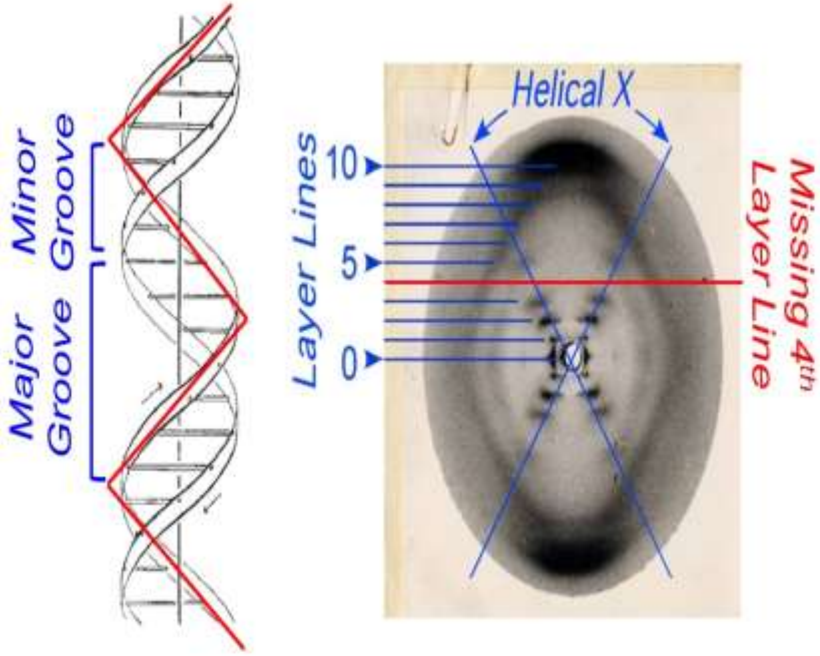
① DNA forms a helix

② Twists every 34 angstrom

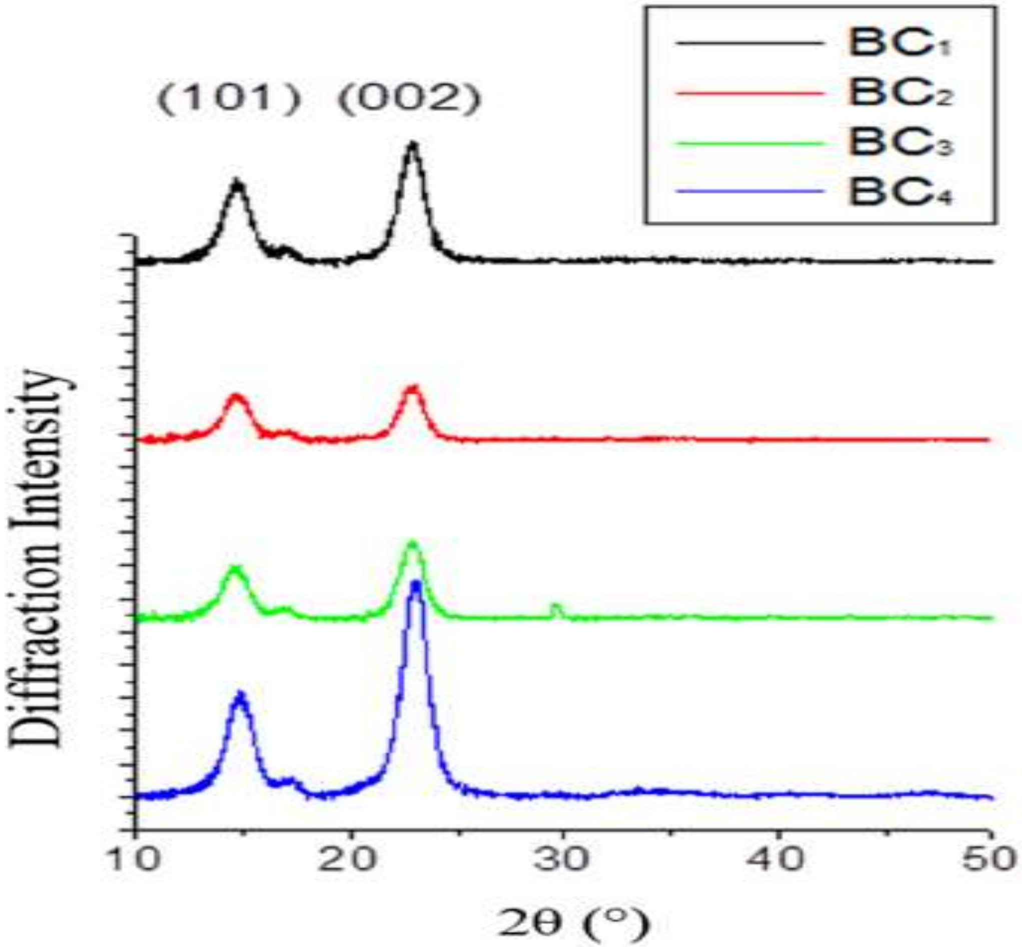
③ 10 bases per twist

④ DNA is double stranded

⑤ Phosphates are on the outside



XRD pattern of Bacterial Cellulose



Applications of XRD

XRD is a nondestructive technique used for:

- **Identification of crystalline phases and orientation(e.g. minerals, inorganic compounds)**
- **To determine structural properties: strain, grain size, epitaxy, phase composition, preferred orientation, order-disorder transformation, thermal expansion of unknown solids**
- **Measurement of thickness of thin films and multilayers**
- **Determination of critical to studies in geology, environmental science, material science, engineering and biology**
- **Measurement of sample purity**

Advantages of XRD

- Measure the average spacings between layers or rows of atoms
- Determine the orientation of a single crystal or grain
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

Strengths

- Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- Provides an unambiguous mineral determination
- Minimal sample preparation is required
- XRD units are widely available
- Data interpretation is relatively straight forward

Limitations

- Homogeneous and single phase material is best for identification
- Must have access to a standard reference file of inorganic compounds (d-spacings, *hkls*)
- Requires tenths of a gram of material which must be ground into a powder
- For mixed materials, detection limit is ~ 2% of sample
- For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated
- Peak overlay may occur