Module 6: Spectroscopic, Diffraction and Microscopic Techniques

(i). Fundamental concepts in spectroscopic and instrumental techniques

(ii). Principle (Beer-Lambert's Law) and applications of UV-Visible Spectroscopy technique

(iii). Principle and applications of X-Ray Diffraction (XRD) technique

(i). Fundamental concepts in spectroscopic and microscopic techniques

Spectroscopy Basics:

- Spectroscopy is a branch of science that studies the interaction between electromagnetic (EM) radiation and matter.
- Spectroscopy is used as a tool for studying the structures of atoms and molecules.
- The basic principle shared by all spectroscopic techniques is to shine a beam of EM radiation onto a sample, and observe how it responds to such a stimulus. The response is recorded as a function of radiation wavelength.
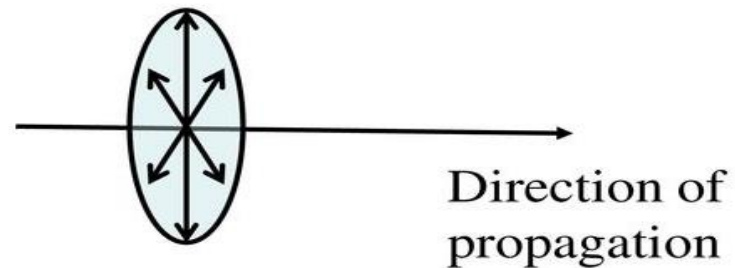
Light is an electromagnetic wave and transverse in nature.

Natural light or ordinary light is unpolarized in nature.
Means vibrations take place symmetrically in all directions in the plane perpendicular to the direction of propagation of light.

Direction of propagation
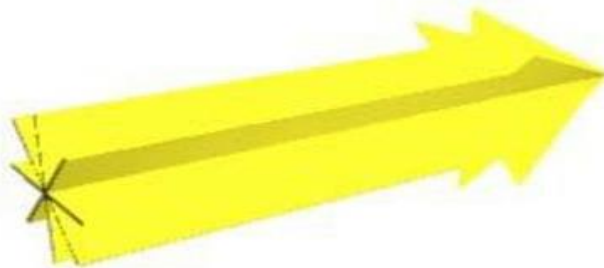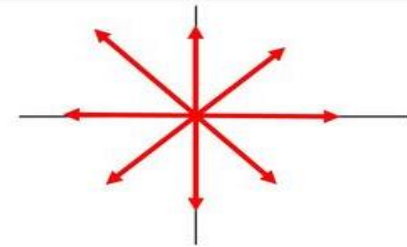
Ordinary light

Types of EM radiation interaction with matter:

- If matter is exposed to EM radiation e.g. IR light (**Fig. shown below**), the radiation can be either absorbed, transmitted, reflected, scattered or undergo photoluminescence.
- Photoluminescence is a term used to designate a number of effects including fluorescence, phosphorescence and Raman scattering.
- Complement of the absorbed light gets transmitted.
- Color of an object that we see is due to the wavelengths transmitted or reflected. Other wavelengths are absorbed. The more absorbed, the darker the color (more concentrated solution).
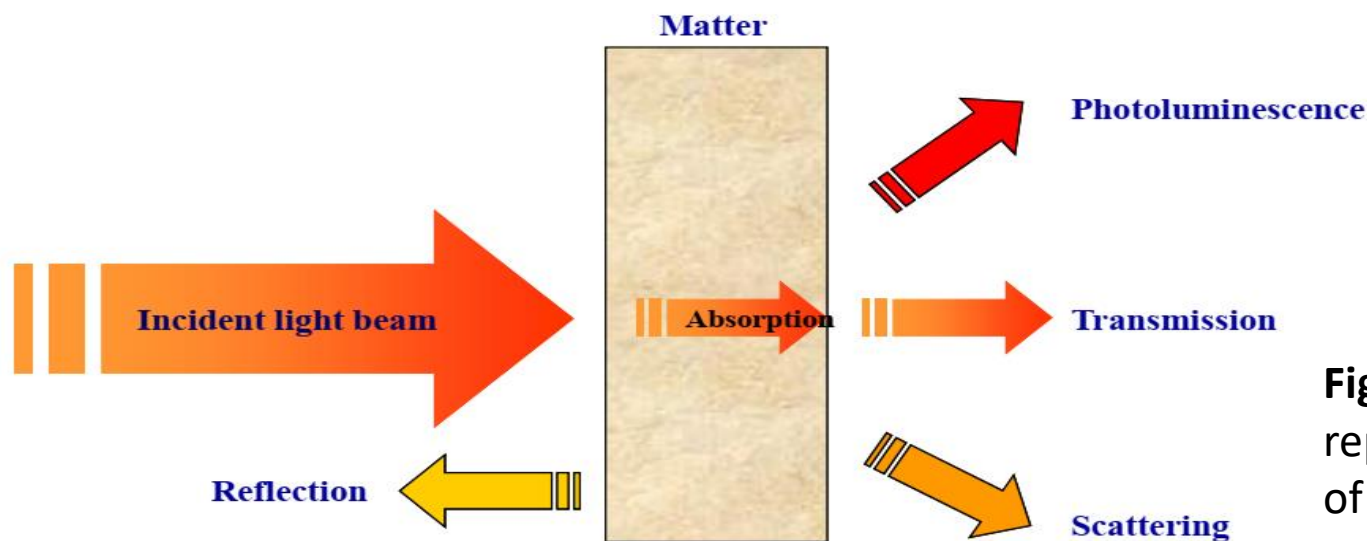

Fig. Schematic representation of interaction of radiation and matter

- Interaction of EM radiation with matter is a quantum phenomenon and is dependent on both the properties of radiation and appropriate structural parts of the samples involved.
- Origin of EM radiation is due to energy changes within matter itself.
- **In spectrochemical methods, we measure the absorbed radiation.**

(ii). Principle and applications of UV-Visible spectroscopy technique

- **Principle:** Different molecules absorb radiation of different wavelengths depending on their structure. An absorption spectrum will show a number of absorption bands corresponding to structural (functional) groups within the molecule. For ex. absorption by carbonyl group in acetone is of the same wavelength as the absorption by carbonyl group in diethyl ketone.

- In UV-Vis spectroscopy, energy is absorbed by a molecule in UV region (1-400 nm) or visible region (400-750 nm) resulting in <u>electronic transition of valence electrons.</u>

Components of a UV-Vis Spectrophotometer
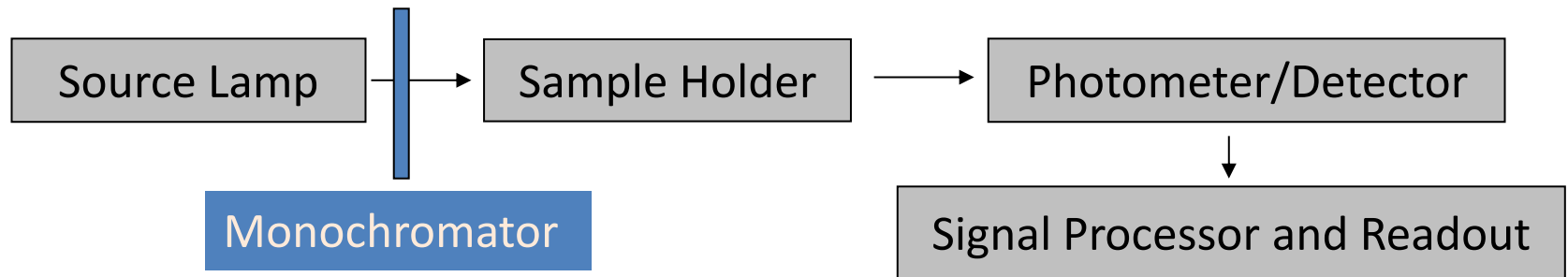
Beer-Lambert Law

- When light passes through a molecular material, absorption can occur. The absorption of light, as it passes through a medium, varies linearly with the distance the light travels and with concentration of the absorbing medium.

- The extent of absorption is given by **Beer-Lambert Law**, as expressed by **$A = \varepsilon cl$,** where **A is the absorption, ε is the absorptivity coefficient**, **l is the path length**, and **c is the concentration of the specific analyte**. Absorptivity characterizes the amount of light absorbed by a specific molecule at a specific wavelength.

Beer-Lambert Law
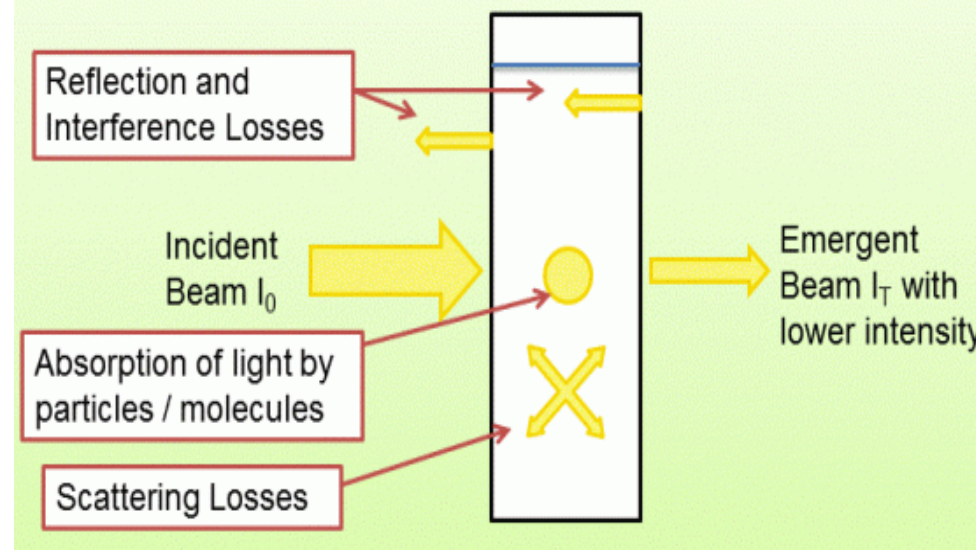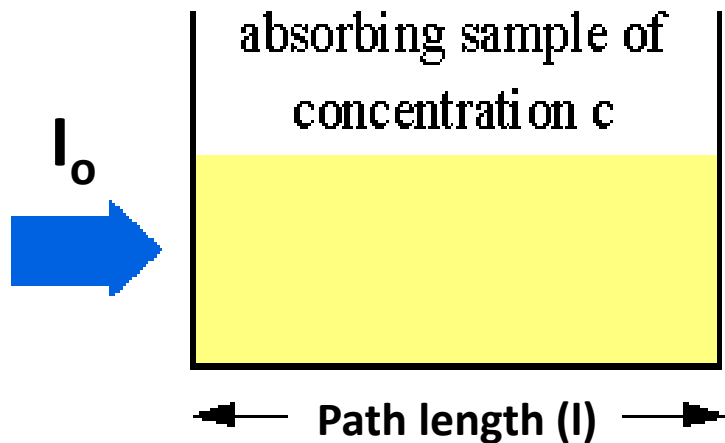
Chromophore: any isolated covalently bonded group that shows a characteristic absorption in the UV-Vis. region. The only molecular moieties likely to absorb light in the 200 to 800 nm region are π-electron functions and hetero atoms having non-bonding electron pairs.

~ λmax: 280 nm

~ λmax: 255 nm
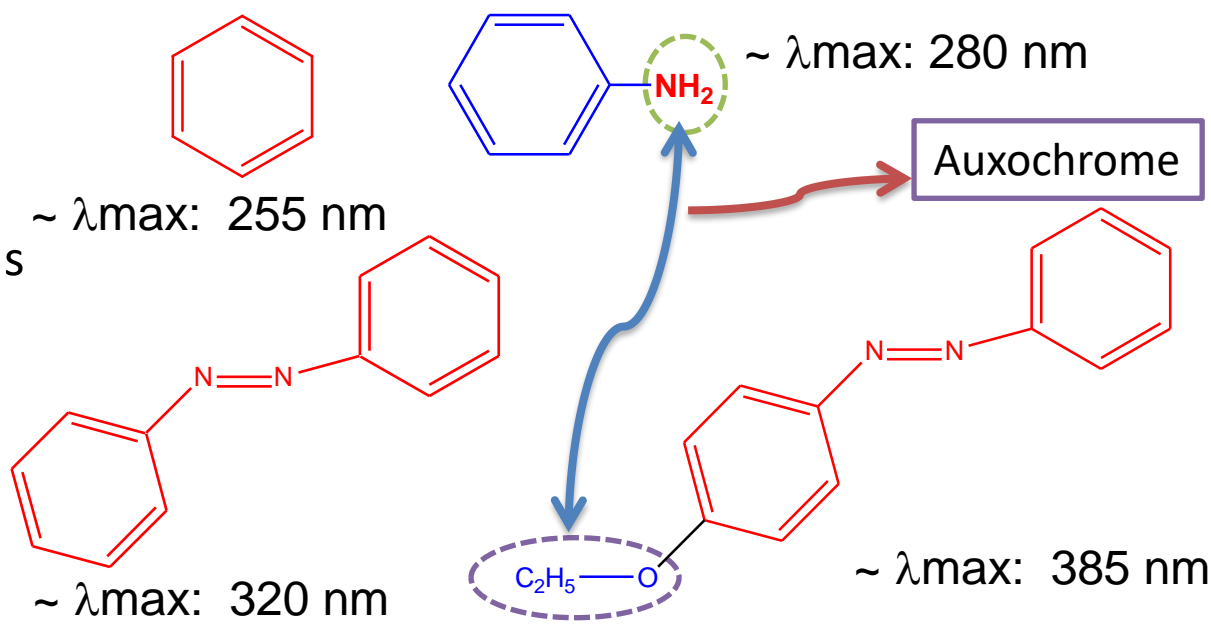
Auxochrome

Auxochrome: group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light. **Ex. COOH, -OH, -SO$_3$H, -NH$_2$, -NH-R, -N-R$_2$**

~ λmax: 320 nm

~ λmax: 385 nm

Electronic excitations in UV- Visible spectroscopy

σ to π* is forbidden transition
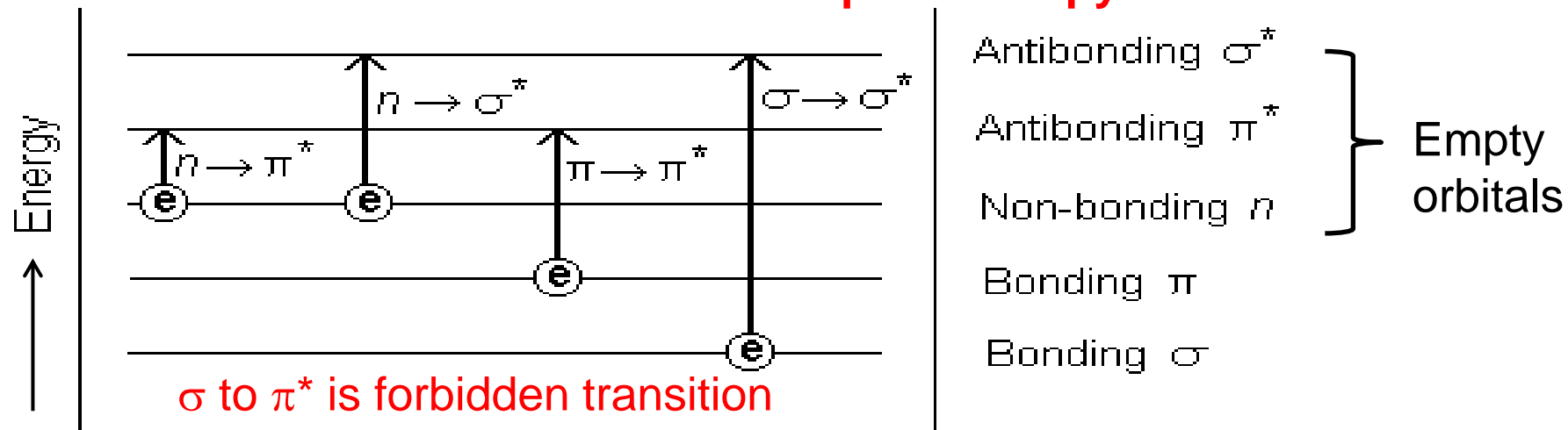
σ to σ^* transitions: Electron in a bonding σ orbital is excited to the corresponding antibonding σ^* orbital. Energy required is large.

n to σ^* transitions: Saturated compounds containing atoms with lone pairs exhibit ***n* to** σ^* transitions. These transitions need lesser energy than σ **to** σ^* transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm.

n to π^* and π to π^* transitions: need an unsaturated group in the molecule to provide the π electrons. Most absorption spectroscopy of organic compounds is based on these transitions and fall in the spectral region between 200 - 700 nm.

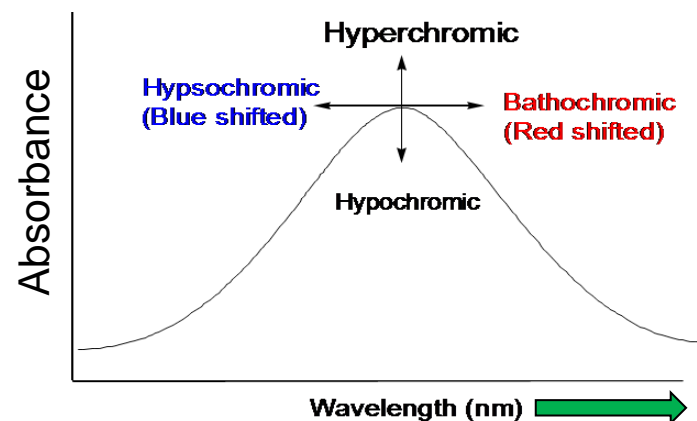**Based on the functional group present and attached to chromophores…**

Bathochromic shift: absorption maximum shifted to longer wavelength (Blue to Red [Red shift]).

Hypsochromic shift: absorption maximum shifted to shorter wavelength (Red to Blue [**Blue shift**]).

Hyperchromism: increase in molar absorptivity

Hypochromism: decrease in molar absorptivity.

# (iii). Principle and applications of X-Ray Diffraction (XRD) technique

- **Principle:** XRD is a technique used 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.
- XRD is a versatile, non-destructive characterization technique widely used in materials science and engineering for identifying unknown crystalline materials.
- XRD is used to study the structure and function of many biological molecules, including vitamins, drugs, proteins and nucleic acids such as DNA.
- XRD is also used to determine structural properties (lattice parameters, strain, grain size, epitaxy, phase composition, orientation, atomic arrangement) and to measure film thickness.
- XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects.

How XRD pattern is produced? Bragg model of diffraction

- Crystals are regular arrays of atoms, whilst X-rays are waves of EM radiation. Crystal atoms scatter incident X-rays, primarily through interaction with the atom's 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, as determined by Bragg's law:
- **$n\lambda = 2d\sin\theta$**, where "n" is an integer, and "λ" is the beam wavelength, "d" is the spacing between diffracting planes and "θ" is the incident angle.
- X-rays scattered from adjacent crystalline planes will combine constructively (constructive interference) when angle θ between plane and X-ray results in path-length difference that is integer multiple "n" of X-ray wavelength "λ".
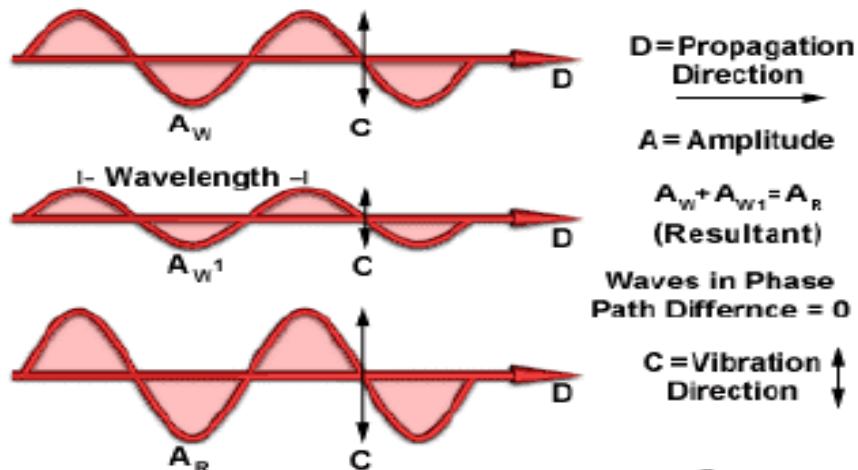
What is diffraction?

- Diffraction refers to a phenomena when a wave encounters an obstacle.
- In classical physics, the diffraction phenomenon is described as the apparent bending of waves around small obstacles and the spreading out of waves past small openings.
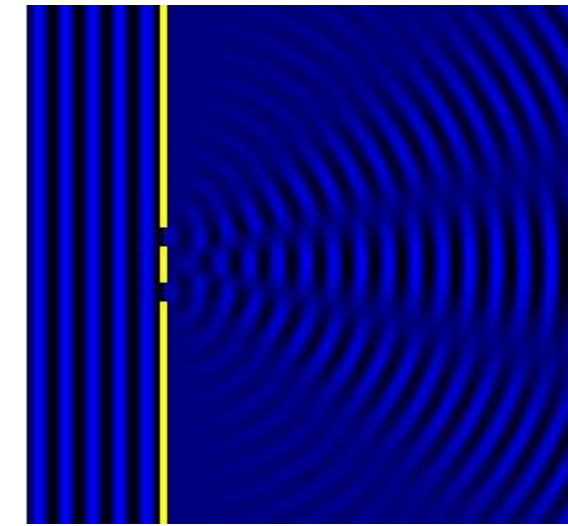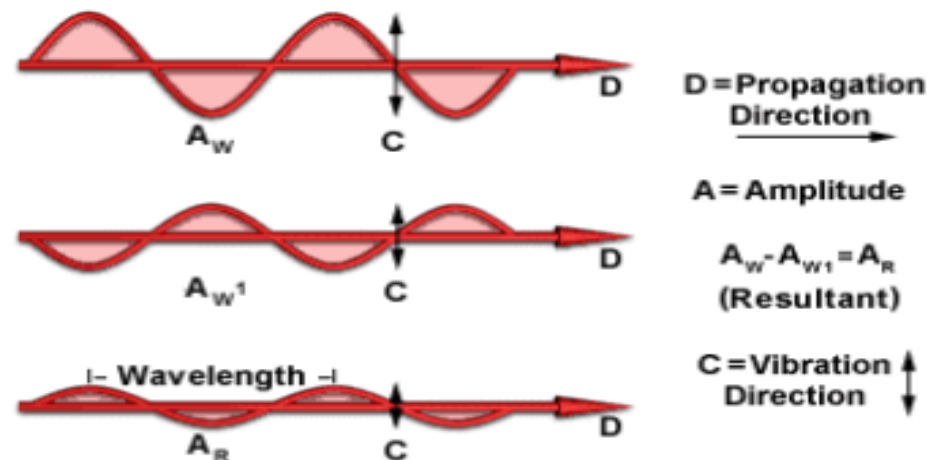
Interference of diffracted waves

- Interaction between diffracted waves is called interference.

- **Constructive Interference**: Waves are in-phase when each of their crests and troughs occur exactly at the same time. Those type of waves stack together to produce a resultant wave that has a **higher amplitude**. For constructive interference, path difference should be multiples of n*λ.

- **Destructive Interference**: If the waves are out of phase by multiples of (n/2)*λ, then destructive interference occurs and the amplitude of the resultant wave will be reduced.

Constructive Interference

A_W C
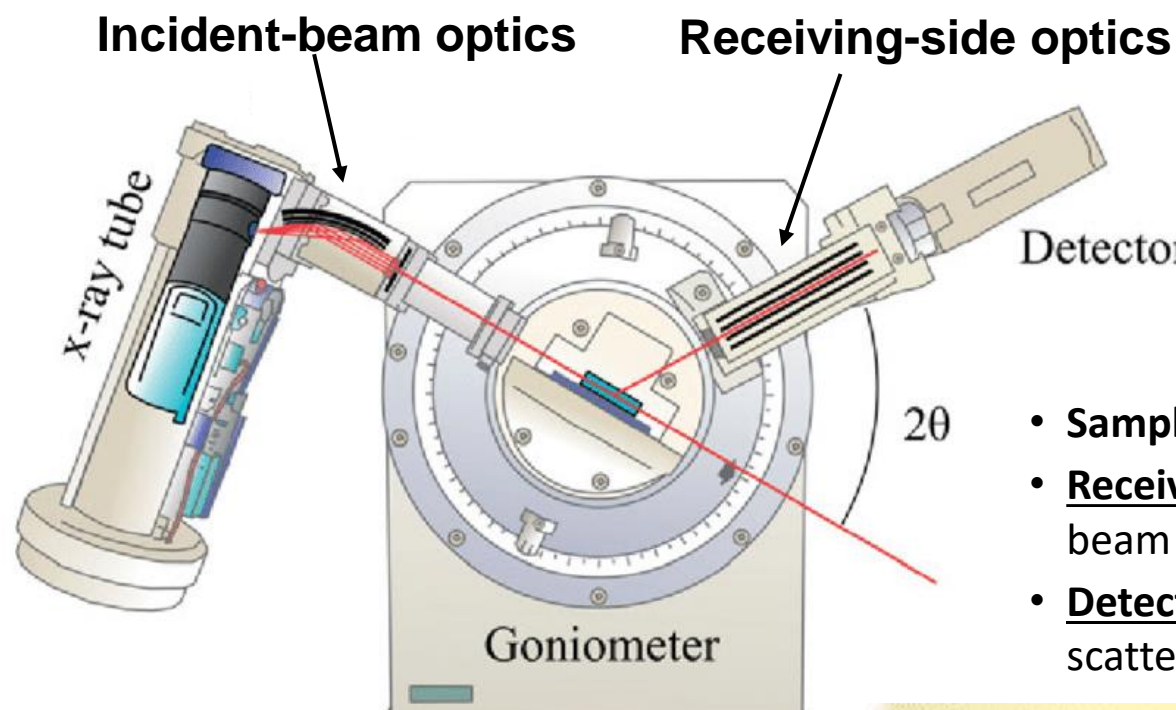|– Wavelength –|
A_{W1} C
A_R C

D = Propagation Direction

A = Amplitude

$A_w + A_{w1} = A_R$ (Resultant)

Waves in Phase
Path Differnce = 0

C = Vibration Direction

path difference = multiple of n*λ

Destructive Interference

A_W C
A_{W1} C
|– Wavelength –|
A_R C

D = Propagation Direction

A = Amplitude

$A_w - A_{w1} = A_R$ (Resultant)
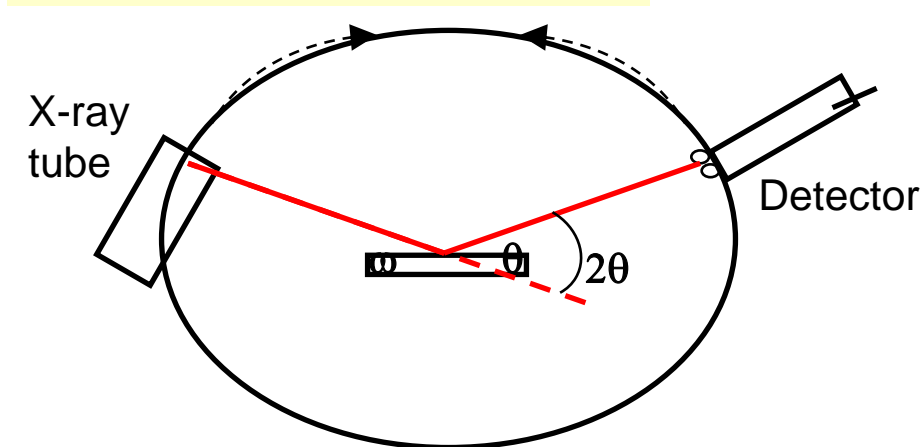
C = Vibration Direction

path difference = multiple of (n/2)*λ

Components of a XRD instrument

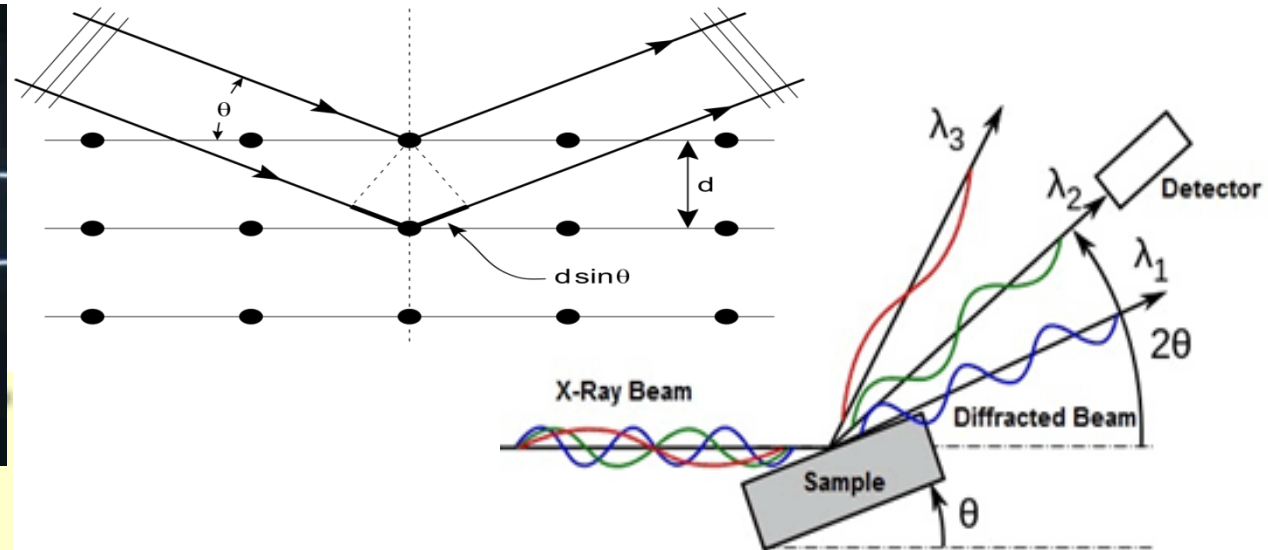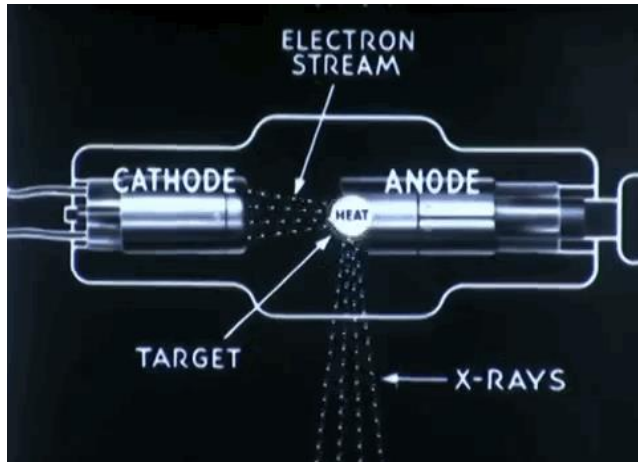**Incident-beam optics**   **Receiving-side optics**
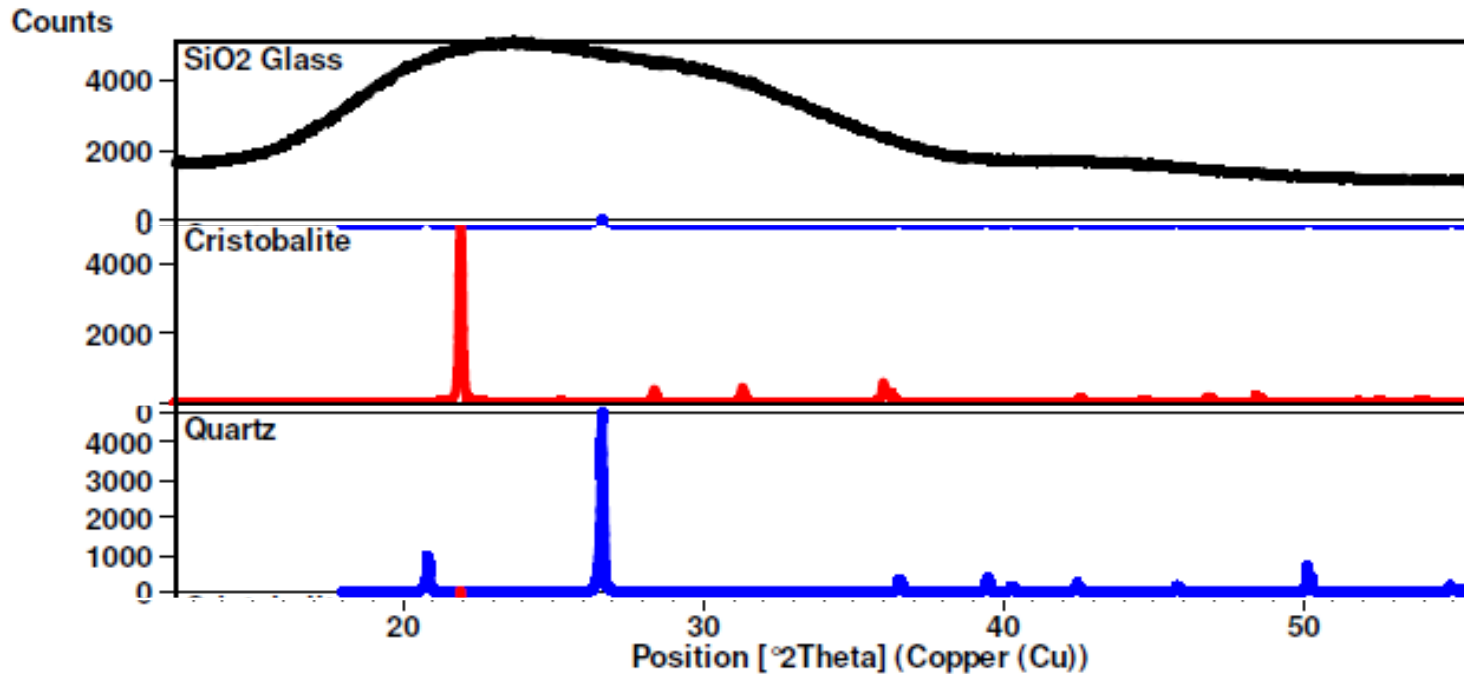

Detector

2θ

Goniometer

- **X-ray tube:** source of X-rays
- **Incident-beam optics:** condition the X-ray beam before it hits the sample.
- **Goniometer:** platform that holds and moves the sample, optics, detector, and/or tube.
- **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.

- Incident angle (ω) is defined between the X-ray source and sample.
- Diffracted angle (2θ) is defined between the incident beam and the detector angle.
- Incident angle (ω) is always ½ of the detector angle 2θ i.e. θ.
- In a typical XRD instrument, the X-ray tube is fixed, the sample rotates at $\theta°$/min and detector rotates at $2\theta°$/min.

ELECTRON STREAM

CATHODE   ANODE

HEAT

TARGET

X-RAYS

θ

d

d sinθ

X-Ray Beam

λ₃

λ₂

λ₁

2θ

Detector

Diffracted Beam

Sample

θ

Vaccum

Anode

Cooling fins

tungsten target

diffracting planes of atoms in crystal

Monochromatic X-ray

Detector

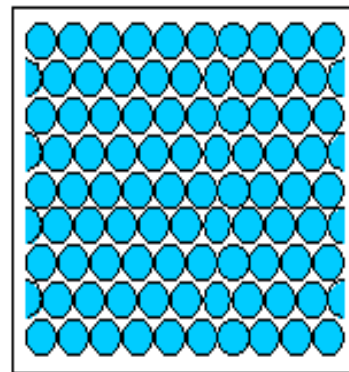X-ray Intensity

2θ

Random Crystals

X-ray tube

Detector

ω   θ   2θ
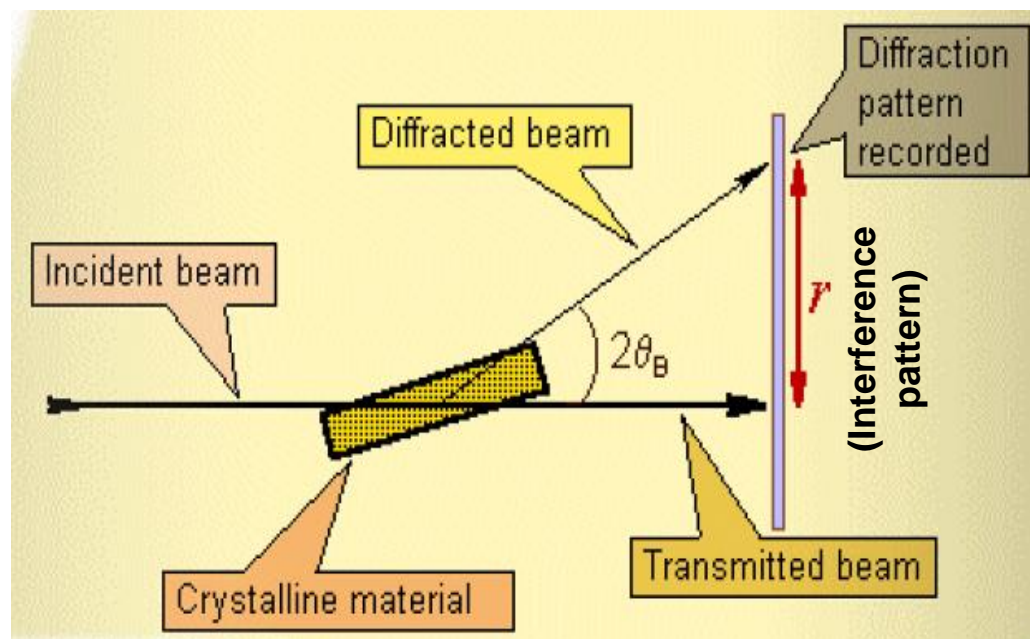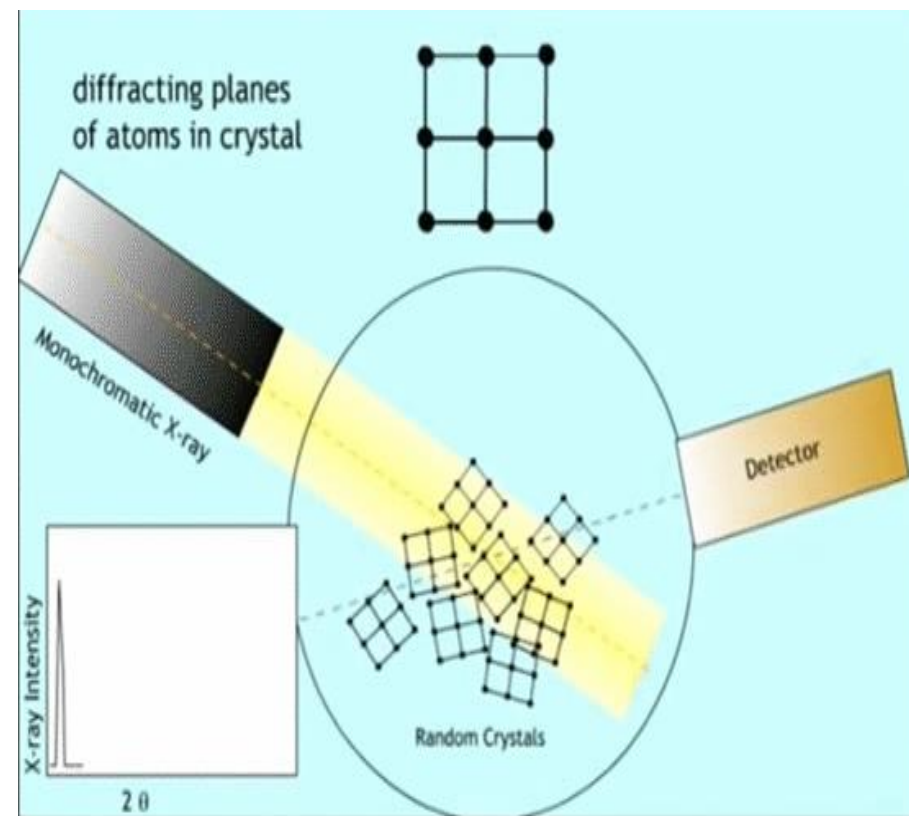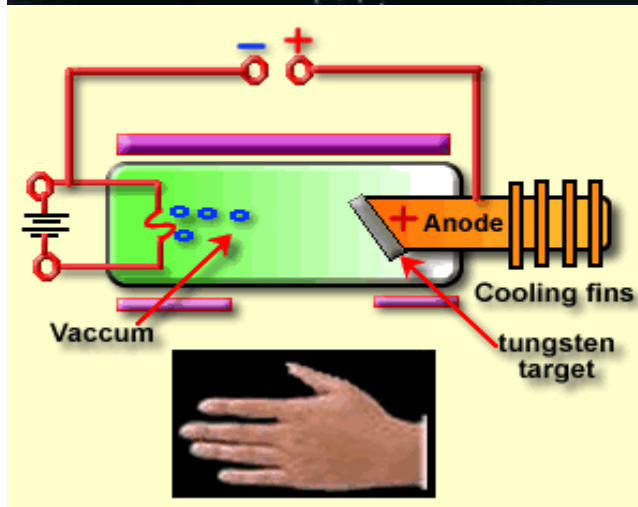
XRD patterns for 3 different forms of SiO$_2$

- These three phases of SiO$_2$ are chemically identical.
- The amorphous glass does not have long-range atomic order and therefore produces only broad pattern.
- Cristobalite form polycrystalline structure.
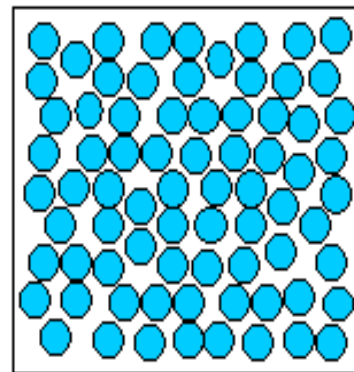- Quartz form single crystal structure.

Single crystal
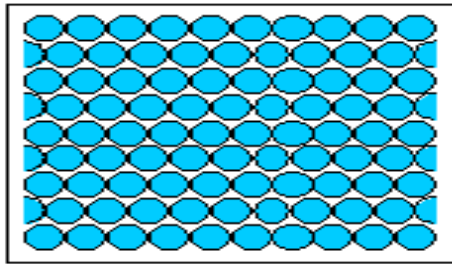Periodic across the whole volume.
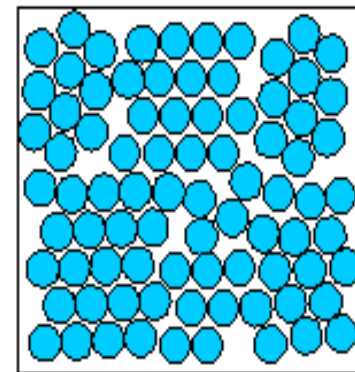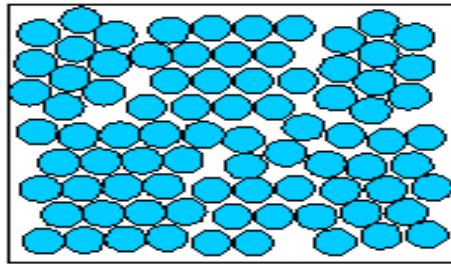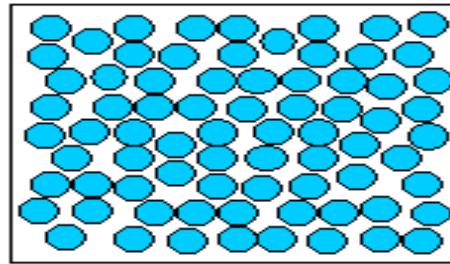
Polycrystal
Periodic across each grain.

Amorphous solid
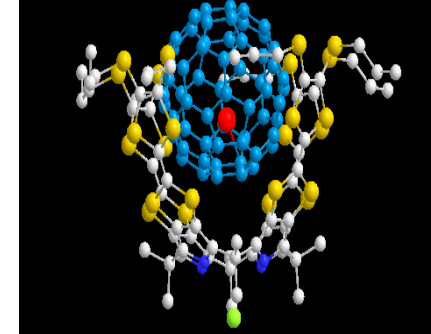Not periodic.

Single crystal
Periodic across the
whole volume.

Polycrystal
Periodic across
each grain.

Amorphous solid
Not periodic.
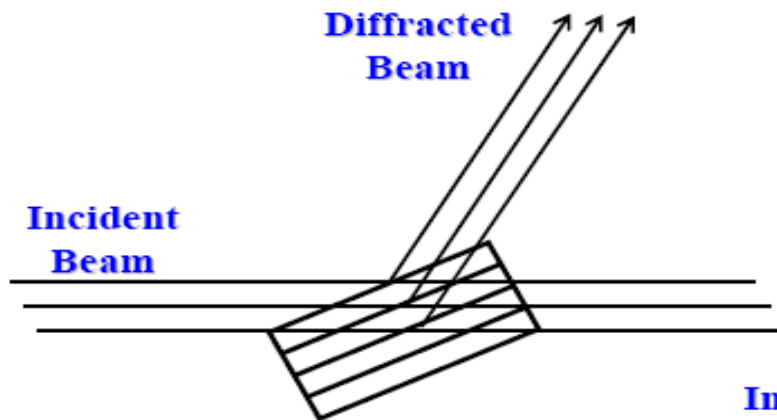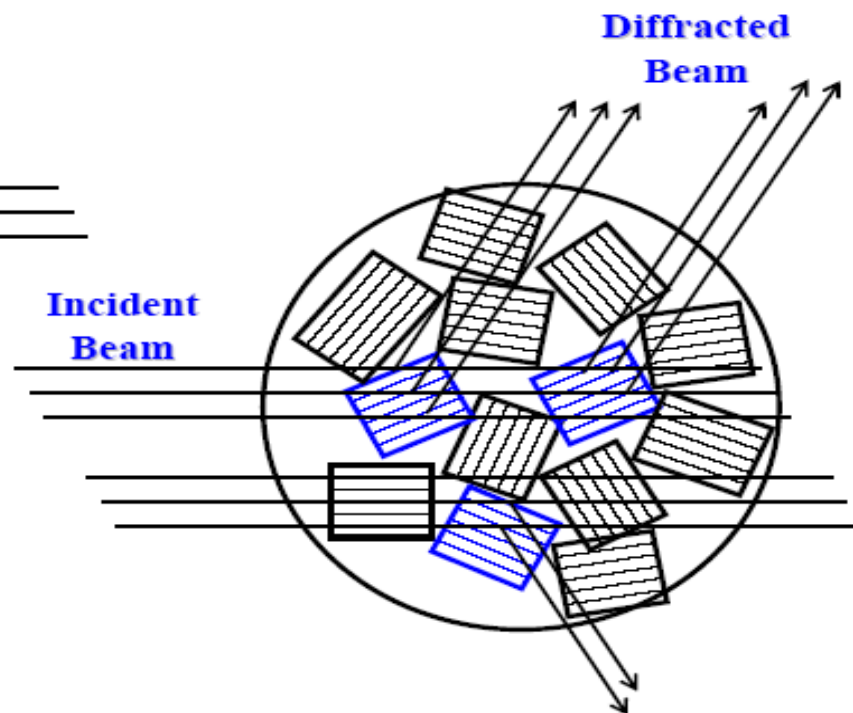
Single Crystal Diffraction

Diffracted Beam

Incident Beam

In powder diffraction only a small fraction of the crystals (shown in blue) are correctly oriented to diffract.

Powder Diffraction

Diffracted Beam

Incident Beam

# Calculation of Crystallite Size using p-XRD data

Crystallites smaller than ~120 nm create broadening of diffraction peaks. This peak broadening can be used to quantify the average crystallite size of nanoparticles using the Scherrer equation - used for nanoparticles characterization. Must know the contribution of peak width from the instrument by using a calibration curve

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Scherrer equation can be written as:

- τ is mean size of ordered (crystalline) domains, which may be smaller or equal to grain size;
- K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

- β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, given in radians
- λ is the X-ray wavelength
- ϑ is the Bragg angle.

- This quantity is also denoted as $\Delta(2\vartheta)$

Fig. Simulated p-XRD patterns for wurtzite CdS spherical particles of different sizes from 1 µm to 1 nm. The inset shows the 1, 2, and 5 nm XRD patterns on an expanded y-axis scale for clarity.
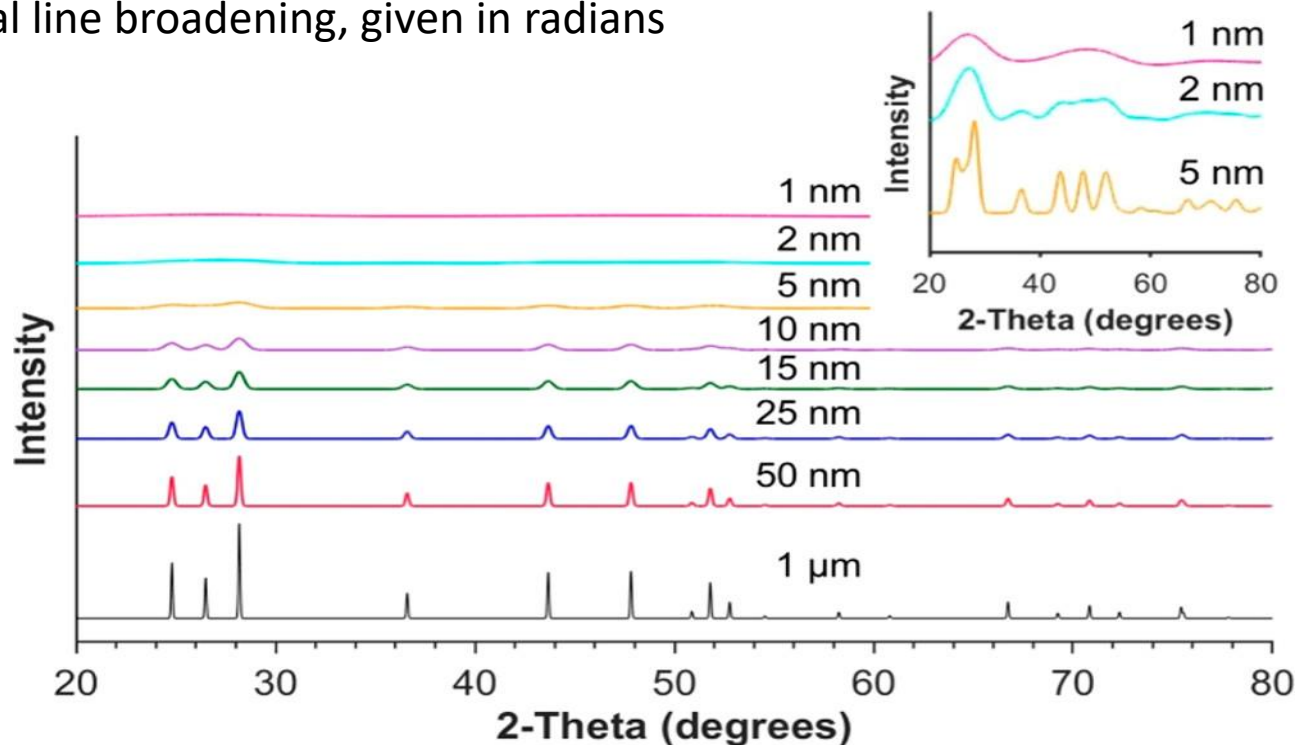
XRD Numericals

Q. 1. In a NaCl crystal, there is a family of planes 0.252 nm apart. If the first-order maximum is observed at an incidence angle of 18.1°, what is the wavelength of the X-ray scattering from this crystal?

Ans.: Use the Bragg equation $n\lambda = 2d\sin\theta$ to solve for θ.

For the first-order, n=1. Then $\lambda = 2d\sin\theta/n = 2d\sin\theta/1$

$\lambda = 2(0.252\times10^{-9}\,m)\sin(18.1°)/1$

$= 0.504*0.31068 = 1.57\times10^{-10}m$ or **0.157 nm**.

Q. 2. Estimate the crystallite size of the given nanomaterial using p-XRD data:

Peak position $2\theta = 21.61°$, FWHM of sample $= 2.51°$, k = 0.9 and $\lambda = 1.5406$ Å (degree to radian = Degree $\times \pi/180$).

Ans.: $2\theta = 21.61°$ ($\theta = 10.805°$) and FWHM = 2.51° (0.043825 radian)

Crystalline grain size calculation by Scherrer's equation: k*λ/β*cosθ

k = 0.9, **λ** = 1.5406 Å (0.15406 nm), **β** = FWHM in radian and **2θ** = Bragg's angle in ° obtained from p-XRD data.

Crystallite size = (0.9*0.15406)/(0.043825*0.982257) nm = **3.22 nm**