INTRODUCTION TO X-RAY DIFFRACTION

By

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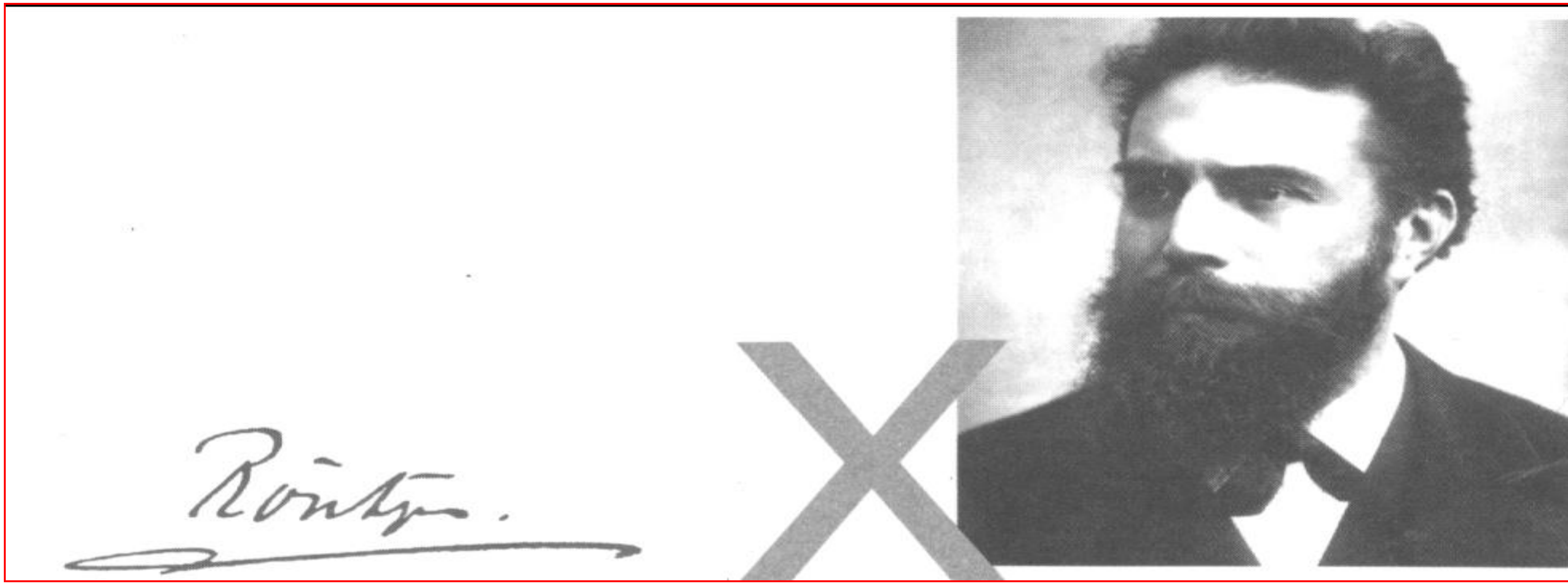
Introduction



1. X-rays were discovered by scientist W. Rontgen in 1895.
2. X-rays are high energy electro magnetic waves having very short wavelength ranging from 0.01 to 10 nm.
3. The longer wavelength (smaller energy : <10 keV) end of X-ray spectrum is known as soft X-rays and shorter wavelength end (higher energy : >10 keV) is known as hard x-rays.

4. In 1912, diffraction pattern of X-rays was first obtained by Max Laue.

Applications of X rays

- X-ray photographs are used to detect bone fracture or presence of foreign object in a human body.
- They are used to cure skin diseases and to destroy tumors.
- They are used to detect flaws and cracks in metallic parts of cars, aeroplanes etc.
- They are used to study crystal structures.

Properties of X-rays

- X-rays travel in a straight line.
- Can not be deflected by electric or magnetic field.
- X-rays have high penetrating power.
- Fluorescent materials glow when X-rays are directed at them.
- Photoelectric emission can be produced by X-rays and also used for elemental composition (XPS, EDAX).
- Ionizes gas molecule when an X-ray beam is passed through gas container.
- X-rays are diffracted by crystals.

Production of X-rays

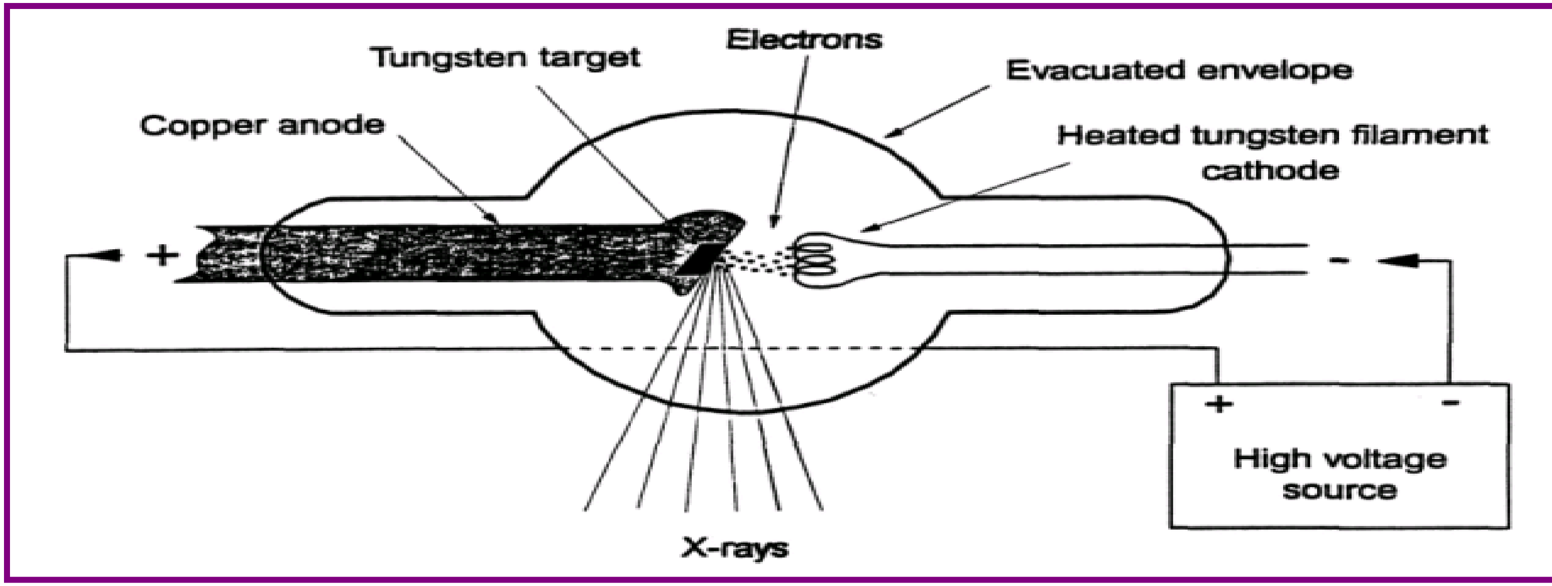
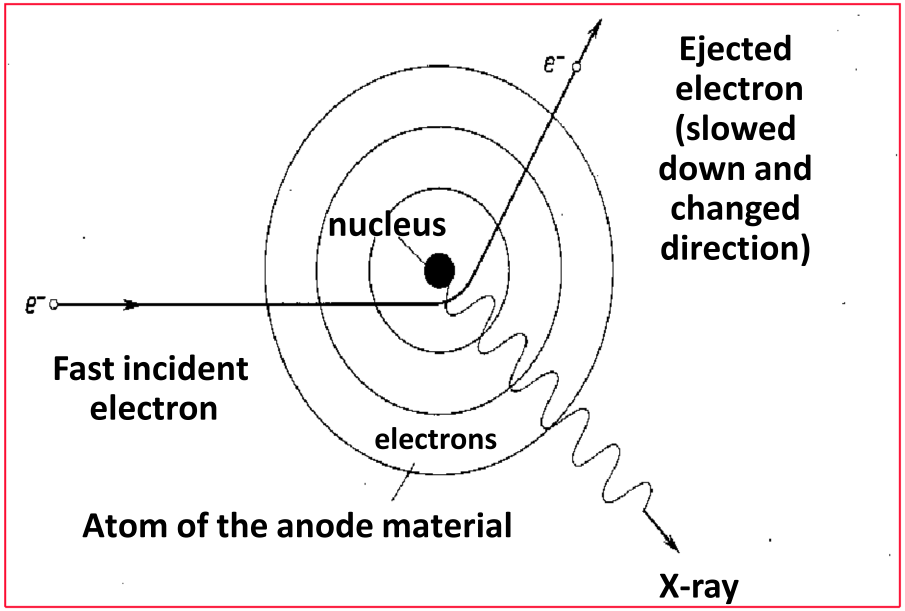


Figure: Schematic diagram of Coolidge X-ray tube

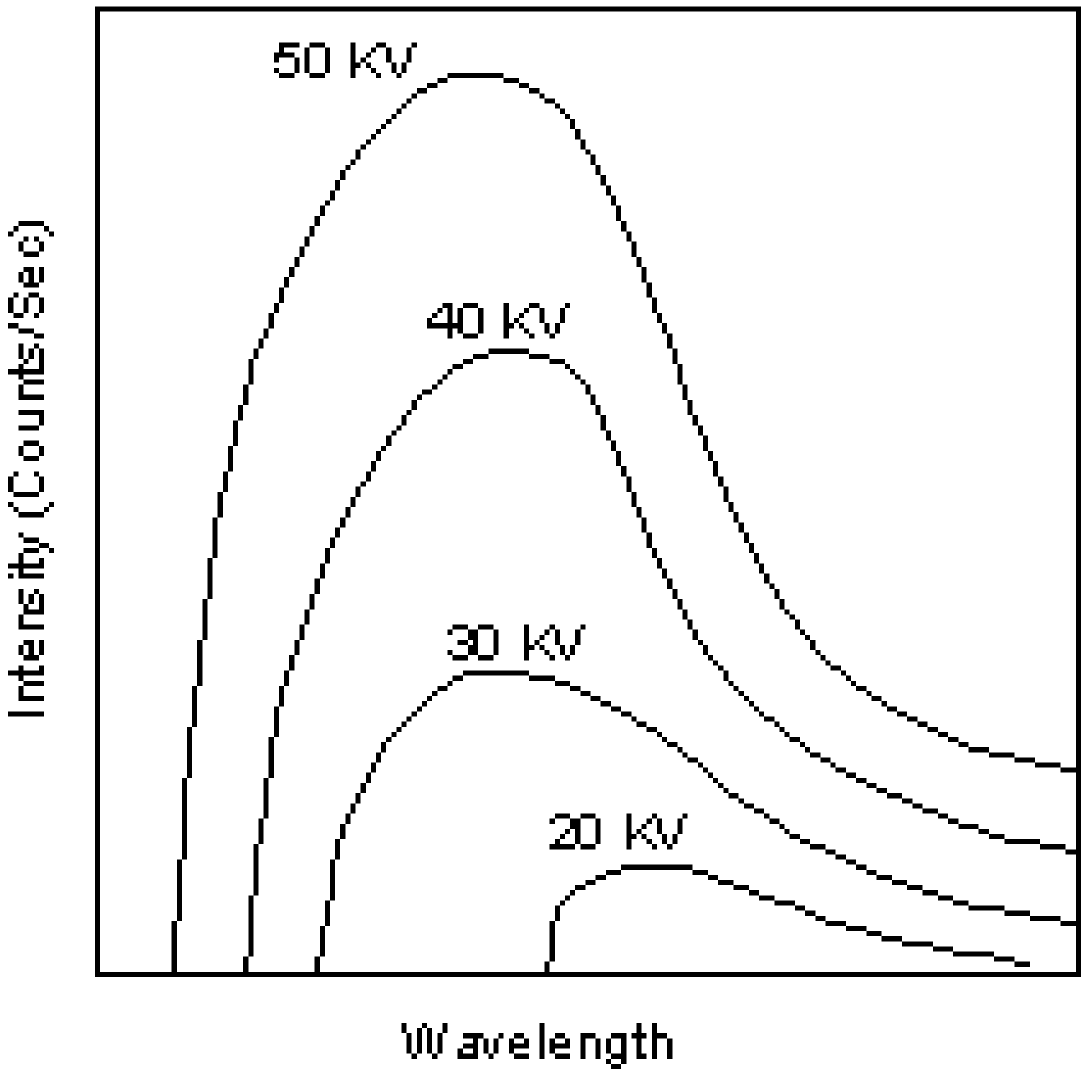
1. Target element should have high melting point and high atomic number.
2. Intensity of X-rays depends upon temperature of filament
3. Frequency (i.e. Energy) of X-rays depends upon P.D. between cathode and anode

The Principle of generation of continuous spectrum



1. Continuous spectrum arises due to the deceleration of the electrons hitting the target
2. This type of radiation is known as bremsstrahlung, German word for "braking radiation"
3. It is also called polychromatic, continuous or white radiation

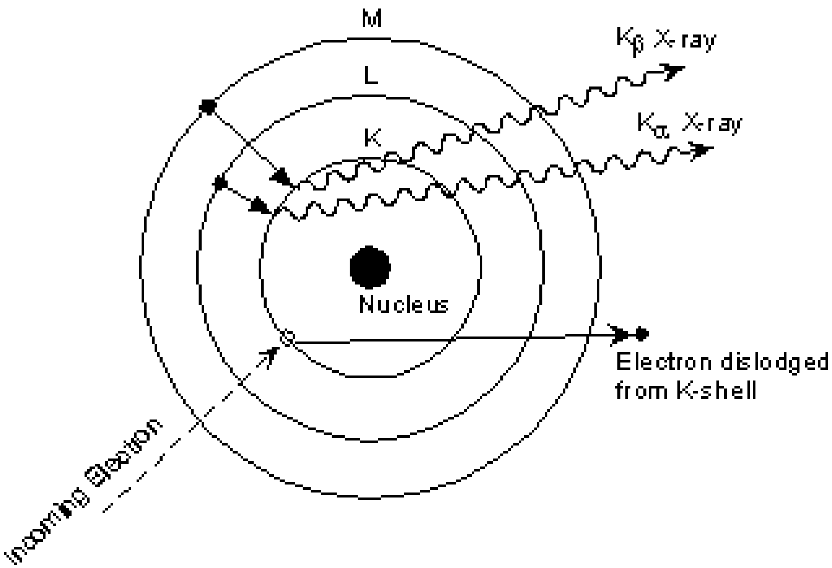
Continuous Spectrum



$$\lambda_{\min} = \frac{hc}{eV}$$

- The minimum wavelength decreases as potential difference increases
- The continuum reaches a maximum intensity at a wavelength of about 1.5 to 2 times the λ_{min} as indicated by the shape of the curve
- Nature of continuous spectrum remains same for all targets at low potential difference
- Total intensity of X-rays emitted from a tube is proportional to atomic no. of target

The Principle of generation of characteristic spectrum



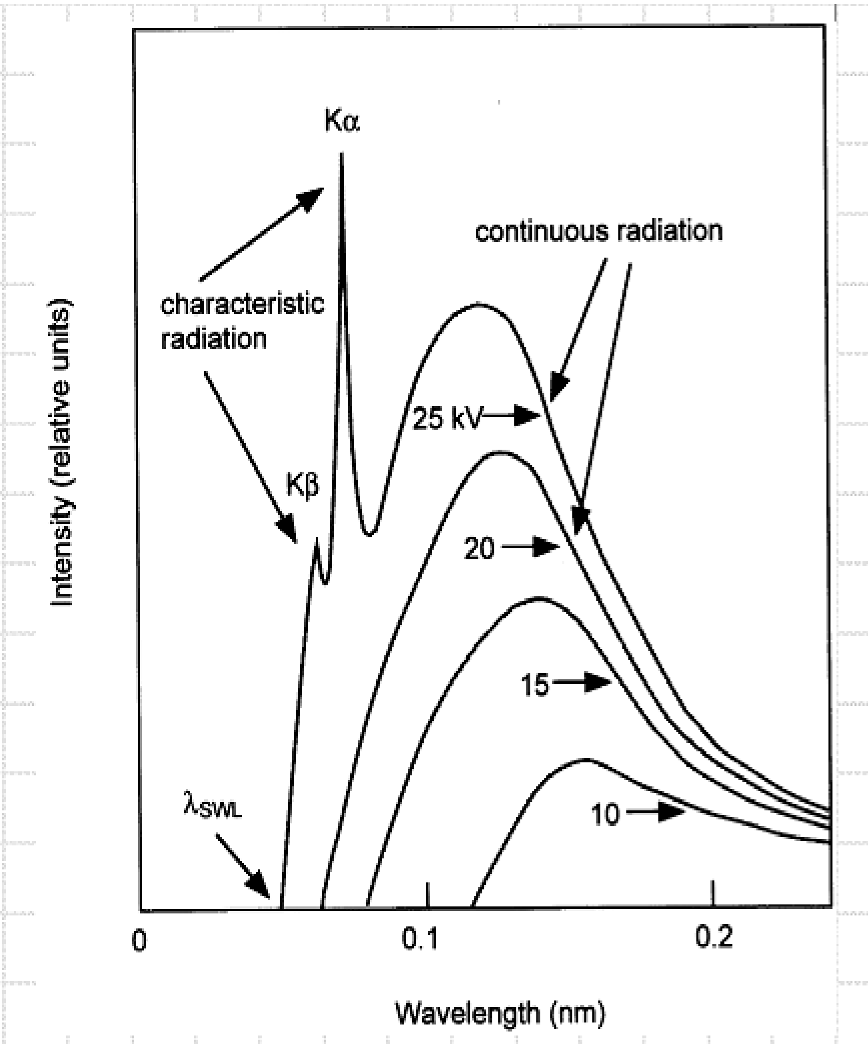
1. An incoming high-energy electron dislodges a k-shell electron in the target, leaving a vacancy in the K shell

2. An outer shell electron then “jumps” to fill the vacancy

3. A characteristic x-ray (equivalent to the energy change in the “jump”) is generated

L-shell to K-shell jump produces a K_α x-ray

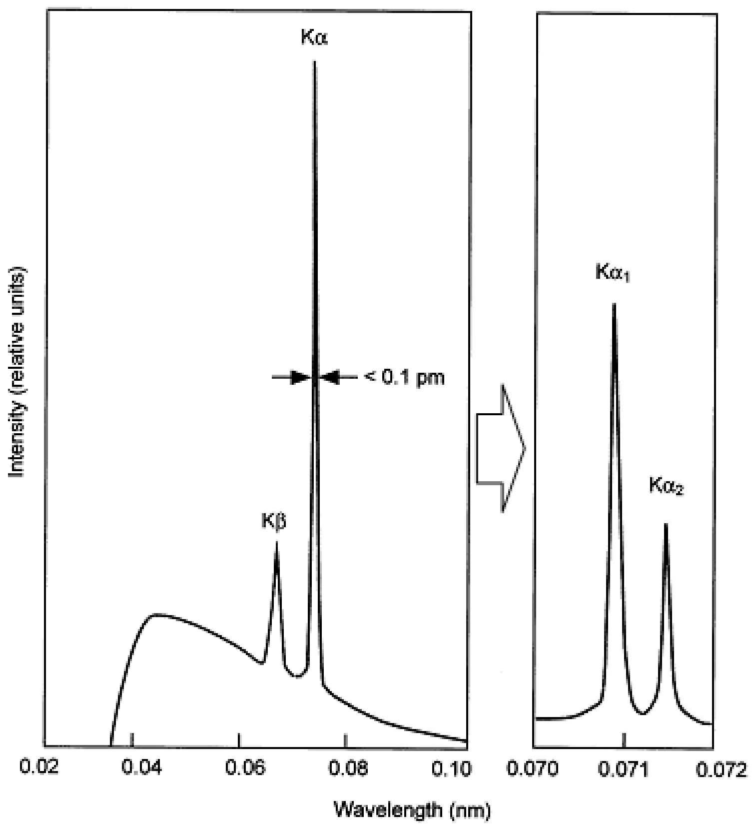
M-shell to K-shell jump produces a K_β x-ray



X-ray spectrum of Mo at different voltage

1. Characteristic spectra is also called as line spectra of target element
2. The spectrum remains all “white” without any peaks till the potential difference reaches a certain higher limit. Above certain potential difference line spectra is observed.
3. Characteristic spectra or line spectra is characteristic of target element.

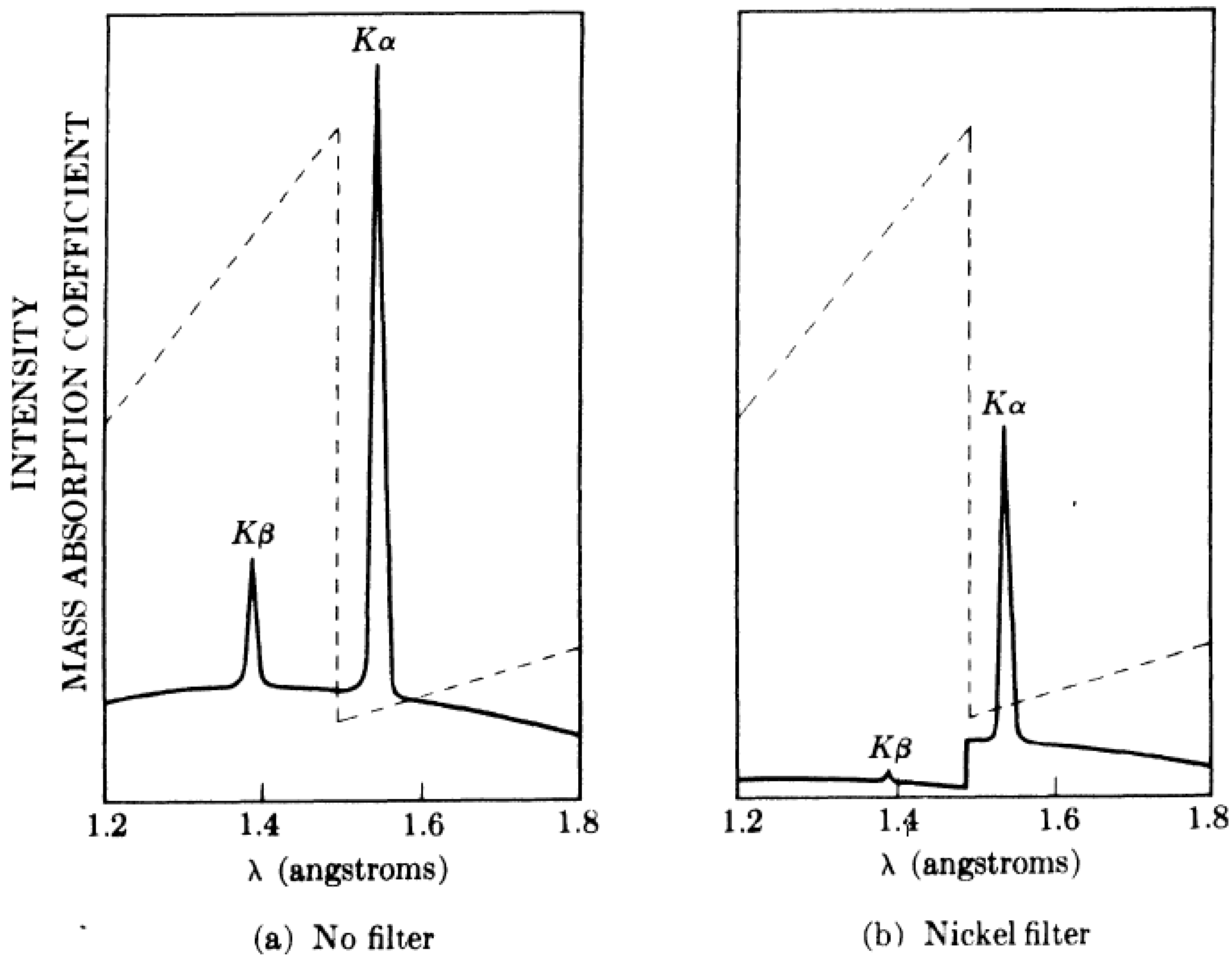
Some Commonly Used characteristic X-ray K wavelengths (Å)



Element	Kα (av.)	$K\alpha_1$	$K\alpha_2$	$K\beta_1$
Cr	2.29100	2.28970	2.29361	2.08487
Fe	1.93736	1.93604	1.93998	1.75661
Co	1.79026	1.78897	1.79285	1.62079
Cu	1.54184	1.54056	1.54439	1.39222
Mo	0.71073	0.70930	0.71359	0.63229

1. Usually only the K-lines are useful in x-ray diffraction
2. There are several lines in the K-set. The strongest are $K\alpha_1$, $K\alpha_2$, $K\beta_1$
3. α_1 and α_2 components are not always resolved – Kα doublet. $K\alpha_1$ is always about twice as strong as $K\alpha_2$, while ratio of $K\alpha_1$ to $K\beta_1$ averages about 5/1.

Use of filter for filtering CuK_β radiation



Characteristic x-ray spectrum of Cu a) without any filter and b) using Ni filter

X-ray Diffraction

Why X-rays are used for diffraction?

- For diffraction of a wave, the size of obstacle or aperture should be comparable to wavelength of wave.
- For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength of radiation.
- In crystals the typical interatomic spacing is of the order of 1 Å so the suitable radiations for diffraction are X-rays, because their wavelengths lies in 0.1 Å to 100 Å range.
- Hence, X-rays can be used for the study of crystal structures.

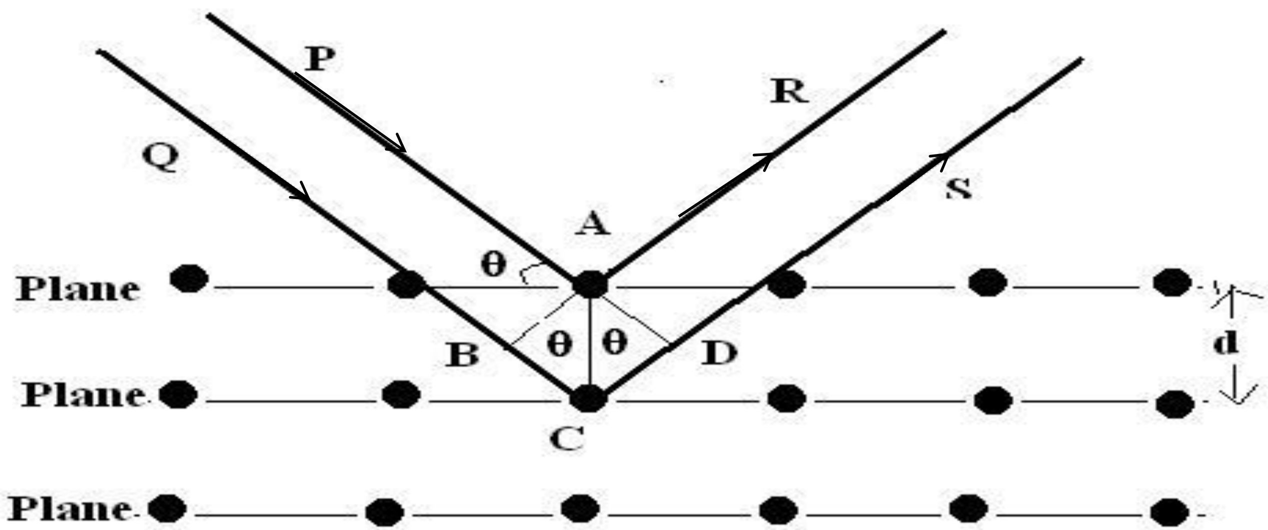
Selection of Anode Material according to different application

Anode Material	Atomic Number	Application
Copper (Cu)	29	Suitable for most diffraction examinations - most widely used anode material.
Molybdenum (Mo)	42	Preferably used for examinations on steels and metal alloys with elements in the range Titanium (Ti) (atomic No. = 22) to approx. Zinc (Zn) (atomic No. = 30)
Cobalt (Co)	27	Often used with ferrous samples, the Iron (Fe) fluorescence radiation would cause interference and cannot be eliminated by other measures.
Iron (Fe)	26	Examination of ferrous samples. Also for use with minerals where Co and Cr tubes cannot be used.
Chromium (Cr)	24	Used for complex organic substances and also radiographic stress measurements on steels.
Tungsten (W)	74	Used where an intensive white spectrum is of more interest than the characteristic.

Bragg's Law

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

- Constructive interference only occurs for certain θ's correlating to a (*hkl*) plane, specifically when the path difference is equal to n wavelengths.



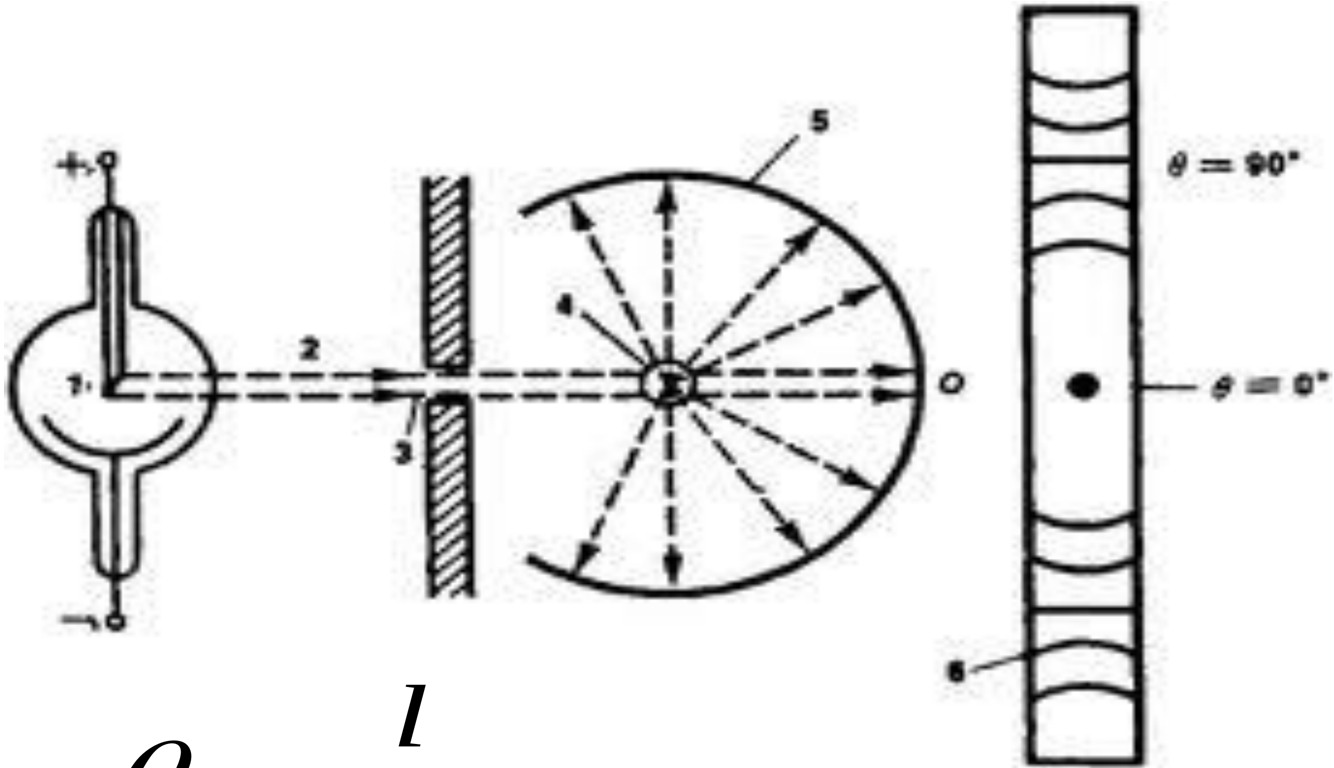
X-RAY DIFFRACTION METHODS

X-Ray Diffraction Method

Laue	Rotating Crystal	Powder
Polychromatic Beam Fixed Angle	Monochromatic Beam Variable Angle	Monochromatic Beam Variable Angle

THE POWDER METHOD

1. This method is useful for samples that are difficult to obtain in single crystal form.
2. Here a monochromatic X-ray beam is incident on a powdered or polycrystalline sample.
3. 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.



1. Target
2. X-ray beam
3. Slit
4. Specimen
5. Debye-Scherrer camera
6. Photographic film

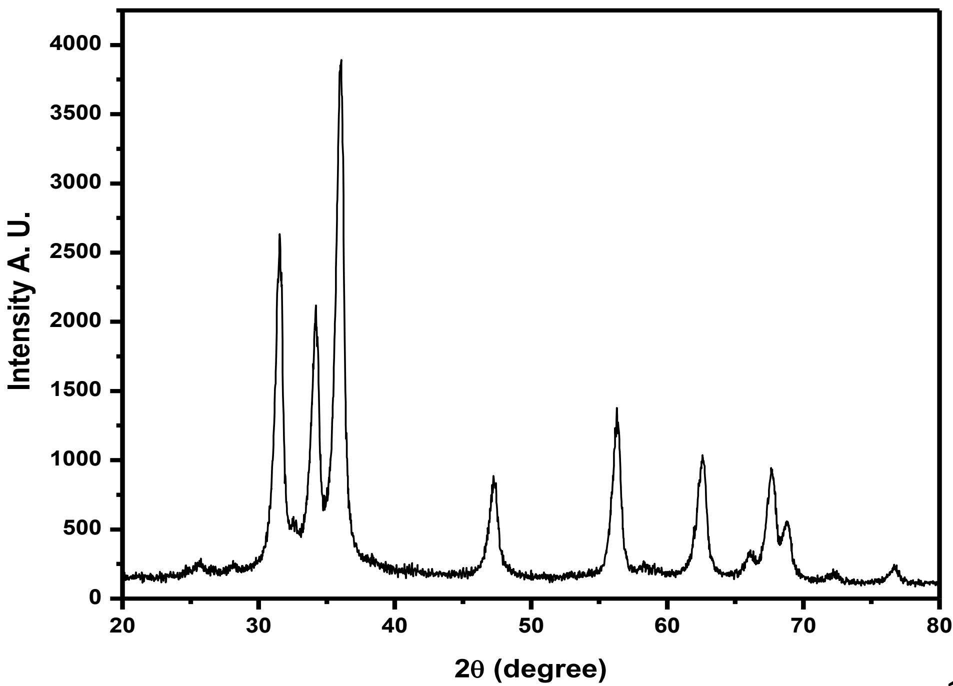
$$\theta = \frac{l}{4R}$$

Schematic Diagram of powder diffraction method

Applications of XRD

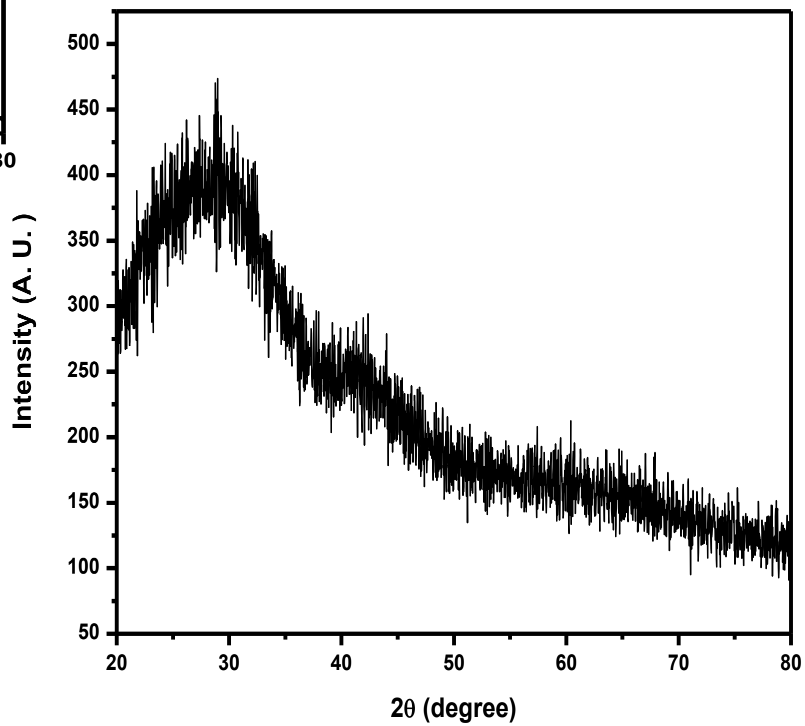
- Differentiation between crystalline and amorphous materials.
- Determination of the structure of crystalline materials.
- Determination of the crystallite size.
- Determination of the orientation of crystals.
- Determination of the standard deviation.
- Measurement of strain, texture coefficient etc

XRD pattern of polycrystalline and amorphous material

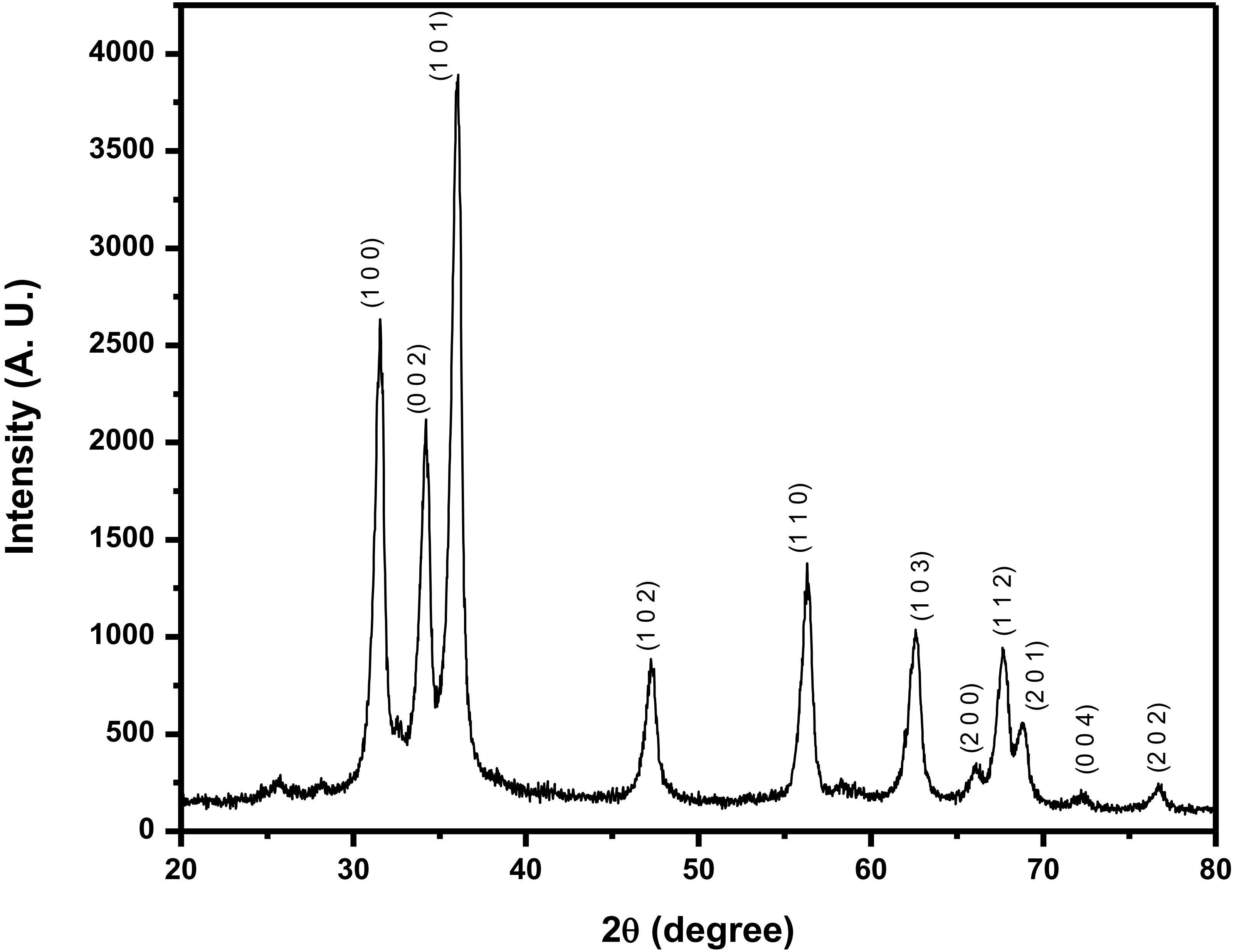


Polycrystalline

Amorphous



Peak indexing of XRD pattern of ZnO sample



Formulae to calculate various parameters using XRD pattern

1. The interplaner distance (d)
(Hexagonal system)

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \frac{l^2}{c^2}$$

2. Bragg's law :

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

3. Crystallite size using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where,

β = FWHM (Full width at half maximum)
D = crystallite size
λ = wavelength of X-ray (1.54056 A^0)

4. Texture coefficient

$$TC = \frac{I_{(hkl)} / I_{0(hkl)}}{\left(\frac{1}{N}\right)\left[\sum I_{(hkl)} / I_{0(hkl)}\right]}$$

Where,

$I_{(hkl)}$ = Measured intensity

$I_{0(hkl)}$ = JCPDS standard intensity

N = number of reflections observed in X-ray diffraction pattern.

5. Standard Deviation

$$\sigma = \frac{\sqrt{\sum I^2{}_{(hkl)} - (\sum I_{(hkl)})^2 / N}}{N}$$

Where, σ = Standard deviation

6. Nelson-Riley Function

$$NRF = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin^2\theta} + \frac{\cos^2\theta}{\theta}\right]$$

Where,

NRF = Nelson-Riley Function

ϴ = Bragg's angle

7.Strain (ε) :

$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon\tan\theta$$

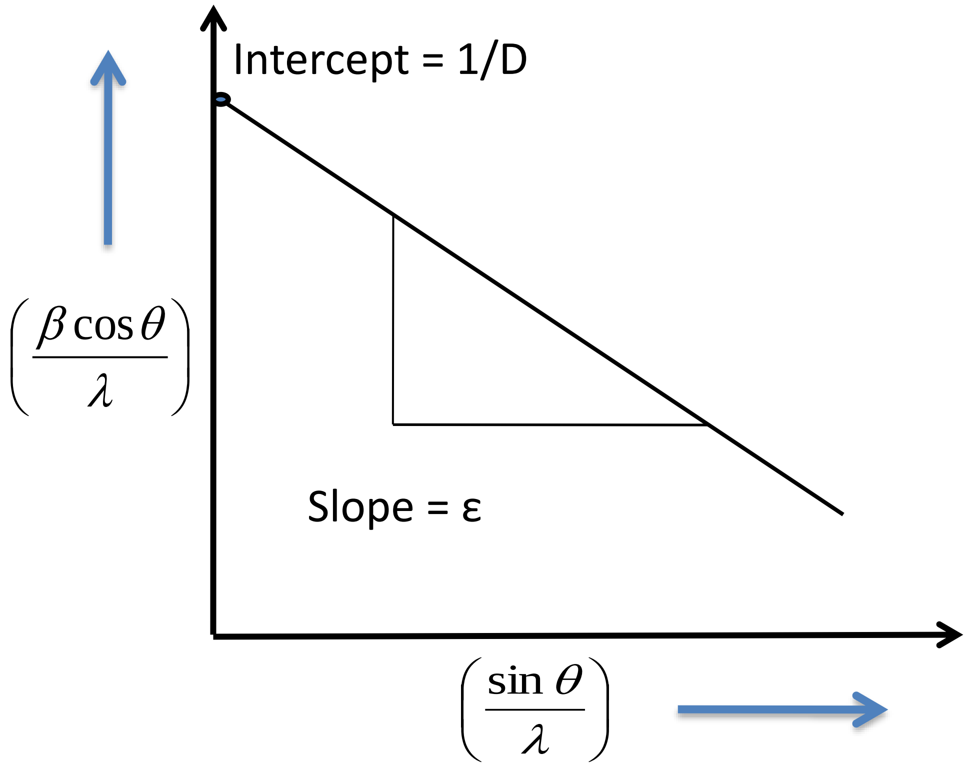
$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon\frac{\sin\theta}{\cos\theta}$$

$$\beta\cos\theta = \frac{\lambda}{D} - \varepsilon\sin\theta$$

$$\left(\frac{\beta\cos\theta}{\lambda}\right) = \frac{1}{D} - \varepsilon\left(\frac{\sin\theta}{\lambda}\right)$$

$$y = c - mx$$

$$y = mx + c$$



Sr. No.	2θ (degree)	Θ (degree)	sinΘ	d_{hkl} observed A^0	(h k l) plane	'd' standard A^0
1	31.6778	15.8389	0.2727	2.8222	(1 0 0)	2.8204
2	34.1601	17.08005	0.2935	2.6226	(0 0 2)	2.6062
3	36.1594	18.0797	0.3101	2.4821	(1 0 1)	2.4806
4	47.4053	23.70265	0.4017	1.9162	(1 0 2)	1.9141
5	56.4841	28.24205	0.4729	1.6278	(1 1 0)	1.6284
6	62.7602	31.3801	0.5204	1.4793	(1 0 3)	1.4793
7	66.0204	33.0102	0.5445	1.4139	(2 0 0)	1.4102
8	67.6551	33.82755	0.5564	1.3837	(1 1 2)	1.381
9	68.9021	34.45105	0.5654	1.3616	(2 0 1)	1.3613
10	72.378	36.189	0.5901	1.3045	(0 0 4)	1.3031
11	76.7111	38.35555	0.6202	1.2413	(2 0 2)	1.2403

Name and formula

Reference code:	01-079-0207
ICSD name:	Zinc Oxide
Empirical formula:	OZn
Chemical formula:	ZnO

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	P63mc
Space group number:	186
a (Å):	3.2568
b (Å):	3.2568
c (Å):	5.2125
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000
Calculated density (g/cm^3):	5.64
Volume of cell (10^6 pm^3):	47.88
Z:	2.00
RIR:	5.26

Status, sub files and quality

Status:	Diffraction data collected at non ambient temperature
Sub files:	Inorganic
	Alloy, metal or intermetalic
	Corrosion
	Modeled additional pattern
Quality:	Calculated (C)

Comments

ICSD collection code:	065121

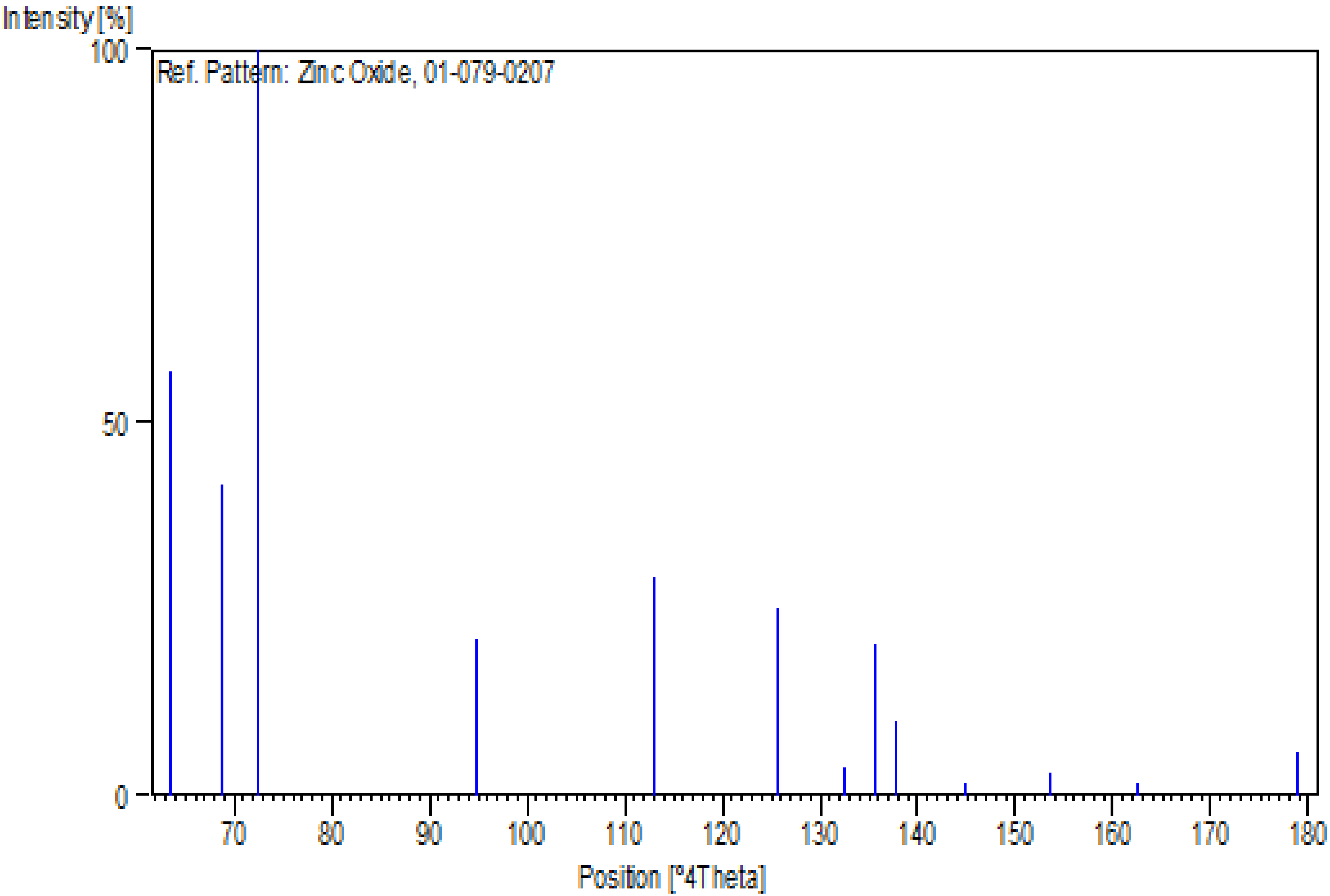
References

Primary reference:	*Calculated from ICSD using POWD-12++*, (1997)
Structure:	Albertson, J., Abrahams, S.C., Kvick, A., *Acta Crystallogr., Sec. B: Structural Science*, **45**, 34, (1989)

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	0	0	2.82049	31.699	57.1
2	0	0	2	2.60626	34.382	41.6
3	1	0	1	2.48062	36.182	100.0
4	1	0	2	1.91416	47.459	21.0
5	1	1	0	1.62841	56.463	29.1
6	1	0	3	1.47933	62.760	25.1
7	2	0	0	1.41024	66.216	3.8
8	1	1	2	1.38101	67.805	20.3
9	2	0	1	1.36130	68.924	10.0
10	0	0	4	1.30313	72.472	1.6
11	2	0	2	1.24031	76.786	3.0
12	1	0	4	1.18297	81.258	1.5
13	2	0	3	1.09497	89.415	5.8

Stick Pattern



Lattice Constant For plane (1 0 0)

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \qquad \text{........(1)}$$

For (1 0 0) plane

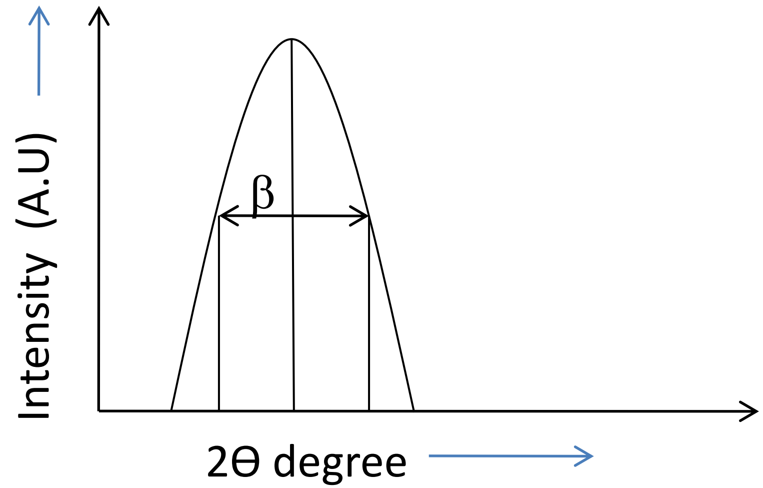
$$\frac{1}{(2.82229)^2} = \frac{4}{3}\frac{1+0+0}{a^2} + \frac{0}{c^2}$$

$$\therefore \qquad a^2 = 10.5618$$

$$\therefore \qquad \mathrm{a} = 3.2499\ \mathrm{A}^0$$

Lattice Constant	Standard value (A^0)	Mean calculated value (A^0)
a	3.2568	3.2499
b	3.2568	3.2499
c	5.2125	5.2624

2Θ degree	Θ degree	β FWHM radian
31.6778	15.8389	0.005861
34.1601	17.08005	0.005861
36.1594	18.0797	0.010885
47.4053	23.70265	0.006699
56.4841	28.24205	0.009211
62.7602	31.3801	0.009211
66.0204	33.0102	0.008373
67.6551	33.82755	0.005861
68.9021	34.45105	0.010048
72.378	36.189	0.013397
76.7111	38.35555	0.010048



1 radian = π/180 = 0.01745

1 degree = 57.25 radian

Crystallite size (D) using Scherrer's formula :

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

$$= \frac{0.9 \times 0.154}{0.005861 \times \cos(0.2763)}$$

$$= \frac{1.386}{0.9620 \times 0.005861}$$

$$D = 24.5883\, nm$$

Similarly remaining values of 'D' can be calculated by using above formula.

Average of crystallite size D in nm = **26.73 nm**

Crystallite Size 'D' in nm
24.5883
24.7460
13.3985
22.6035
17.0855
17.6297
19.7428
28.4705
16.7306
12.8203
17.5923

NRF : Nelson – Riley Function

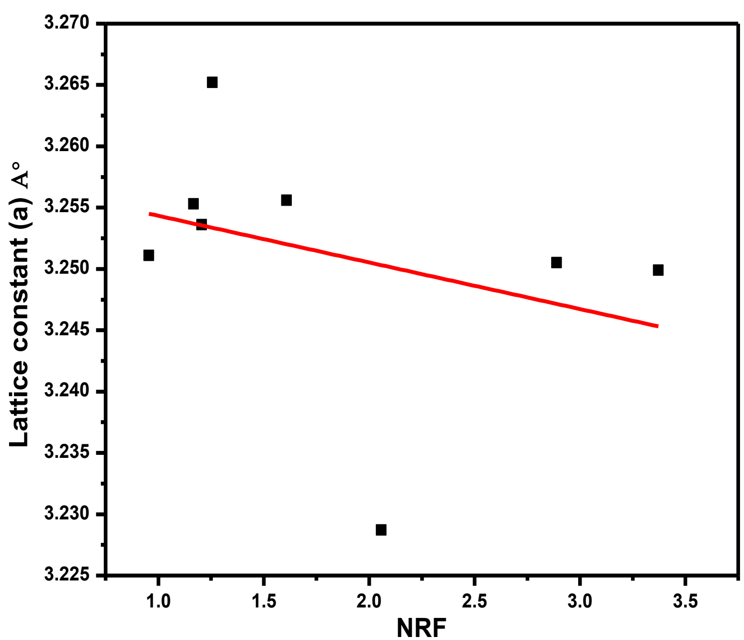
$$NRF = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$$

$$= \frac{1}{2}\left(\frac{\cos^2(0.2263)}{\sin(0.2263)} + \frac{\cos^2(0.2263)}{0.2263}\right)$$

$$= \frac{1}{2}\left(\frac{0.9225}{0.2727} + \frac{0.9985}{0.2309}\right)$$

$$= \frac{1}{2}[3.381908 + 3.339043]$$

$$NRF = 3.3714$$



(h k l) plane	NRF	a (A^0)
(1 0 0)	3.3714	3.2499
(0 0 2)	3.0899	
(1 0 1)	2.889	3.2505
(1 0 2)	2.0575	3.2287
(1 1 0)	1.6084	3.2556
(1 0 3)	1.3663	3.1784
(2 0 0)	1.2567	3.2652
(1 1 2)	1.2052	3.2536
(2 0 1)	1.1674	3.2553
(0 0 4)	1.0682	
(2 0 2)	0.9557	3.2511

Average value of a=3.2581 Å

Strain

Sinϴ/λ	β cosϴ/λ
0.1770	0.00366
0.1905	0.003637
0.2013	0.006717
0.2608	0.00398
0.3070	0.005268
0.3378	0.005105
0.3534	0.004559
0.3611	0.003161
0.3670	0.005379
0.3830	0.00702
0.4026	0.005116

$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon\tan\theta$$

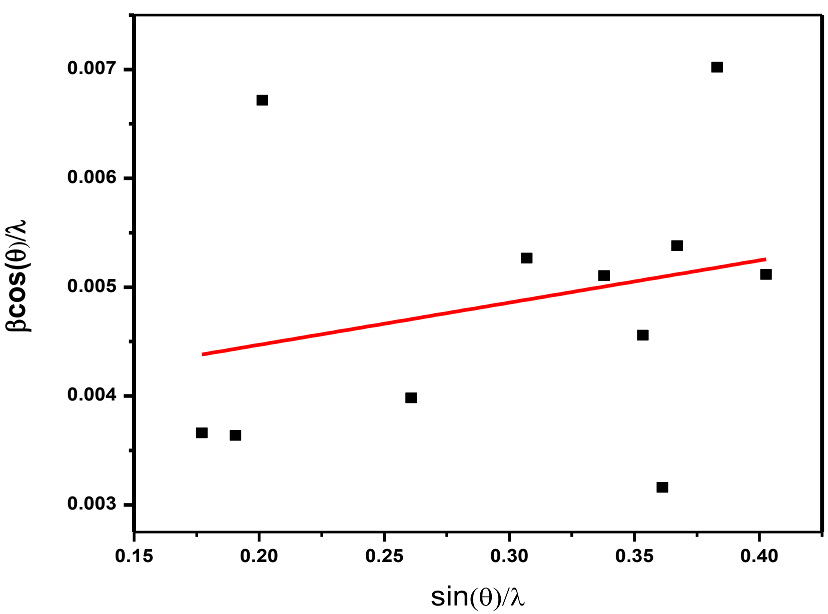
$$\beta = \frac{\lambda}{D\cos\theta} - \varepsilon\frac{\sin\theta}{\cos\theta}$$

$$\beta\cos\theta = \frac{\lambda}{D} - \varepsilon\sin\theta$$

$$\left(\frac{\beta\cos\theta}{\lambda}\right) = \frac{1}{D} - \varepsilon\left(\frac{\sin\theta}{\lambda}\right)$$

$$y = c - mx$$

$$y = mx + c$$



D = 1/intercept

=1/0.00369

D = 271.0071 Å

D = 27.1007 nm

Slope (ε) = 0.00388

Texture Coefficient:

$$TC = \frac{I_{(hkl)} / IO_{(hkl)}}{\frac{1}{N} \sum [I_{(hkl)} / IO_{(hkl)}]}$$

$$= \frac{66.09/57.1}{\frac{1}{11}[12.60108]}$$

$$= 1.010379$$

The reflection intensities from XRD pattern contain information related to the preferential or random growth of polycrystalline thin films which is studied by calculating the texture coefficient TC(hkl). TC for the (0 0 2) plane has relatively higher value than (1 0 0) and (2 0 0) plane. This result conforms that the c-axis crystal orientation of ZnO.

(h k l) plane	Texture coefficient
(1 0 0)	1.010379
(0 0 2)	1.198195
(1 0 1)	0.872941
(1 0 2)	0.846753
(1 1 0)	0.929637
(1 0 3)	0.792255
(2 0 0)	1.196848
(1 1 2)	1.0686
(2 0 1)	1.086811
(0 0 4)	0.938412
(2 0 2)	1.059168

Standard Deviation

$$\sigma = \frac{\sqrt{\sum I^2_{(hkl)} - \left(\sum I_{(hkl)}\right)^2 / N}}{N}$$

$$\sigma = \sqrt{\frac{20338.42 - \left(345.2/11\right)}{11}}$$

$$\sigma = 29.39607$$