X-RAY DIFFRACTION: Basics and Techniques

A PART OF

B.Sc. Physics (Hons.) Old syllabus: Paper-IX

B.Sc. Physics (Hons.) Semester: V (CBCS); Course: CC-XII

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What are X-rays?

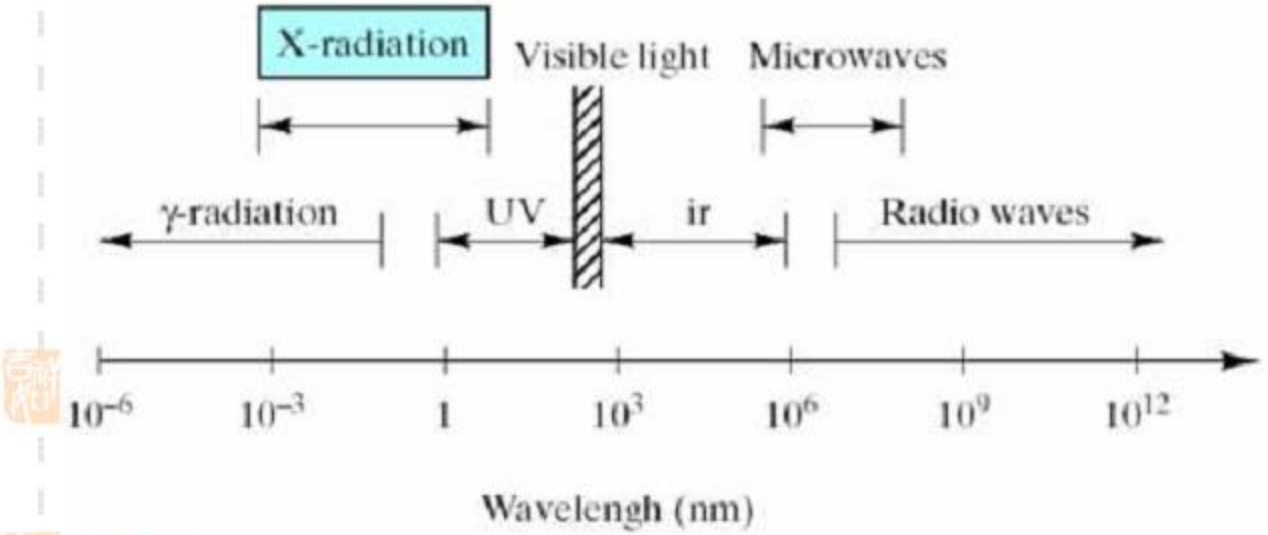
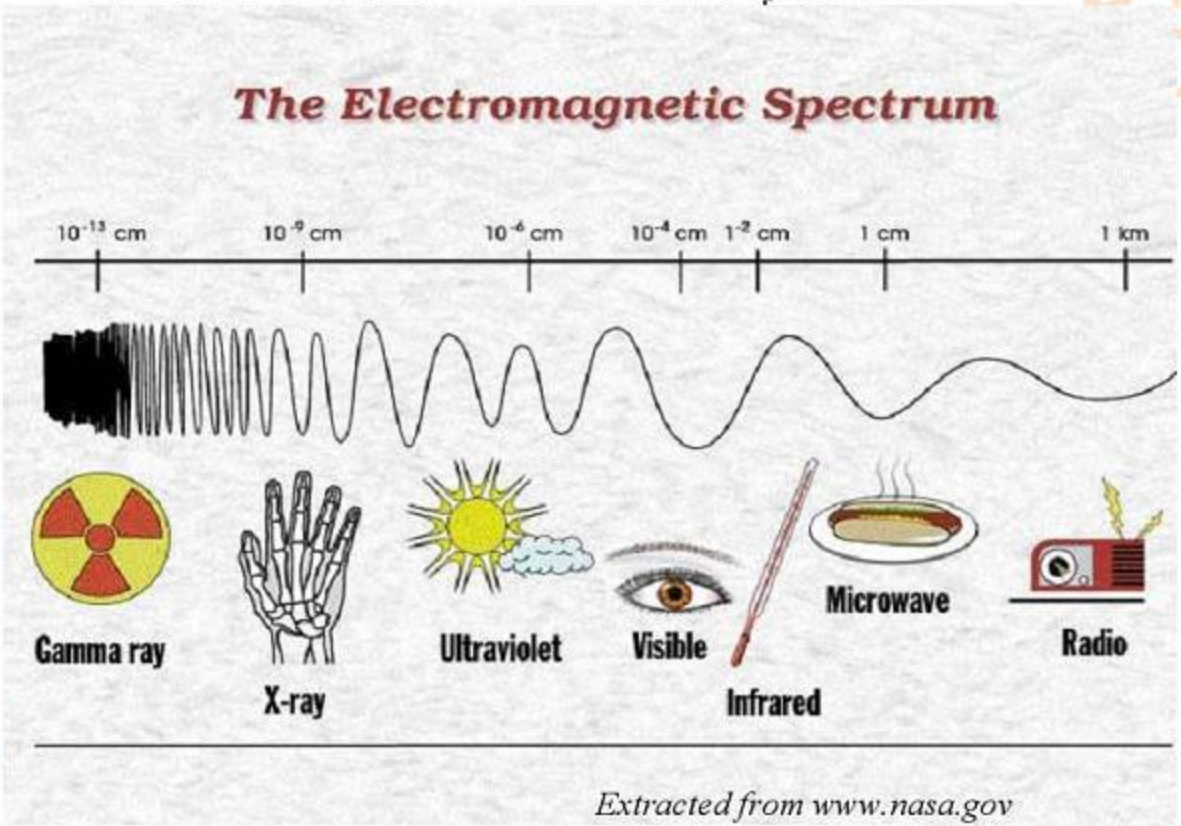


Figure 3-34 *Electromagnetic radiation spectrum. X-radiation represents that portion with wavelengths around 0.1 nm.*

What are X-rays?

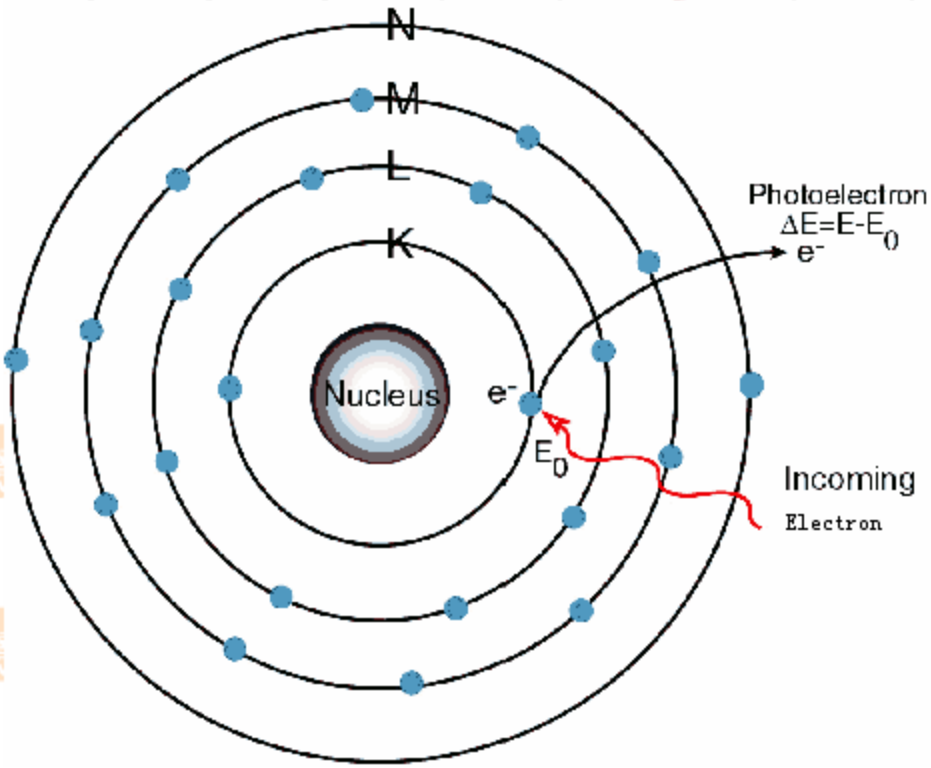


Extracted from www.nasa.gov

X-rays were discovered in 1895 by Wilhelm Röntgen.

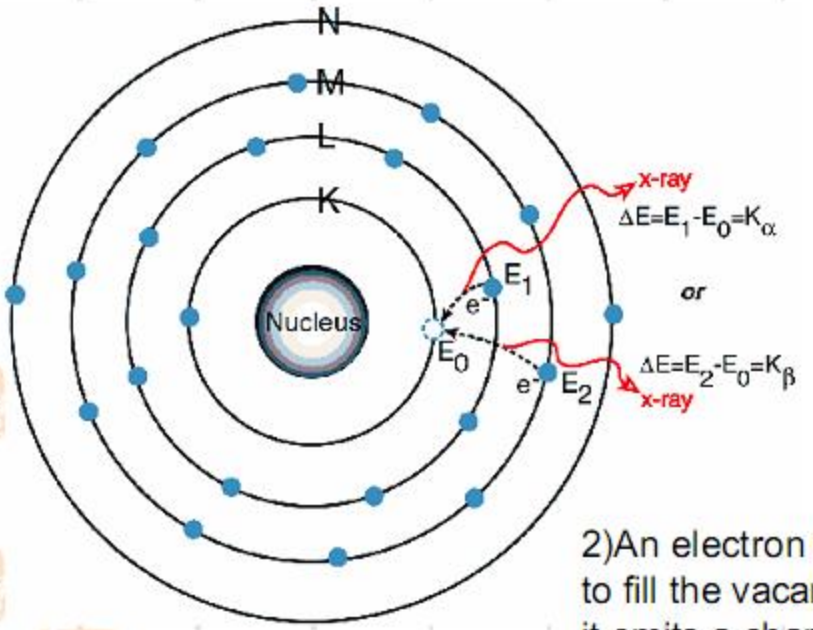
E=hν h=Planck's number= 4.136×10^{-15} eV.s

X-rays production process example

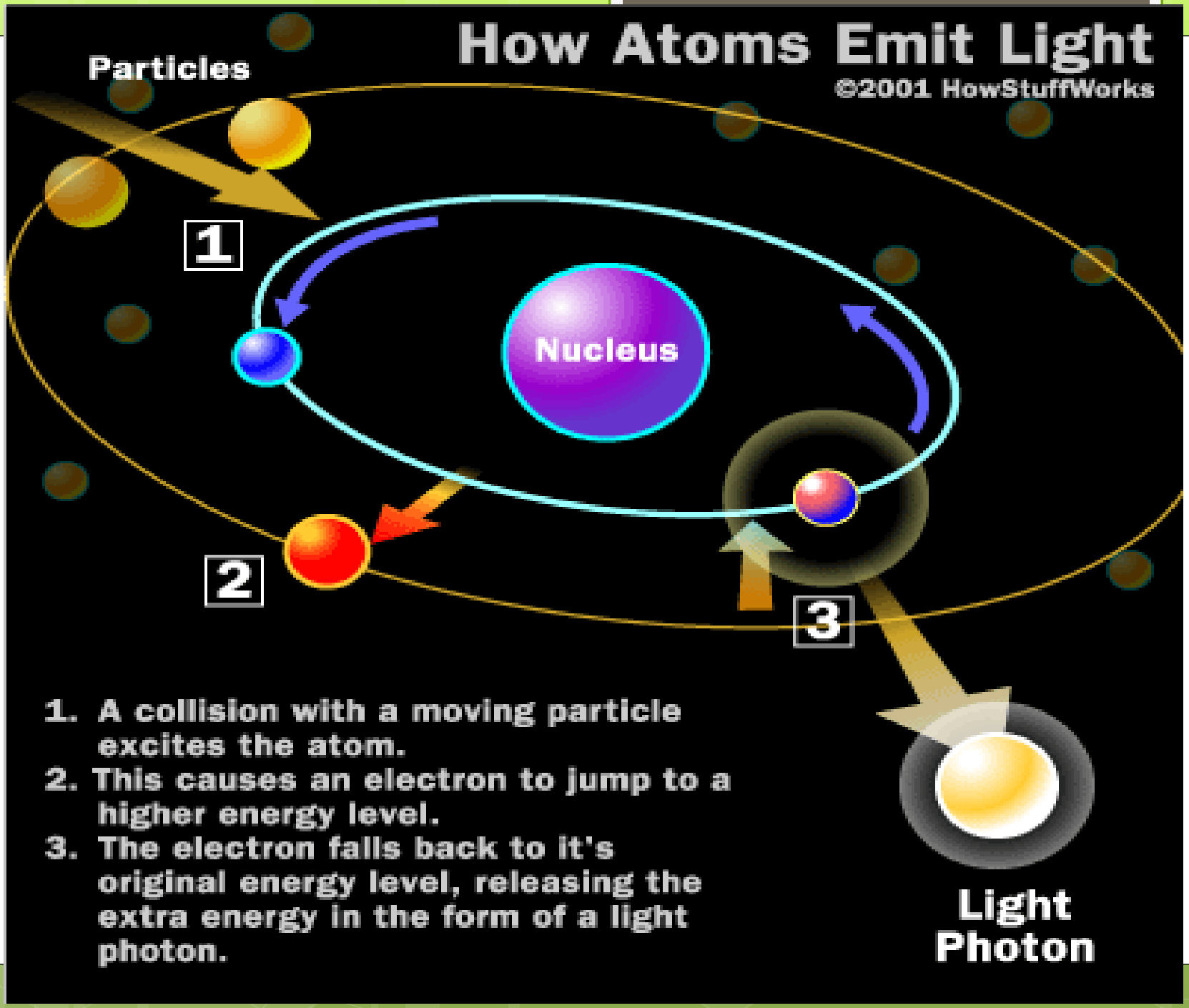


1) An electron in the K shell is ejected from the atom by an external electron

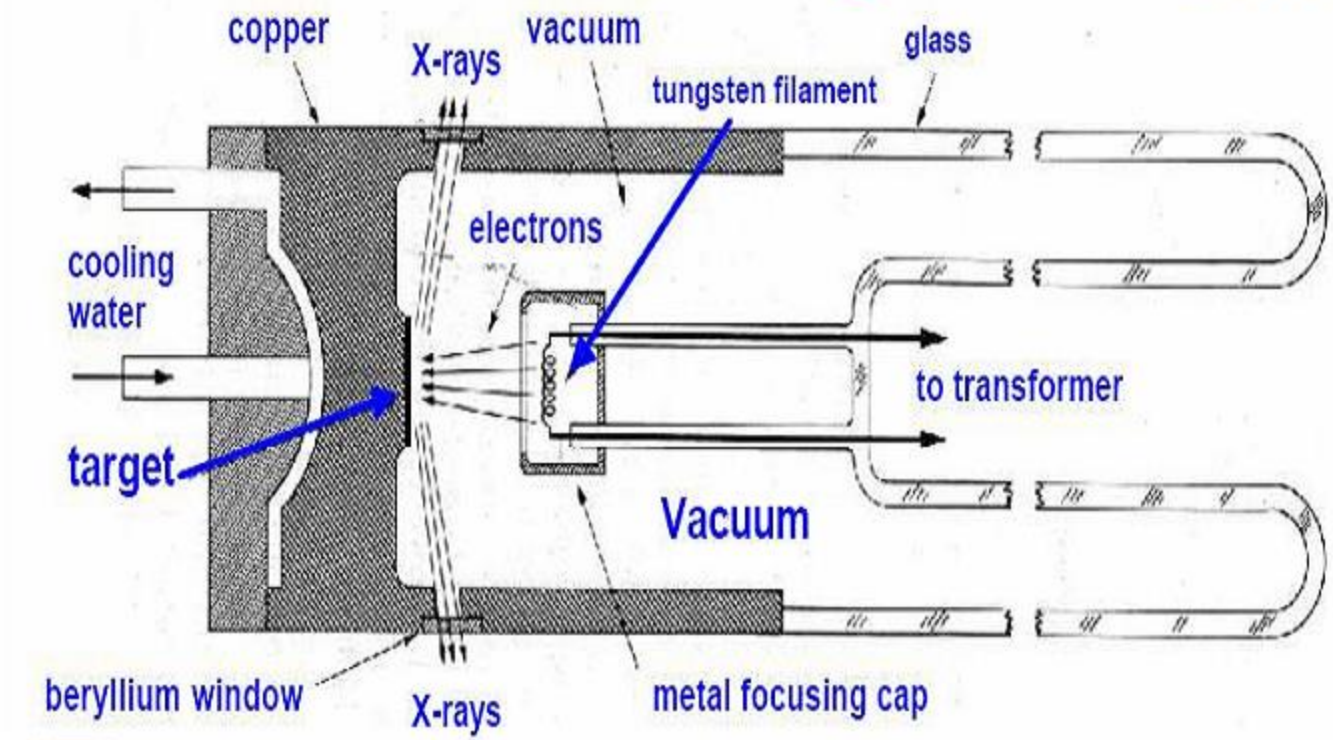
X-rays production process example



2)An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.


How Atoms Emit Light
©2001 HowStuffWorks
Particles
1
Nucleus
2
3
1. A collision with a moving particle excites the atom.
2. This causes an electron to jump to a higher energy level.
3. The electron falls back to it's original energy level, releasing the extra energy in the form of a light photon.
Light Photon

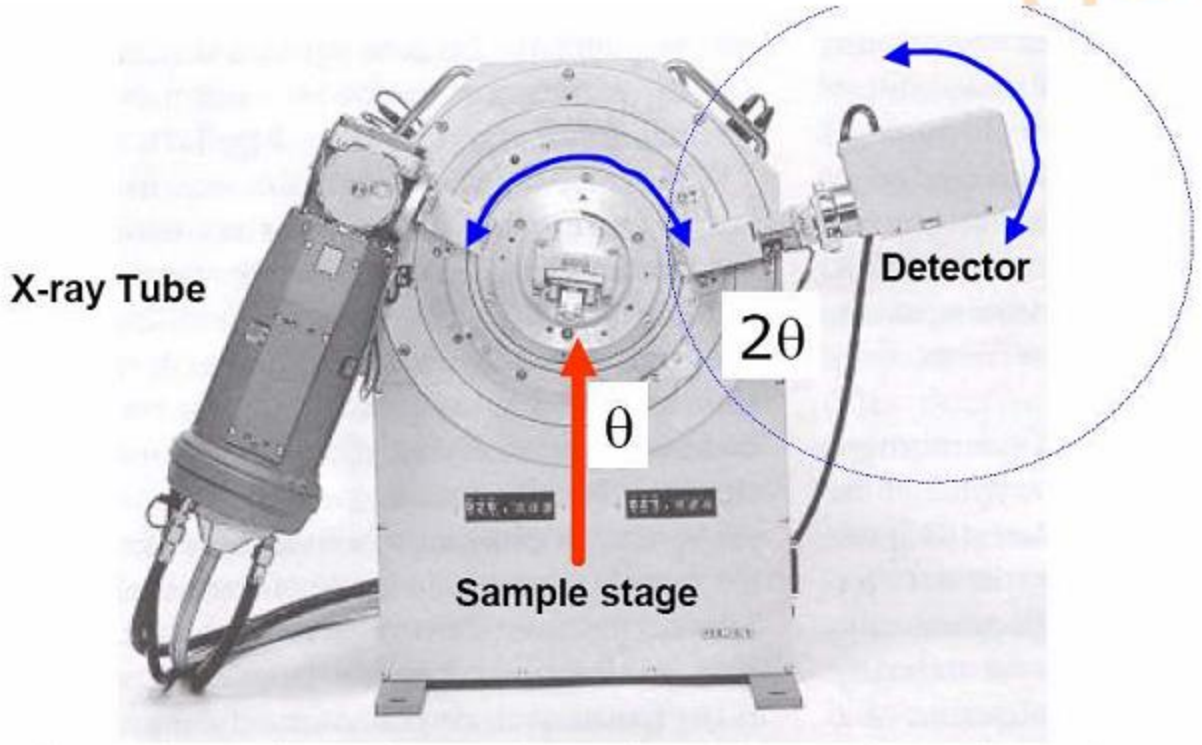
Production of X-rays

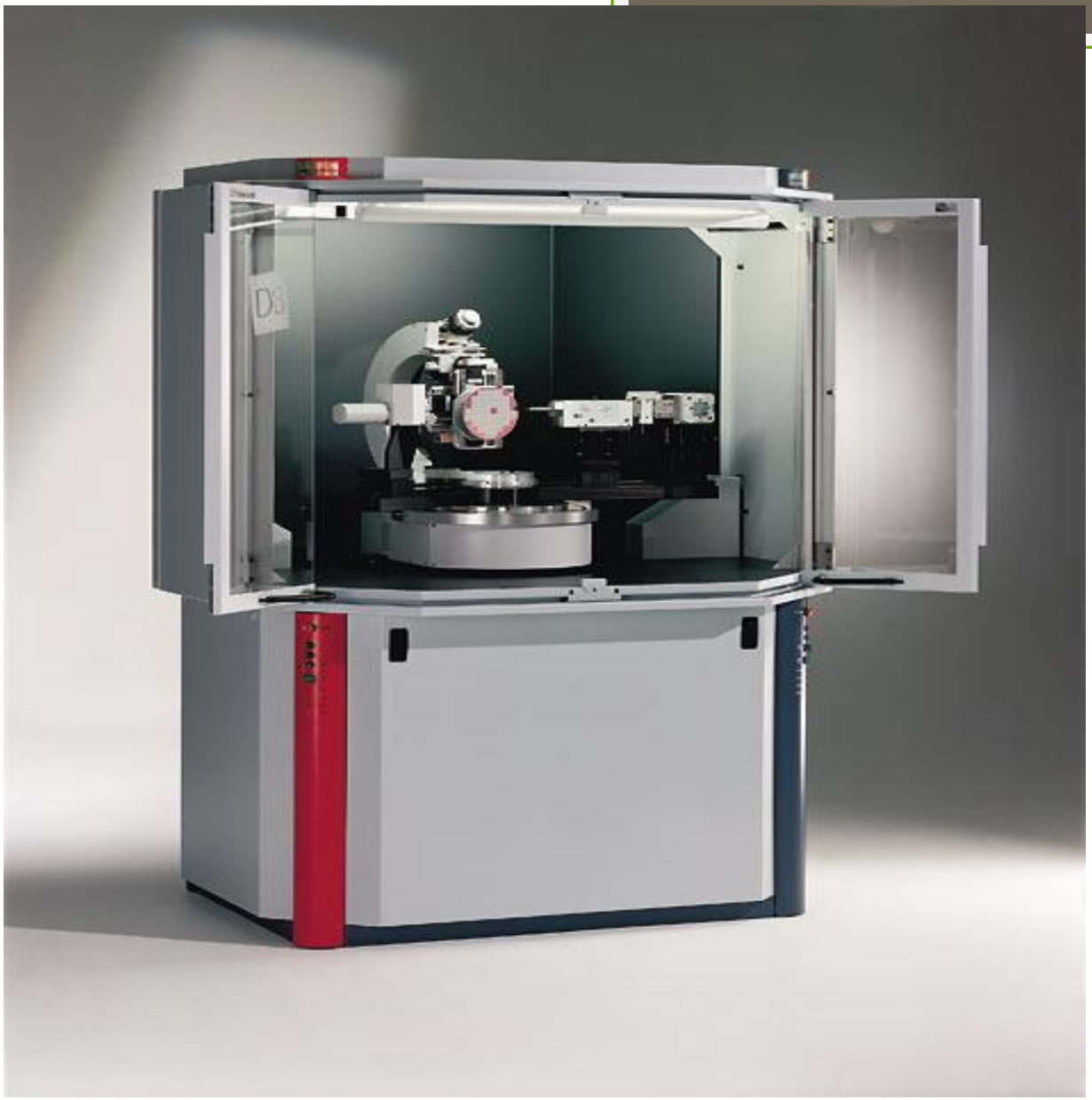


X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, Cu, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target

Efficiency is almost 1% and most of the energy of electrons is converted into heat

Typical XRD Machine





Essential Parts of the Diffractometer

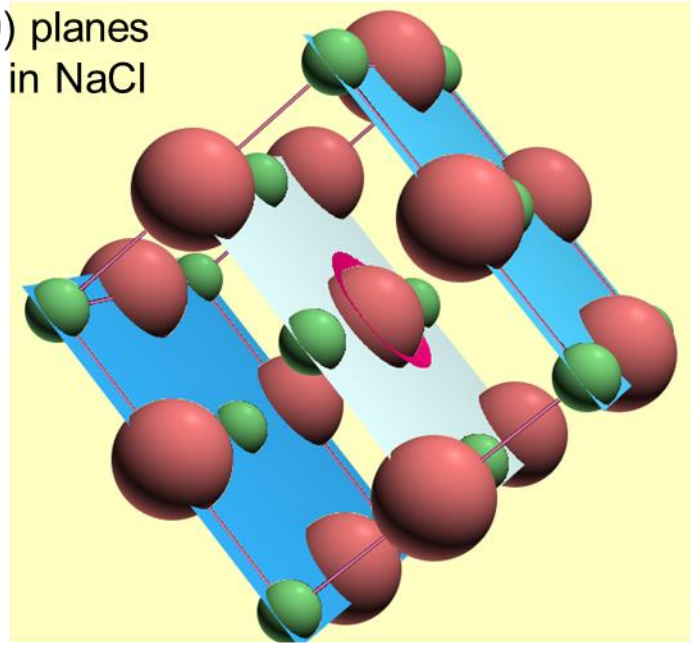
- X-ray Tube: the source of X Rays
- Incident-beam optics: condition the X-ray beam before it hits the sample
- The goniometer: the platform that holds and moves the sample, optics, detector, and/or tube
- The sample & sample holder
- Receiving-side optics: condition the X-ray beam after it has encountered the sample
- Detector: count the number of X Rays scattered by the sample

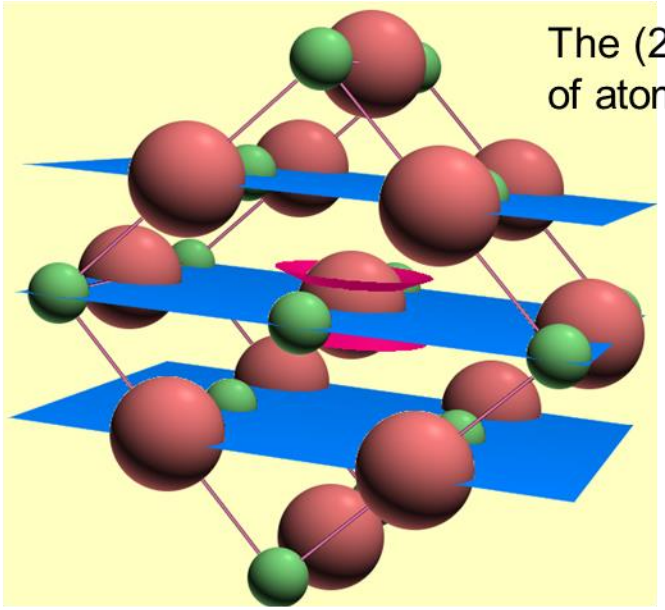
Instrumentation

- Production of X-Rays
- Collimator
- Monochromator
  - Filter
  - Crystal monochromator
- Detector
  - Photographic methods
  - Counter methods

Crystalline materials are characterized by the orderly periodic arrangements of atoms.

The (200) planes of atoms in NaCl



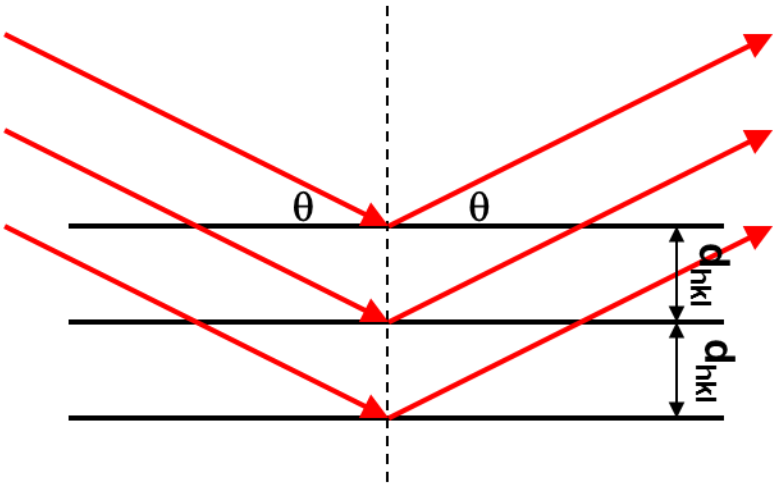


The (220) planes of atoms in NaCl

- The unit cell is the basic repeating unit that defines a crystal.
- Parallel **planes of atoms** intersecting the unit cell are used to define directions and distances in the crystal.
  - These crystallographic planes are identified by **Miller indices**.

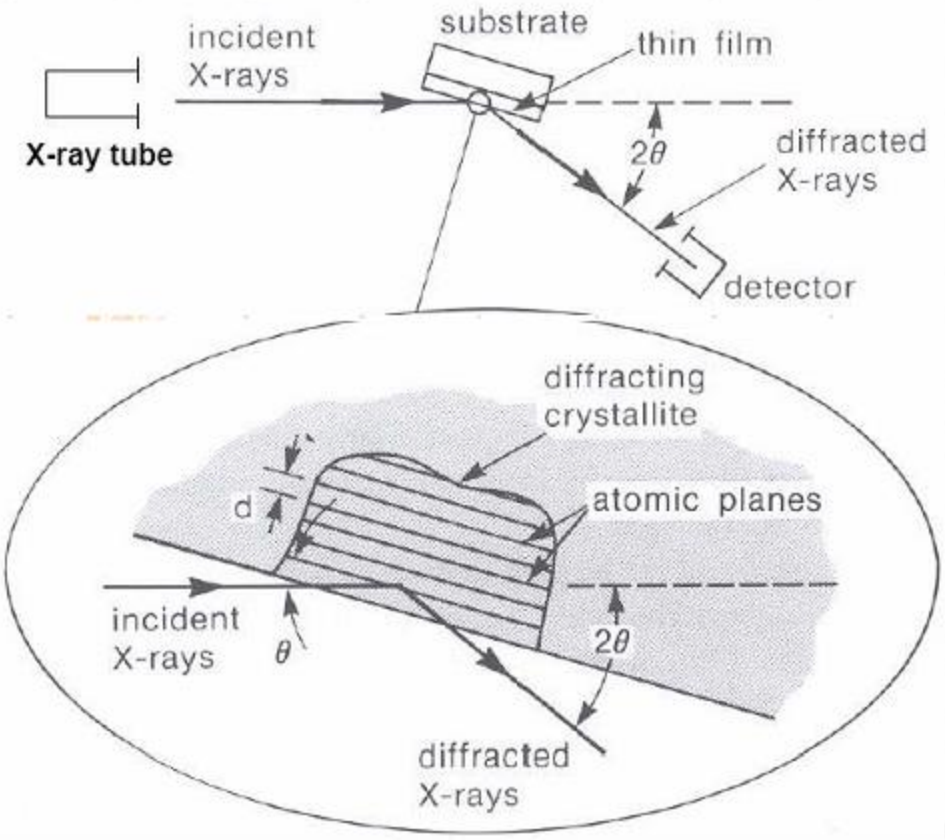
Bragg's law is a simplistic model to understand what conditions are required for diffraction.

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



- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - In our diffractometers, the X-ray wavelength λ is fixed.
  - Consequently, a family of planes produces a diffraction peak only at a specific angle θ.
  - Additionally, the plane normal must be parallel to the diffraction vector
    - Plane normal: the direction perpendicular to a plane of atoms
    - Diffraction vector: the vector that bisects the angle between the incident and diffracted beam
- **The space between diffracting planes of atoms determines peak positions.**
- **The peak intensity is determined by what atoms are in the diffracting plane.**

Basic Features of Typical XRD Experiment



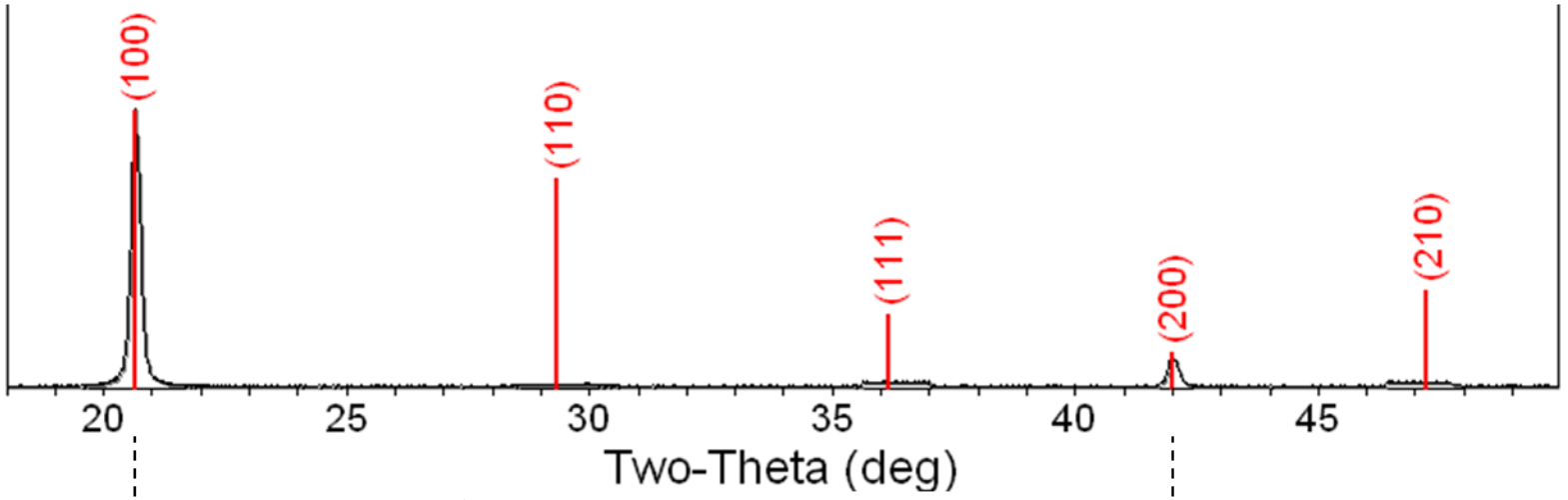
1) Production

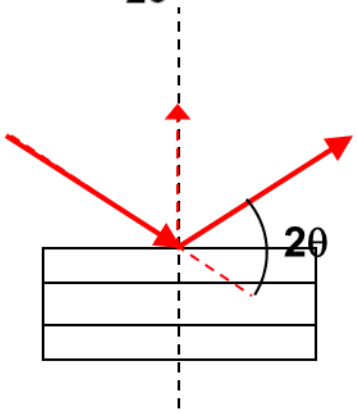
2) Diffraction

3) Detection

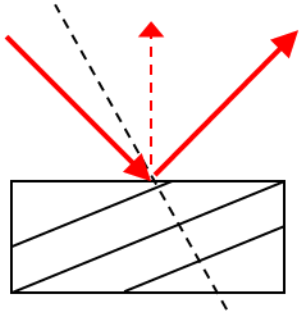
4) Interpretation

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

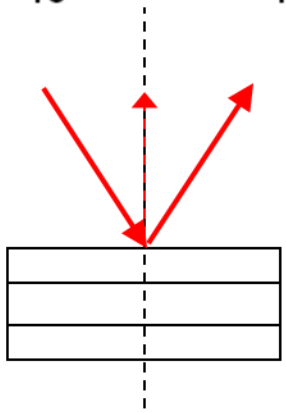




At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.



The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.



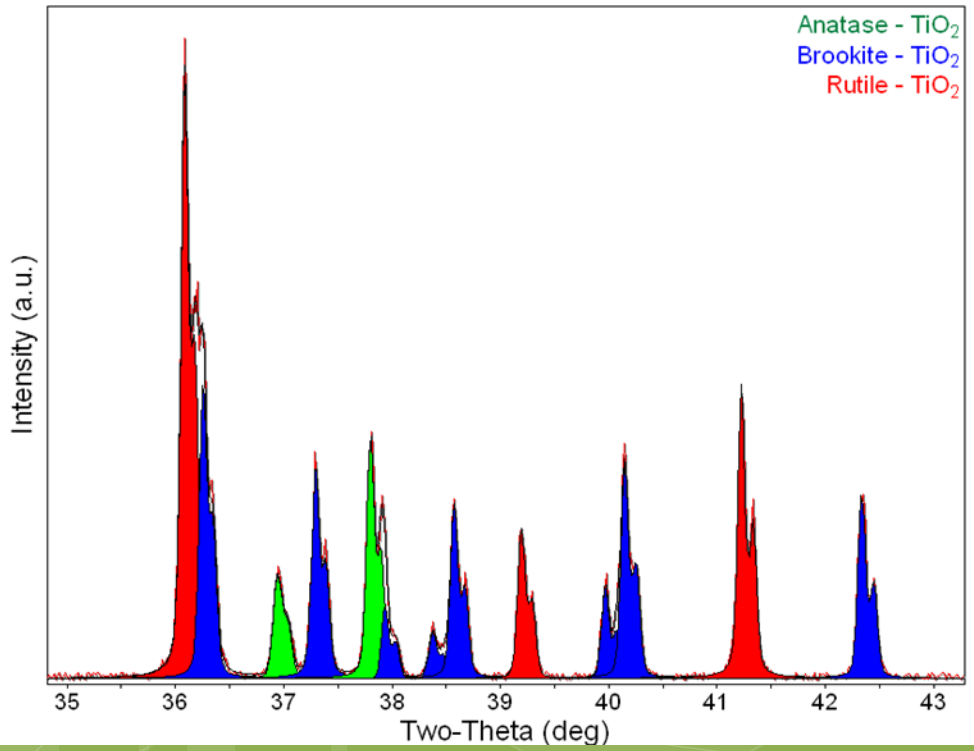
The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

You can use XRD to determine

- 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
- *We have in-situ capabilities, too (evaluate all properties above as a function of time, temperature, and gas environment)*

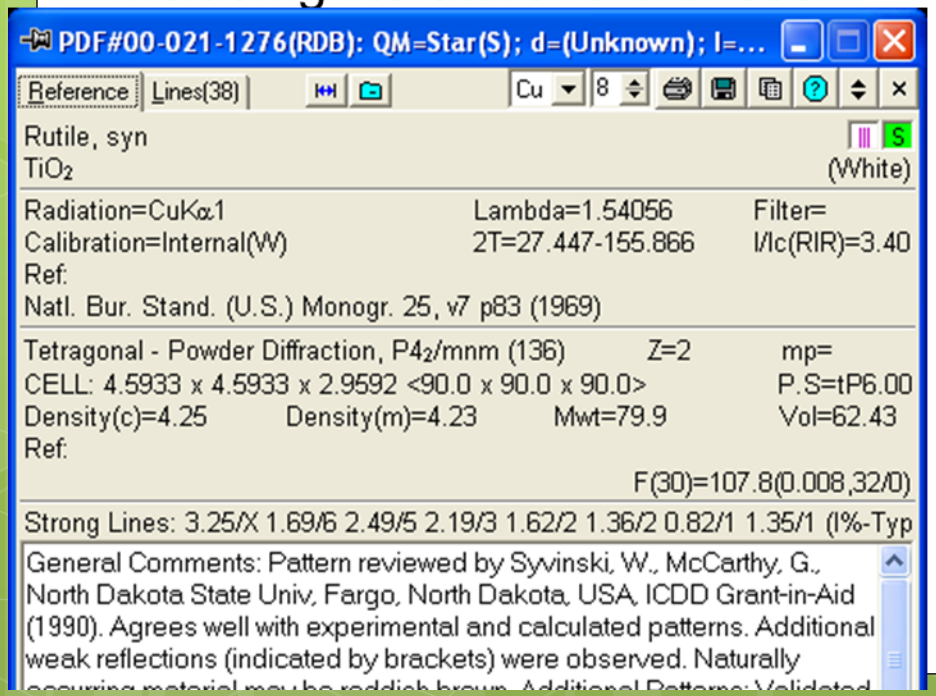
Phase Identification

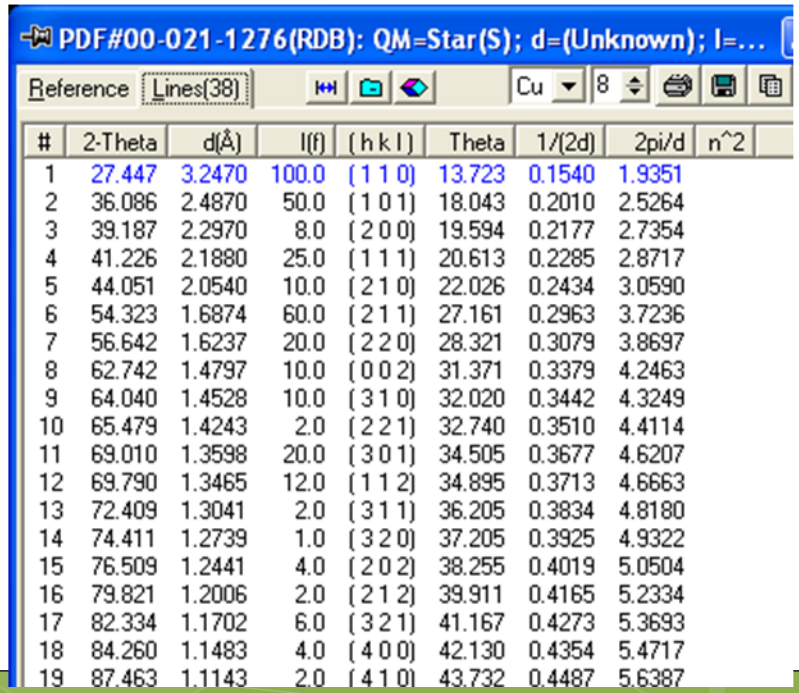
- The diffraction pattern for every phase is as unique as your fingerprint
  - Phases with the same chemical composition can have drastically different diffraction patterns.
  - Use the position and relative intensity of a series of peaks to match experimental data to the reference patterns in the database



Databases such as the Powder Diffraction File (PDF) contain dI lists for thousands of crystalline phases.

- The PDF contains over 200,000 diffraction patterns.
- Modern computer programs can help you determine what phases are present in your sample by quickly comparing your diffraction data to all of the patterns in the database.
- The PDF card for an entry contains a lot of useful information, including literature references.

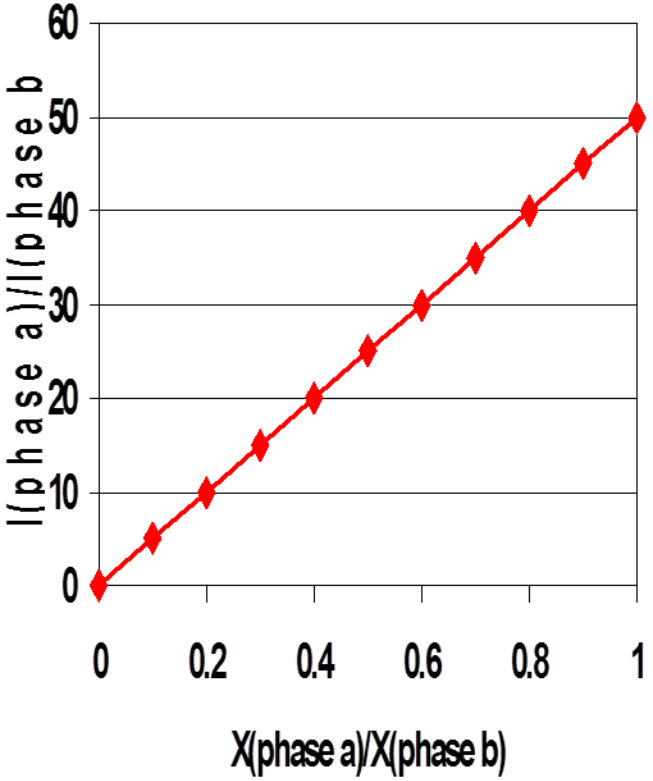




#	2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
1	27.447	3.2470	100.0	(1 1 0)	13.723	0.1540	1.9351	
2	36.086	2.4870	50.0	(1 0 1)	18.043	0.2010	2.5264	
3	39.187	2.2970	8.0	(2 0 0)	19.594	0.2177	2.7354	
4	41.226	2.1880	25.0	(1 1 1)	20.613	0.2285	2.8717	
5	44.051	2.0540	10.0	(2 1 0)	22.026	0.2434	3.0590	
6	54.323	1.6874	60.0	(2 1 1)	27.161	0.2963	3.7236	
7	56.642	1.6237	20.0	(2 2 0)	28.321	0.3079	3.8697	
8	62.742	1.4797	10.0	(0 0 2)	31.371	0.3379	4.2463	
9	64.040	1.4528	10.0	(3 1 0)	32.020	0.3442	4.3249	
10	65.479	1.4243	2.0	(2 2 1)	32.740	0.3510	4.4114	
11	69.010	1.3598	20.0	(3 0 1)	34.505	0.3677	4.6207	
12	69.790	1.3465	12.0	(1 1 2)	34.895	0.3713	4.6663	
13	72.409	1.3041	2.0	(3 1 1)	36.205	0.3834	4.8180	
14	74.411	1.2739	1.0	(3 2 0)	37.205	0.3925	4.9322	
15	76.509	1.2441	4.0	(2 0 2)	38.255	0.4019	5.0504	
16	79.821	1.2006	2.0	(2 1 2)	39.911	0.4165	5.2334	
17	82.334	1.1702	6.0	(3 2 1)	41.167	0.4273	5.3693	
18	84.260	1.1483	4.0	(4 0 0)	42.130	0.4354	5.4717	
19	87.463	1.1143	2.0	(4 1 0)	43.732	0.4487	5.6387	

Quantitative Phase Analysis

- With high quality data, you can determine how much of each phase is present
  - must meet the constant volume assumption (see later slides)
- The ratio of peak intensities varies linearly as a function of weight fractions for any two phases in a mixture
  - need to know the constant of proportionality
- RIR method is fast and gives semi-quantitative results
- Whole pattern fitting/Rietveld refinement is a more accurate but more complicated analysis



ESTIMATION OF UNIT CELL PARAMETERS AND CRYSSTALLITE SIZE OF SAMPLE

- **Unit Cell or Lattice Parameters: using Bragg's Law**

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

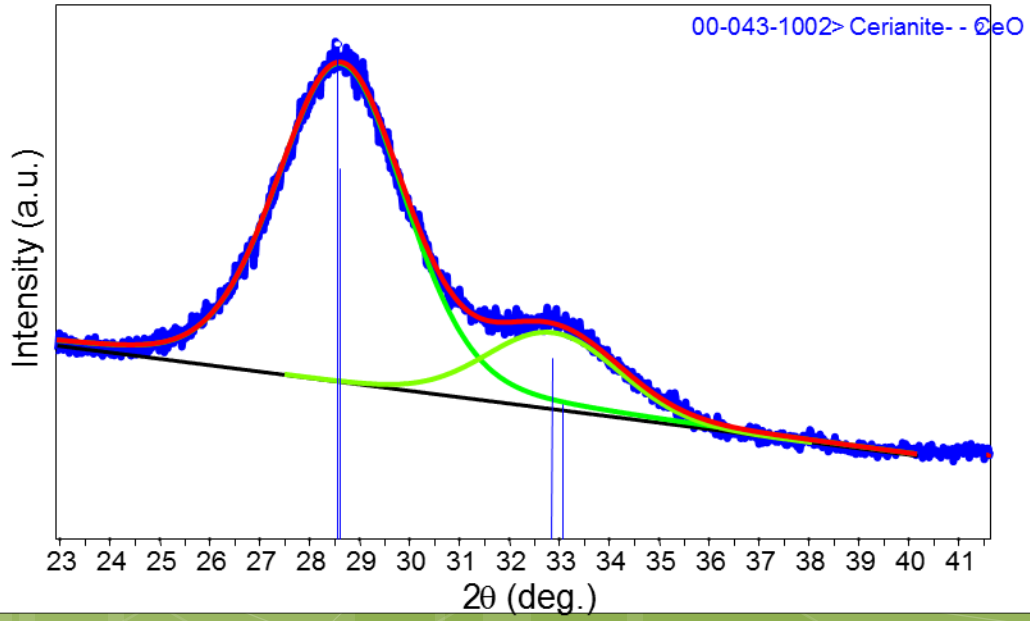
$$1/d^2 = (h^2+k^2)/a^2 + l^2/c^2 \quad \text{(Cubic crystal structures)}$$

$$= 4/3[(h^2+hk+k^2)/a^2] + l^2/c^2 \quad \text{(Hexagonal crystal)}$$

$$= (h^2+k^2)/a^2 + l^2/c^2 \quad \text{(Tetragonal crystal structures)}$$

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



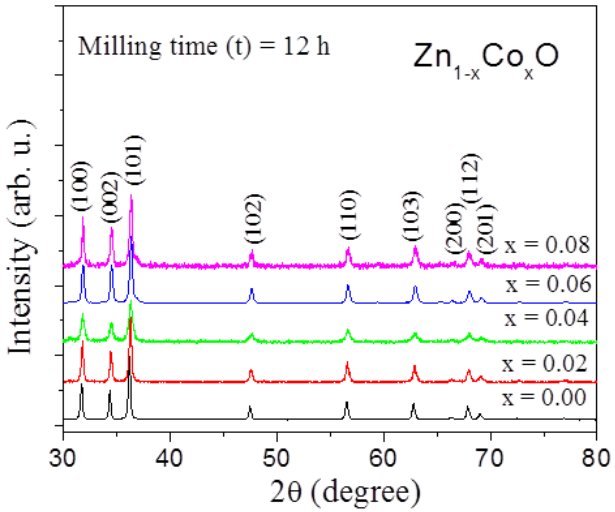
$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

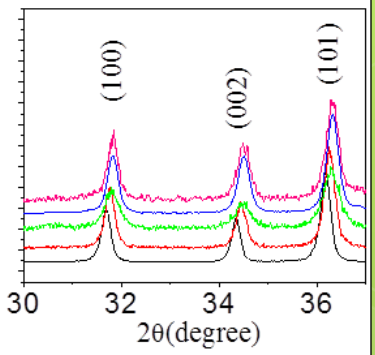
Part-A: Oxide Semiconductors doped with magnetic ions (3*d* or 4*f* elements):

1. Study of Co-doped ZnO ($0 \le x \le 0.08$) bulk powders prepared by mechano-synthesis (Ball milling) route :

Ball milling process

- ✓ Starting materials:
  ZnO , SnO_2 (99.99%)
  And CoO (99.99%)
- ✓ Sample: ball (gm)- 1:10
- ✓ Low temperature (<70°C)
- ✓ Milling time:
  1, 4, 8 and 12 hrs





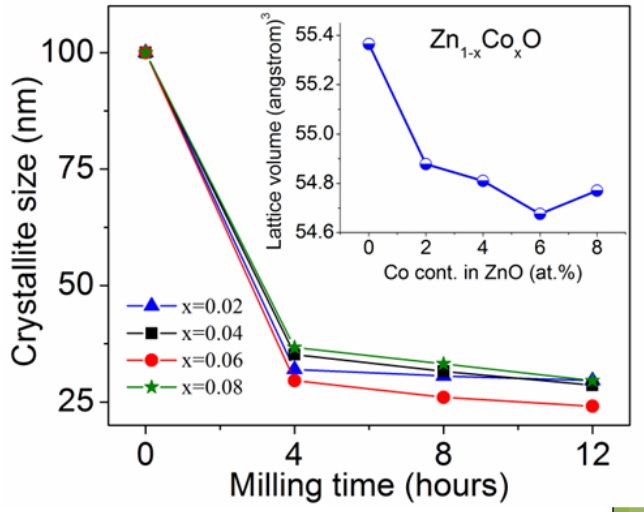
- Peak shifting due to Co ion substitution

- ❑ Hexagonal ZnO wurtzite structure.
- ❑ No secondary or impurity phases are detected from XRD.

✓ Particle size are estimated using Debye-Scherer formula

$$t = 0.9\,\lambda/\beta\cos\theta \ldots\ldots (1)$$

- ❑ Decrease in lattice parameter indicates the insertion of smaller Co^{2+} ion (0.6 Å) replacing Zn^{2+} ions (0.74 Å).



S. Ghosh et al. **Journal of Magnetism and Magnetic Materials 322, 1979 (2010)**

Mixture of Two sample phases: ZnO & CoO

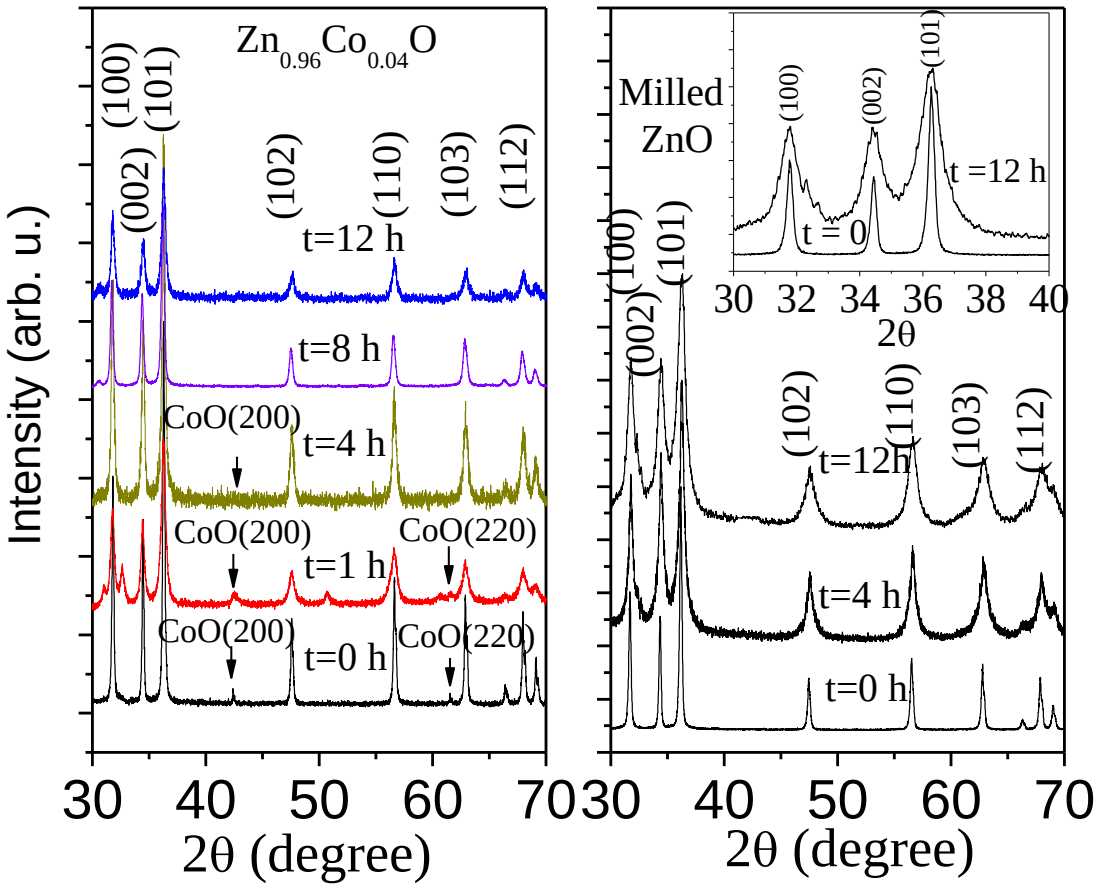


Fig.: Evolution of XRD peaks on different milling time.

THNAK YOU