

X-Ray Diffraction

X-ray diffraction (XRD) is an effective method for determining the crystal structure of materials. It detects crystalline materials having crystal domains greater than 3-5 nm. It is used to characterize bulk crystal structure and chemical phase composition.

Crystalline & Amorphous materials

Materials can be classified as

- Crystalline material : Crystalline material can be single crystal or polycrystalline
- Amorphous material

Crystalline material

Crystalline materials are composed of atoms arranged in a regular ordered pattern in three dimensions. This periodic arrangement is known as crystal structure. It extends over distance much larger than the interatomic separations. In a single crystal, this order extends through the entire volume of the material. There are seven crystal systems: cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic. Different crystal structures are based on framework of one of the 14 Bravais lattice.

Parallel planes of atoms intersecting the unit cell are used to define directions and distances in the crystal. The 'd spacing' is defined as the distance between adjacent planes. The orientation and interplaner spacing (d) of these lattice planes are defined by three integers h,k,l called Miller Indices. The (hkl) designate a crystal face or family of planes throughout a crystal lattice.

Polycrystalline materials consist of many small single crystal regions called grains. Grains are separated by grain boundaries. The grains can have different shapes and sizes and are disoriented with respect to each other.

Amorphous materials: When the atoms are not arranged in a regular periodic manner, the material is called amorphous. Such materials possess only short range order (distance less than a nanometer).

X-Ray Diffraction :

X-ray is a form of electromagnetic radiation having range of wavelength from 0.01-0.7 nm which is comparable with the spacings between lattice planes in the crystal. Spacing between atoms in metals ranges from 0.2-0.3 nm. When an incident beam of X-rays interacts with the target atom, X-ray photons are scattered in different directions. Scattering is elastic when there is no change in energy between the incident photon and the scattered photon. In inelastic scattering, the scattered photon loses energy. These scattered waves may superimpose and when the waves are in phase then the interference is constructive and, if out of phase, then destructive interference occurs. Atoms in crystal planes form a periodic array of coherent scatterers. Diffraction from different planes of atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal.

Bragg's law

The X-ray beams incident on a crystalline solid will be diffracted by the crystallographic planes. Bragg's law is a simple model explaining the conditions required for diffraction. It is given as $n\lambda = 2d_{hkl} \sin \theta$, where d_{hkl} is the spacing between two planes hkl, n is an integer and λ is the wavelength. For parallel planes of atoms, with a spacing d_{hkl} between the planes, constructive interference occurs only when Bragg's law is satisfied. In diffractometers, the X-ray wavelength is fixed. Consequently, a family of planes produces a diffraction peak only at a specific angle θ . The spacing between diffracting planes of the atoms determines the peak positions. The peak intensity is determined by the atoms in the diffracting plane. Fig. 1 explains the Bragg's law. Two in-phase incident waves, beam 1 and beam 2, are deflected by two crystal planes (Z and Z_1). The diffracted waves will be in phase when the Bragg's Law, $n\lambda = 2d \sin \theta$, is satisfied. In order to keep these beams in phase, their path difference (SQ + QT) has to equal one or multiple X-ray wavelengths ($n\lambda$) i.e $SQ + QT = n\lambda$ or $SQ + QT = 2PQ \sin \theta = 2d \sin \theta = n\lambda$. Hence the

path difference depends on the incident angle (θ) and spacing between the parallel crystal planes (d).

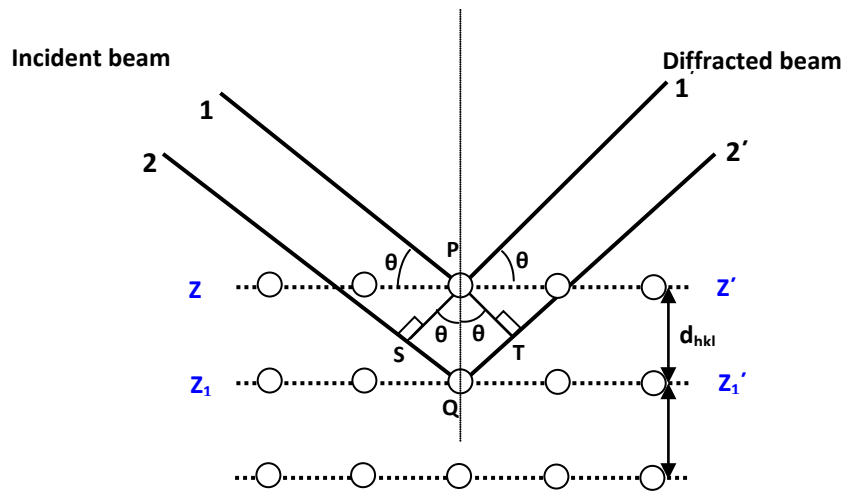


Fig. 1. Braggs analysis for X-ray diffraction by crystal planes

Working principle and Instrumentation

The instrument is called an X-ray diffractometer. In the diffractometer, an X-ray beam of a single wavelength is used to examine the specimens. By continuously changing the incident angle of the X-ray beam, a spectrum of diffraction intensity versus the angle between incident and diffraction beam is recorded.

The main components of diffractometer are

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

The basic components of the diffractometer are shown in Fig 2. The ' θ ' is the angle between the X-ray source and the sample, whereas 2θ is the angle between the incident beam and the detector. The incident angle θ is always half of the detector angle 2θ . The basic function of a diffractometer is to detect X-ray diffraction from materials and to record the diffraction intensity as a function of the diffraction angle (2θ). The X-ray radiation generated by an X-ray tube passes through Soller slits which collimate the X-ray beam. The X-ray beam passing through the slits strikes the specimen. X-rays are diffracted by the specimen and form a convergent beam at the receiving slits before they enter a detector.

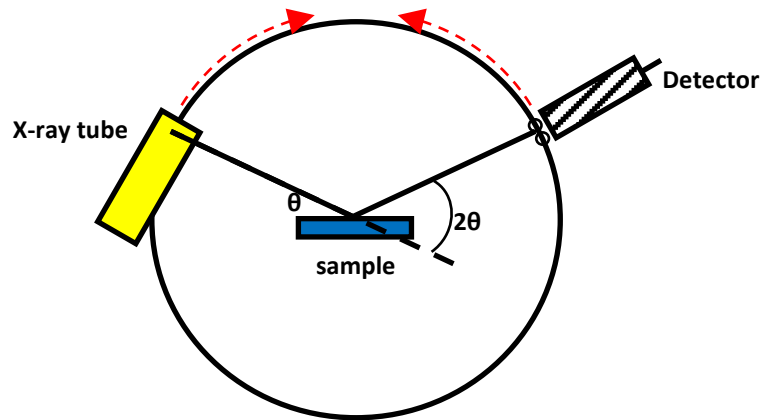


Fig. 2. Basic components of X-ray diffractometers

The diffracted X-ray beam passes through a monochromatic filter to suppress wavelengths other than K_{α} radiation and decrease any background radiation, before being received by the detector. The K_{α} radiation is generated by bombarding of target surface (Cu, Fe, Cr) by accelerated electrons. Most commonly a copper target is used generating K_{α} wave length of 0.154 nm.

Relative movements among the X-ray tube, specimen and the detector ensure the recording of diffraction intensity in a range of 2θ .

An instrument can be operated in two ways:

- tube is fixed, the sample and the detector rotates (THETA : 2-THETA arrangement)
- sample is fixed and the tube and the detector rotates (THETA:THETA arrangement)

Powder diffraction

A single crystal produces only one family of peaks in the diffraction pattern. A polycrystalline sample contains thousands of crystallites. Therefore, all possible diffraction peaks are observed. Powder diffraction is used for characterization of polycrystalline materials. The basic assumption of powder diffraction is that for every set of planes, there are statistically relevant number of crystallites that are properly oriented to diffract the incident beam. The diffraction pattern is the fingerprint of any crystalline phase. The position, intensity, shape and width of the diffraction lines gives information on the samples. Powder diffraction data consists of a record of photon intensity versus detector angle 2θ . Diffraction data can be reduced to a list of peak positions and intensities. Each d_{hkl} corresponds to a family of atomic planes (hkl). However, individual planes cannot be resolved in by this method; this is a limitation of powder diffraction versus single crystal diffraction

Applications

Catalysts are extensively characterized by XRD technique. The major applications of XRD are discussed below.

1. Phase Identification

The catalysts are generally composed of mixture of several phases. The diffraction pattern for each phase is as unique as a fingerprint. Phases with the same chemical composition can have drastically different diffraction patterns. Phase identification is based on the comparison of the diffraction pattern of the specimen with that of pure reference phases or with a database. Databases such as the Powder Diffraction File (PDF) contain lists for thousands of crystalline phases. The PDF contains over 200,000 diffraction patterns. Modern computer programs can determine the phases present in a

sample by quickly comparing the diffraction data to all of the patterns in the database. Various crystalline phases can be quantified based on the fact that each phase of the mixture gives its characteristic diffractogram independently of the others and the intensity depends on the amount present in the mixture. The intensity of the diffraction line (hkl) from a phase α is given by

$$I_{\alpha}(hkl) = \frac{K_{\alpha}(hkl) \times X_{\alpha}}{\rho_{\alpha} \times (\mu / \rho)_m}$$

X_{α} = weight fraction of phase α
 ρ_{α} = mass fraction of phase α
 $(\mu / \rho)_m$ = mass absorption coefficient of the mixture
 $K_{\alpha}(hkl)$ = constant for a given phase structure α ,
 diffraction line (hkl) and set of experimental conditions

Peak intensities are generally measured from peak heights on the assumption that peak height is proportional to peak area

2. Determination of average crystallite size

Ideally, a Bragg diffraction peak is a line without width. In reality, diffraction from a crystal specimen produces a peak with a certain width. This is known as peak broadening. The peak width depends on the size of the crystals. Peak width is inversely related to crystal size; that is, peak width increases with decreasing crystal particle size.

The average crystallite size can be determined by Scherrer formula using elementary line broadening analysis. The Scherrer formula assumes that the breadth of the diffraction peak of crystallites (small single crystals) mainly depends on the characteristics of crystallites (size and the defect in the lattice). Elementary analysis of the broadening assumes that lattice deformation is negligible. According to Scherrer, the thickness of crystallite, L , can be determined by

$$L = \frac{k \lambda}{\beta \cos \theta}$$

k = constant ; λ = wavelength of X-ray source ;
 β = breadth of diffraction profile = Full width at half maxima
 θ = half of the diffraction angle/Bragg angle

The diffraction corresponding to the most intense peak is selected to calculate the average crystallite size using Scherrer relation. The Scherrer formula assumes that crystallite size is the major source leading to line broadening effect of the diffractions peaks, but ~~there is always~~ a line broadening can also be due to instrumental factors such as slit width, sample size, imperfect focusing or misalignment of diffractometers.

3. Spacing between atomic planes of a crystal

Based on Bragg's Law, information on spacing between atomic planes can be obtained when constructive interference occurs. Knowing the spacing of crystallographic planes by diffraction methods, the crystal structure of materials can be determined. The plane spacing of cubic crystal is related to the lattice parameter (a) by the following equation.

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

From Braggs Law, $n\lambda = 2d \sin \theta$.

Combining ,

$$\sin^2 \theta = \frac{n^2 \lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

Examples

1. XRD pattern of oxide supports

Titania and zirconia are used as catalyst support or as active catalyst itself. They can be identified from their XRD pattern by comparison with the standard files. For any unknown sample the peaks are identified by comparison with the standard data. For oxides calcined at 400-500 °C, the typical XRD profiles of titania and tetragonal zirconia are shown in Fig 3.

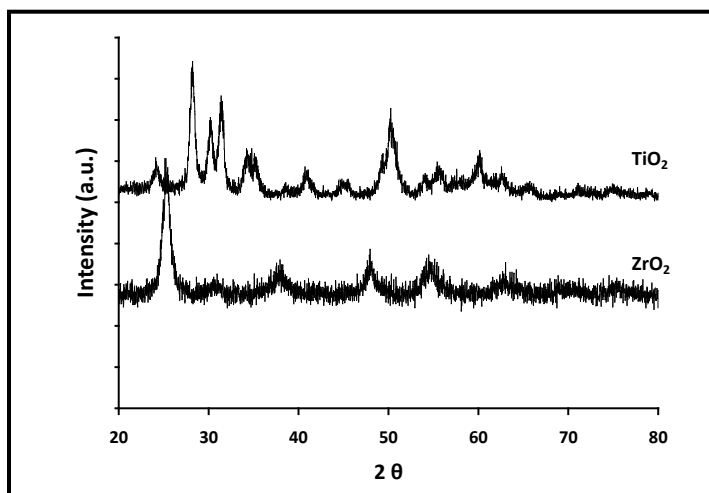


Fig. 3. XRD profiles for titania and zirconia prepared by precipitation method

Solved problem

1. A cubic crystal was placed in an x-ray diffractometer using incoming x-rays with a wavelength $\lambda = 0.154$ nm. The various peak intensities recorded at different 2θ values are given in following table.

2θ (deg)	40.3	58.3	73.2	154.2	131.2
$h\ k\ l$	110	200	211	400	321
Relative intensity	100	15	23	2	18

Determine the followings

- i. Calculate the crystal size (Given, $k=0.9$; $\beta = 0.0098$)
- ii. Calculate the value for the lattice constant (Assume first order diffraction with $n = 1$.)

Solution

i. The crystal size can be calculated using the peak corresponding to $2\theta = 40.3$ having highest peak intensity.

Hence, $k = 0.9$; $\beta = 0.0098$; $\lambda=0.154$ nm; $\theta=20.15$, the crystal size L can determined using the Scherrer equation as follows

$$L = \frac{k\lambda}{\beta \cos \theta} = \frac{0.9 \times 0.154}{0.0098 \times \cos(20.15)} = \frac{0.1386}{0.0098 \times 0.9387} = 15.1 \text{ nm}$$

- ii. The plane spacing of cubic crystal is related to the lattice parameter (a) by the following equation.

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2} \quad [1]$$

From Braggs Law,

$$n\lambda = 2d \sin \theta \quad [2]$$

$$\text{or, } n^2 \lambda^2 = 4d^2 \sin^2 \theta$$

$$\text{or, } d^2 = \frac{n^2 \lambda^2}{4 \sin^2 \theta} \quad [3]$$

From [1] and [3] Combining ,

$$a^2 = \frac{n^2 \lambda^2}{4 \sin^2 \theta} (h^2 + k^2 + l^2)$$

Using the peak corresponding to $2\theta = 40.3$ having highest peak intensity with [hkl] value of [110] the lattice constant ' a ' for cubic crystal can be calculated as follows.

Or

$$a^2 = \frac{1^2 \times 0.154^2}{4(\sin 20.15)^2} (1^2 + 1^2 + 0) = 0.1 \text{ nm} \quad [\because \sin 20.15 = 0.3436]$$

Or, $a = 0.342 \text{ nm}$
