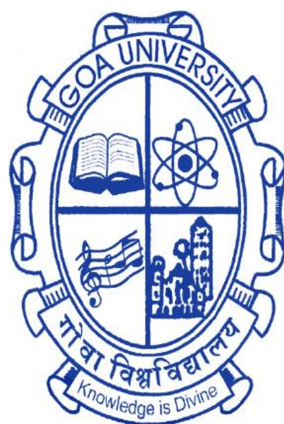
X-ray Diffraction: Principle and Applications

M.Sc. Dissertation

by

Ms. Pearl F. Sequeira



School of Chemical Sciences

Goa University

Goa – 403206

APRIL 2022

X-ray Diffraction:
Principle and Applications

DISSERTATION

Submitted in partial fulfilment of
The degree of M.Sc. (Inorganic Chemistry)

By

Ms. Pearl Fronia Sequeira

To

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Goa – 403206

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DECLARATION

I hereby declare that the matter presented in this dissertation entitled ***'X-ray Diffraction: Principle and Applications'*** was carried out by me during the year 2021-2022 under the guidance of Dr. Kedar Umakant Narvekar. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigation.

Ms. Pearl F. Sequeira
M.Sc. Student
School of Chemical Sciences,
Goa University

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THANK YOU…

Ms. Pearl F. Sequeira

M.Sc. Student

School of Chemical Sciences,

Goa University

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X-ray Diffraction: Principle and Applications

Introduction

X-Ray Diffraction (XRD) is a method or instrument accustomed determine the atomic and molecular structure of a crystal by diffracting a beam of X-rays altogether directions. generally, the function of the XRD tool is to spot and analyse the phase of material, in the type of powder or solid from inorganic samples, within the form of polycrystalline and amorphous. XRD are often used for qualitative and quantitative chemical analysis. Max von Laue and Co., in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths almost like the spacing of planes during a space lattice. X-ray diffraction is now a standard technique for the study of crystal structures and atomic spacing.

Within the quantitative chemical analysis, the info presented is including of two theta angels, peak intensity, and therefore the amount of lattice constant. For chemical analysis, the info includes phase analysis, which may be in the form of identification of the sort of phase, phase composition (percentage), crystallite size, orientation, and others[1]. X-ray diffraction is predicated on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to supply monochromatic radiation, collimated to concentrate, and directed toward the sample.

Within the analysis using XRD instruments, the essential principle of XRD is to diffract light through the crystal slit. Diffraction of light by lattices or crystals can occur if the diffraction comes from a radius that features a wavelength like the distance between atoms, which is about 1 Angstrom. The radiation is employed within the type of X-ray radiation, electrons, and neutrons. X-ray may be a photon with high energy which contains a wavelength starting from 0.5 up to 2.5 Angstrom. When an X-ray beam interacts with a material, a number of the beams are absorbed, transmitted, and a few of it is scattered diffracted. This scattered diffraction is what XRD detects. The scattered X-ray beam cancels each other out because the phases are different and a few are mutually reinforcing because the phase is similar. X-ray beams that reinforce one another are called diffraction beams. When X-rays are fired at the crystal lattice of the material to be tested, the rays are diffracted and form certain patterns called fingerprints [2].

It might appear that the technique isn't generally applicable to organic analysis due to the need of working with crystalline compounds. However, when organic compounds can't be identified directly (if they're liquids, for example) it's frequently possible to convert them to crystalline derivatives which have characteristic patterns. Many of the classical derivatives can he used for X-ray identification, and standard patterns of variety of derivatives are published (1-7). Standard samples are prepared, and therefore the X-ray patterns of an outsized number of organic compounds are obtained in the laboratory. Among the applications which are made from the technique to organic analysis are identification of dibasic acids directly, identification of aldehydes and ketones as 2,4-dinitrophenylhydrazones, fatty acids as p-bromoanilides, and amines as picrate derivatives [3].

The application of this XRD instrument is extremely widely used. This XRD instrument is most frequently used for the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). One among them is that the characterization of unknown materials using XRD instruments is incredibly useful for studies in geology, archaeology, ecology, materials science, engineering, and biology. Other applications of XRD instruments are the characterization of crystalline materials, identification of fine-grained minerals, determination of unit cell dimensions, and measurement of sample purity [1].

Definition

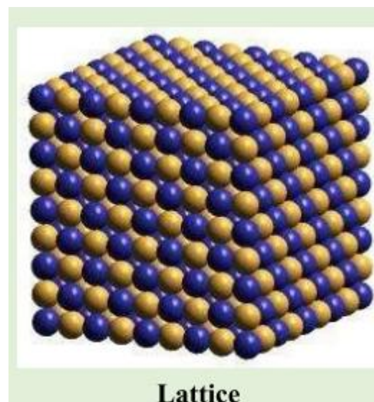
X-ray diffraction (XRD) is a versatile, non-destructive technique to analyse material properties like phase composition, preferred crystal orientations (texture), and other structural parameters, like average grain size, crystallinity, strain, crystal defects and many more of powder samples, solid samples or maybe liquid samples.

X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice [2]. Identification of phases is achieved by comparing the X-ray diffraction pattern obtained from an unknown sample with patterns of a reference database. This process is extremely almost like the identification of finger prints in crime scene investigations. The foremost comprehensive database is maintained by the ICDD (International Centre of Diffraction Data). Alternatively, it's possible to create up a reference database from experimental diffraction patterns of pure

phases and/or patterns published within the scientific literature or derived from own measurements [4].

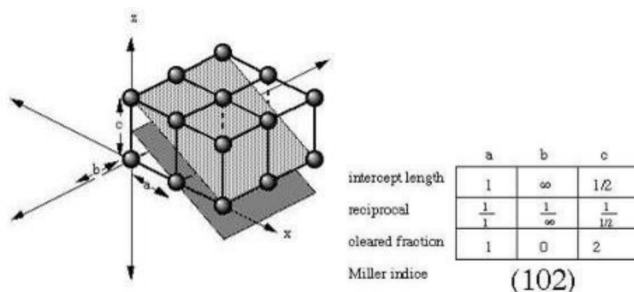
Basics of Crystallography

- The atoms are arranged in a regular pattern, and there is as smallest volume element that by repetition in three dimensions describes the crystal. This smallest volume element is called a unit cell.
- Crystals consist of planes of atoms that are spaced a distance d apart, but can be resolved into many atomic planes, each with a different d spacing.


Lattice

- The dimensions of the unit cell are described by three axes: *a*, *b*, *c* and the angles between them *α*, *β*, and *γ* are the lattice constants which can be determined by XRD.

Miller Indices



- Crystal structures are made up of a series of planes of atoms in which each plane is spaced with a distance d with each other. But various atomic planes in a crystal can be resolved with different d-spacing. For distinguishing different planes there is a coordinate system introduced by William Hallowes Miller called Miller indices (i.e. *h*, *k*, *l*).
- Miller indices- the reciprocals of the fractional intercepts which the plane makes with crystallographic axes.
- Reciprocals are taken to avoid ∞ in the indices [5].

Theory of diffraction

The interaction of waves with periodic structures produces diffraction effects if the wavelength and therefore the periodicity of the crystals, are of comparable magnitude. X-rays may easily be produced with wavelengths matching the unit cell dimensions of crystals, but electrons or neutrons of appropriate energy also can be used for diffraction experiments on crystals. Considering that atoms have diameters of the order of Angstroms (1 Å = 10^{-10} m), unit cells have dimensions of several Å. This suggests that crystals with sizes of microns or larger contains billions of unit cells, which repeat periodically in all three dimensions, i.e., they possess long-range order. This type of order distinguishes crystalline materials from amorphous ones, e.g., glasses, which have only short-range order. Since the "quality" of diffraction effects in XRD depends strongly on the strict and undisturbed periodicity of atoms, any kind of deviation from the perfect order will show within the X-ray diffraction diagram. Even small crystallite size could be a deviation from the theoretically infinite perfect crystal. Other deviations from the ideal order could also be replacements of atoms by others (common in solid solutions), slight geometric deviations of atoms from their ideal position because of internal strain (e.g., from incomplete annealing or massive grinding), or larger two- or three-dimensional aberrations (e.g., dislocations or stacking faults).

1. The atom form factor

Electromagnetic waves with wavelengths of the order of 10−10 m are called X- rays. The electric field of such waves interacts with the charges of all electrons of an atom, which then emit an almost spherical wave with an equivalent wavelength as the incident radiation. The amplitude of this outgoing wave is proportional to the number of electrons within the atom, and, hence, to the atomic number. Light elements with few electrons, e.g., carbon or oxygen, are therefore "poor" scatterers for X-rays, whereas heavy elements like lead are "good" scatterers. Detection limits are severely influenced by this effect. The amplitude of the scattered wave is described by the atom form factor f. Because of interference within individual atoms, especially larger ones, the amplitude of the outgoing wave and hence the atom form factor varies also with the scattering angle 2θ (Figure 1).

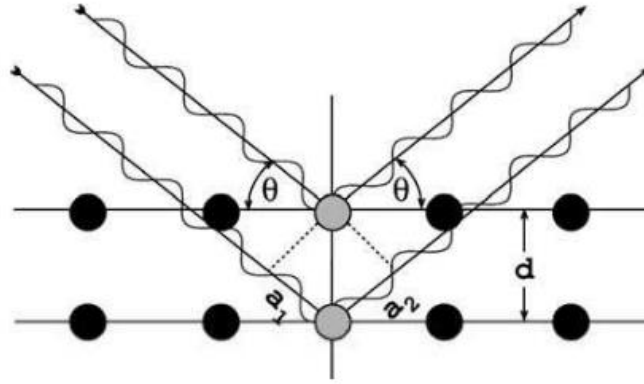


Figure 1. Geometric derivation of Bragg's law: Constructive interference occurs when the delay between waves scattered from adjacent lattice planes given by $a_1 + a_2$ is an integer multiple of the wavelength λ [6].

2. Bragg's Law and Diffraction

A typical derivation of the Bragg equation (1) is straightforward to understand but leaves an honest deal unexplained. a rather more critical approach, although a bit more demanding, is more interesting and provides a far better introduction to the utilization of X-ray diffraction in structure determination. Usually, the treatment begins with a diagram that shows a regular array of scattering points, drawn in order that they lie on a set of parallel lines, distance d apart. Interference between parallel beams of X-rays, reflected as if from a mirror from these lines of points, is then considered. The condition for constructive interference, that the rays reflected from adjacent lines should differ in path length by an integral number, n, of wavelengths, then easily results in the Bragg equation.

$$n \lambda = 2d \sin\theta \quad (1)$$

However, in this derivation it's not explained why the angles of incidence and reflection should be equal. for instance, why should a diagram like Figure 2 not are used? Here, the condition for constructive interference between the parallel rays scattered from X and Y is easily seen to be

$$n\lambda = d (\sin\theta_1 + \sin\theta_2) \quad (2)$$

It is clearly not necessary for θ_1 to equal θ_2, and it's easy to see that the same reflection condition will apply to the entire set of scattering centres that lie on the line XY or its extension, and are placed d apart. However, it's important to understand that in X-ray diffraction experiments we are counting on a cooperative effect, which we'll only observe intense diffracted X-ray beams at sharply defined angles if very large numbers of scattering centres (typically over 107) are

producing radiation that's in phase. We therefore got to establish what's required to realize this condition for all the centres during a regular three-dimensional array.

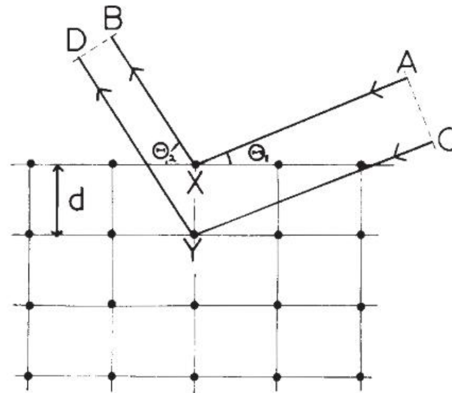


Figure 2. Alternative diagram, showing the path difference between parallel rays.

The easiest way to begin this problem is to look at the path difference that exists between rays scattered from centres that lie a distance l apart in a line within the top plane, as shown in Figure 3. The path difference between rays AB and CD is

$$\text{path difference} = l\,(\cos\theta_1 - \cos\theta_2) \qquad (3)$$

Constructive interference between all the scattering points at any spacing in such a line is simply possible if $\theta_1 = \theta_2$. If the argument is extended to consider scattering points that exist in several parallel lines drawn across the surface—that is, to consider all the scattering points in the plane—it is seen that the incident and scattered beams must both lie in a plane perpendicular to the surface.

Of course, vector algebra (2) may be used to give these results more succinctly and elegantly, but there's a danger that a clear physical understanding of the Bragg conditions for reflection will then be lost [7].

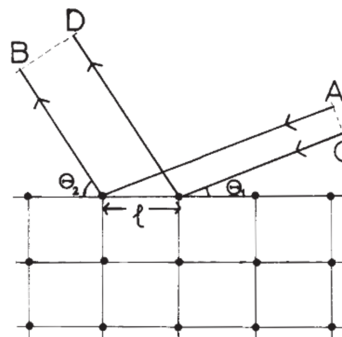


Figure 3. Reflection from points in the top Bragg plane [7].

Without any diffraction effects, the incidence of a primary X-ray beam onto a sample volume would produce scattering in all directions. Diffraction redistributes intensity from the entire scattering sphere into distinct directions. Therefore, intensity peaks arise in certain directions, whereas in directions between peaks the intensity decreases drastically. The intensity integrated over the sphere, however, remains constant because of energy conservation. In what directions can we observe such peaks, also called reflections? a way of describing these directions is the notion of scattering lattice planes and interference between the wavelets scattered by neighbouring lattice planes. Figure 2 illustrates this case. Constructive interference and hence a so-called Bragg reflection is obtained when the path of the wavelet scattered of the lower of the 2 planes is longer by an integer number of wavelengths λ than that of the wavelet scattered off the upper plane. a reflection will thus occur when

$$n\lambda = 2d \sin\theta. \quad (1)$$

This is the so-called Bragg equation, where λ is the wavelength of the radiation, n is an integer number, θ is the angle between the lattice planes and the incident beam and d is the distance of the lattice planes for which the peak occurs [6].

3. The interference function

Interference occurs among the waves scattered by the atoms when crystalline solids are exposed to X-rays. There are 2 types of interference depending on how the waves overlap one another. Constructive interference occurs when the waves are moving in phase with each other. Destructive interference occurs when the waves are out of phase.

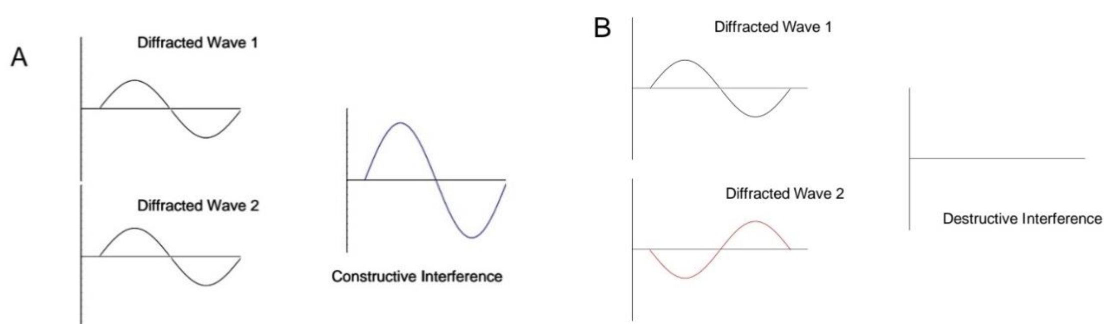


Figure 4. Constructive and Destructive interferences

One might argue that small deviations from the perfect Bragg angle θ (Figure 2) should also produce significant intensity, as long as the phase delay isn't far away from λ and therefore constructive interference still occurs to some extent, although not at maximum intensity. Indeed, this is often the case in sufficiently small crystals. In large crystals, whenever at an

angle 2θ the phase delay isn't exactly λ, a position somewhere within the crystal can be found that gives rise to a phase delay of λ/2 and hence destructive interference. Therefore, in large crystals even minor deviations from the ideal Bragg angle result in cancellation by interference and thus sharp peaks result. for tiny crystals, however, the peaks broaden. This influence of crystal size is modelled by the interference function

$$S = \frac{(\sin \pi h N)^2}{N(\sin \pi h)^2}$$

where N is the number of unit cells in the crystal and h the index of the reflection [6].

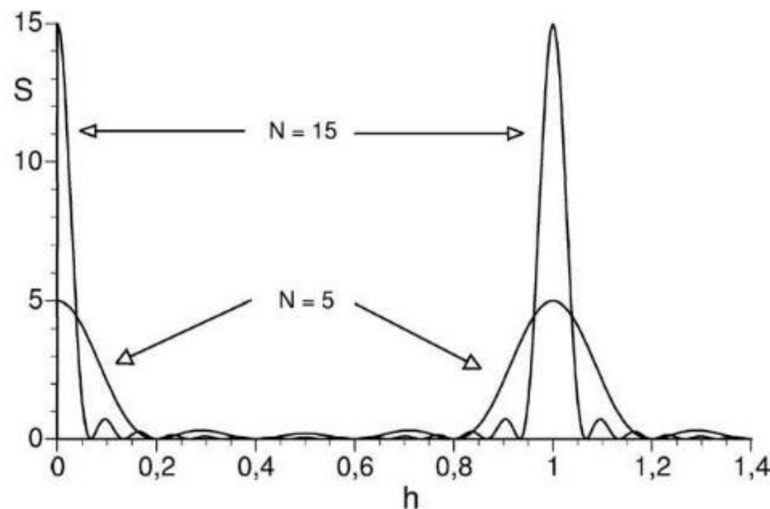


Figure 5. Plot of interference function S against the continuous variable h for N = 5 and N = 15. Note that the area under the peaks remains constant irrespective of N.

4. The structure factor

As a next step we've to put the diffraction by crystals on a quantitative basis so as to know why different types of structures, i.e., different mineral phases show unique sets of diffraction peaks and why these peaks have characteristic relative intensities. Two quantities ought to be considered, when waves interact: their amplitude and their relative phase. Both parameters make up a complex number. The process of interference of waves scattered by atoms at different positions within a unit cell and with different amplitudes reduces to easily adding of these complex numbers to give the structure factor F as

$$F(hkl) = \sum_{n=1}^{N} f_n e^{2\pi i(hu+kv+lw)}$$

In which h, k and l are the Miller indices of the respective set of lattice planes giving rise to the reflection. This equation gives the amplitude of a diffracted wave, but experimentally we observe the intensity, which is proportional to $|F(hkl)|^2$.

5. The Scherrer equation

Scherrer Equation, was developed in 1918, to calculate the nano crystallite size (D) by XRD radiation of wavelength λ (nm) from measuring full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. The first scientist, Paul Scherrer, published his results in a paper that included what became known as the Scherrer equation in 1981.This can be attributed to the fact that “crystallite size” is not synonymous with “particle size”, while X-Ray diffraction is sensitive to the crystallite size inside the particles. A widely used tool to determine the average crystallite size (D) is X-ray powder diffraction combined with the well-known Scherrer equation:

$$FWHM(\beta) = \frac{(K \times \lambda)}{(D \times \cos\theta)}$$

in which FWHM is the full width at half-maximum of the diffraction peak, K is a shape constant, D is the crystallite size and θ is the Bragg angle. K is a constant related to crystallite shape, normally taken as 0.9. The value of β in 2θ axis of diffraction profile must be in radians. The θ can be in degrees or radians, since the cosθ corresponds to the same number [8].

This equation is obtained based on the idea that every atom (scattering centre) scatters the incoming radiation independently, and once scattered the radiation doesn't interact with the other atoms. The derivation for this equation is often seen for instance in Klug & Alexander (1974) and it doesn't depend upon the sort of atoms inside the crystal, the structure factor of the reflection or the linear absorption coefficient. Cullity & Stock (2001) argue that this equation is valid just for crystallite sizes up to 200 nm. This limit, however, is related to the resolution of the diffractometer [9].

Single-Crystal XRD

Single-crystal X-ray diffraction, commonly cited as X-ray crystallography, is an analytical technique within which X-ray methods are employed to determine with certainty the actual arrangement of atoms within a crystalline specimen. The science of X-ray crystallography originated in 1912 with the discovery by Laue that crystals diffract X-rays. Since that point, single-crystal X-ray diffraction has developed into the foremost powerful method known for obtaining the atomic arrangement in the solid state[10]. In single crystal X-ray diffraction, a single crystal is rotated around various axes so as to find a large number of various reflections. The atomic arrangement within the crystal (the crystal structure) are often determined from the angular positions and the intensity of those reflections.

A four-circle goniometer (sample holder) is required in order to observe all possible reflections. Single-crystal diffractometers are dedicated instruments, mainly utilized in research institutes and departments [4]. There are many classes of chemical compounds like natural products, organometallic complexes, inorganic salts, metal cluster systems, and organic and inorganic reaction products for which the structure can't be deduced even with all of the other methods combined. X-ray crystallography is uniquely capable of unambiguously determining the entire three- dimensional molecular structures (including the absolute stereochemistry) of chemical substances. Modern X-ray crystallographic data often permits routine location and refinement of solvent molecules and hydrogen atoms. a major reason for the increased use of X-ray crystallographic methods is the remarkable improvement in instrument performance achieved through the introduction of two-dimensional detectors, most recently CMOS (Complementary Metal Oxide Semiconductors) systems. The range of materials which will be studied by X-ray crystallography has recently been extended by the provision of higher-flux X-ray sources (e.g., microfocus sources, rotating anode generators, X-ray optics, liquid-metal sources, synchrotron beam lines) and more sensitive X-ray detectors (CMOS detectors), by the employment of high-speed computers with large amounts of mass storage and also the development of latest algorithms for solving and refining large and problematic structures (e.g. twinned specimens, incommensurate structures). These advances, coupled with progress in the related fields of crystal growth, cryo-crystallography, and crystal-mounting techniques, now permit X-ray structure determinations to be carried out on very small specimens (minimum dimensions of a couple of microns), on materials with very large unit cells (e.g., axis length 400 Å) and on materials that are liquids at room temperature or that undergo solid- state phase changes.

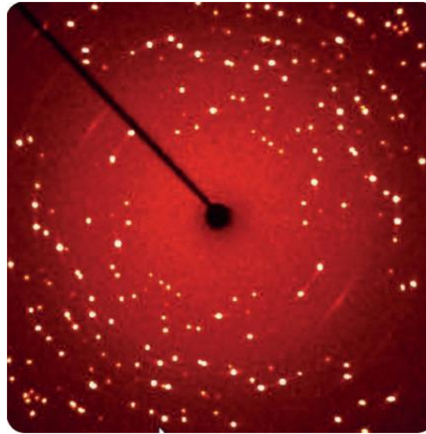


Figure 6. An example of an X-ray diffraction pattern (one-minute rotation image) produced by a randomly oriented single-crystal specimen on a 2D detector [10].

Single-crystal XRD Instrumentation

The basic hardware components of a typical automated single-crystal X-ray diffractometer system include:

- An X-ray source consisting of a high-stability X-ray generator, a copper or molybdenum or silver target X-ray tube, a tube shield with associated shutters, attenuators and safety interlocks, a monochromator or X-ray mirror system, and an incident-beam collimator.
- A three- or four-circle goniometer system that allows the specimen to be precisely oriented in any position while remaining in the X-ray beam.
- A video camera for aligning the specimen and indexing crystal faces.
- A CMOS-based two-dimensional X-ray detector system. A low-temperature attachment for cooling the specimen during data collection.
- A microprocessor-based interface module that receives commands from a host computer and carries out all real- time instrument control functions to drive goniometer motors, monitor the detector system, open and close the shutter and monitor collision sensors and safety inter- locks.
- A host computer with a large hard disk mass storage device, a video monitor and keyboard, and diffractometer control programs to control the data collection strategy and to send commands to the microprocessor.

Structure determination calculations could also be carried out on the pc used for data collection or they'll be performed on a second computer linked to the diffractometer system. A large

variety of hardware configurations are available, depending upon the necessities of the individual laboratory.

The most critical mechanical component in an X-ray diffractometer system is the goniometer assembly, which must be capable of keeping the specimen centred within the incident X-ray beam while at the same time changing its orientation so as to collect many thousands of frames of data in reciprocal space. The most commonly used kind of goniometer is illustrated in Figure 7. The most important and costliest component of any modern single-crystal diffractometer system is its detector system. Most new instruments purchased since 2011 use a detector system based upon 2D CMOS technology (Figure 8) [10].

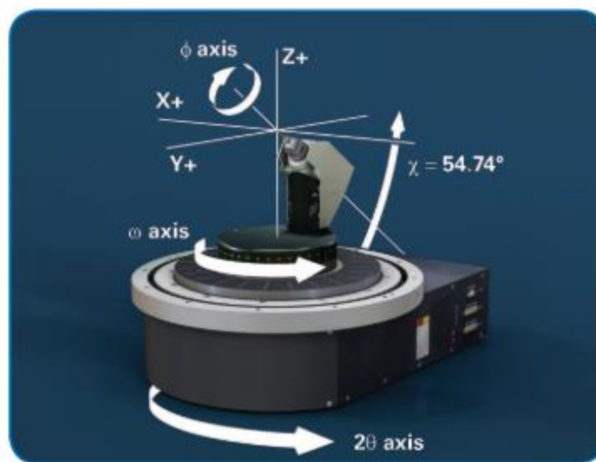


Figure 7. Diagram of axes for three- circle goniometer (χ is fixed at 54.74°) [10].

Figure 8. Commercial CMOS based single-crystal X-ray detector [10].

Experimental Procedure

The first step in a crystal structure analysis is concerned with the selection and mounting of a suitable specimen. Ideally, a crystal whose structure is to be determined must be a single crystal of 0.1 mm to 0.5 mm size, not cracked and not twinned. Micron-sized crystals are not uncommon with the higher-intensity microfocus sources. The techniques required to obtain such crystals vary considerably depending on the types of compounds to be analysed. Stable crystals of typical organic, organometallic or coordination complexes can usually be grown by slow recrystallization from common solvents. Other types of compounds may require the use of sublimation, zone refinement, solvent-diffusion, low-temperature and/or inert-atmosphere techniques in order to isolate suitable specimens.

- Once a suitable specimen has been selected, it is glued or otherwise securely attached to a goniometer head (sample holder) in an arbitrary orientation.
- The goniometer head is then placed on the base of the goniometer assembly and the crystal is optically aligned in the centre of the incident X-ray beam using a video camera or microscope. The orthogonal X-, Y-, and Z-translations on the goniometer head are adjusted until the specimen is centred for all crystal orientations.
- A preliminary rotational image is then collected with the 2D detector to screen the specimen for analysis and to select suitable parameter values for subsequent steps.
- In order to determine the unit cell, a preliminary set of frames is measured using an automatic routine. For example, three sets of frames are collected in different parts of reciprocal space.
- These frames are then processed to locate spots on individual frames and to then determine the centers of reflections.
- An auto-indexing routine selects the appropriate reduced primitive unit cell and calculates the corresponding orientation matrix and lattice constants.
- This preliminary unit cell is then refined using a non-linear least-squares algorithm and converted automatically to the appropriate crystal system and Bravais lattice. This new cell is refined by the non-linear least-squares algorithm to yield an accurate orientation matrix which may be used to index crystal faces and to carry out integration calculations after intensity data collection[10].

Figure 9. A commercial CMOS-based single-crystal X-ray diffractometer system [10].

Strengths

- No separate standards required
- Non-destructive
- Detailed crystal structure, including unit cell dimensions, bond-lengths, bond-angles and site-ordering information
- Determination of crystal-chemical controls on mineral chemistry
- With specialized chambers, structures of high pressure and/or temperature phases can be determined
- Powder patterns can also be derived from single-crystals by use of specialized cameras (Gandolfi)

Limitations

- Must have a single, robust (stable) sample, generally between 50-250 microns in size
- Optically clear sample
- Twinned samples can be handled with difficulty
- Data collection generally requires between 24 and 72 hours [11].

Powder X-ray Diffraction

Powder XRD is used on microcrystalline powder samples. PXRD are often relatively quick as compared to single crystal XRD because of the significantly reduced difficulty within the sample preparation step. It is very challenging to grow high-quality single crystals of sufficient size to perform single crystal XRD measurements for several materials but powder XRD can be performed on much smaller crystal sizes [12].

In X-ray powder diffraction, the sample consists of an infinitely large number of small crystallites, ideally randomly oriented with respect to each other. Because all orientations are present, it is only necessary to vary the angle of incidence and the angle of diffraction. A powder diffractogram is obtained by counting the detected intensity as a function of the angle between the incident and the diffracted beam [4].

Ideally, when preparing a sample for powder XRD, the particle size should be as homogenous as possible and fewer than ~ 10 µm in diameter. All the microcrystals will be randomly oriented but too small particle sizes or too much variation in the particle sizes in a sample can result in broadening of the peak structures and potentially complicate the structural assignments.
Techniques like ball-milling or manual grinding with a mortar and pestle can be suitable for the preparation of bulk powders for XRD. it's possible to make measurements either on the loose, uncompacted powders or to compact the powder into pellets to try and achieve higher signal-to-noise ratios.

One issue with powder XRD is that while the sample preparation is comparatively straightforward, it's demanding in terms of the amounts of sample required for a measurement. Powder XRD is popular within the pharmaceutical analysis due to the short sample preparation times and the amount of data that can be recovered on the crystalline phases of the substrate. Powder-based methods are also widely employed in mineralogy for both research and industrial applications. this could be used to evaluate material performance but also for aging and dating specimens of historical interest [12].

Principle of the Powder method

The principles of the powder method are shown in Fig. 10. A monochromatic beam of X-rays strikes a finely powdered sample that, ideally, has crystals randomly arranged in every possible orientation. In such a powder sample, the varied lattice planes are present in every possible orientation. for every set of planes, therefore, at least some crystals must be oriented at the Bragg angle, θ, to the incident beam and thus diffraction occurs for these crystals and planes. The diffracted beams could also be detected either by surrounding the sample with a strip of photographic film (Debye–Scherrer and Guinier focusing methods) or by employing a movable detector, like a Geiger counter, scintillation counter or image plate, connected to a chart recorder or computer (diffractometer).

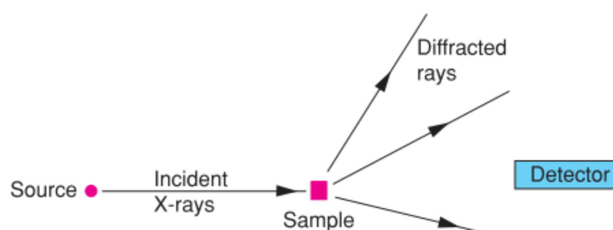


Figure 10. X-ray diffraction experiment

The first powder photography, the Debye–Scherrer method, is little used nowadays, but more modern methods operate a similar principle, it's easy to understand and it provides a really good introduction to the principles of X-ray diffraction. For any set of lattice planes, the diffracted radiation forms the surface of a cone, as shown in Fig. 11.

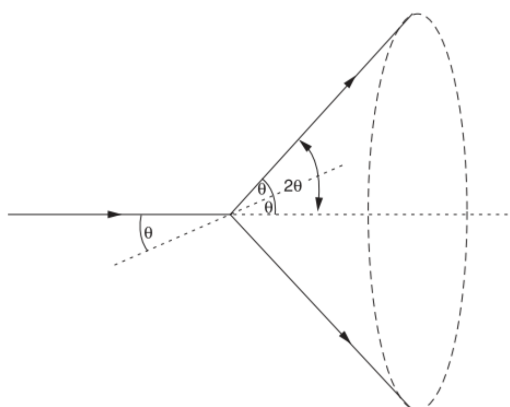


Figure 11. Formation of a cone of diffracted radiation

The sole requirement for diffraction is that the planes be at the Bragg angle θ to the incident beam; no restriction is placed on the angular orientation of the planes about the axis of the incident beam. in a finely powdered sample, crystals are present at every possible angular position about the incident beam and also the diffracted beams that result appear to be emitted from the sample as cones of radiation (each cone is actually a large number of closely spaced diffracted beams). If the Bragg angle is θ, then the angle between diffracted and undiffracted beams is 2θ and the angle of the cone is 4θ. Each set of planes gives its own cone of radiation. The cones are detected by a thin strip of film wrapped round the sample, Fig. 12;

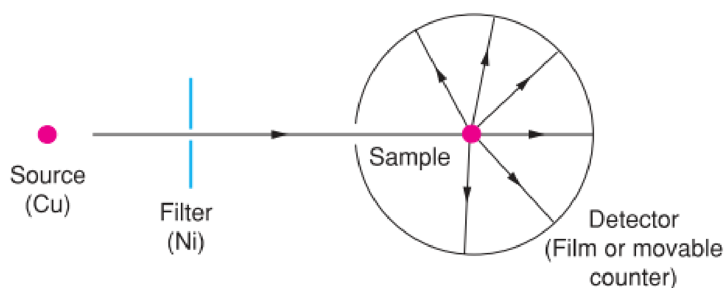


Figure 12. The powder method

Each cone intersects the film as two short arcs, Fig. 13, which are symmetrical about the 2 holes within the film (these allow entry and exit of incident and undiffracted beams). In a well-powdered sample, each arc appears as a continuous line, but in coarser samples the arcs could also be spotty because of the relatively small number of crystals present.

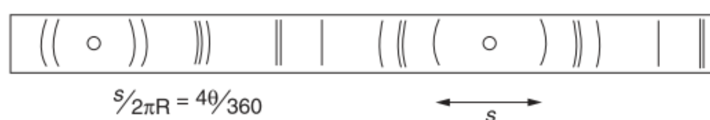


Figure 13. Schematic Debye-Scherrer Photograph

The other modern and more widely-used powder technique is diffractometry, which gives a series of peaks on a strip of chart paper or on a computer screen. A convergent incident beam is again used to give good resolution of peaks. Both peak positions and intensities (peak heights or areas) are readily obtained, which makes this a very useful and rapid method of phase analysis.

The most important use of the powder method is in the qualitative identification of crystalline phases or compounds. Whereas most chemical methods of analysis give information about the

elements present in a sample, powder XRD is very different, and perhaps unique, in that it tells which crystalline compounds or phases are present but gives no direct information about their chemical constitution [13].

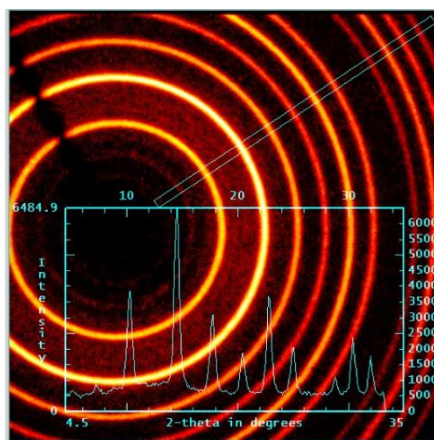


Figure 14. Powdered XRD: Circular diffraction pattern [14]

Strengths

- Powerful and rapid (<20 min) for identification of an unknown mineral
- Wide availability of XRD units
- Requires minimal sample preparation
- Provides unambiguous mineral determination in most cases
- Relatively straightforward data interpretation

Limitations

- If the material belongs to a family of phases with very similar XRD patterns, it may not be possible to identify unambiguously the phase concerned; for instance, many niobates and tantalates have very similar XRD patterns, e.g., LiNbO3 and LiTaO3, as do many compounds of adjacent rare earth elements
- Access to a standard reference file of inorganic compounds is required
- Material, in tenths of a gram quantity, must be ground into a powder
- For unit cell determinations, indexing of patterns for non- isometric crystal systems is complicated
- For mixed materials, detection limit is » 2% of sample isometric crystal systems is complicated Peak overlay may occur and worsens for high angle "reflections" X-ray [2].

Examples of Single Crystal and Powder XRD diffraction patterns with their crystal structures

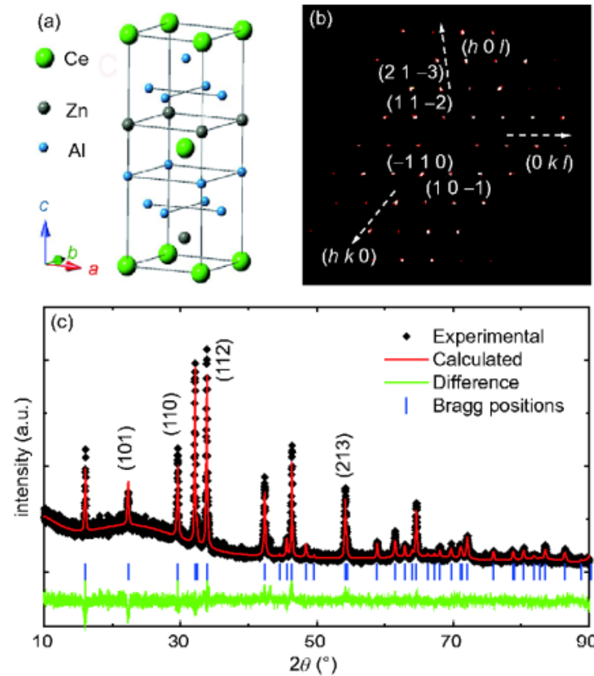


Figure 15. (a) Crystal structure of CeZnAl3; (b) single crystal X-ray diffraction pattern of CeZnAl3 measured perpendicular to the [111] direction; (c) powder X-ray diffraction pattern of powdered CeZnAl3 single crystals [15].

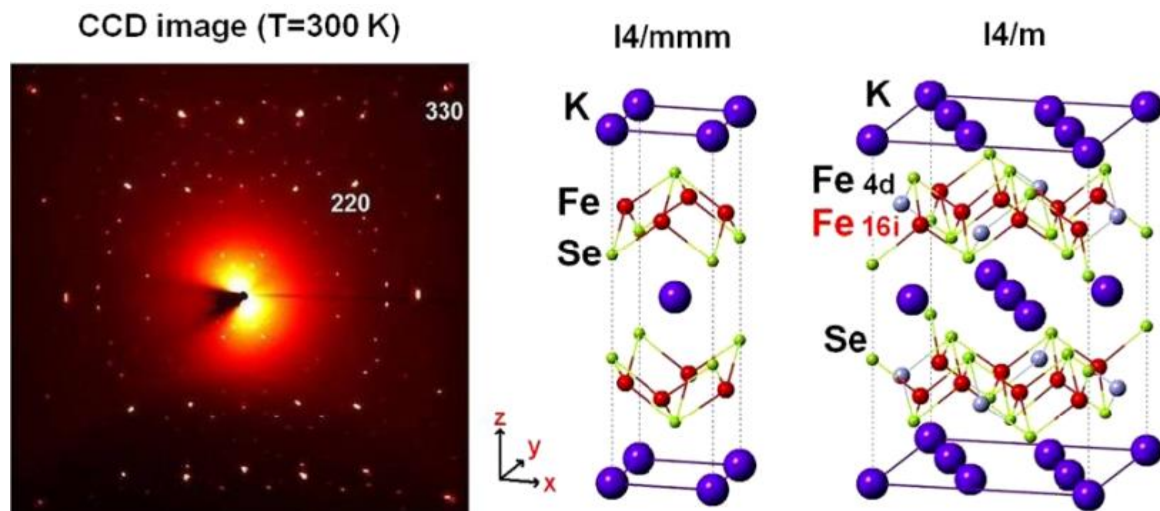


Figure 16. Single-crystal x-ray diffraction pattern (CCD image) of K0.8Fe1.6Se2 at 300 K. Structural models of the basic (I4/mmm) and larger (I4/m) unit-cells of the 122-type tetragonal structure are also shown[16].

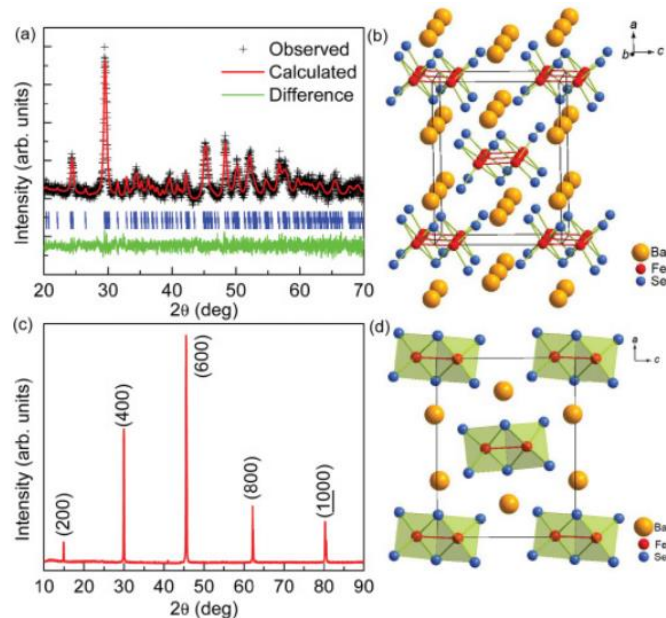


Figure 17. (a) Powder XRD patterns of BaFe2Se3.
(b) Crystal structure of BaFe2Se3. The big orange, small red, and medium blue balls represent Ba, Fe, and Se ions. (c) Single crystal XRD of BaFe2Se3. (d) The arrangement of double chains of edgesharing Fe-Se tetrahedra along the b axis[17].

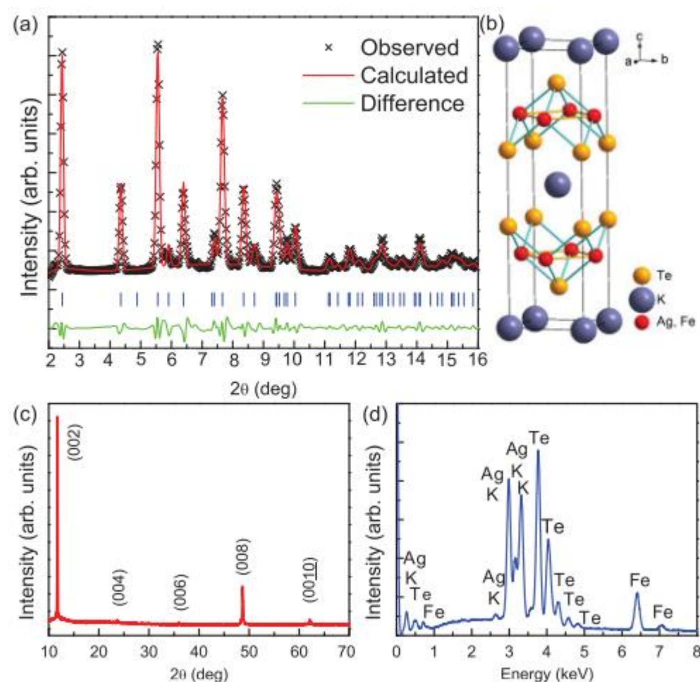


Figure 18. (a) Powder XRD patterns of KFe0.85Ag1.15Te2. (b) Crystal structure of KFe0.85Ag1.15Te2. The big blue, small red, and medium orange balls represent K, Fe/Ag, and Te ions. (c) Single-crystal XRD of KFe0.85Ag1.15Te2. (d) The EDX spectrum of a single crystal [18].

Diffractometer system

1. Instrumentation

The x-ray spectrometer, has had a long and uneven history in the field of x-ray diffraction. It was first used by W. H. and W. L. Bragg in their early work on x-ray spectra and crystal structure, but it then passed into a long period of relative disuse during which photographic recording in cameras was the most popular method of observing diffraction effects. The few spectrometers in use were all homemade and confined largely to the laboratories of research physicists. In recent years, however, commercially made instruments (based mainly on a design developed by Friedman about 1943) have become available, and their use is growing rapidly because of certain particular advantages which they offer over film techniques. Initially a research tool, the x-ray spectrometer has now become an instrument for control and analysis in a wide variety of industrial laboratories. Depending solely on the way it is used, the x-ray spectrometer is really two instruments:

- An instrument for measuring x-ray spectra by means of a crystal of known structure.
- An instrument for studying crystalline (and non-crystalline) materials by measurements of the way in which they diffract x-rays of known wavelength. The term spectrometer has been, and still is, used to describe both instruments, but, properly, it should be applied only to the first instrument. The second instrument has been aptly called a diffractometer: this is a term of quite recent coinage but one which serves well to emphasize the particular use to which the instrument is being put, namely, diffraction analysis rather than spectrometry [19].

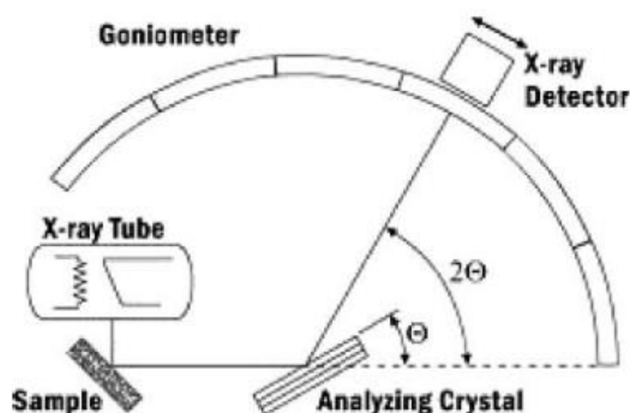


Figure 19. Schematic diagram of a diffractometer system [2]

X-ray diffractometers contains three basic elements: an X-ray tube, a sample holder, and an X-ray detector (Connolly, 2007). X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced.

These spectra contain several components, the most common being K_{α} and K_{β}. K_{α} consists, in part, $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ features a slightly shorter wavelength and twice the intensity of $K_{\alpha 2}$. the precise wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the 2 is used. Copper is the most common target material for single-crystal diffraction, with CuK_{α} radiation= 1.5418 Å.

These X-rays are collimated and directed onto the sample. as the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies Bragg's law, constructive interference occurs and a peak in intensity appears. A detector records and processes this X-ray signal and converts the signal to a count rate, which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle u while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data are collected at 2θ from 5˚ to 70˚, angles that are preset in the X-ray scan. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering, and biology. Other applications include characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, and measurement of sample purity.

With specialized techniques, X-ray diffraction (XRD) can be used to determine crystal structures by using Rietveld refinement, determine modal amounts of minerals (quantitative

analysis), characterize thin film samples, and make textural measurements, such as the orientation of grains, in a polycrystalline sample (Brindley and Brown, 1980) [2].

2. Types of Detectors

In modern powder diffractometers different types of detectors can be used, depending on the application. In the following the most common types are presented

a. Point detectors

Two types of point detectors are widely used for almost all diffraction applications: gas-filled proportional counters and scintillation counters. The selection of the appropriate detector heavily depends on the choice of tube anode material.

b. Gas proportional counter

Gas-filled proportional counters consist of a metal cylinder with an entrance window for X-ray photons. The cylinder is cross-sected by a thin wire attached to a high-voltage positive potential. The detector is filled with a noble gas, either argon or xenon. The incoming X-ray photon ionizes the atoms of the counting gas. The ionization electrons are accelerated to the wire and are ionizing further atoms (charge avalanche). At the counting wire an impulse with an amplitude proportional to the energy of the absorbed X-ray photon is generated and recorded by a pulse-height discriminator. This detector type is the optimum choice for standard wavelengths as Cu Ka, Co Ka, and Cr K_α radiation. The detector has a very low background and a good energy resolution.

c. Scintillation counter

Scintillation counters consist of a crystal and a photomultiplier. The crystal is capable to convert an X-ray photon into a UV or visible photon. The incoming X-ray photon is absorbed in the crystal (for example: NaI, doped with Tl). The resulting light impulse is recorded by the photomultiplier as an amplitude proportional to the energy of the absorbed X-ray photon. Scintillation detectors have a lower energy resolution than gas proportional counters for Cu K_α radiation. However, they are preferred for short wavelengths (e.g., Mo K_α or Ag K_α).

The main properties of point detectors regarding their applications are

- high dynamical range (~106)
- possibility to use a diffracted beam monochromator

- low (background) noise
- can be used with focusing or parallel beam geometry
- cost-effective

d. Line detectors

Line detectors cover a certain angular range in 2θ. They resemble a large number of adjacent single detectors. Line detectors are thus much faster than point detectors. Different types are on the market. The first commercial line detectors used a wire and a counting gas. Since 2001 semiconductor detectors define the new standard. The PANalytical X'Celerator with its unique semiconductor RMTS (Real Time Multiple Strip) technology was the first detector of that kind on the market. The X'Celerator overcame the problems of the gas-filled detectors, which have a small dynamic range and need regular maintenance because of aging of counting gas and detector wires. The current state-of-the art PANalytical $PIXcel^{3D}$ detector consists of smaller strips than the X'Celerator. The strips are subdivided in segments so that the PIXcel resembles a solid-state area detector. It has a better resolution and the highest linearity of all detectors available for laboratory XRD equipment. The detector can be used in point detection mode, in line detection mode and as an area detector. This makes it also the ideal detector for measurements of epitaxial layers, reflectometry and small-angle X-ray scattering, which require a very large dynamic range. Secondary monochromators are exclusively available for these detectors, to improve energy resolution and suppress sample fluorescence.

Most line detectors have an active length of a few degrees so that the deviations from the ideal focusing geometry are not too large. The use as a scanning detector further reduces this defocusing effect. Line detectors are primarily designed for focusing geometry, but can also be used with parallel beam geometry in reflection or transmission. In order to maintain an acceptable resolution in these cases, the width of the beam has to be small.

The main properties of line detectors regarding their applications are:

- very fast measurements and/or improvement of counting statistics
- investigation of time-resolved processes
- small sample amounts and areas can be investigated
- excellent angular resolution (in case of solid-state types)
- outstanding linearity (in case of PIXcel)

e. Area detectors

Area detectors can record larger parts of the Debye rings or even complete rings at low angles. They are suited for special applications like micro-diffraction and texture analysis. They are also widely used for single crystal diffraction. Different designs are on the market.

The main properties of area detectors in powder diffraction are

- very fast measurements and/or improvement of counting statistics
- usage of a bigger part of the Debye-Scherrer rings, which allows analysis of small spots (micro-diffraction) and small sample quantities.
- improved analysis of highly textured samples
- resolution sometimes less than with line detectors, but solid-state detector like PIXcel^{3D} without compromise [4].

Applications

1. Powder X-Ray Diffraction in Science and Technology

i. Polymorph study

PXRD is useful in identification and characterization of polymorph, monitoring the stability, method development and validation for identification and quantification of drugs in Pharmaceutical Industries. X-rays are partially scattered by atoms once they strike the surface of a crystal. The part of the X-ray that's not scattered simply passes through subsequent layer of atoms, where again a part of the X-ray is scattered and part of it passes through to the next layer. This causes an overall diffraction pattern, just like how a grating diffracts a beam of light. in order for an X-ray to diffract, the sample must be crystalline and the spacing between atom layers must be close to the radiation wavelength. If beams diffracted by two different layers are in phase, constructive interference occurs and the diffraction pattern shows a peak. However, if they're out of phase, destructive interference occurs appear and no peak is observed. Diffraction peaks only occur if it follows Bragg’s Law. Since, a highly regular structure is required for diffraction to occur, only crystalline solids diffract, the PXRD of amorphous materials don't depict any significant peak in diffraction pattern.

ii. Variable Temperature and Relative Humidity study by PXRD

Solid phase transitions like polymorph inter-conversions are routinely examined by X-ray diffractometer using variable temperature sample stages (VT-XRD). Both sub ambient and elevated temperature stages are available which will help to review the sample behaviour at variable temperature conditions. VT-XRD helps to directly identify the crystalline phase as a function of temperature. XRPD is also commonly used to investigate the structure of variable hydrates that are crystalline and contain nonstoichiometric water within channels within the crystal lattice. The quantity of water present in a variable hydrate occurs as a function of the change in relative humidity (RH) in the environment of the sample. The peak positions in the diffractogram refers to dimensions of the unit cell so a change in the size of the unit cell because of the presence of water can be screened by comparison of XRPD patterns under different RH environments.

iii. Use of PXRD in Pharmaceutical industry

XRD is the key technique for drug analysis. It serves a significant role in all stages of drug development, testing and production. It's an important part of analytical research and development, quality control of the active ingredients, excipients and final products Minor changes may cause major batch-to-batch inconsistency that may cause critical problems and result in problems in the manufacturing of the pharmaceutical dosage form, the quality of the formulation, the bioavailability and drug stability.

Many new drug moieties exhibit different forms (polymorphs or solvates) that show changes in their physical properties. Differences in these forms can affect the standard or efficacy of the new drug. It helps in elucidation of the relevant polymorphic and pseudo-polymorphic forms in pharmaceutical development. The materials starting from Active Pharmaceutical Ingredients to finished dosage forms need to be properly screened by XRD because it ultimately causes changes in diffraction patter and affects the bio-availability.

iv. PXRD use in Forensic studies

PXRD is beneficial in trace analysis. It is used to contact traces of paint flakes, hair, glass fragments, stains of any description and loose powdered materials. Identification and comparison of trace quantities of material can help in the conviction of a suspect of his involvement in a crime.

v. Use of PXRD in glass industry

Glasses are amorphous in nature. The X-ray pattern of amorphous compounds doesn't contain any significant peak. However, there are many uses of PXRD in the glass industry. It includes identification of crystalline particles that makes faults in bulk quantity of glass, measurements of crystalline coatings for texture, crystallite size and crystallinity.

vi. Crystallinity study by PXRD

The XRD analysis of crystalline compounds gives a diffraction pattern consisting of a well-defined, narrow, sharp and significant peak while amorphous materials don't give clear peaks rather the pattern has noise signals, smeared peak or it can have some order bumps. Many polymers depict semi-crystalline behaviour and produce halo pattern. Powder XRD are often

used to determine the crystallinity by comparing the integrated intensity of the background pattern to that of the sharp peaks. Different scientists have reported variable methods to seek out the percentage crystallinity and crystallinity index. Ashish Chauhan and Balbir Kaith have widely used it for polymer characterization.

vii. Studying phase transitions by PXRD

Under certain conditions, like 0°C for water at 1 atm, a brand-new arrangement of atoms or molecules may become stable, resulting in a phase change. At this point new diffraction peaks will appear or old ones disappear according to the symmetry of the new phase. If the material melts to an isotropic liquid, all sharp lines will disappear and get replaced by a broad amorphous pattern. If the transition produces another crystalline phase, one set of lines will suddenly get replaced by another set. In some cases, however lines will split or collapse, e.g., if the material undergoes a continuous, second order phase change. In such cases the symmetry may change because the present structure is distorted rather than replaced by a totally different one. For instance , the diffraction peaks for the lattice planes (100) and (001) can be found at two different values of q for a tetragonal phase, but if the symmetry becomes cubic the 2 peaks may coincide [20].

viii. Other less standard applications of PXRD

- Isostructurality and isomorphism studies
- Solid state miscibility studies and solid solution characterization
- Polymorphism studies
- Temperature dependent XRPD analysis: phase transformations, solid state reactions, thermal expansion
- Texture analysis. Determination and characterisation of the preferred crystallographic orientations
- Strain and residual stress analysis
- Microstructural characterization. Crystallite size and micro strain determination.
- Grazing-incidence analysis: phase analysis as a function of the penetration in film samples.
- Determination of strain - relaxed states and composition of semiconductor heteroepitaxial layers.
- Resolution and refinement of crystalline structures.

- Full profile analysis of a powder pattern is important or highly recommended for a few of the most important applications of the PXRD method. To carry out properly a full profile analysis on a powder pattern, it's necessary to understand at least the cell parameters and also the space group of the crystalline phase or phases observed. There is chance to index and thus to find the cell of an unknown phase [21].

2. Identification of Counterfeit Pharmaceuticals

Counterfeit pharmaceuticals are illegally manufactured and widely distributed throughout the world, which presents a major threat to public health. Counterfeit pharmaceuticals are unapproved and unregulated products which may contain dangerous or harmful ingredients or an insufficient amount of the active pharmaceutical ingredient (API) patients require to stabilize or improve their health. Historically, counterfeit pharmaceuticals have been found to contain the incorrect amount of API, contain a different API, no API, or incorrect excipients within the counterfeit product.

XRD has been shown to be a useful technique in the analysis of suspect counterfeit pharmaceutical products. Counterfeit dosage forms were then analysed and compared to the authentic dosage form XRD spectra to determine if the counterfeit products could be differentiated from the authentic products. Various authentic pharmaceuticals, that are commonly counterfeited, were chosen for this study. The bulk powder excipients and API standards that composed these authentic pharmaceuticals were then selected for analysis. Bulk powder acetylsalicylic acid was selected to be used for sample preparation method experiments because a large abundance of the powder was available for experimentation.

From the results, it was determined that the APIs were not distinguishable in the authentic dosage form XRD spectra, and therefore could not be used to distinguish authenticity as originally assumed. Instead, it was determined that counterfeit products contain different excipients with different crystalline structure than the authentic product. Even in cases where the excipients used in the counterfeit product were the same or similar, this difference in the crystalline structure caused a significant shift in peaks. It was confirmed that a shift greater than 0.2^{o} in the 2θ-diffraction angle is indicative of a counterfeit product. The method developed can be used to distinguish counterfeit pharmaceuticals from authentic pharmaceuticals by examining the overall XRD spectrum for missing peaks, additional peaks and peak shifts [22].

3. Characterization of Epitaxial thin films

Among the most famous epitaxial thin films are GaN films for LED applications, the development of which led to the awarding of the Nobel Prize in Physics in 2014. The GaN heteroepitaxial films for these LEDs were grown on sapphire substrates after overcoming the large lattice mismatch between them. Though a symmetric similarity for c-axis growth of GaN (hexagonal) on the c-plane of sapphire (trigonal) exists, these two materials are totally different in the crystallographical sense. Complex domain structures and large mosaic spread (tilt/twist) of GaN epitaxial films were caused mainly by the large lattice mismatches. In the pursuit of new characteristics comparable to GaN-LEDs, recent studies have concentrated on growing functional thin films epitaxially crystallographically different substrates. In this process, XRD analysis is very helpful to characterize their orientation relationships, crystalline quality, etc.

Multidimensional detectors, especially in 2D mode are used in characterizing polycrystalline thin films as well as functional epitaxial thin films such as (La,Sr)MnO3/ZnO double heterostructure on sapphire and Epitaxial growth of α-MoO3 on sapphire [23].

4. In situ observation of bimetallic alloy nanoparticle formation and growth using high-temperature XRD

Bimetallic alloy nanoparticles have attracted considerable attention in many areas of science and technology, because their optical, magnetic, or catalytic properties differ significantly from those of their monometallic counterparts. For instance, bimetallic nanoparticles often exhibit enhanced surface catalytic activity for different chemical reactions, which is attributed to the modifications in the surface electronic structure in combination with modified surface morphologies, because of the atomic neighbourhood of two dissimilar types of atoms. Electrocatalytic activity of bimetallic nanoparticles is critically sensitive to the structure, composition, and particle size of the alloy phases. The clarification of the structure-reactivity relationships of Pt-M (M = Fe, Co, Cu, Ni, etc.) alloy nanoparticle catalysts has been notoriously hampered by limited alloy crystal uniformity, because of the presence of multiple alloy phases (ordered, disordered, different compositions) in the thermally annealed catalyst materials.

The thermal preparation of nanoparticle alloys with controlled properties was studied and the insight into the alloy formation dynamics was clarified. In situ measurements of the alloy formation process of bimetallic Pt-Cu alloy nanoparticles using high-temperature X-ray diffraction (HT-XRD) was reported. HT-XRD is a powerful technique to study in situ the formation of ordered or disordered crystallographic phases, combined with particle size. The Pt-Cu alloy system is of great technological interest, because single-phase $PtCu_3$ alloy nanoparticles serve as precursors for core-shell nanoparticle electrocatalysts with significantly improved activity for the electroreduction of oxygen in realistic fuel cells.

Annealing temperature and annealing time were correlated with atomic lattice parameters, alloy phase composition, and particle size, and their role and relative time scales were clarified in the alloy formation process. In doing so, entire Vegard-type structure-composition relations of the Pt-Cu nanoparticle system were mapped out over a wide temperature range. This technique gives atomic-scale insight in the phase formation behaviour of a nanoscale bimetallic cubic Pt-Cu alloy system [24].

5. Characterization and bioanalytical applications of fluorescent carbon dots

In the characterization of the C-dots, XRD is mainly used to provide the information of crystal structure and particles size. Liu et al. used unsubstituted hexa-peri- hexabenzocoronene as the precursor to synthesize C-dots. After pyrolysis at high-temperature, oxidative exfoliation, surface functionalization and reduction treatment, C-dots with a size of ~60 nm in diameter and 2~3 nm thickness were obtained, and the fluorescence quantum yield was 3.8 %. As shown in Fig.20 XRD spectrum showed apparent wide- angle pattern, with the peaks corresponding to the (002), (100), (004) and (110) planes, respectively, indicating the high degree of crystallinity of the nanoparticles. Mao et al. prepared photoluminescent C-dots via a facile one-step pyrolysis of poly (acrylic acid) in the presence of glycerol. The structure and optical properties of the C-dots were thoroughly investigated. XRD pattern showed a broad (002) peak around $2\theta=24°$, further confirming the graphite structure of the white fluorescent C-dots. Bourlinos et al. [99] directly calcined octadecyl ammonium citrate salt at 300 °C to prepare C-dots, the corresponding XRD pattern displayed two superimposed reflections, confirming the existence of highly disorder carbon and surface modified carbon alkyl groups [25].

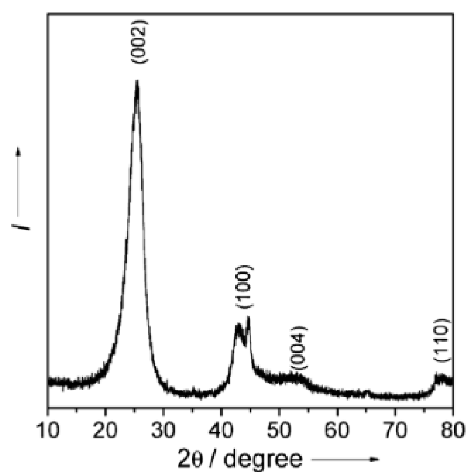


Figure 20. Wide-angle X-ray diffraction pattern of C-dots [25].

6. Quantitative and qualitative analysis of minerals using RockJock program

RockJock is a computer program that determines quantitative mineralogy in powdered samples by comparing the integrated X-ray diffraction (XRD) intensities of individual minerals in complex mixtures to the intensities of an internal standard. Analysis without an internal standard (standardless analysis) also is an option. Carefully weighed samples containing an internal standard (zincite) are ground in a McCrone mill. Randomly oriented preparations then are X-rayed, and the X-ray data are entered into the RockJock program. Minerals likely to be present in the sample are chosen from a list of standards, and the calculation is begun. The program then automatically fits the sum of stored XRD patterns of pure standard minerals (the calculated pattern) to the measured pattern by varying the fraction of each mineral standard pattern, using the Solver function in Microsoft Excel to minimize a degree of fit parameter between the calculated and measured pattern. The calculation analyzes the pattern (usually 20 to 65 degrees two-theta) to find integrated intensities for the minerals. Integrated intensities for each mineral then are determined from the proportion of each mineral standard pattern required to give the best fit. These integrated intensities then are compared to the integrated intensity of the internal standard, and the weight percentages of the minerals are calculated. The results are presented as a list of minerals with their corresponding weight percent. To some extent, the quality of the analysis can be checked because each mineral is analysed independently, and, therefore, the sum of the analysis should approach 100 percent. Also, the method has been shown to give good results with artificial mixtures. The program is easy to use, but does require

an understanding of mineralogy, of X-ray diffraction practice, and an elementary knowledge of the Excel program [26].

7. Influence of the silver modification on the Nickel reducibility in Ni-Mg/ SiO_2 catalyst precursors for edible oil hydrogenation

The edible oil hydrogenation is an important process in the fats and oil industry due to its wide applications, such as modification of the oils physical characteristics for specific uses and increase of its stability towards oxidation. The hydrogenation of fatty acids proceeds simultaneously with their cis/trans isomerization. The presence of the trans fatty acids (TFA) in the edible products is undesirable because of their unfavourable effect on the human health. The catalysts used in the industry are essentially metallic nickel finely dispersed on the various oxide supports such as alumina, silica and natural earths. However, Ni-containing composites isomerise some of the naturally occurring cis fatty acids to the trans ones. The decrease in the TFA content in the hydrogenated products continues to be a scientific challenge. A field where much progress has been made is the design of new hydrogenation catalysts. It is seen that the magnesium-promoted nickel catalyst supported on di-atomite demonstrates high hydrogenation activity as well as high TFA production. In order to inhibit the TFA isomer formation, the Ni-Mg/diatomite catalyst is additionally modified by silver. This idea arose from the earlier investigations on Ni-Ag/kieselgel catalysts, suitable for the edible fats production. The effects of the silver presence and content on the structure and the state of nickel species in the Ni-Mg/diatomite materials were elucidated as catalyst precursors for edible oil hydrogenation. The changes of the sample structures are established by in situ XRD analysis in H_2 atmosphere.

In this study it is concluded that the silver modification of Ni- Mg/SiO2 material effect on the structure and the state of nickel and silver species in the synthesized precursors. The studied materials display reflections of nickel hydrosilicate compounds better formed in the silver-free sample. Most probably, the addition of silver decreases BET surface area of the modified materials due to Ag_2CO_3 blocking effect of the pore system. The presence of hydrosilicate-type phases in all reduced samples although with lower intensity indicates that the reduction of Ni^{2+} ions to the metallic nickel is not yet completed at the end of the procedure. The silver-species in the materials are easily reduced to the metallic silver in contrast to the reduction of nickel-containing ones [27].

8. Quantitative X-ray diffraction analysis of clay-bearing rocks

X-ray powder diffraction is the best available technique for the identification and quantification of all minerals present in clay-rich rocks (clay stones, mud- stones, and marls). Accurate quantitative mineral analysis is very important in petrological studies, engineering, and industrial applications of rocks that contain clay minerals. Whereas mineral identification is comparatively simple and unambiguous if modern software and good mineral databases are available.

The quantitative mineral analysis technique allows us to measure accurately mineral compositions of rocks, including clay mineral content. The technique is especially well-suited to clay-rich samples, because diagnostic reflections of clays are weak compared to non-clay minerals. The advantage of this method is that all minerals, including the clay groups, are quantified individually and directly as the wt.% of the bulk rock, without normalization and without a size separation and analysis from oriented preparations. The quality of the results is often judged by the departure of totals from 100%, provided the amorphous components are negligible or were quantified separately. In organic-rich rocks, or rocks containing amorphous metal oxides or hydroxides, this method can reveal the presence of such material by the departure of mineral content sum from 100% [28].

9. Use of waste marble powder in brick industry in Turkey

The usability of waste marble dust as an additive material in industrial brick is investigated. Marble wastes were collected from marble deposits which are located at Southwest of Turkey and industrial brick mortar was obtained from a brick company in Istanbul. Waste marble dust and brick mortar were prepared for various processes of industrial brick investigation. waste material in several proportions was mixed with industrial brick mortar starting amount of 0 wt.% up to 80 wt.%. in 41 x 8 x 8 mm rectangular prisms for testing of physico-mechanical properties of the samples having different marble dust composition. These prepared prisms were pressed and sintered at three different temperatures 900, 1000 and 1100 °C. Flexural strengths of the test samples were given at three different temperature values of 900, 1000 and 1100 °C. Archimedes water displacement test was conducted with different water absorption percentage values at 900, 1000 and 1100 °C temperatures. XRD analyses was administered for

the additives which contain mainly calcite and little amount of dolomite minerals. It had been found that the quantity of marble dust additive had positive effect on the physical, chemical and mechanical strength of the produced industrial brick. With increasing demands of the development industry, bricks quality and price become more important day by day in Turkey. Additionally, the usage of marble wastes for the production of industrial bricks has significant important role on the recycling waste marble powder within the brick production together with an excellent contribution to economy and ecology of the country [29].

10. Single crystal XRD application

Single-crystal XRD is a powerful characterization technique that can provide the absolute structure of a molecule. While structure determination is the most typical reason chemists use XRD, there are a range of special X-ray techniques, like anomalous scattering and photocrystallography, which give more information about a molecule.

Anomalous scattering can distinguish between atoms of comparable molecular weights. This technique is especially valuable for characterization of heteropolynuclear metal complexes (compounds that have more than one metal atom with different identities). Anomalous scattering has also been utilized in protein crystallography as a technique to help resolve the phase of the diffracted beam, which is very important for structure determination.

Photocrystallography involves single-crystal XRD coupled to photochemistry. By irradiating a sample with light in the solid state, we are able to observe small structural changes and monitor those changes by XRD. Examples of this technique include observing isomerization of a molecule by light as well as characterization of reactive intermediates [14].

Conclusion

In the past few years, powder XRD systems have become more and more efficient for the pharmaceutical industry because of innovations and improvements in detection and source emission technology. X-ray diffraction methods are especially significant for the analysis of solid materials in forensic science. They're often the sole methods that allow a further differentiation of materials under laboratory conditions. Minerals are the building blocks of the solid Earth. Some minerals are readily recognized by their distinctive colours or crystal forms, but in most cases, powder X-ray diffraction is the primary and most definitive method used to identify minerals. The high flux and density of X-rays produced at synchrotrons provide the microelectronics industry with a robust probe of the structure and behaviour of a large array of solid materials that are being developed to be used in devices of the future. X-ray diffraction studies are also used to obtain information on the short and intermediate range structure of glasses [2]. Advances in PXRD instrumentation and software have improved the efficacy of pharmaceutical drugs, efficiency of solid-state characterization and rapid analysis of composites and materials. Variable temperature and humidity techniques are especially powerful in understanding structural changes of pharmaceutical drugs to boost the stability and screen the drug substances under variable conditions. XRD in association with DSC, TGA, DTA, FTIR techniques can solve numerous problems encountered in industries for pharmaceutical formulation and pharmaceutic developments. The excellence of this technique is catering to academic research and commercial use in industries. Powder X-ray diffraction technique is a key analytical technique to serve the growth and development of Science and Technology [20]. The accuracy, relevance, sensitivity and availability of XRD increase its roles in various fields. But one question which might appear, what are the limits that it would be faced. It can only analyse single phase at a time, need controlled diffracted patterns, low sensitivity for mixed complex hybrid mixture and sometimes hybrid peaks appeared for top angle reflections. So, advanced simulation methods are preconditioned to fix the issues to get more appreciation of the XRD wealth info. Development of easier data interpretation methods are also appreciating for both in labs and industrial applications. For carbon-based nanomaterial, XRD takes prolonged time to simulate all structural properties. Thus, there's necessity to create a standard control library of simulated controlled diffracted patterns of varied nanomaterial phases which would occupy all structural properties of these matters. it would make XRD pattern diffraction peak analysis easier, faster, sensitive and less time-consuming method in future not just for carbon matters but also for others [30].

What is the future of XRD?

Both powder and single crystal XRD methods became workhorse techniques for materials and pharmaceutical analysis. While many measurements still benefit from the energy tunability and photon doses available at advanced light source infrastructures like synchrotrons, there has been an excellent proliferation within the number of lab-based X-ray sources that are available.

One area of development for both powder and single crystal XRD is the application of these methodologies to new sample types. This includes complex materials like nanocomposites and polymer species as well as thin film. There are also developments to try and make XRD measurements under more extreme pressures that materials may experience when being used in each application. This includes the development of sample delivery systems that mimic ‘in operando’ conditions or high temperatures and pressures to explore how the material behaviour changes as a function of these additional variables.

Multiplex X-ray measurements, where XRD measurements are performed alongside other experiments, like X-ray fluorescence or absorption, are also becoming increasingly common, where a comprehensive characterization of both elemental composition and structural arrangements can be performed in a single experiment [12].

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