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Review Article

X-RAY DIFFRACTION METHODS – ARTICLE REVIEW

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Abstract:

X-ray diffraction (XRD) is an important and widely used material characterization technique. With the recent development in material science technology and understanding, various new materials are being developed, which requires upgrading the existing analytical techniques such that emerging intricate problems can be solved. Although XRD is a well-established non-destructive technique, it still requires further improvements in its characterization capabilities, especially when dealing with complex mineral structures. The present review conducts comprehensive discussions on atomic crystal structure, XRD principle, its applications, uncertainty during XRD analysis, and required safety precautions. The future research directions, especially the use of artificial intelligence and machine learning tools, for improving the effectiveness and accuracy of the XRD technique, are discussed for mineral characterization. The topics covered include how XRD patterns can be utilized for a thorough understanding of the crystalline structure, size, and orientation, dislocation density, phase identification, quantification, and transformation, information about lattice parameters, residual stress, and strain, and thermal expansion coefficient of materials. All these important discussions on XRD analysis for mineral characterization are compiled in this comprehensive review, so that it can benefit specialists and engineers in the chemical, mining, iron, metallurgy, and steel industries.

Keywords: X-ray diffraction; mineral characterization; crystal structure; Bragg's law; lattice parameters; crystallography; unit cell.

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INTRODUCTION ORIGIN OF X-RAYS:

The X-ray region of the electromagnetic spectrum consists of wavelengths in the region of about 0.1 to 100\AA . For analytical purposes, the range of 0.7 to 2.0\AA is the most useful region. X-rays are generated when high velocity electrons impinge on a metal target. The process of producing X-rays may be visualized in terms of Bohr's theory of atomic structure. An atom is composed of a nucleus and numerous electrons. The electrons are arranged in layers or shells with the valence electrons in the outer shell. The different shells, or layers of electrons are called the K shell, L shell, M shell, and so on. For example, a sodium atom contains filled K and L shells and one electron in the M shell. An atom is shown schematically in fig 1.1

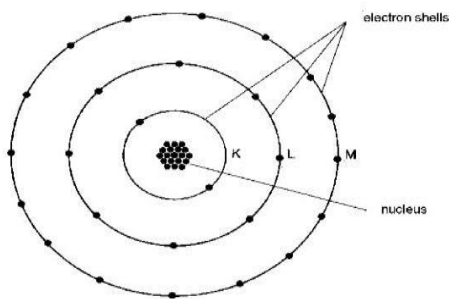


Fig.1.1:schematic diagram of the electronic structure of an atom.

Whenever a fast moving electron impinges on an atom, it may knock out an electron completely from one of the inner shells of that atom. Following the loss of inner-shell electron one of the outer electrons will fall into the vacated orbital, with the simultaneous emission of an X-ray photon. The energy of the emitted X-ray photon is equal to the difference in energy between the two levels involved for instance if a K-shell loses its one electron, and it is replaced by the electron from the L-shell, the resulting X-ray is termed as K X-ray and its energy E_K is given as follows:

$$E_K = E_L - E_K$$

where E_L and E_K are the energies of L- and K-shell electrons respectively. These K lines have been further divided into K_{α} and K_{β} depending on whether the electron falling into the K shell comes from the closest shell or the nearest shell, i.e., L or M shell. Similar to above, the L series of X-rays is obtained when an electron in the L shell is ejected and replaced by the electron from the outer shell. Again, L-lines have been further divided into L_{α} and L_{β} , and depending upon whether electron falling into the K orbit comes from the closest shell or the next nearest shell, i.e., M or N shell.

The customary notations used to identify the emitted X-rays are illustrated in Fig.1.2

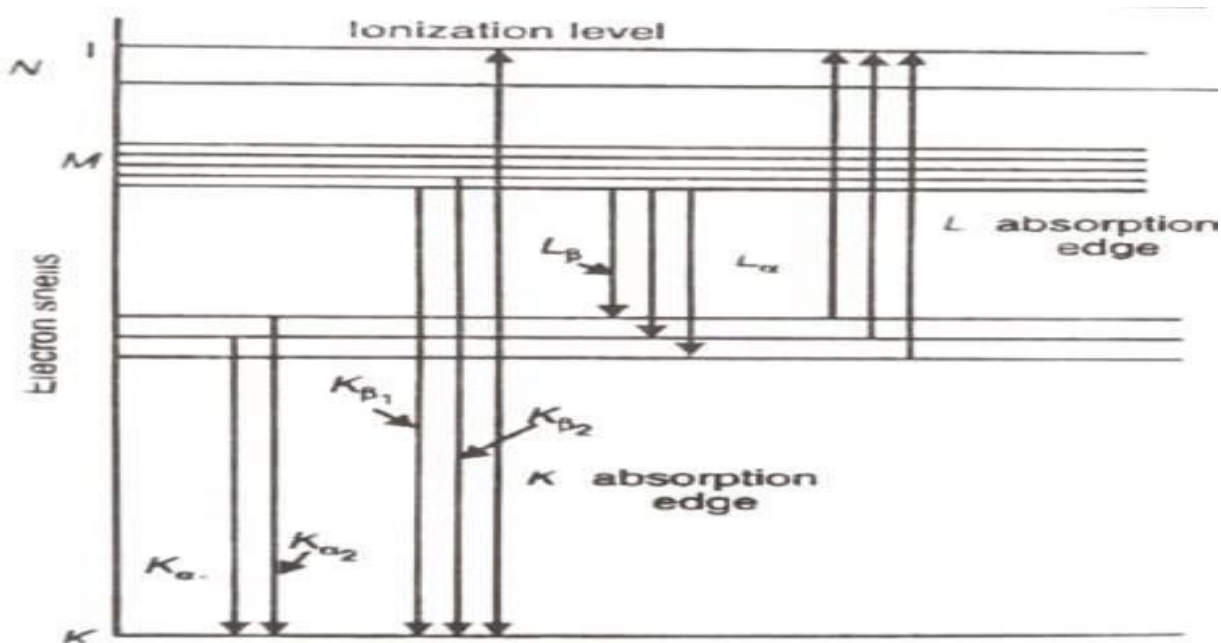


Fig.1.2 energy level diagram for a hypothetical atom

If an electron is dislodged from K shell, it may be replaced by an electron from an L M shell. The electrons descending from the shell would emit X-rays with a frequency

$$\nu = (E_{\{L\}} - E_{\{K\}})/h$$

Lines originating from transitions between L and K shells are termed as K lines. The slight difference in the energy levels of the different electrons in the L shell results in the emission lines at slightly different frequencies. These lines are termed as $K_{\{21\}}$ and K_{α} . Similarly, electrons descending from the M shell to the L shell would emit X-rays with the frequency $\nu = (E_{\{M\}} - E_{\{L\}})/h$

By these transitions, L lines are emitted

Generally, the spectrum of X-rays emitted from a given target element may have either a series of sharp and characteristic lines, as discussed above or may have a complicated spectrum of X-rays with faintly sharp spectral lines superimposed on the continuum. The difference depends on whether we are using primary X-rays (in the former case) or high-energy electrons (in the latter case) to bombard the target element and eject an inner electron.

X – RAY CRYSTALLOGRAPHY

X-ray crystallography is a tool used for determining the atomic and molecular structure of a crystal.

The underlying principle is that the crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a

crystallographer can produce a 3D picture of the crystal, as well as their chemical bonds, their disorder and various other information can also be determined.

The method revealed the structure and function of many biological molecules including; vitamins, drugs, proteins and nucleic acids such as; DNA. Note that the double helix structure of DNA discovered by James Watson and Francis Crick was revealed by X-ray crystallography. Recent advances in image reconstruction technology have made X-ray crystallography.

Bragg's law for x-ray diffraction

Bragg pointed out that the unlike reflection of ordinary light, reflection of X-ray can take place only at a certain angle which is determined by the wavelength of x-ray and distance between the plane of in the crystal. Two geometrical facts are worth remembering:

(1) The incident beam, the normal to the reflecting plane, and the diffracted beam are always coplanar.

(2) The angle between the diffracted beam and the transmitted beam is always 2θ . This is known as the diffraction angle, and it is this angle, rather than θ , which is usually measured experimentally.

Suppose a beam of x-ray falls on the crystal at glancing angle (tangential angle) θ , then some of these rays will be reflected from the upper plane at same angle θ .

While some of these rays will be absorbed and get reflected from the successive layer

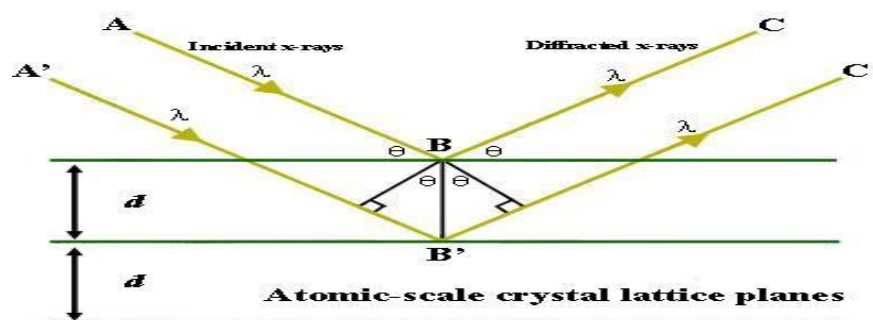


Fig 1.3 The Bragg's Law So, here

angle will be $\angle XBY = \theta$ & $\angle YBB' = \theta$

$AB = A'B$ & $CB = C'B$

Path difference = $XB + B'Y$

Path difference is defined as an integral multiple of wavelength = $n\lambda$ $\lambda = XB + B'Y$

Now for $\triangle XBB'$;

$\sin \theta = XB'/BB'$

$XB' = BB' \sin \theta$

$XB' = d \sin \theta$

Now for $\triangle YBB'$;

$\sin \theta = YB'/BB'$

$YB' = BB' \sin \theta$

$YB' = d \sin \theta$

SINGLE CRYSTAL X RAY DIFFRACTION

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond-lengths, bond-angles, and details of site-ordering. Directly related is single-crystal refinement, where the data generated from the X-ray analysis is interpreted and refined to obtain the crystal structure. Single crystal x ray diffraction instrumentation. X-ray diffractometers consist of three basic elements, an X-ray tube, a sample holder, and an X-ray detector. 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 impact of the electrons with the target material. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K\alpha$ and $K\beta$. $K\alpha$ consists, in part, of $K\alpha_1$ and $K\alpha_2$. $K\alpha_1$ has a slightly shorter wavelength and twice the intensity as $K\alpha_2$. The specific wavelengths are characteristic of the target material. 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 two is used. Molybdenum is the most common target material for single-crystal diffraction, with $MoK\alpha$ radiation = 0.7107\AA . These X-rays are collimated and directed onto the sample. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs. 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. X-rays may also be produced using a synchrotron, which emits a much stronger beam.

Single-crystal diffractometers use either 3- or 4-circle goniometers. These circles refer to the four angles (2 , X , 4 , and 2) that define the relationship between the crystal lattice, the incident ray and detector. Samples are mounted on thin glass fibers which are attached to brass pins and mounted onto goniometer heads. Adjustment of the X, Y and Z orthogonal directions allows centering of the crystal within the X-ray beam.

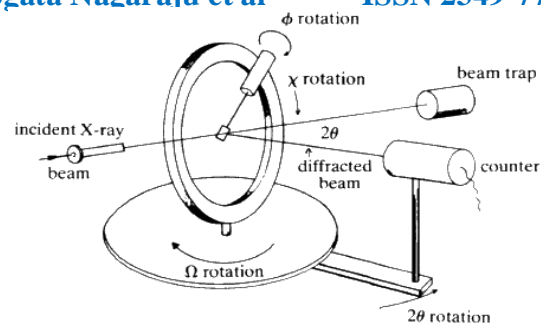


Fig 1.4 : 4- circle diffractometer

X-rays leave the collimator and are directed at the crystal. Rays are either transmitted through the crystal, reflected off the surface, or diffracted by the crystal lattice. A beam stop is located directly opposite the collimator to block transmitted rays and prevent burn-out of the detector. Reflected rays are not picked up by the detector due to the angles involved. Diffracted rays at the correct orientation for the configuration are then collected by the detector.

Modern single-crystal diffractometers use CCD (charge-coupled device) technology to transform the X-ray photons into an electrical signal which are then sent to a computer for processing.

ROTATING CRYSTAL METHOD

Rotating Crystal Method:

The rotating crystal method was developed by Schiebold in 1919. The arrangement of this method (a) The X-rays are generated in the X-ray tube and then the beam is made monochromatic by filter

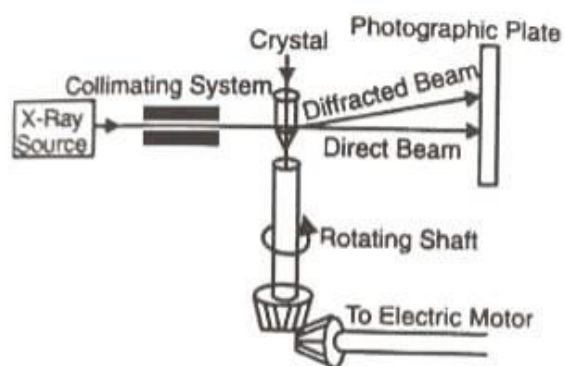


Fig 1.5: The rotating crystal method

From of the filter, parallel the X-rays. beam is then allowed to pass through collimating system which permits a fine pencil of parallel X rays.

From the collimator, the X-ray beam is made to fall on a crystal mounted on a shaft which can rotate at a uniform angular rate by a small motor.

Now the shaft is moved to put the crystal into slow rotation about fixed axis. This causes the set of Bragg's planes coming successively into their reflecting positions, i.e., the value of θ satisfies the Bragg relation. Each plane will produce a spot on the photographic plate. One can take a photograph of diffraction pattern upon a photographic plate perpendicular to X-ray beam or upon film in a cylindrical camera, the axis of which coincides with the axis of rotation of the crystal.

POWDER DIFFRACTION METHOD

X-ray powder method is usually carried for polycrystalline materials.

The powder method of x-ray diffraction was devised independently in 1916 by Debye and Scherrer in Germany and in 1917 by Hull in the United States.

Basically, this method involves the diffraction of monochromatic x-rays by a powder specimen. In this connection, "monochromatic" usually means the strong K characteristic component of the general radiation. x-ray tube operated above the K excitation potential of the target material. "Powder" can mean either an actual, physical powder held together with a suitable binder or any specimen in polycrystalline form.

The method is thus eminently suited for metallurgical work, since single crystals are not always available to

the metallurgist and such materials as polycrystalline wire, sheet, rod, etc., may be examined nondestructively without any special preparation.

There are three main powder methods in use, differentiated by the relative position of the specimen and film:

1) Debye-Scherrer method. The film is placed on the surface of a cylinder and the specimen on the axis of the cylinder. Focusing method. The film, specimen, and x-ray source are all placed on the surface of a cylinder.

2) Pinhole method. The film is flat, perpendicular to the incident x-ray beam, and located at any convenient distance from the specimen. In all these methods, the diffracted beams lie on the surfaces of cones whose axes lie along the incident beam or its extension; each cone of rays is diffracted from a particular set of lattice planes.

In the Debye-Scherrer and focusing methods, only a narrow strip of film is used and the recorded diffraction pattern consists of short lines formed by the intersections of the cones of radiation with the film.

Debye-Scherrer powder diffraction method

The given polycrystalline material is grinding to fine powder and this powder can be taken either in a capillary tube made up of non-diffracting material or is just struck on a hair with small quantity of binding material and fixed at the center of cylindrical Debye-Scherrer camera as shown in fig.

- Debye Scherrer cylindrical camera
- Film mounted in camera
- Film on stretch out

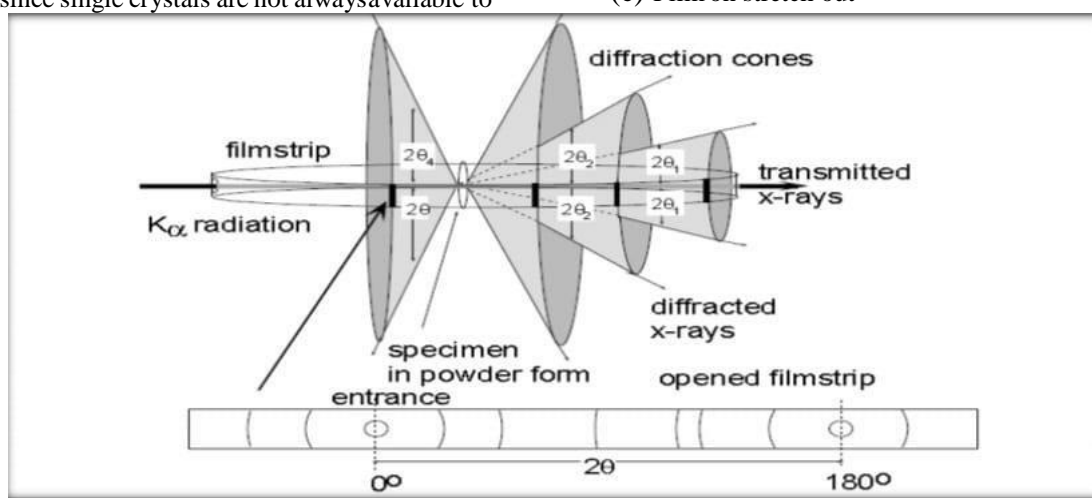


Fig : 1.6: Debye – Scherrer powder diffraction setup and analysis

A stripe of X-ray photographic film is arranged along the inner periphery of the camera.

A beam of monochromatic X-rays is passed through the collimator to obtain a narrow fine beam of X-rays.

This beam falls on the polycrystalline specimen and gets diffracted.

The specimen contains very large number of small crystallites oriented in random directions.

For each set of planes and for each order, there will be such a cone of reflected X-rays. These intersections with a photographic film sets with its plane normal to the incident beam, form a series of concentric circular rings.

In this case, a part of the reflected cone is recorded on the film and it is a pair of curves, the resulting pattern is shown in Fig.(c).

Diameter of these rings or corresponding curves is recorded on the film, and using this the glancing angle and interplanar spacing of the crystalline substance can be determined. Figure (b) shows the film mounted in the camera and the X-ray powder pattern obtained.

The film on spread-out is shown in Fig (c). The distance between any two corresponding curves on the film is indicated by the symbol S.

In case of cylindrical camera, the diffraction angle Θ is proportional to S. Then,

$$\Theta = S/4R$$

where R is representing the radius of the camera. S is the distance between any two corresponding curves on the film

$$\Theta_1 = S_1/4R, \Theta_2 = S_2/4R, \Theta_3 = S_3/4R$$

If S_1, S_2, S_3 etc. are the distance between

symmetrical lines on the stretched film, then,

Using these values of Θ_n equation $n\lambda = 2d \sin \Theta_n$ Where $n = 1, 2, 3$. order of diffraction

$d =$ Interplanar spacing

$\Theta_n =$ Angle of diffraction for nth order.

In a Debye-Scherrer arrangement, after exposing a powder of a crystalline material to monochromatic X-rays, the developed film strip will exhibit diffraction patterns such as indicated in fig. 1.6. Each diffraction peak (dark line) on the film strip corresponds to constructive interference at planes of a particular interplanar spacing (d_{hkl}). The problem now consists of "indexing" the individual lines i.e., determining the Miller indices (hkl) for the diffraction lines:

rays scatter from atoms in a material and therefore contain information about the atomic arrangement.

STRUCTURAL ELUCIDATIONS;

Structure of crystals:

The analytical applications of x-ray diffraction are numerous. The method is non destructive and gives information on the molecular structure of the sample. Perhaps its most important use has been to measure the size of crystal planes. The patterns obtained are characteristic of the particular compound from which the crystal was formed. For example, as shown in Fig. 1.7, NaCl crystals and KCl crystals give different diffraction patterns. A mixture containing 1% KCl in NaCl would show a diffraction pattern of NaCl with a weak pattern of KCl. On the other hand, a mixture containing 1% NaCl in KCl would show the diffraction pattern of KCl with a weak pattern of NaCl.

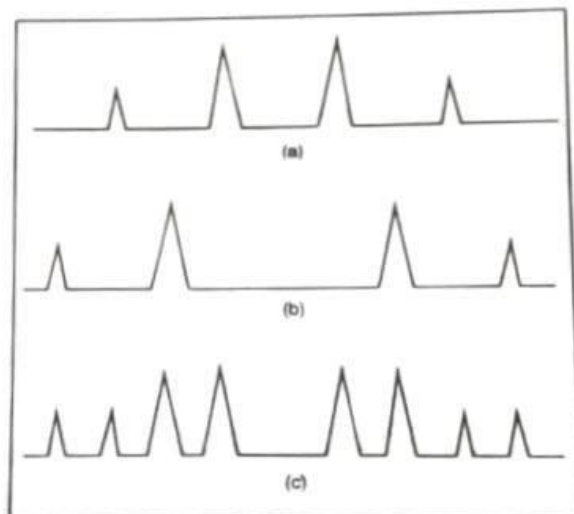
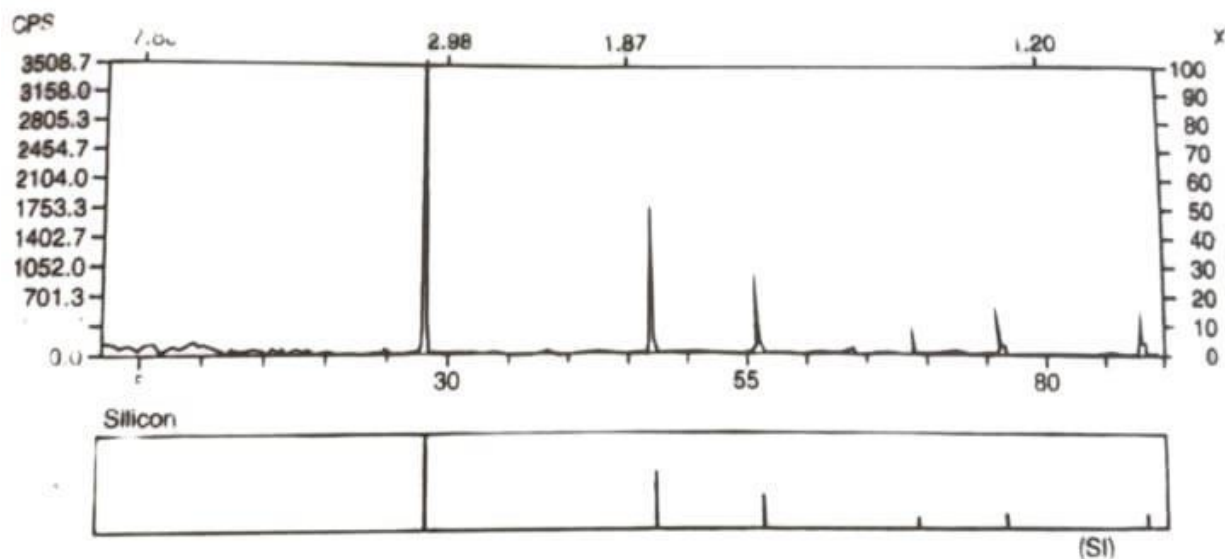


Fig 1.7: Hypothetical x- ray patterns of two salts: (a) x – ray pattern of salt A,

(a) X – ray pattern of salt B ,(c) x -ray pattern of a mixture of salts A and B,

If, on the other hand, the crystal is a mixed crystal of sodium potassium chloride, in which the sodium and potassium ions are in the same crystal lattice, there would be changes in the crystal's lattice size. When there is a large excess of sodium over potassium, the pattern would be similar to that of sodium chloride.

Comparing diffraction patterns from crystals of unknown composition with patterns from crystals of known compounds permits the identification of unknown crystalline compounds. It is also possible to identify a substance



as being a single compound that would give a superimposed pattern for each type of crystal present.

Fig 1.8 : X- ray diffraction pattern of unknown material (upper spectrum) The lower was retrieved from the memory bank and is of silica

Particle size determination

A variety of X-ray techniques may be used to determine the size of particles or crystallinities.

(a) Spot counting method-This method is used for determining size of particles larger than 5 microns.

If the powder diffraction pattern of such a specimen is obtained, it will consist of a series of lines. Fatigue weakens the metal and can result in the metal breaking. It is occasionally necessary to check moving parts for metal fatigue, such as airplane wings (which move slightly during flight), combustion engine parts, and bridges.

CONCLUSION:

For materials including metals, minerals, plastics, pharmaceuticals, and semiconductors XRD apparatus provide highly accurate tools for non-destructive analysis.

The diffraction systems are also supported by an extensive range of application software. X-ray Diffraction is a very useful to characterize materials for following information.

- Phase analysis
- Lattice parameter determination
- Strain determination
- Texture and orientation analysis
- Order-disorder transformation and many more things.

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