

CRYSTAL CHARACTERIZATION TECHNIQUES

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ABSTRACT:

Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their properties. Characterization essentially involves evaluation of the chemical composition, structure, optical, mechanical, electrical and thermal properties of the grown crystals. Different types of characterization techniques are available to study the physical and chemical properties of the crystal.

INTRODUCTION:

A complete description of the physical and chemical properties of a material of interest is termed as characterization of that material[1-5]. These assessment techniques are used for the study of the physical and chemical properties of the grown crystals assist us to trigger rapid progress in the growth process and to improve the quality of the crystal. The information on the process that occurred during growth of a single crystal is provided by the post growth analysis[6-11]. Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their properties.

Characterization essentially involves evaluation of the chemical composition, structure, optical, mechanical, electrical and thermal properties of the grown crystals[12-18]. Different types of characterization techniques are available to study the physical and chemical properties of the crystal. Some of them are

- SINGLE XRD STUDIES
- POWDERED XRD STUDIES
- FT-IR SPECTROSCOPY
- UV SPECTROSCOPY

- **DIELECTRIC STUDIES**
- **NON LINEAR OPTICAL(NLO) STUDIES**

SINGLE XRD STUDIES:

A wide range of technological products is based on the use of single crystals. Electronic properties of single crystals are employed in the semiconductor industry, magnetic properties of single crystals are employed to built magnetic storage devices, mechanical properties(e.g. yield strength)and chemical properties(e.g. corrosion rate)of single crystals are employed in material science. Even the understanding of many polycrystalline materials has been gained by studies of single crystal studies[19-24].

In most cases, the properties of a single crystals are not only a function of the type and the quality of the crystals, but strongly dependent on its orientation. The determination of single crystal orientation thus represents an essential step towards the successful use of single crystals in technological applications[25-30], clear understanding of the crystal structure and the precise knowledge of its orientation often help greatly to optimize the crystal performance.

Single crystal XRD technique offers single crystal structure analyses on wide range of problems dealing with single crystal X-ray diffraction. Such as crystal selection and mounting, determination of the crystal system[31-35], Space group and unit cell parameters, data collections and processing, Structure solution refinement, preparation of molecular illustrations etc.A typical diagram of a single crystal X-ray diffractometer is shown below.

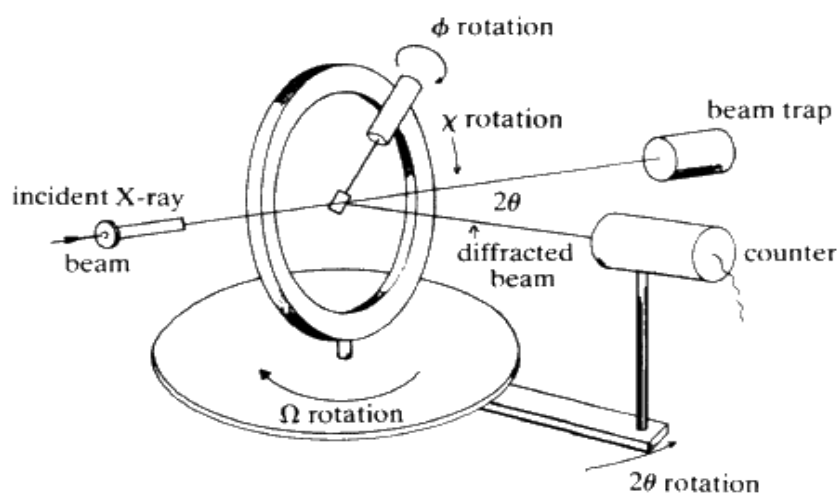


Figure.1 Single crystal X-ray diffractometer

POWDERED XRD STUDIES:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

Fundamental Principles of X-ray Powder Diffraction (XRD):

X-ray diffraction finds the geometry or shape of a molecule using X-rays. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long range order. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction[36-39].

X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel. If the wavelength of these scattered X-rays did not change (meaning that X-ray photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) in that only momentum has been transferred in the scattering process[40-45]. These are the X-rays that we measure in diffraction experiments, as the scattered X-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process

(Compton Scattering), X-rays transfer some of their energy to the electrons and the scattered X-rays will have different wavelength than the incident X-rays.

Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction[46-50]. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. The peaks in a X-ray diffraction pattern are directly related to the atomic distances given by

Bragg's law: $2d\sin\theta = n\lambda$

Where d is the inter-plane distance, θ is the scattering angle, n is an integer representing the order of the diffraction peak and λ the wavelength of the X-ray.

Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. It is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials. It is also a common method for determining strains in crystalline materials. An effect of the finite crystallite sizes is seen as a broadening of the peaks in an X-ray diffraction as explained by the Scherrer Equation. This technique is perhaps the most widely used X-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a

Powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).

The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material

properties are highly dependent on structure. Powder diffraction data can be collected using either transmission or reflection geometry, as shown below. Because the particles in the powder sample are randomly oriented, these two methods will yield the same data.

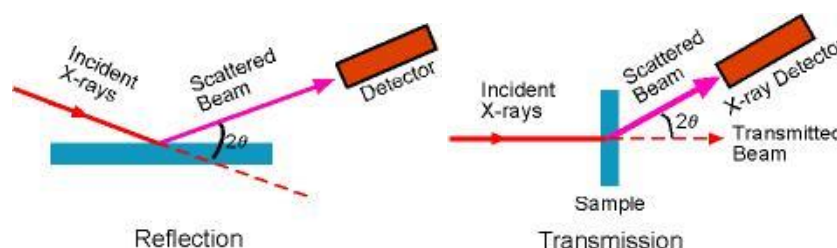


Figure.2 Two methods of data collection in powder diffraction technique

Applications:

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds) 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
- measurement of sample purity

With specialized techniques, XRD can be used to:

Determine crystal structures using Rietveld refinement

Determine of modal amounts of minerals (quantitative analysis)

- characterize thin films samples by:
 - determining lattice mismatch between film and substrate and to inferring stress and strain
 - determining dislocation density and quality of the film by rocking curve measurements
 - measuring superlattices in multilayered epitaxial structures
 - determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements

make textural measurements, such as the orientation of grains, in a polycrystalline sample.

FTIR-FOURIER TRANSFORM INFRARED SPECTROSCOPY:

Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for identifying types of chemical bonds in a molecule by producing an Infrared absorption spectrum that like a molecular “finger print”

Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of various infrared light wave lengths by the material of interest. These Infrared absorption bands identify specific molecular component and structures.

Working Process of FT-IR:

The normal instrumental process is as follows:

❖ The Source:

Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

❖ The Interferometer:

The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferometer signal then exits the interferometer.

❖ The Sample:

The beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

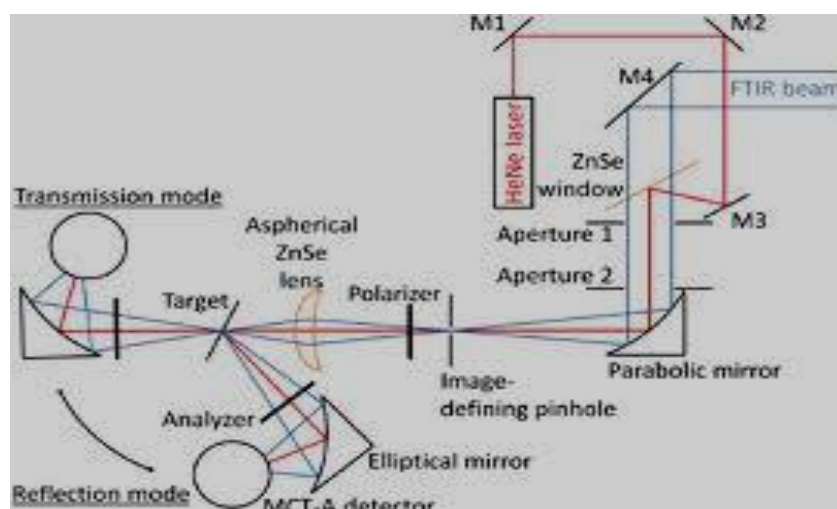


Figure.3 FTIR Instrumentation Diagram

❖ **The Detector:**

The beam finally passes to the detector to final measurement. The Detectors used are specially designed to measure the special interfero-gram signal.

Advantages of FT-IR:

✓ **Speed**

All of the frequencies are measured simultaneously, most measurement by FT-IR are made in a matter of seconds rather than several minutes.

✓ **Sensitivity**

It is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher results in much lower noise levels.

✓ **Mechanical Simplicity**

The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus there is very little possibility of mechanical breakdown.

FT-IR technique has brought significant practical advantages to infrared spectroscopy. It has possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by order technology. It has made the use of infrared analysis virtually limitless.

Application of FTIR:

It can identify unknown materials.

- It can identify variation.
- It can determine the quality of example.
- It can determine the amount of component in a mixture. FTIR is much more sensitive.

UV- SPECTROSCOPY:

UV-Spectroscopy is used to study the optical properties of materials. Ultraviolet and visible spectroscopy is the electronics spectroscopy. When a molecule absorbs light of a particular wavelength an electron can be raised from its highest occupied molecular orbit causing an electronic transition. UV and visible light have sufficient energy to cause only the two electronic transitions namely $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, this means that only compounds with π electrons or non bonding electrons can produce UV spectra.

Silver chloride, if exposed to sunlight will undergo change in color and finally become black. Ritter found that the action considerably increases. If silver chloride is exposed beyond the action considerably region of 400nm to 10nm is called an ultraviolet spectrum. Sun is the natural source of UV radiations detection of UV radiations can be done by four methods.

- Photographic plates, which quickly blackens, when exposed to UV radiation.
- Fluorescence, process by which certain substance emit visible light when exposed to UV
- Phosphorescence process by which substances continuous to emit visible light even exposed UV is removed.
- Photo electric effect, using UV as light source to emit electrons.

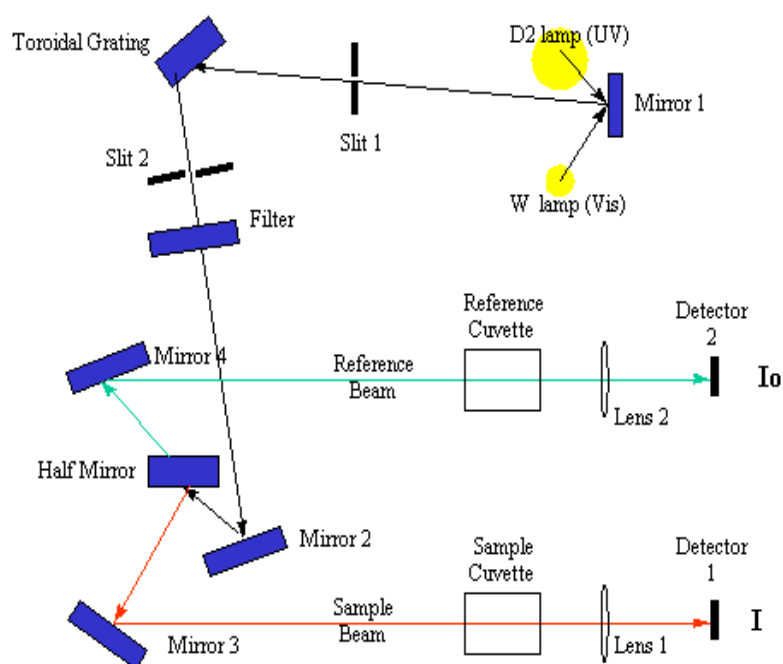


Figure.4 UV-Visible Spectrophotometer

The functioning of this instrument is relatively straight forward. A beam of light from a visible or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic beam in turn is split into two equal beams by a half-mirrored device.

One beam, the sample beam passes through a small transparent container containing a solution of the compound being studied in a transparent solvent. The other beam, the reference passes through an identical cuvette containing only the solvent.

The intensities of these light beams are then measured, by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as I_0 . The intensity of the sample beam is defined as I . Over a short period of time, the spectrometer automatically scans all the component wavelength in the manner described.

The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm.

Application of UV visible spectroscopy:

- UV absorption spectroscopy is used to determine the dissociation constants of acids and bases.
- UV absorption spectroscopy is generally used for the qualitative determination of compounds that absorb UV.
- UV absorption spectroscopy is one of the best methods for detecting impurities in organic compounds.
- UV absorption spectroscopy can characterize those type of compounds whiz absorb UV radiation.
- UV absorption spectroscopy can be used to study the kinetics of reaction.

DIELECTRIC STUDIES

A dielectric (or an insulator) is a material in which all the electrons are lightly bound to the nuclei of the atoms. Thus there are no free electrons to carry current. Hence the electrical conductivity of a dielectric is very low. The conductivity of an ideal dielectric is zero.

Example:

Glass, Plastic, Mica, Oil.

The molecule of dielectrics may be classified as,

- (a) Polar molecule
- (b) Non-Polar molecule

(a)Polar molecule:

Polar molecule is one in which the centre of gravity of the positive charges is separated from the center of gravity of the negative charges by a finite distance. The Polar molecule is thus an electric dipole and has an intrinsic permanent dipole moment.

Example: HCl, CO.

(b)Non-Polar molecule:

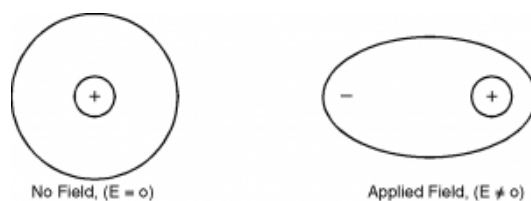
Non-Polar molecule is one in which the centre of gravity of the positive charges (protons) coincides with the center of gravity of the negative charges (electrons). The Non- Polar molecules have symmetrical and zero electric dipole moment.

Example: H_2 , CO_2 , O_2 , N_2

Dielectric constants can be determined practically and it may usually contributed by four parts.

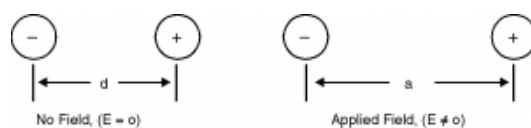
- Electronic Polarizability.
- Ionic Polarizability.
- Dipolar Polarizability
- Space Charge Polarizability

Electronic polarization: Electronic polarization occurs due to displacement of the centre of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field.



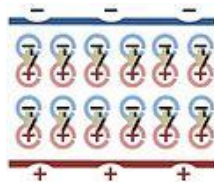
Example: Monoatomic gases exhibit only electronic polarization.

Ionic Polarization: Ionic polarization occurs in ionic materials. It occurs when an electric field is applied to an ionic material then cations and anions get displaced in opposite directions giving rise to a net dipole moment.

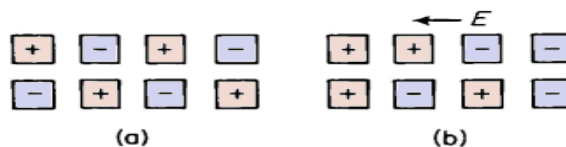


Example: Polyatomic gases

Dipolar Polarization: A material must have molecules with their own dipolar momentum (which can rotate freely). The external field aligns these dipoles to some extent and thus induces a polarization of the material.



Space Charge Polarization: Surfaces, grain boundaries, interphase boundaries may be charged i.e they contain dipoles which may become oriented in an external field and thus contribute to the polarization of the material. Conducting granules in insulated matrix may play role of induced dipoles and cause the space charge polarization.



NON LINEAR OPTICS (NLO) STUDIES:

Nonlinear optics is the study of the interaction of intense electromagnetic fields with materials to produce modified that are different from the input fields in phase, frequency and amplitude. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. In fact, the beginning of the field of nonlinear optics is often taken to be the discovery of second harmonic generation by Franken. Nonlinear optical phenomena are “nonlinear” in the sense that they occur when response of a material system to an applied optical field in nonlinear manner. For example, second harmonic generation occurs as a result of the part of the atomic response that depends quadratically on the strength of the applied optical field. Consequently, the intensity of the light generated at the second harmonic frequency tends to increase as the square of the intensity of the applied laser light.

CONCLUSION:

A complete description of the physical and chemical properties of a material of interest is termed as characterization of that material. These assessment techniques are used for the study of the physical and chemical properties of the grown crystals assist us to trigger rapid progress in the growth process and to improve the quality of the crystal. The information on the process that occurred during growth of a single crystal is provided by the post growth analysis. Characterization of a crystal essentially consists of determination of chemical composition, structure, defects and study of their properties.

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