Chapter 2

Instrumentation Techniques

2.1 Introduction:

The detailed information of the instrumentation techniques and characterization techniques including its principle, functionality and procedure is described in this section. The experimental techniques involve the determination of structural analysis and optical characteristics. The various properties of Rare Earth (RE) doped transition metal oxide (TiO_2/ZrO_2) – Polyacrylicacid (PAA) nanocomposites were investigated by following experimental techniques.

2.2 X-ray Diffraction(XRD):

The development of shine a beam of X-rays through a copper sulphate crystal has been successfully done with recording its diffraction on a photographic plate. After being developed, the plate showed a large number of well-defined spots arranged in a pattern of intersecting circles around the spot produced by the central beam [1].

Crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray powder diffraction (XRD) is a rapid analytical technique that is primarily used for phase identification of a crystalline material providing information on unit cell dimensions. The analysed material is finely ground, homogenized to determine the average bulk composition.

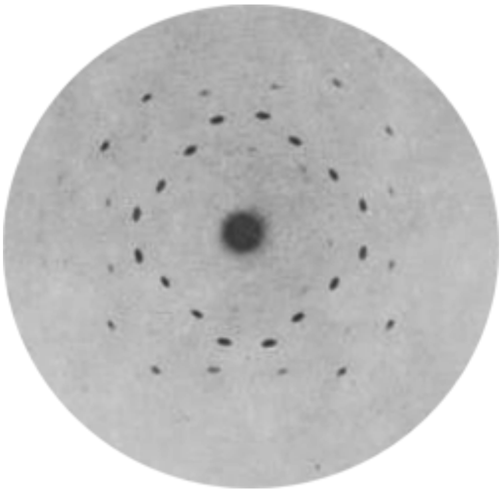
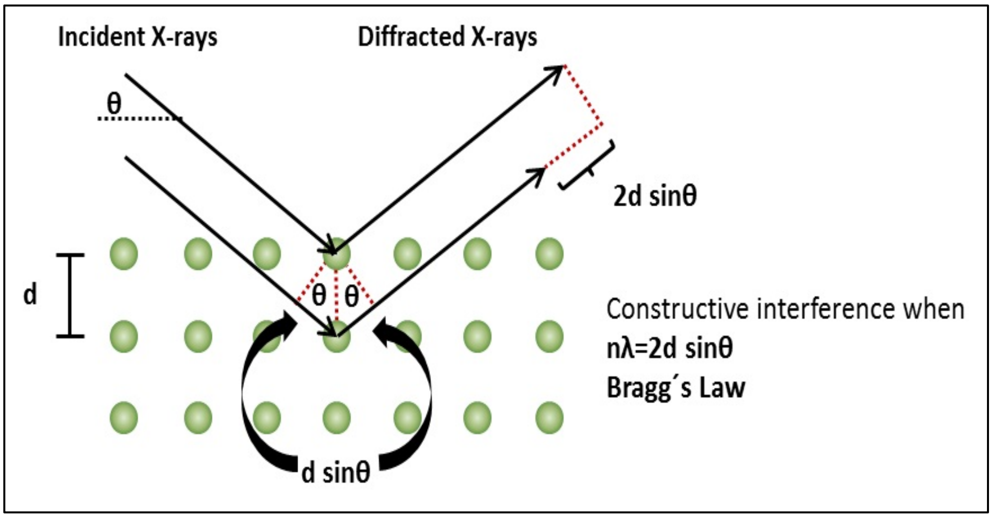


Figure 2.1: One of the first X-ray diffraction patterns obtained by Laue and his collaborators using some crystals of the mineral Blende [2]

Working Principle, Theory, Formulae and Calculations

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. A cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample, generates these X-rays. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

Figure 2.2: Diffraction of X-rays by two successive atomic planes



Crystallite Size

Scherrer gave the formula for the crystallite size determination. It is also known as the Scherrer equation [3]. It relates the size of crystallites in a solid to the broadening of peak in its diffraction pattern.

The Scherrer equation can be written as:

$$d = K\lambda/\beta \, Cos \, \theta$$

where,

d = crystallite size

K = dimensionless shape factor with the value of 0.94

λ = wavelength of X-ray used

β = full width at half maximum (FWHM)

θ = Bragg diffraction angle

The Scherrer equation is limited to nano scale particles.

Instrumentation

X-Ray Diffractometer is a powerful tool for powder diffraction applications such as routine qualitative and quantitative phase analysis, non-ambient analysis, structure solution and refinement, crystallite size and degree of crystallinity calculation [3].

Features

- High Speed Rate (1000°/min)
- High Precision Angle Reproducibility (+/- 0.0001°)
- Fast Measurement and Highly Reliable Data
- Extremely precise angular values thanks to stepper motors with optical encoders
- Easy to handle

GNR APD 2000 PRO X-ray Diffractometer used in the present work for x-ray diffraction studies.

Figure 2.3: Actual image of the instrument GNR APD 2000 PRO XRD

Technical Specifications

X-Ray Generator-

Maximum Output Power	3 kW (option: 4 kW)
Max Output Voltage	60 kV
Max Output Current	60 mA (option: 80 mA)
Voltage Step Width	0.1 kV
Current Step Width	0.1 mA

X-Ray Tube-

Type	Glass (option: Ceramic), Cu Anode, Fine Focus (options: any kind of X-Ray tube)
Focus	0.4 x 12 mm LFF (other options available)
Max Output	3.0 kW

Goniometer-

Configurations	Vertical and Horizontal θ /2θ geometry
Vertical Scan Angular Range	- 60° < 2 Theta < + 168° (accordingly)
Horizontal Scan Angular Range	- 110° < 2 Theta < + 168° (accordingly)
Smallest selectable step size	0.0001°
Modes of operation	Continuous scan, step scan, theta or 2 theta scan, fast scan, theta axis oscillation

Detector-

Type	Scintillation counter Nal
Count rate	2 x 10(6) cps (Nal); 2 x 10(7) cps (Yap(Ce))

Strengths and Limitations

Strengths

- Powerful and quick (< 20 min) procedure for identification of an unknown mineral.
- Minimal sample preparation is required.
- XRD units are widely available.
- Data interpretation is relatively straight forward.

Limitations

- Standard reference file of inorganic compounds (d-spacings, hkls) is a must.
- Requires tenths of a gram of material which must be ground into a powder.
- For mixed materials, detection limit is ~ 2% of sample.
- Peak overlay may occur and worsens for high angle 'reflections’.

Applications

- Phase Composition of a Sample – Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry – Index peak positions – Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure – By Rietveld refinement of the entire diffraction pattern Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain – Indicated by peak broadening – Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width

2.3 Energy Dispersive X−ray Spectroscopy (EDS):

EDS is an analytical technique used to study the chemical composition or constituents of the samples. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The investigation of a sample is done through the interactions between electromagnetic radiation and matter. Using an energy dispersive spectrometer, the energy of emitted X-rays are measured. These characteristic X-rays provide quantitative information about the composition of samples in terms of elements present in the sample. X-ray analysis is a commonly feature found in modern SEM which is referred as Energy Dispersive X-ray Spectroscopy. As the emitted X-rays are the characteristic of the atomic structure of an element, the elemental composition of the specimen can be measured by EDS.

Energy Dispersive X – ray Spectroscopy (EDS) system equipped with the SEM machine JEOL make MODEL JSM 5810 LV., carried out quantitative elemental composition analysis.

Figure 2.4: Actual image of Energy Dispersive X-ray Spectroscopy (EDS)

Figure 2.4 represents an experimental set up of EDS, which is attached to the Scanning Electron Microscope **JEOL** make **JSM 5810 LV**. It is consists of following four components:

1. Electron Beam source
2. X−ray detector
3. Pulse processor
4. Analyzer

The energy of emitted X−rays which is determined from the voltage measurement, transferred to a computer for display and further data evaluation. From the spectrum of X−ray energy versus counts, the elemental composition of the specimen can be determined. The specifications of EDS are shown below:

Model:	JOEL JSM-5610
Resolution:	With LaB_6 filament 2 nm at 30 kV, with W filament 3.5 nm at 30 kV
Accelerating Voltage:	0.2 to 30 kV
Magnification:	up to 2,50,000 X

2.4 Particle Size Analyzer (DLS):

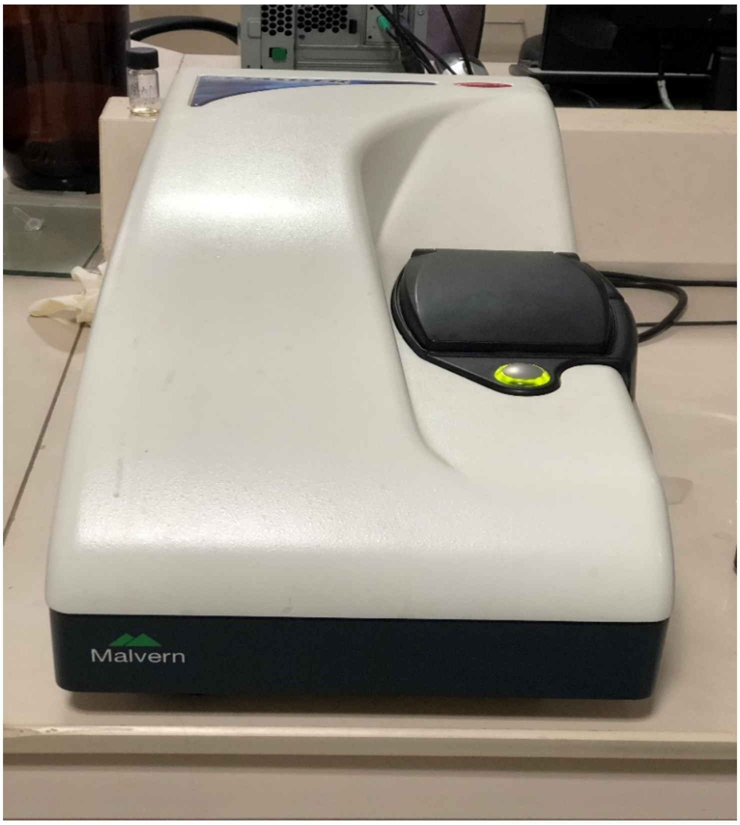


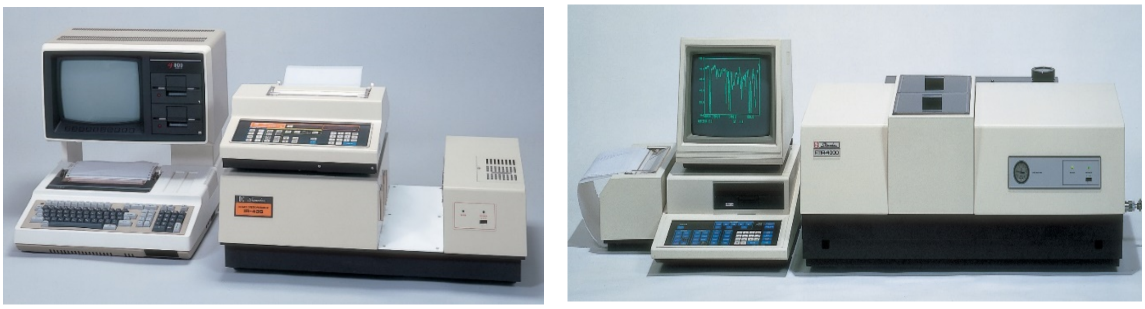
Figure 2.5: Actual image of Malvern Nano ZS Particle Size Analyzer

The distribution of the hydrodynamic diameters of the nanoparticles were determined using a Malvern Nano ZS particle size analyzer by Dynamic Light Scattering (DLS) technique.

2.5 Fourier Transformation Infra-Red Spectroscopy(FTIR):

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material [4].

Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.



(a) **(b)**

Figure 2.6: (a) In 1981, the IR-435, a dispersive instrument featured an integrated microcomputer and room for optional ROM memory; accurate spectrum recordings of rapid reaction processes and automatic peak detection became possible, **(b)** In 1984 Shimadzu’s first Fourier Transform Infrared Spectrophotometer was launched [5].

Working Principle, Theory, Formulae and Calculations

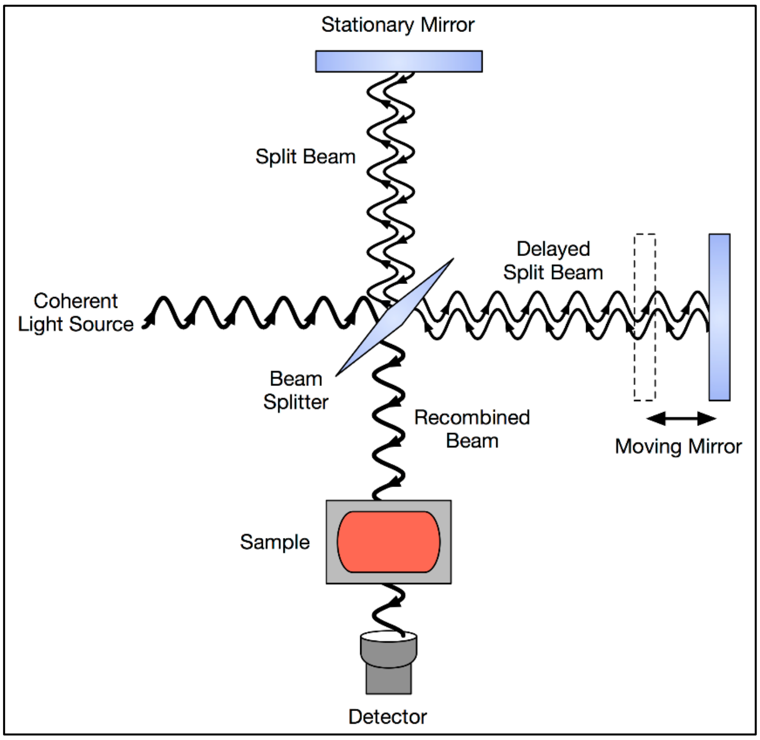


Figure 2.7: Analytical information of FTIR spectrometer

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. The two beams reflect of their respective mirrors and are recombined when they meet back at the beam splitter. Since the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal that exits the interferometer is the result of these two beams “interfering” with each other. The resulting signal is called an interferogram, which has the unique property, that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source.

This implies that as the interferogram is measured, all frequencies are being measured at the same time. So, the utilization of the interferometer brings about very quick estimations. Since the analyst requires a frequency spectrum to make a unique proof, the deliberate interferogram signal can't be interpreted straightforwardly. A means for "decoding" the individual frequencies is required. This can be cultivated through a notable mathematical method called the Fourier transformation. This transformation is performed by the computer which at that point gives the client the ideal otherworldly data for analyst.

Instrumentation

For many routine sample analyses, the FT/IR-4700 can be paired with the ATR-PRO ONE single bounce ATR with a choice of prisms including a high throughput monolithic diamond, Germanium (ideal for carbon-black samples) or ZnSe. A choice of clamps with pressure up to 10,000 psi ensures the best sample contact with the crystal [6].

In the presented work, FTIR spectroscopic studies were done using JASCO FT/IR-4700 spectrometer with ATR-PRO ONE.

Figure 2.8: Actual image of the instrument JASCO FT/IR-4700 spectrometer

Features

- Wave Number Extension
- Excellent Signal-to-Noise Ratio

Technical Specifications

Standard Wavenumber Measurement Range	7,800 to 350 cm^{-1}
Maximum Resolution	0.4 cm^{-1}
Optical System	Single beam
Sample Chamber	Size: 200 mm (W) × 260 mm (D) × 185 mm
Optical path	Center focus, light axis 70 mm high
Interferometer	45º Michelson interferometer; Corner cube mirror interferometer, with auto-alignment mechanism, sealed structure, DSP control
Light Source	Standard: High-intensity ceramic source
Detector	DLaTGS (with Peltier temperature control)
Optional Detectors	W-MCT, M-MCT, N-MCT, Si, InSb, InGaAs
Signal-to-Noise Ratio (4 cm-1, 1 min, near 2,200 cm-1)	35,000:1

Strengths and Limitations

Strengths

- Speed
- Sensitivity
- Mechanical Simplicity
- Internally Calibrated
- Accurate and reproducible.

Limitations

- The sampling chamber of an FTIR can present some limitations due to its relatively small size.
- Mounted pieces can obstruct the IR beam. Usually, only small items as rings can be tested.
- Several materials completely absorb Infrared radiation; consequently, it may be impossible to get a reliable result.

Applications

- It a very reliable technique for positive identification of virtually any sample.
- The sensitivity benefits enable identification of even the smallest of contaminants.
- FT-IR is an invaluable tool for quality controller quality assurance applications.
- The practical use of infrared for quantitative analysis have been dramatically increased by the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms.
- Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

2.6 Photoluminescence spectroscopy(PL):

Photoluminescence is the emission of light which is caused by the irradiation of a substance with other light. The term embraces both fluorescence and phosphorescence, which differ in the time after irradiation over which the luminescence occurs. It is used in many photonic devices, for example in light emitting diodes and on phosphor screens [7].

Working Principle, Theory, Formulae and Calculations

Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials. Light is focused onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be depraved by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence.

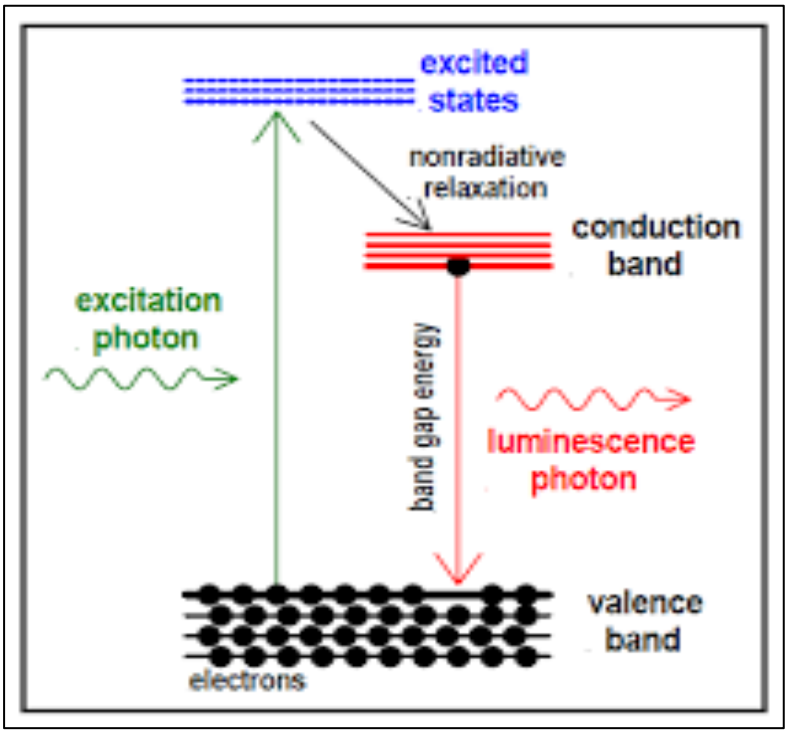


Figure 2.9: Principle of photoluminescence spectroscopy

Forms of photoluminescence

- Resonant radiation
- Fluorescence
- Phosphorescence

Instrumentation

The fluorescence spectrometer primarily has a source of light, monochromators, a sample holder and a detector.

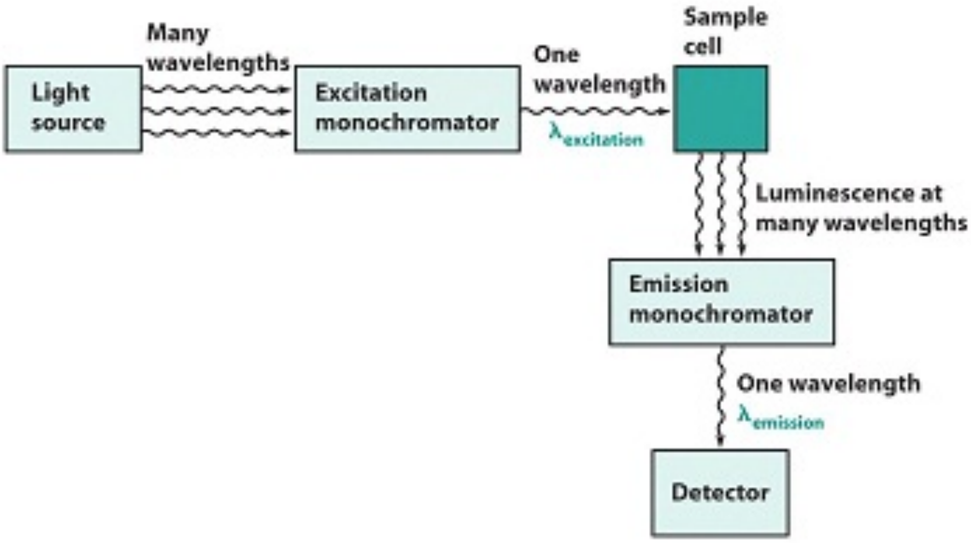


Figure 2.10: Block diagram of fluorescence spectrometer

PL measurements done for the present study were done using JASCO FP-6500 spectrofluorometer.

Figure 2.11: Actual image of the instrument JASCO FP-6500 spectrofluorometer

Features

- Wavelength accuracy
- Wavelength Repeatability
- Resolution
- Stray light
- Detection Limit
- Photometric stability
- UV-30 filter, L-39 filter, R-60 filter and secondary low pressure mercury lamp are built in the FP-6500 [8].

Strengths and Limitations

Strength

- Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials

Limitations

- The main scientific limitation of photoluminescence is that many optical centers may have multiple excited states, which are not populated at low temperature.
- The disappearance of luminescence signal is another limitation of photoluminescence spectroscopy

Applications

- Detection of Aggregation-caused quenching (ACQ) properties
- Detection of Aggregation-induced emission (AIE) properties

2.7 UV-Vis Spectroscopy (UV-Vis):

UV-Visible (UV-Vis) Spectrometers perform absorption and reflectance spectroscopy using light in the visible and adjacent ranges. UV-Vis spectroscopy is a powerful analytical chemistry technique for determining concentration of analytes in a sample and tracking chemical reactions. When purchasing a UV Visible spectrometer, it is important to consider the instrument’s wavelength range, the lamp’s lifetime, the image capture system and software, the resolution, and the amount of sample that is needed for input [9].

Working Principle, Theory, Formulae and Calculations

Although modern UV-Vis spectrometers differ greatly from the first DUs, all operate on the same basic principle. Light intensity is measured from UV-Vis source lamps before and after the light passes through a sample. The amount of light absorbed corresponds to the molecular concentration in the sample.

When the molecules or atoms or ions of a sample moves from one energy state to another energy state the electromagnetic radiation absorbed or emitted, the measurement and explanation of the same is Spectroscopy.

UV spectroscopy is type of absorption spectroscopy in which light of UV region (200-400 nm) is absorbed by the molecule, which results in the excitation of the electrons from the ground state to higher energy state.

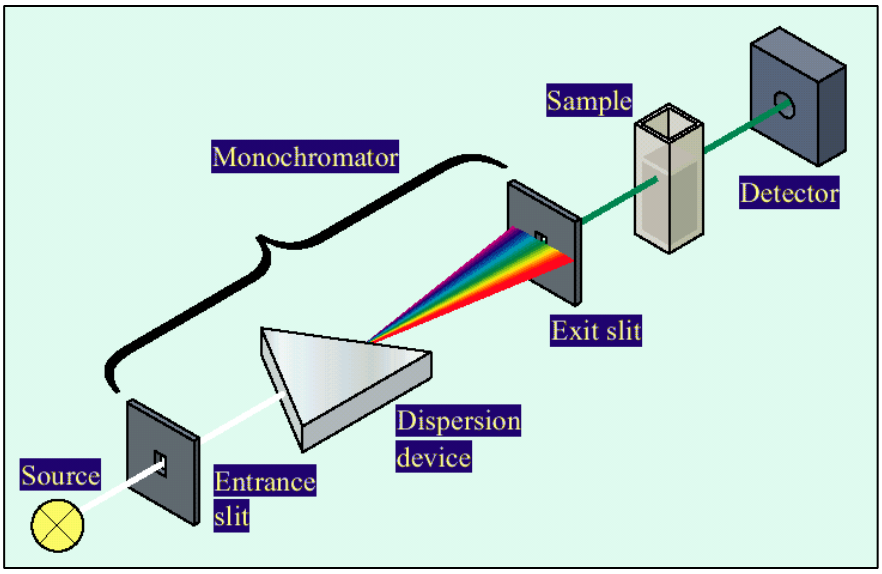


Figure 2.12: A simple view of essential components of UV-Vis spectrometer

Basically, spectroscopy is related to the interaction of light with matter.

The more easily excited the electrons, the longer the wavelength of light it can absorb. There are four possible types of transitions (π–π*, n–π*, σ–σ*, and n–σ*), and they can be ordered as follows: σ–σ* > n–σ* > π–π* > n–π*

The absorption of ultraviolet light by a chemical compound will produce a distinct spectrum which aids in the identification of the compound.

Lambert – Beer Law

Lambert – Beer Law states that the absorbance of a sample at a given wavelength is proportional to the molar absorptivity of the substance (a constant at each wavelength), the path length and the concentration of the absorbing substance.

$$A = \varepsilon \, l \, c$$

A = measured absorbance

ε = the molar absorptivity of the substance, l = path length and

c = concentration of the substance

Experimental measurements are usually made in terms of transmittance (T). The instrument measures the intensity (I) of light passing through the sample and compares it to the intensity of incident light (I0) on the sample. The transmittance is given by I/I0. The following equation gives the relation between absorbance and transmittance.

$$\mathbf{A = - \log (T) = - \log (I/I0)}$$

The UV – Visible spectrometer can also be configured to measure reflectance. In this case, the spectrometer measures the intensity of light reflected from a sample (I) and compares it to the intensity of light reflected from a reference material (I0). The ratio I/I0 is called the reflectance.

The UV-Visible Spectrometer comprises of four basic components namely, light source, sample holder, monochromator and detector. Light emitting diodes (LED) have been used for visible wavelengths [10].

Absorption Co efficient (α cm-1)

The absorption coefficient determines the amount of light or photon absorbed in a material. This is very important parameter for optical properties. The formula to determine absorption co efficient is given below.

$$\boldsymbol{\alpha = (2.303 * \text{Absorbance}) / t}$$

Where, t = path length,(thickness of the film or thickness of the sample holder)

Extinction Coefficient (K)

The extinction coefficient is also known as absorption index. It is a measure of fraction of light lost due to scattering and absorption per unit distance of the penetration medium. It is a measure of how well the material scatters and absorbs electromagnetic radiation. If the material has a low extinction co efficient, the electromagnetic wave can pass through very easily [11]. The formula of extinction co-efficient is given below.

$$\boldsymbol{K=\alpha\lambda/4\pi}$$

Where, α = absorption co efficient λ = absorbed wavelength

Optical Bandgap (Eg eV)

The bandgap is defined as the energy difference between the top of the valance band and the bottom of the conduction band. There is a distinction between optical bandgap and electrical bandgap. The optical bandgap is the energy to create an exciton (bound electron – hole pair) but not to separate the electron and hole while the electrical bandgap is the energy to create electron hole pair and to separate them. As per definition, the optical conductivity is slightly lower than electrical conductivity. The optical bandgap can be determined using Tauc's relation.

$$\alpha = A(h\nu - Eg)1/n$$

A = constant, hν = photon energy &
n = constant which depends on the type of transition
= 1/2 for direct allowed transitions, = 2 for indirect allowed transitions
= 3/2 for direct forbidden transitions, = 3 for indirect forbidden transitions

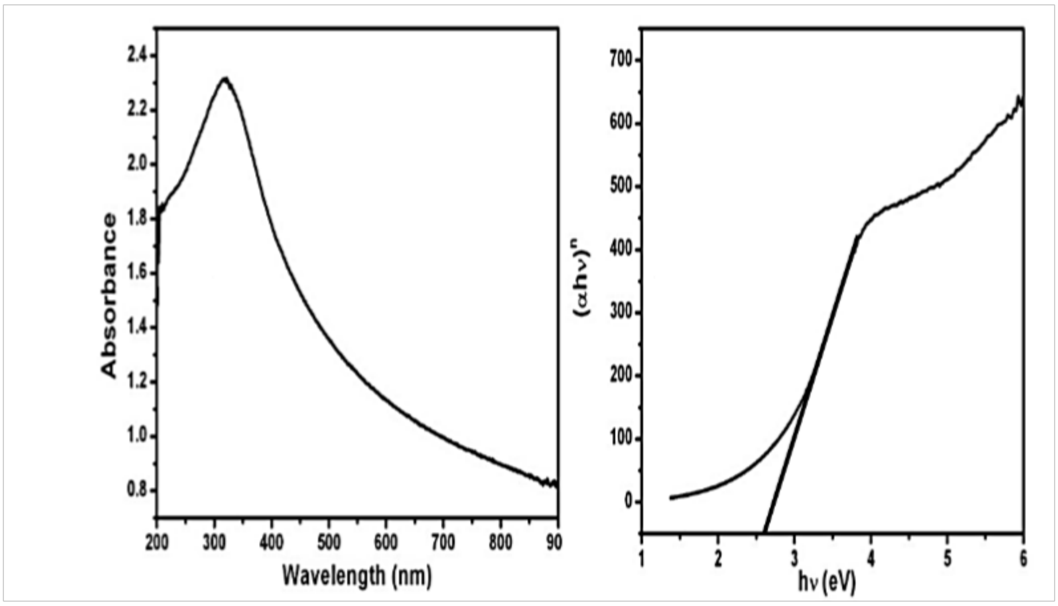


Figure 2.13: Absorption spectra and their corresponding Tauc's Plot

To determine optical bandgap, the absorption spectra is taken and from that absorption co efficient (α) is calculated. The graph between (αhν)n and hν is plotted. It is also known as Tauc's plot. The extrapolation of straight line region in Tauc's plot gives the bandgap energy.

Refractive Index (η)

The refractive index of the material is a measure for how much the speed of light is reduced inside the medium. The refractive index of the thin film or powder material can be determined by UV – Visible absorption spectra. V Kumar and J K Singh have proposed a relation to calculate the refractive index [12].

$$\eta = KE_g{}^C$$

η = refractive index, Eg = bandgap
K = constant = 3.3668, C = constant = - 0.32234

Instrumentation

UV-Vis spectroscopic measurements were done using UV-3600 Shimadzu spectrometer.

There are four basic components to a simple single beam UV/Vis spectrophotometer; a light source, a monochromator, a sample, and a detector. High sensitivity, high resolution, and an ultra-low stray-light level are achieved in this model.

Figure 2.14: Actual image of the instrument Shimadzu UV-3600 spectrometer

Features

- High Sensitivity
- High Resolution, Ultra-Low Stray-Light, and Wide Wavelength Range
- Wide Range of Optional Accessories [13]

Strength and Limitations

Strength

- Quick analysis ability
- Easy to operate

Limitations

- The stray light of UV-Vis spectrophotometer could influence spectra measurement accuracy of the absorption in substance it measures.
- Affecting the measurement accuracy and reduce the sensitivity of the instrument due to the amount of noise.

Applications

- Detection of Impurities in organic molecules.
- Structure elucidation of organic compounds.
- Quantitative determination of compounds that absorb UV radiation.
- Molecular weights of compounds can be measured spectro-photometrically by preparing the suitable derivatives of these compounds.
- UV spectrophotometer may be used as a detector for HPLC.
- Used to detect the presence or absence of functional group in the compound.
- Kinetics of reaction can also be studied using UV spectroscopy.
- Many drugs can be examined by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

References:

[1] Celebrating 100 years of X-ray crystallography, S. W. Wilkins; https://journals.iucr.org/a/issues/2013/01/00/me0486/

[2]https://www.xtal.iqfr.csic.es/Cristalografia/parte_10-en.htmlhttps://www.gnr.it/products/x-ray-diffraction/apd-2000-pro/

[3] N.R. Khalida, E.Ahmeda, Zhanglian Hon, M.Ahmada, Yuew Zhang Sadia Khalida, Ceramics International, 2013, 201339, 7107–7113. (Basics of X-Ray Powder Diffraction, Scott A Speakman, Ph.D.)

[4] Early history of Fourier transform spectroscopy, Pierre Connes, Infrared Phys. Vol. 24, No. 2/3. pp. 69-93, 1984

[5] https://www.shimadzu.eu/60-years-infrared-spectrophotometers

[6] https://jascoinc.com/products/spectroscopy/ftir-spectrometers/specifications/

[7] A Brief History of Fluorescence and Phosphorescence before the Emergence of Quantum Theory, Bernard Valeur and Mario N. Berberan-Santos

[8] https:// www.jascoinc.com › docs › product-spec-sheets › FP6500_072

[9] Evolution of UV-Vis Spectrophotometers, John Buie, 2011

[10] Skoog, et al. Principles of Instrumental Analysis. 6th ed. Thomson Brooks/Cole. 2007, 349-351.

[11] http://www.chemguide.co.uk/analysis/uvvisible/spectrometer.html.

[12] V Kumar and J K Singh, Indian Journal of pure and Applied Physics, 48, 2010, 571-574.

[13] https://www.upc.edu/sct/ca/documents_equipament/d_85_id-406.pdf