Chapter 3

Characterization Techniques

3.1 Introduction

In material science different instrumentation techniques are used for the purpose of characterization and investigation of different properties of material.

In the present thesis, the materials were prepared with an intention to change its structural and optical properties. This was done by using different synthesis techniques. The characterization of materials was done by X- ray diffraction to obtain structural information on an atomic scale for both crystalline and non-crystalline (amorphous) materials. The optical properties were determined by UV-Visible spectroscopy. The surface morphology was analyzed by Scanning Electron Microscopy. Different structural and optical parameters were also evaluated using these techniques.

3.2 X-ray diffraction (XRD)

X-ray diffraction is a nondestructive technique to determine crystal structures of metals, alloys, minerals, inorganic compounds, polymers and organic materials and to derive information such as crystallite size, lattice strain, crystalline phase and orientation.

3.2.1 Fundamental Principles of X-ray Diffraction

X-rays are electromagnetic radiation having lower wavelength. X-rays are generated in a cathode ray tube by heating a filament to produce electrons. These electrons are accelerated by applying voltage and bombarded on the target material. When electrons have sufficient energy to displace inner shell electrons of the target material, characteristic X-rays are produced. They consist of several components, the most common being K_α and K_β. The characteristic wavelength of X-ray depends on target material (Cu, Fe, Mo, Cr). The most common target material for powder diffraction is Cu. The wavelength of the K_α line in Cu is 1.5418 A° **[1]**.

In 1912, Max von Laue discovered that crystalline substances act as diffraction grating for X-ray wavelengths as the wavelength of X-rays is of the order of inter atomic spacing in crystals. These diffracted X-rays will interfere constructively or destructively. When a certain geometric requirement is met, the X-rays from crystalline material will interfere constructively. X-ray diffraction follows the principle of elastic scattering i.e. the change of direction of the electromagnetic waves motion without any energy loss.

Crystals are regular arrangement of atoms. The inter atomic spaces act as grating lines for diffraction. If many atoms are together then the scattered waves from all the atoms can interfere. If the scattered waves are in phase they interfere constructively and we get diffracted beam in certain direction. The direction of diffracted beam depends on incident wavelength and nature of crystalline material. The relation between the wavelength of X-rays and the spacing of the atomic planes was given by W. L. Bragg in 1913 **[2]**. A pattern of scattered X-rays or the diffraction pattern is mathematically related to the structural arrangement of atoms causing the scattering.

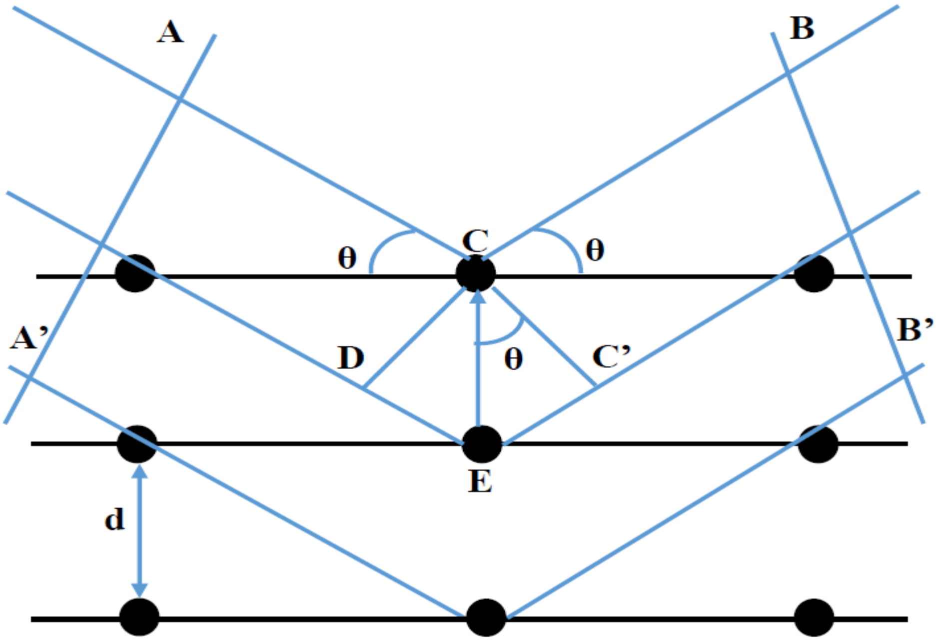

Figure:1 Diffraction of X-rays by crystal

A regular arrangement of atoms is shown in figure.1. Each plane of atoms reflects the incident wave. If the X-ray beam of wavelength λ is incident on a crystal plane at an angle θ, the diffracted wave makes the same angle with the atomic plane as does the incident wave. The difference in the path length between incident wave front AA’ and diffracted wave front BB’ must be an integral number (n) of wavelengths (λ) for constructive interference. Therefore the path difference δ must be

$$\delta = n\lambda \qquad (1)$$

Where n is an integer. Since lines CC’ and CD are also wave fronts,

$$\delta = DE + EC' = 2EC' \qquad (2)$$

From elementary trigonometry,

$$\delta = 2CE \sin\theta \qquad (3)$$

As CE is the inter planar spacing

$$\delta = 2d \sin\theta \qquad (4)$$

By combining (1) and (4),

$$n\lambda = 2d \sin\theta \qquad (5)$$

This equation is known as Bragg’s Law. By varying the angle θ, the Bragg’s Law conditions are satisfied by different d – spacing in polycrystalline materials.

3.2.2 Instrumentation for X-ray diffraction

The basic components of X-ray diffractometer are the X ray source, detector and assembly. The components lie on the circumference of circular arc.

Figure 2 shows geometry of an X-ray Diffractometer. The angle between the plane of specimen and the X-ray source is θ. The angle between the projection of X-ray source and the detector is 2θ. The X-ray diffraction pattern produced with this geometry is known as θ-2θ scan. In this geometry the X-ray source is fixed, and the detector moves through a range of angle. The 2θ measurement range is from 0° to 170°. The target range depends on crystal structure of material.

The θ-2θ geometry is the most common geometry. The other useful geometry is θ – θ geometry. In θ – θ geometry both X-ray source and the detector move in the vertical plane in opposite direction above the center of the specimen.

The diffractometer circle is also known as the goniometer circle. It is the circle centered at the specimen, and both the x ray source and the detector lie on the circumference of the circle.

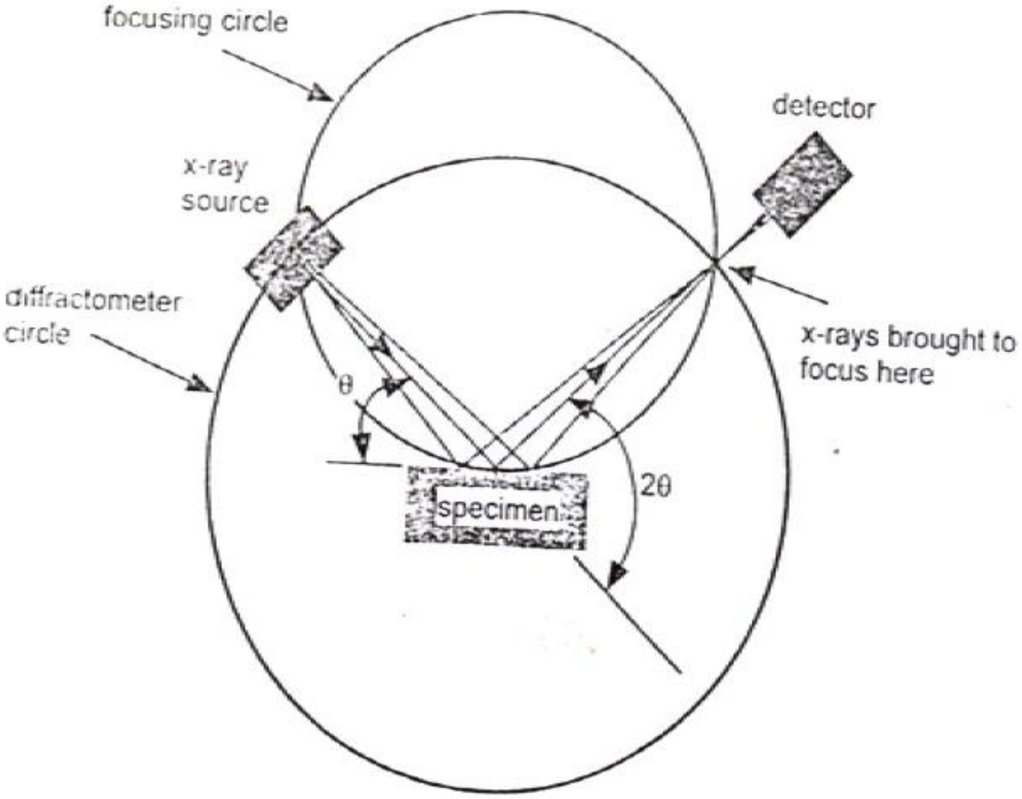

Figure 2: Geometry of an X-ray Diffractometer [2]

3.2.3 X-ray diffraction pattern

The X-ray diffraction pattern consists of a several peaks. The X-ray diffraction pattern is a plot of peak intensity versus diffraction angle (2θ). The peaks are also called reflections. Each reflection corresponds to x-ray diffracted from a specific set of planes of a crystal. The intensity is proportional to the number of x-ray photon of particular energy counted by detector. The position of the peak in x-ray diffraction pattern depends on the crystal structure of the material. The number of peak depends on the symmetry of crystal structure. As symmetry of crystal structure decreases the number of diffraction peak increases. The 2θ value of peak gives the information about the position of particular plane. The width of an individual peak, often defined as the full width at half the maximum (FWHM), can be used to determine crystallite size and the presence of lattice distortions (strain) in the crystal.

The Powder Diffraction data for the crystals has been compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). It is a collection of single phase x-ray powder diffraction patterns in the form of tables of interplanar spacing (d) and corresponding relative intensities. There are more than 100000 patterns in the database.

X-ray diffraction is most widely used for identification of unknown crystalline materials. Different structural parameters or information can be evaluated form x-ray diffraction pattern. Some of them are Crystallite size, Phase composition, Dislocation density, preferred orientation of different planes, Lattice strain and Lattice parameters.

Crystallite Size

The formula for the crystallite size determination was given by Scherrer. 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:

$$\boldsymbol{d = \frac{K\lambda}{\beta \cos\theta}}$$

Where,

d = crystallite size

K = dimensionless shape factor with the value of 0.94

λ = wavelength of X-ray used

β = line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening in (radians)

θ = Bragg diffraction angle

The Scherrer equation is limited to nano scale particles.

Phase Composition

The phase composition can also be determined from the x-ray diffraction pattern e.g. if two different phase of TiO_2 i.e. Anatase and Rutile exist together in material, the amount of one of the phase (Rutile) can be given by the following relation **[4]**.

$$\mathbf{X_R = [1 + 1.26(I_A/I_R)]^{-1}}$$

Where,

X_R = the mass fraction of Rutile

I_A = the intensity of the highest peak for Anatase

I_R =the intensity of the highest peak for Rutile.

Lattice Strain

In present work, the lattice strain is calculated using following relation **[5]**.

$$\eta = \left[\frac{\lambda}{t\cos\theta} - \beta\frac{\pi}{180}\right]\frac{1}{\tan\theta}$$

Where,

t = grain size

λ = wavelength of X-ray

β = full width at half maximum of the diffraction peak

θ = angle of diffraction.

Crystallinity Index

A parameter termed as the crystallinity index has been used to describe the relative amount of crystalline portion in material. The crystallinity Index can be calculated using following equation **[6]**.

$$CI = (I_{max} - I_{min})/ I_{max}$$

$$CI\ \% = \{(I_{max} - I_{min})/ I_{max}\} \times 100\ \%$$

Where,

I_{max} = height of the highest peak

I_{min} = height of the minimum of the highest peak

Lattice Parameters

The lattice parameters ‘a’ and ‘c’for tetragonal crystal structure can be calculated as mentioned below **[7]**.

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where, d = inter planar spacing determined using bragg’s equation

h, k, l = the miller indices of the lattice plane.

3.3 UV-Visible Spectroscopy

3.3.1 Introduction

UV-Visible absorption spectroscopy is an important technique to study the optical properties of material. It is also referred to as absorption spectroscopy or reflectance spectroscopy. Molecules absorb in the region of electromagnetic spectrum and undergo electronic transitions. In UV-Visible spectroscopy, the material is exposed to ultraviolet and visible radiation. The typical range or radiation wavelength for UV-Visible spectroscopy is 200 nm – 900 nm.

The basic principle of UV-Visible spectroscopy is transition of π- electrons or nonbonding electrons to higher anti-bonding molecular orbitals by absorbing energy in the form of ultraviolet or visible light **[8]**. The valence electron in a molecule can be found in one of the three types of electron orbital: σ – bonding (single bond) orbitals, π – bonding (multiple bond) orbitals and non – bonding (lone pair electrons) orbitals.

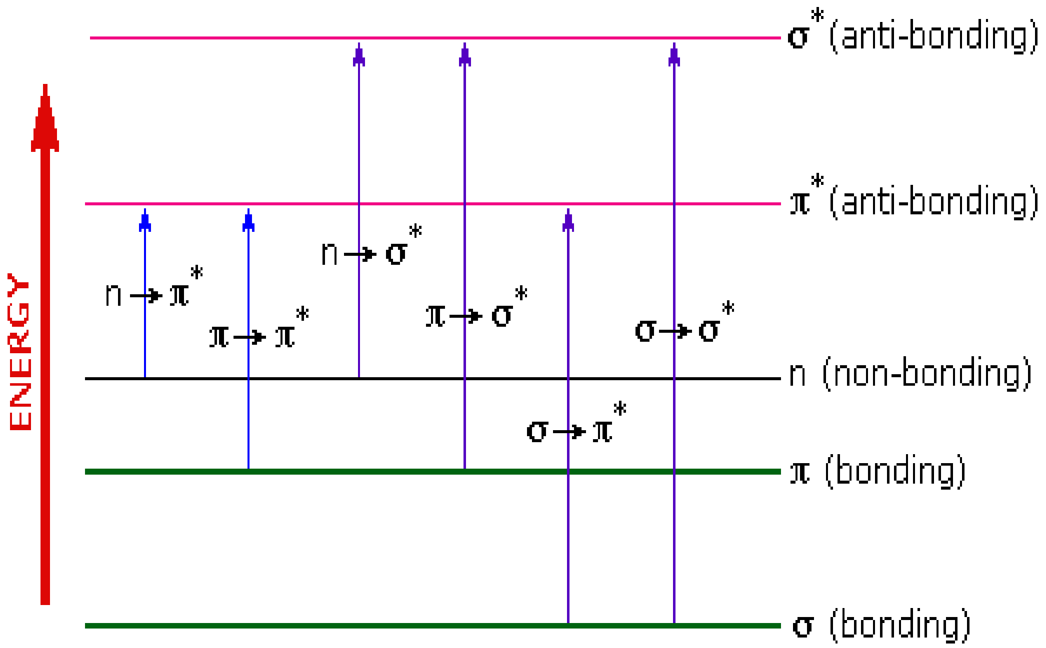

Figure 3: Different transitions between the bonding and anti-bonding electronic states [9].

σ – bond electrons have the lowest energy and they are the most stable electrons. High energy is required to displace these electrons to upper energy levels. The transition of these electrons requires absorption of lower wavelengths of ultraviolet radiations.

π – bond electrons have much high energy compared to σ – bond electrons and therefore they are relatively unstable. Less energy is required to displace these electrons and therefore they absorb ultraviolet and visible radiation.

Non – bonding electrons are electrons with high energy levels than π –electrons and σ – electrons. These electrons can be easily excited by ultraviolet or visible radiations **[10, 11]**. Figure 3 shows different transitions between the bonding and anti – bonding electronic states.

In UV-Visible spectroscopy most of the absorption occurs due to the transitions of π – electrons and non – bonding electrons.

3.3.2 The UV-Visible Spectrometer

The instrument used for UV-Visible spectroscopy is called UV-Visible Spectrometer. The instrument is based on 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.

$$\mathbf{A = \varepsilon\ l\ c}$$

Where,

A = measured absorbance

ε = the molar absorptivity of the substance

l = path length

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 (I_0) on the sample. The transmittance is given by I/I_0. The following equation gives the relation between absorbance and transmittance.

$$\mathbf{A = -\log (T) = -\log (I/I_0)}$$

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 (I_0). The ratio I/I_0 is called the reflectance.

The UV-Visible Spectrometer comprises of four basic components namely, light source, sample holder, monochromator and detector. The UV-Visible spectrometer needs a light source which gives the entire visible spectrum plus the near ultraviolet radiation. For this purpose, combination of different lamps is used. Deuterium lamp gives UV part of the spectrum whereas tungsten or halogen lamp gives visible part. Instead, the Xenon arc lamp with continuous emission from 160 – 900 nm can be used. Recently, light emitting diodes (LED) have been also used for visible wavelengths **[12]**. The monochromator consists of prism but currently gratings are used instead of prism. The detector is typically photomultiplier tube or photodiode. The sample holder for UV-Visible spectroscopy is often called as a cuvette or cell. The cuvette is made up of glass or quartz. The sample holder contains a dilute solution of the testing substance. The solvent is chosen so that it doesn’t absorb significant amount of light in the wavelength range 200 – 900 nm. Different solvents and their absorption wavelengths are given in table 1.

Table 1: Different solvents and their minimum wavelengths

Solvent	Minimum Wavelength (nm)
Ethanonitrile	190
Water	191
Cyclohexane	195
Hexane	201
Methanol	203
Ethanol	204
Ethoxyethane	215
Dichloromethane	220
Trichloromethane	237
Tetrachloromethane	257

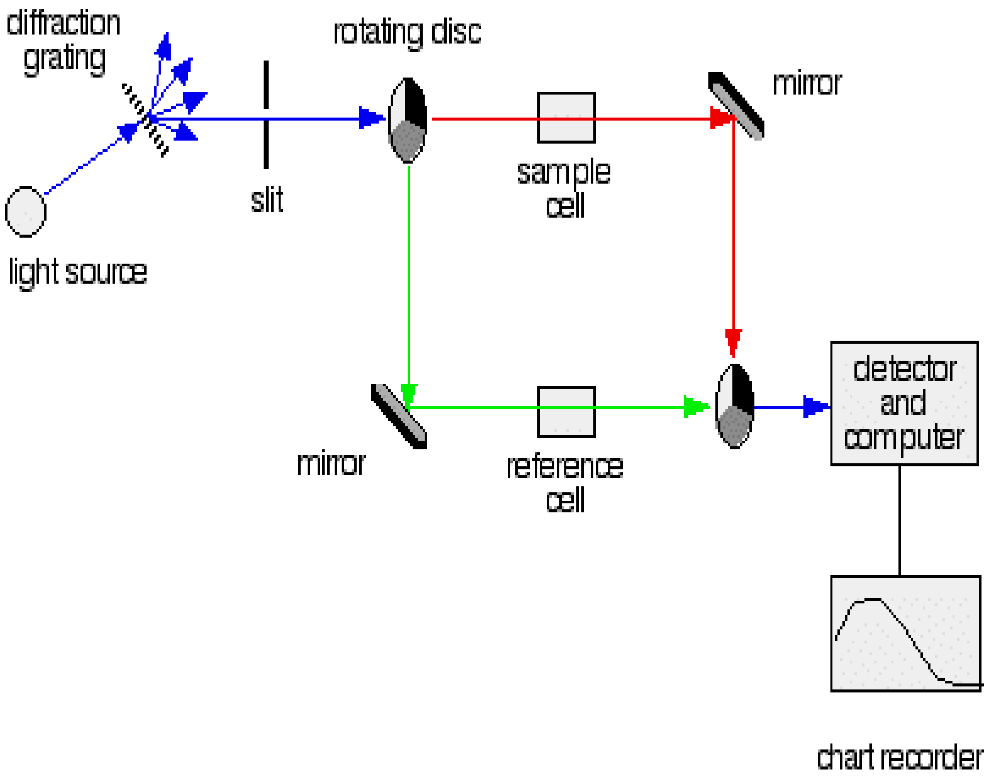

Figure 4: Schematic of UV-Visible Spectrometer [13]

Two types of arrangements are used in the UV-Visible spectrometer, single beam and dual beam. Figure 4 shows schematic diagram of dual beam UV-Visible spectrometer. The working of this instrument is very simple. A beam of light is separated into its component wavelengths by a prism or diffraction grating. The monochromatic beam from grating hits the rotating disc. The rotating disc is made up of three different segments, black section, mirrored section and transparent section.

If monochromatic light hits the transparent section it will straight away pass through the sample cell. From there it will divert to second rotating disc by mirror. The disc is rotating such that when the light arrives from the first disc, it meets the mirrored section of section of second disc. That bounces it onto the detector.

If the monochromatic beam hits the mirrored section of the first rotating disc, it is bounced down along the green path. From mirror it will pass through the reference cell. The light gets to the second disc where it meets the transparent section and goes straight to the detector.

If the monochromatic light meets the black section of first rotating disc, it is blocked and for a short while no light passes through the spectrometer. This just allows the computer to make allowance for any current generated by the detector in the absence of light.

3.3.3 Applications of UV-Visible Spectrometer

The UV- Visible Spectroscopy is very important technique to study optical properties of different materials. The UV-Visible spectroscopy has many applications in organic and biological chemistry. One of the most basic applications is to determine concentration of chromophore. The UV-Visible spectroscopy is also useful for the identification of organic compounds. By comparing the peaks on a given UV-Visible spectrum with a list of known peaks, it is possible to identify some structural features of unknown molecules. The identification of impurity in the material or different functional groups can also be done by UV – Visible spectroscopy.

It can be also used to study the optical properties of thin films like reflectance, transmittance or thickness of the film. Several methods have been developed to measure thickness of the film using UV-Visible Spectroscopy.

The UV-Visible spectroscopy gives the information about different optical constants like refractive index, extinction co-efficient, absorption co-efficient, optical conductivity, dielectric constants, etc. Jan Tauc has given a relation to determine the optical bandgap of material using UV-Visible absorption spectra.

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.

$$\boldsymbol{\alpha = \frac{2.303 \times Absorbance}{t}}$$

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 **[8]**. The formula of extinction co efficient is given below.

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

Where, α = absorption co efficient

λ = absorbed wavelength

Optical Bandgap (E_g 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.

$$\boldsymbol{\alpha = A(h\nu - E_g)^{1/n}}$$

Where,

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

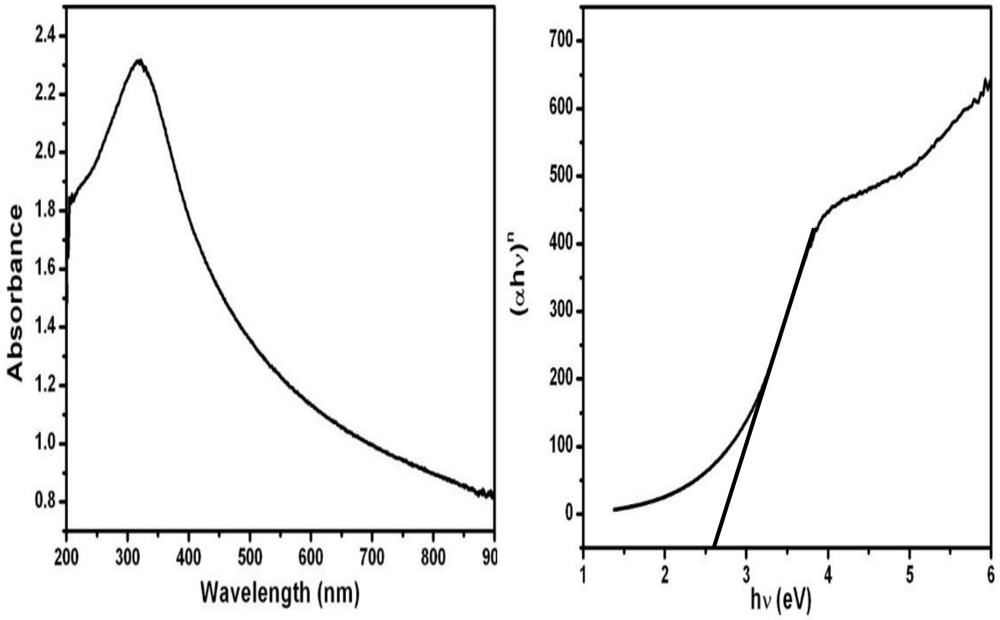

Figure 5: Absorption spectra and their corresponding Tauc's Plot

To determine optical bandgap, the absorption spectra is taken and from that absorption co efficient (α) is calculated. The graph between $(\alpha h\nu)^n$ 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. Both the absorption spectra and Tauc's plot are shown in figure 5.

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 **[14].**

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

Where,

η = refractive index

E_g = bandgap

K = constant = 3.3668

C = constant = - 0.32234

Optical Conductivity (σ)

Optical conductivity is a material property. The term optical conductivity means the electrical conductivity in the presence of an alternative electric field. The term optical here covers the entire frequency range and it is not restricted only to the visible region of spectrum **[15]**. The formula for optical conductivity is given below.

$$\boldsymbol{\sigma = \frac{\alpha \eta c}{4\pi}}$$

Where,

c = velocity of light

α = absorption co efficient

η = refractive index

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