CHAPTER - 3

Characterization

3.1 Introduction

In order to do systematic analysis, the experiment divided into ***three parts***. In the first part, undoped as well as doped $CdWO_4$ crystals have been synthesized with different dopants by Hydrothermal Method. In the second part of our experiment, we synthesized Cerium doped $CdWO_4$ by varying pH of the reaction medium at constant temperature by same method. Europium doped $CdWO_4$ with different pH of solution were synthesized in third part. After that the obtained samples were characterized by PL, XRD, TEM and FTIR. The details of the experimental set up and the instruments having been used for characterization of the synthesized phosphor has been explained in this chapter.

This chapter provides information of research techniques used in our study. The prepared phosphors were characterized by using techniques such as powder X-ray diffraction (XRD), Photoluminescence Spectroscopy (PL), Transmission Electron Microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

The instruments used for characterization in this study are as follows:

- X-ray diffraction technique (XRD) by Bruker D8 Advance X-ray diffractometer.
- Spectrofluorophotometer (SPF) by Shimadzu – RF 5301 PC.
- Fourier Transform Infrared Spectroscopy (FTIR) by Jasco FTIR- 4100, spectrophotometer.
- Transmission Electron Microscopy (TEM) by Tecnai 20 G2 FEI.

3.2 X-ray Diffraction (XRD)

3.2.1 Fundamentals of X-ray

After the radical invention of X-ray by Rontgen (November 8th, 1895), a large number of experiments were designed by different eminent scientists to find out the properties of this radiation and its dealings with matters. In 1915, M. Laue received the Nobel Prize in Physics for discovery of X-ray diffraction by crystals. After that, the X-ray diffraction (XRD) technique was known for study the structure of crystalline materials. XRD also attracted utmost interest as a unique non-destructive tool to extract the structural features of polycrystalline materials [1-3].These features play significant roles in analysis of different structural properties of the materials, and so their applications have added vital prominence in material science.

X-rays with energies in the range about 100 eV to 100 keV are classified as electromagnetic waves, which lies between γ-rays and ultraviolet radiation. X-ray wavelengths are shorter than those of uv rays and typically longer than those of γ-rays Their wavelengths are varying from 10 nm to 1 pm. X-rays have much shorter wavelength than visible light, which makes it possible to examine structures much smaller than what can be perceived using a regular microscope. It can be used in X-ray microscopy to acquire high resolution images, but also in X-ray crystallography determine the positions of atoms in crystals. The useful range of X-rays for crystal studies is between 0.05 nm to 0.25 nm, which is very close to inter-atomic space (0.2nm) in crystals. X-rays are produced in an X-ray tube when electrons strike a metal target. X-

ray tube consists of two metal electrodes; one is made by tungsten known as cathode and second is made by metal known as anode. When tungsten filament is heating at high negative potential, the electrons are emitted and moving towards the anode. The attenuation of energy of the electrons due to impact with the metal anode is displayed as X-rays. Only less than 1% of energy of the accelerated electron beam is converted to X-rays, the remaining is dissipated as heat in metal anode having water cooling system [4].

When an electron is removed from inner-shell, at the same time a hole (vacancy) is created in the electron shell and the atom will be remaining unstable. Assume this hole is generated in innermost K shell and it is filled by an electron from following outer L, M shell. At the same time, X-ray photon with definite energy equal to the difference in the electron energy levels is produced. Transitions from L to K results emission of $K\alpha_1$ and $K\alpha_2$ respectively. Similarly transition from M to K results emission of K_β X-ray as shown in figure 3.1. If the $K\alpha_1$ and $K\alpha_2$ lines cannot be resolved, the characteristic line is normally called the $K\alpha$ line and the wavelength is given by the weighted average of the $K\alpha_1$ and $K\alpha_2$ lines [4]. In our experiment we used Cu source having $K\alpha_1$ (1.5406 nm) and $K\alpha_2$ (1.54439 nm) and average of the $K\alpha_1$ and $K\alpha_2$ is found to be 1.54184 nm.

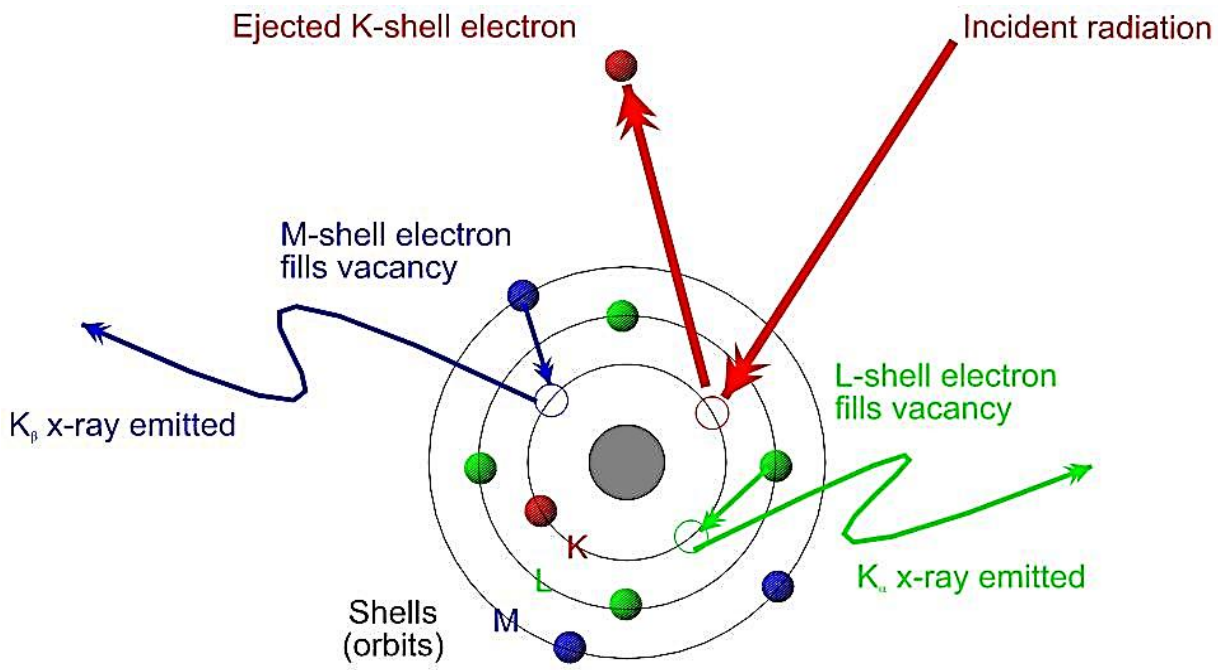


Figure 3.1 Characteristic X-ray productions.

3.2.2 X-ray diffractometer

X-ray diffraction (XRD) is a versatile, non-destructive characterization method used for finding atomic and molecular structure of a crystal, crystal size, atomic parameters, stress measurement, etc.[4]. It works on the principle of *diffraction*. A crystal is a periodic array of atoms or molecules and hence it can act as scattering centers for X-rays. Electrons around the atoms or molecules are responsible for elastic scattering of the X-rays, resulting the diffraction. If X-ray falls on these periodic arrangements of atoms or molecules, destructive and constructive diffraction pattern obtained according to Bragg's Diffraction law:

$$\mathbf{2d_{hkl} \sin \theta = n\lambda}$$

Where d_{hkl} is the inter-atomic spacing; θ is the incident angle which is also called as Bragg angle and λ is the wavelength of the incident x-ray used [4-10]. Figure 3.2 shows the schematic representation of X-ray diffraction pattern by a crystal for understanding of Bragg's law.

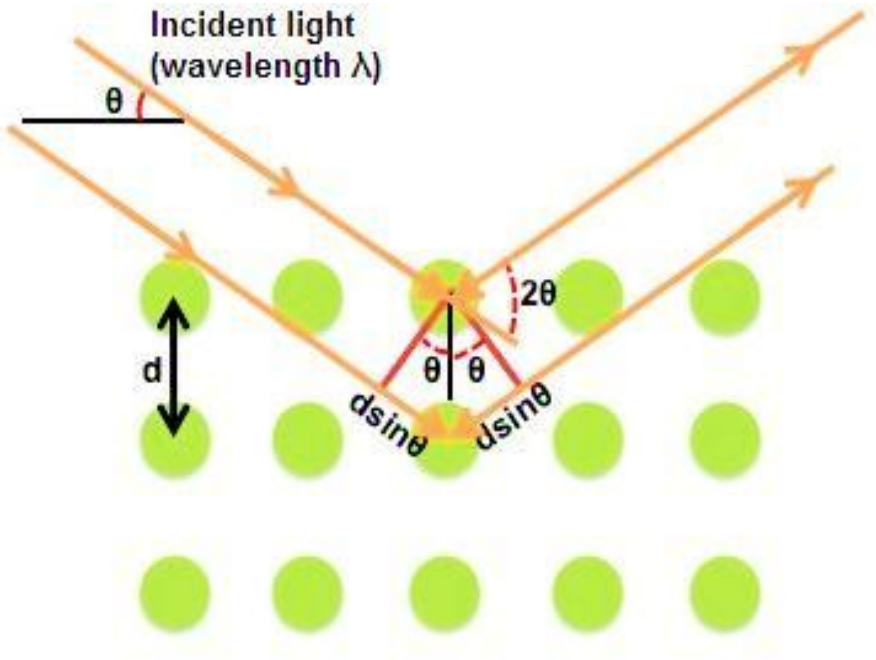


Figure 3.2 Schematic representation of x-ray diffraction pattern.

There are three basic components of an X-ray diffractometer: X-ray source, sample stage and X-ray detector. Source and detector are set on the circumference of a circle, which is known as focusing circle. An angle between the plane of the sample and plane of the X-ray source is θ considered as the Bragg angle. An angle between the projection of the X-ray source and the detector is 2θ.

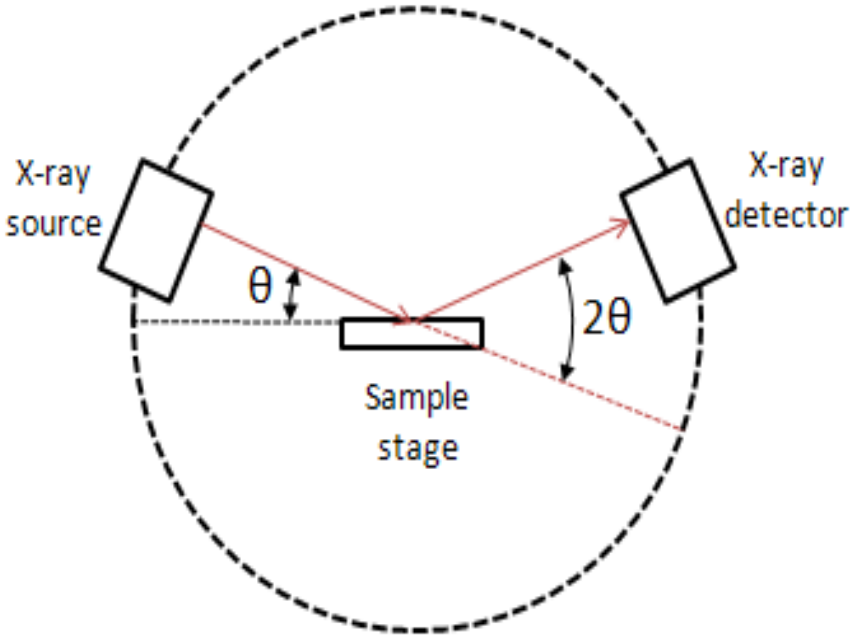


Figure 3.3 Goniometer circle

The goniometer is the central part of an X-ray diffractometer and is provide the specimen stage. The diffractometer circle also referred as the goniometer circle in which specimen is at center which is shown in figure 3.3. The X-ray source and the detector are mounted on goniometer arms [4]. This circle makes four different geometries which are employed to record X-ray patterns. The X-ray source is static and the detector travels through a selected range of angles in first geometry and is called the θ-2θ geometry. The second geometry is called θ-θ geometry in which both the X-ray source and the detector moves in the vertical plane in mutually opposite directions. Other two geometries are called ω geometry and ϕ geometry, are not widely used. Production of X-ray is depending on the

target metal, suitable operating voltage is required to knock out K electron. In our analysis, we supplied 40 kV operating voltage and 30 mA operating current to produce X-ray from copper (Cu) target.

3.2.3 Analysis of X-ray Pattern

X-ray diffraction patterns also known as reflections which contain of a series of peaks. The peak intensity is plotted on the ordinate (y-axis) and the obtained diffraction angle (2θ) along the abscissa (x-axis). The intensity is proportional to the number of X-ray photons of a particular energy counted by the detector in unit time for that particular angle 2θ. Since it is not possible to measure absolute value of intensity, it is usually expressed in arbitrary units. Each peak in the diffraction pattern corresponds to a specific set of planes by diffracted X-ray through specimen with certain intensity.

The intensity of the peaks depend on different factors i.e. structure factor, slit width, incident intensity and operating parameters used in the X-ray source. The positions of the reflections in an X-ray diffraction pattern depend on the shape and size of the unit cell of the $CdWO_4$crystal structure. It is also depends on the wavelength of the X-ray used. The full width at half the maximum height can be used to determine crystallite size and the presence of lattice distortions (strain) in the $CdWO_4$. At low values of 2θ, each reflection looks as a single sharp peak. For larger values of 2θ (above 80˚) each reflection involves of a pair of peaks, which attribute to diffraction of the $K\alpha_1$ and $K\alpha_2$ wavelengths. At small 2θ values of the separation of the peaks is quite less, but increases at higher 2θ values. The separation between $K\alpha_1$ and $K\alpha_2$ peaks increases from 0.05˚ at 20˚ (2θ) to 1.08˚ at 150˚ (2θ).

Broadening of X-ray diffraction peaks arises mainly due to three factors:

1. Crystallite size

Due to the effect of small crystallite sizes, the peaks become broader. Therefore, analysis of peak broadening can be used to determine the crystallite size.

Scherrer has derived a mathematical relation for broadening of X-ray diffraction peaks on the basis of small crystallite size.

$$B_{crystallite} = \frac{k\lambda}{L\cos\theta}$$

Where,

k = constant between 0.9 to 1.39

λ = wavelength of X-ray used

θ = Bragg angle

2. Lattice strain

   The lattice strain in the crystals also causes broadening of the X-ray peak, which can be expressed by the mathematical relationship,

$$B_{strain} = \eta tan\theta$$

   Where, η = strain in the material

3. Instrumental Effect

Improper focusing, disturbance in alignment of goniometer can causes the broadening of X-ray peaks.

3.2.4 Recording of X-ray spectra

XRD analysis of our samples has been done at two different scientific research institutes: One at under UGC-CSR Indore Center, Madhya Pradesh and Other at ERDA, Vadodara, Gujarat. The XRD analysis was carried out by Bruker D8 Advance X-ray diffractometer installed at the Indore Centre under UGC Consortium for scientific research facility shown in figure 3.4. The typical sample holder of the diffractometer has 9 sample changer, making it possible to measure up to 9 samples in one attempt. The diffractometer have a 1-D position sensitive detector based on silicon drift detector system which decreases the measurement time significantly without reduction in the diffracted intensity. The maximum count rate handled by this detector is around 10^8cps [4]. The inset in the photograph of the XRD system is the sample holder. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha). The X-rays were detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye Detector).

Figure 3.4 XRD instrument at UGC-CSR, Indore Centre.

Powder X-ray diffraction (XRD) patterns of some samples were recorded with a Japan Rigaku D/max-RB diffractometer (figure 3.4) in Electrical Research and Development Association (ERDA) at Vadodara. The scanning rate is 2˚/min and Cu K-alpha radiation ($\lambda = 0.15406$ nm) is used. The supplied operation voltage and current were fixed at 40 kV and 40mA, respectively.

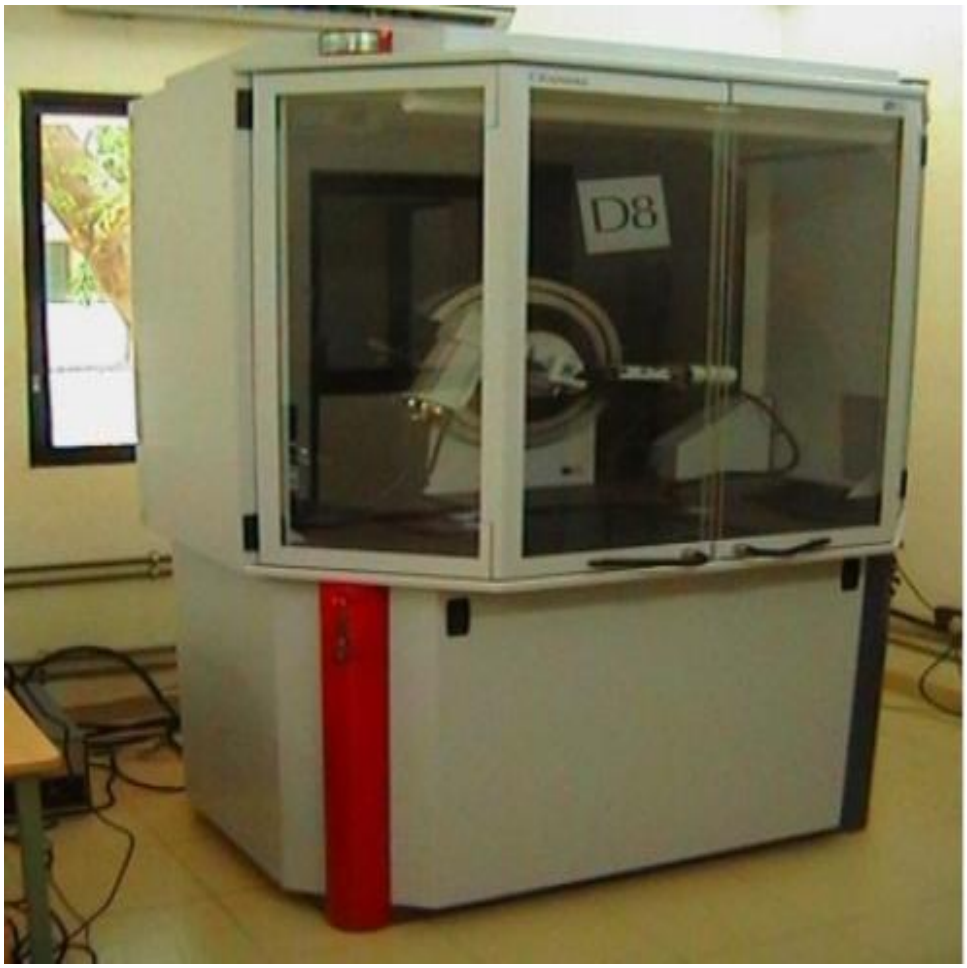


Figure 3.5 XRD instrument at ERDA, Vadodara.

3.2.5 Analysis of XRD Data

Computation of lattice parameters, unit cell volume and average crystallite size (using Debey-Scherrer formula) were performed in order to determine crystal structure and phase produced for all samples using Powder X program [4]. Calculation of XRD data had done by "Powder X" program (available free online or can get by e-mail: chengdon@aphy.iphy.ac.cn) provided by Cheng Dong, Institute of Physics, National Laboratory for Superconductivity, Institute of Physics, Chinese Academy of Sciences,

Beijing[4]. As obtained XRD file was imported to Powder X program. $K\alpha_2$ elimination was done by DONG's method. Noise elimination was performed by adaptive smoothing. Back ground substraction was performed via Sonnerveld method. Lastly peak search and indexing were done.

Application of X-ray Diffractometer

- To identify crystalline orientation and phases.
- To determine atomic arrangement of crystal.
- To measure thickness of thin films and multi-layers.
- To determine structural properties: Lattice parameters, Quantification of strain, Phase composition, Orientation order-disorder transformation, Thermal expansion etc.
- To detect dislocations and defects.
- To estimate substitutional dopant concentration.

3.3 Photoluminescence Spectroscopy

3.3.1 Introduction

The Photoluminescence Spectroscopy of the samples was investigated on a Shimadzu spectrofluorophotometer at room temperature with a xenon lamp as excitation source. It is the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. While relatively simple in concept, determining the reflectance or transmittance involves careful consideration of the geometrical and spectral conditions of the measurement [11]. It deals with visible light, near-ultraviolet, and near-infrared region of the spectrum. It is an instrument which takes advantage of luminescent properties of phosphor in order to provide information regarding their concentration and optical nature of sample. In photoluminescence, absorption of an ultraviolet or visible photon promotes a valence electron from its ground state to an excited state with conservation of the electron's spin. This phenomenon is called excitation. The excited states are not stable and will not stay indefinitely. If we observe a molecule in the excited state, at some random moment it will spontaneously return to the ground state. This return process is called decay, deactivation or relaxation. Under some special conditions, the energy absorbed during the excitation process is released during the relaxation in the form of a photon. This type of relaxation is called emission. Photon absorption occurs on a very short time scale (~10^{-15}seconds). If the molecule is excited beyond the first excited electronic state, it will usually rapidly lose energy via internal conversion, to reach the lowest energy singlet

excited state. In this process it takes ~10^{-12} seconds. In most cases, the excited state will vibrationally relax to reach the lowest energy state within the excited state [12].

3.3.2 Basics of PL Instrument

For study of excitation or emission spectra, information of the sample and knowledge of parameters used in recording the spectra such as slit width, optical filters, etc. are required. Recording of an excitation or emission spectrum is not simple task as it varies slightly from one instrument to another.

The PL instrument consist of light source, excitation and emission monochromators, sample holder (stage), optical filters and photomultiplier tube (detector). White light source is used in PL instrument. Xenon lamp is used as white light source which can provide an optimal light range approximately 250nm to 1000 nm. In our case, for $CdWO_4$ samples light range from 220nm to 650nm is used. The function of monochromators is to separate white or polychromatic light into various colors or wavelengths. It makes possible to choose a single desired excitation or emission wavelength to execute an emission or excitation scanning [5, 13-15]. To execute an excitation scan, the emission monochromator is adjusted at the desired wavelength and after that the excitation monochromator is scanned through the essential wavelength range. According to Stoke's law, the excitation scan wavelength shorter than the fixed emission wavelength. On the other side, emission scanning is performed by selecting a suitable excitation wavelength and emission monochromator is scanned by the needed

wavelength range. Mostly, the emission scanning occurs in longer wavelength than the fixed excitation wavelength [5].

After passing through excitation and emission monochromator light intensity is adjusted by excitation and emission slit widths. To obtain better resolution and signal-to-noise ratio of spectra, large emission slit width and small excitation slit width are assigned for excitation scan, while large excitation slit width and small emission slit width are assigned for emission scan [5,13-15]. After monochromators light is passing through optical filters which select transmit light in a particular range of wavelength, while blocking the remainder. Optical filters are often required to remove undesirable wavelengths in the excitation beam or to remove scattered light from the emission spectrum. A detector detects the light emitted from the sample as photon flux. This is usually performed by a PMT (photomultiplier tube). A PMT is a current source where the current is proportional to the light intensity or number of photons. A PMT multiplied the individual photons and detected as an average signal or counted as individual photons [5, 13-15].

For a typical excitation scan, a desired emission wavelength 610 nm (say) is monitored and the excitation monochromator is scanned throughout the required excitation wavelength range, 220 to 400 nm (say). In doing so, an optical filter of 515nm (say), which is within the maximum value to be scanned (400 nm in this case) and the monitored emission wavelength (610 nm) is selected. The filter remove second order artifact, in this case 305 nm (half of 610 nm), which might have creep and alter the excitation spectrum, if the filter has not been used. Similarly, an excitation wavelength,

286 nm (say), is monitored in recording an emission spectrum, 400 to 700 nm (say). In this case, a filter of 350 nm (say), which is between the monitored excitation wavelength (286 nm) and minimum value of emission (400 nm) is selected. This filter remove second order artifact at around 572 nm (double of 286 nm) which might have creep and alter the emission spectrum, if the filter has not been used. This will be elucidated in chapters 4, 5 and 6.

It is always useful to know sample's absorption or emission wavelength before making emission or excitation examinations. Even if proper spectroscopy data are not available, looking at the sample can provide valuable information. For example, samples that are transparent will most likely absorb in the UV and are likely to emit (if indeed there is emission) in the blue region of electromagnetic spectrum. Samples that have yellow color will absorb in the 400 nm region and will probably emit green or orange; samples that are blue will absorb at around 600-700 nm and will have dark red or even infrared emission [5,13]. However, if both the excitation and emission wavelengths of the sample are unknown then pre-scans are required to know either excitation or emission wavelength. In such case, a random value of excitation wavelength may be operated and scanned throughout the entire range of emission wavelength. The maximum peak intensity of the emission spectrum is considered and corresponding excitation spectrum is then recorded. The excitation maximum may not be the wavelength selected in recording the emission spectrum but it is the required excitation wavelength to be monitored in recording an emission spectrum of the sample to give maximum emission intensity. Further, validity or precision of the sample's emission spectrum can be checked by

comparing the color of light observed by naked eyes and the color of light determined from CIE (International Commission on Illumination; from French, Commission Internationale de l'éclairage) chromaticityco-ordinates and CIE diagram [5,16,17].

3.3.3 Excitation and Emission Spectra

An emission spectrum is the intensity - wavelength distribution of an emission measured with certain constant excitation wavelength. On the other hand, an excitation spectrum is the intensity - wavelength distribution of an excitation measured with certain constant emission wavelength. Such spectra can also be presented on different scale like photo energy, wave number and frequency. However, wavelength scale is not difficult to interpret visually. To obtain accurate spectra are difficult and therefore directly recorded uncorrected spectra are generally used [5, 13-15]. In most cases, the emission occurs at longer wavelengths than applied wavelength for excitation. This difference called **Stokes shift or down conversion** which is due to a variety of factors; some of these factors are intrinsic property of phosphor, impurity, method of synthesis, reaction parameter and size of particles. In some cases, the emission occurs at shorter wavelength than applied wavelength for excitation. This difference known as Anti Stoke shift or Up conversion.In emission spectrum presence of four- five Gaussian components indicates the excited states of emission centre are relaxed and degenerated under the influence of perturbation.

3.3.4 Spectrofluorophotometre

The PL of the samples was investigated on a Shimadzu spectrofluorophotometer at room temperature with a xenon lamp as excitation source. We have done PL analysis of our

samples at Display Materials Laboratory, Applied Physics Department, Faculty of Technology, The M S University of Baroda, Vadodara, Gujarat. The information and write up of spectrofluorophotometer are collected from the laboratory as given below:

1. Optical System of Spectrofluorophotometer: The spectrofluorophotometer irradiates a sample with excitation light and measures the fluorescence emitted from the irradiated sample to perform a qualitative or quantitative analysis. A typical configuration of the spectrofluorophotometer is schematically described, figure-3.6, taking the RF-5301 PC instrument as an example. The excitation monochromator (1) isolates a band of a particular wavelength from the light from the Xenon lamp to obtain excitation light. Since brighter excitation light will contribute to higher sensitivity of the spectrofluorophotometer, the excitation monochromator incorporates a diffraction grating with a larger aperture to collect the largest possible amount of light. The cell holder (2) holds a cell filled with sample. The emission monochromator (3) selectively receives fluorescence emitted from the sample and its photomultiplier tube measures the intensity of the fluorescence. This monochromator has a diffraction grating whose size is the same as that of the excitation monochromator to collect the greatest possible amount of light. The photomultiplier tube (4) is for monitoring. Generally, the Xenon lamps used on spectrofluorophotometer are characterized by very high emission intensity and an uninterrupted radiation spectrum. However, their tendency to unstable light emission will result in greater signal noise if no counter measure is incorporated. In addition, the non-uniformity in the radiation spectrum_ of the Xenon lamp and in the spectral sensitivity

characteristics of the photomultiplier tube (these criteria are generally called instrument functions) causes distortion in the spectrum. To overcome these factors, the photomultiplier tube (4) monitors a portion of excitation light and feeds the resultant signal back to the photomultiplier tube (5) for fluorescence scanning [18-20].

2. Design of the Spectrofluorophotometer: Figure 3.6 illustrated the optical system of the RF-5301PC instrument. A 150 W Xenon lamp (1) serves as the light source. The uniquely designed lamp housing contains generated ozone in it and decomposes the ozone by means of the heat produced by the5lamp. The bright spot on the Xenon lamp is magnified and converged by the ellipsoidal mirror (2) and then further converged on the inlet slit of the slit Assy. (excitation side) (3) by the concave mirror (4). A portion of the light isolated by the concave grating (5) passes through the outlet slit, travels through the condenser lens (11) and illuminates the sample cell. (The concave grating in both the monochromators is a highly-efficient ion-blazed holographic grating). To achieve light - source compensation, a portion of the excitation light is reflected by the beam splitter quartz plate (6) and directed to the Teflon reflector plate 1 (7). The diffusely reflected light from the reflector plate I (7) then passes through the aperture for light quantity balancing (21) and illuminates the Teflon reflector plate 2 (8). Reflected by the reflector plate 2 (8), the diffuse light is attenuated to a specific ratio by the optical attenuator (9) and then reaches the photomultiplier for monitoring (10). The fluorescence occurring on the cell is directed through the lens (13) to the emission monochromator that comprises the slit Assy. (14) and the concave grating (15). Then, the isolated lights introduced

through the concave mirror (16) into the photomultiplier for photometry (17) and the resultant electrical signal is fed to the preamplifier. The spectra recorded using the above instrument displays the spectra along with the peak data the same can be copied to any other format, which is user-friendly software. Figure 3.7 shows photographs of spectrofluorophotometer and powder sample holder.

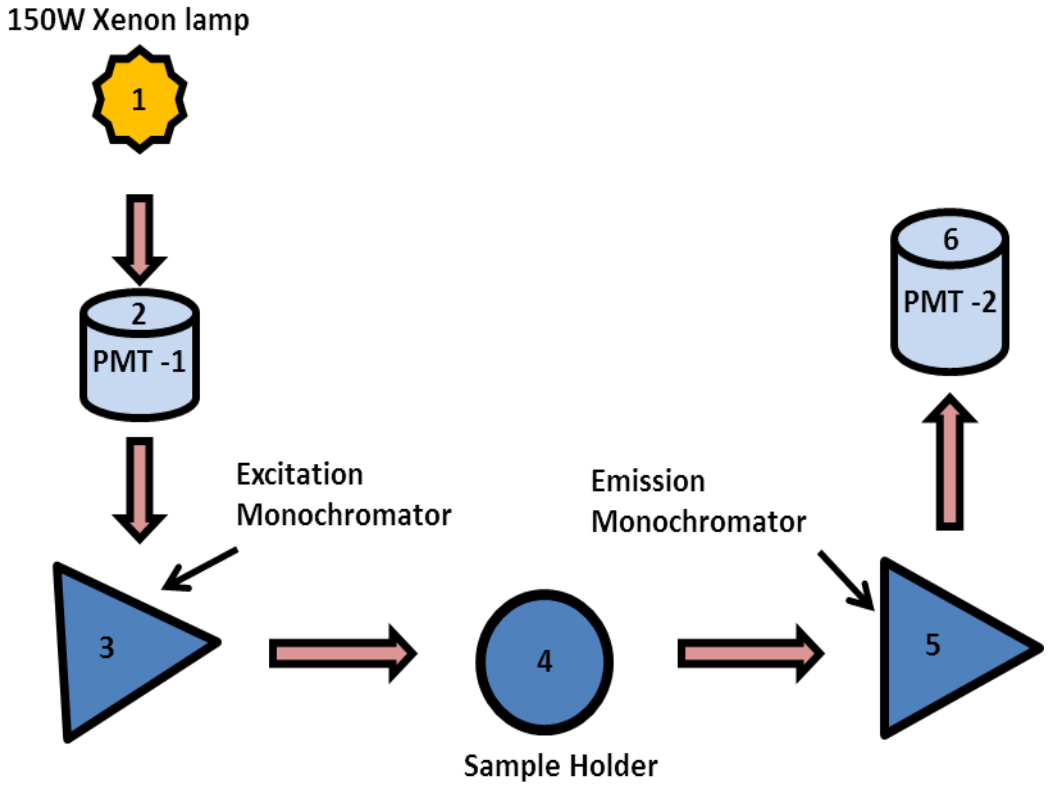
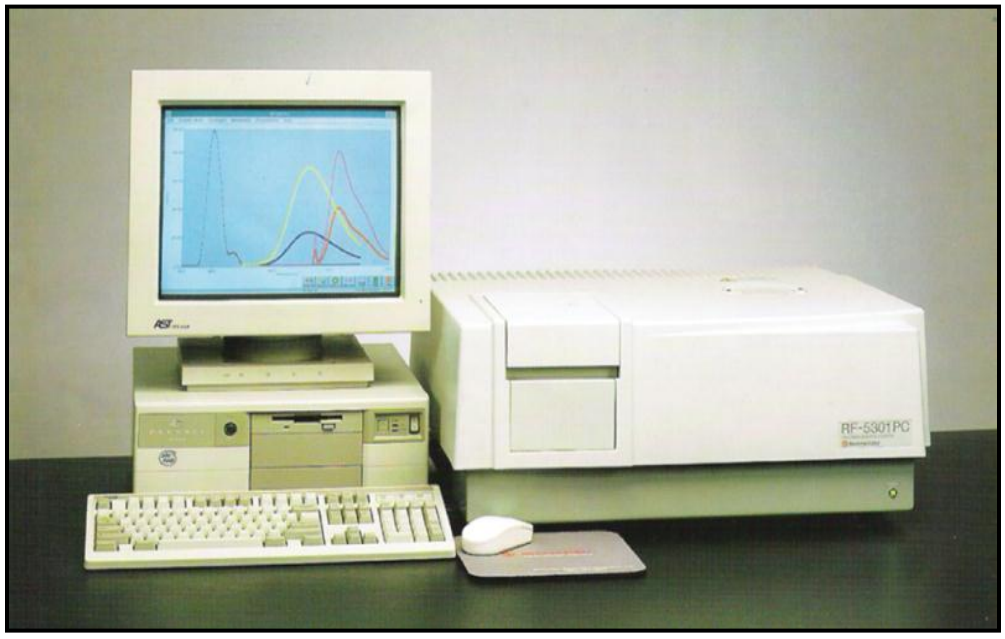


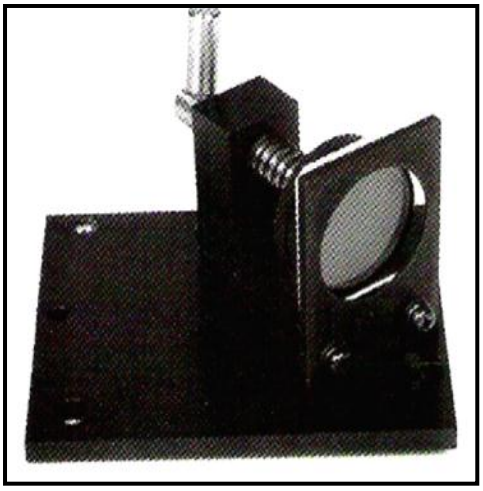
Figure 3.6 Constitution of RF-5301 PC.

(1) 150 W Xenon lamp (2) Excitation monochromator,(3) Sample holder,

(4) Emission monochromator,(5)Photomultiplier tube - 1, (6) Photomultiplier tube - 2



(a)



(b)

Figure 3.7 a) Spectrofluorophotometer (b) RF-5301 PC with Powder Sample Holder

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) can provide very useful information about functional group. The method can be used to examine functional group of organic materials and inorganic materials. Since no two compounds have similar atomic combination, no two compounds formed the similar infrared spectrum and hence infrared spectroscopy can effectively be used for identification of different samples [5, 18-20].

The FTIR technique is to count the absorption of various infrared radiations by the target material, to develop an IR spectrum that can be used to recognize functional groups and molecular structure in the sample. Two methods can be used for the FTIR analysis depending sample's chemical characteristics i.e. Transmission mode and Absorption mode. IR spectra are collected from the sample by Microscope, FTIR under transmission mode (Transmittance), and using clean area as background. An infrared spectrum represents a pattern of a sample with absorption peaks which correspond to the frequencies of vibrational bonds of the constituent of the sample by Microscope FTIR under absorption mode (Absorbance).

1. Infrared Spectroscopy: Infrared spectroscopy has been an effective technique for material analysis in the laboratory for over seventy years. 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.

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.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.

Most interferometers employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place. The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the

signal which 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 means that as the interferogram is measured; all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. It means of "decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis [18-20].

2. The Sample Analysis Method: The normal instrumental method is given as follows:

The original infrared spectroscopy is of dispersive nature where prism or grating is used as a dispersive medium of frequencies emitted from an infrared source. The amount of energy at each frequency passing through sample is measured by detector. Due to this scanning process over the entire frequency range become slow. Interferometer is an instrument which can measure all the frequencies simultaneously rather than individually. It generates a signal called interferogram, which has the exceptional property that signal made by data points contain information about every infrared frequency coming from source. This means that all the frequencies are measured simultaneously as the interferogram is measured results into extremely fast measurement. The measured

interferogram explicated by a mathematical technique called Fourier transform and named as Fourier Transform Infrared (or FT-IR) spectroscopy [5, 21-23].

To first step to measure a typical FT-IR spectrum of a sample is to assess the background or reference (without the sample). That is, a thin ~1 mm translucent pellet of KBr is scanned. Dimension of KBr pellet makes probable recognition of impurities in the KBr and instrumental artifacts, which may change the real identity of the sample. Then spectrum of the sample is measured by making a pellet, which is a mixture of the sample and KBr in the ratio ~ 1:10.

A glowing black-body is the source emitting Infrared energy and this beam passes through an aperture which controls the amount of energy presented in the sample "Spectral encoding" takes place when this beam enters the interferometer. When beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. Sample are having unique characteristic under which specific frequencies of energy are absorbed. Finally, the beam passes to the detector for final measurement to measure the special interferogram signal.

The measured signal is digitized and sent to the computer where the Fourier transformation takes place and final infrared spectrum is then presented to the user for interpretation and for further manipulation.

Advantages of FT-IR:

- Sensitivity: The Sensitivity of FT-IR is much higher, which reduces desired noise levels and initiate fast scan.

- Speed: FT-IR can measure all the frequencies at the same time in fraction of seconds.
- 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.
- Internal Calibration: These instruments employ a He-Ne laser as an internal wavelength calibration standard. These instruments are self-calibrating and never need to be calibrated by the user.

Figure 3.8 FTIR Instrument Jasco-4100

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it is a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it is batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis.

Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis. Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

3.5 Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electron instead of light. In light microscope resolution is limited which is related to wavelength of light. TEM uses electron as light source and their much lower wavelength makes it possible to get a resolution a thousand times better than with a light microscope. We can see objects to the order of a few angstrom (10^{-10}m).Due to high magnifications; TEM is valuable tool in material science as well as medical science [24]. Figure 3.9 shows layout of optical components in a basic TEM.

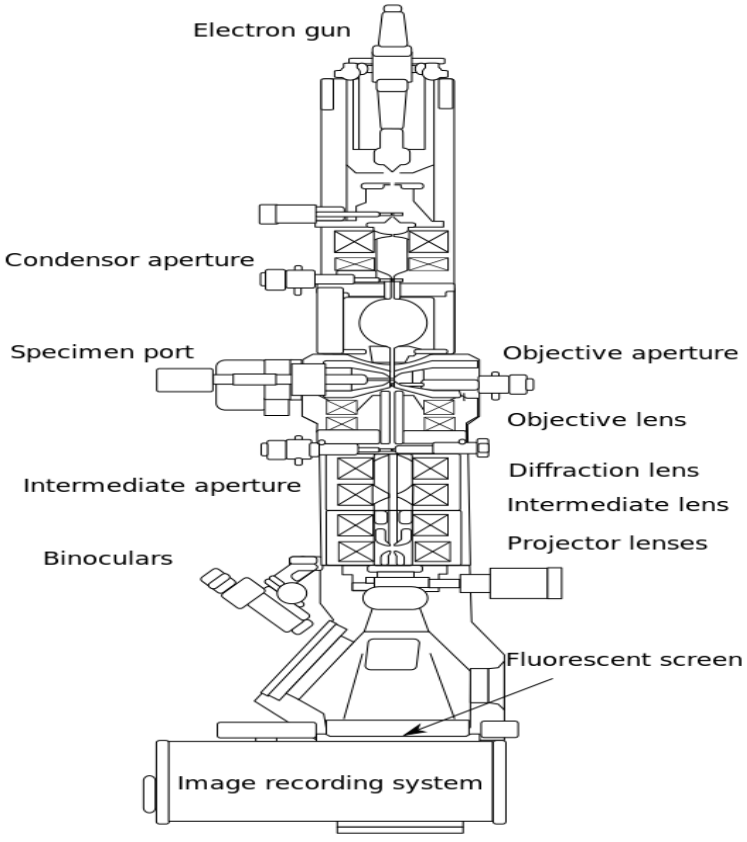


Figure 3.9 Layout of optical components in a basic TEM [25]

The uncertainty principle sets a fundamental limit on the spatial resolution while using a beam of particles with de Broglie wavelength. Thus, smaller the wavelength of the source, higher will be the resolution of the system. In the transmission electron microscopy, much smaller wavelength electrons (0.03Å) are used instead of photons ($\lambda >$ 1000 Å) providing much higher resolution. During TEM analysis, a thin sample is bathed with a collimated beam of accelerating electrons uniformly over the illuminated area. Electrons being charged in nature, can be easily deflected using an external electric or magnetic field and can be accelerated using external potential [26]. As the electrons travel through the sample, they are either scattered or are transmitted unaffected through the sample. The probability of scattering is described in terms of the interaction cross-section or the mean free path and can be elastic or inelastic. This results into a non-uniform distribution of electrons in the beam that comes out of the sample, which contains all the structural information of the sample [27].

The scattered (diffracted) electrons deflected away from the optical axis of the microscope are blocked using an aperture and thus the transmitted electron beam generates a contrast on the fluorescent screen depending on its varying intensity. In the case of nanomaterials, the crystalline structures interact with the electron beam mainly by diffraction rather than absorption, though the intensity of the transmitted beam depends largely on the density and thickness of the material though which it passes. The intensity of the diffraction thus depends on the orientation of the planes of atom in the crystal relative to the electron beam. Angular distribution of electrons due to diffraction can be viewed in the form of scattering patterns, usually called diffraction patterns, and spatial

distribution of electrons can be observed as contrast in images of the sample. Figure 3.8 shows the layout of the various components of a transmission electron microscope. The transmitted electron beam strikes the fluorescent screen and generates an image with varying contrast. The darker areas with higher contrast are those from where fewer electrons have been transmitted due to high density or thickness of the sample while the areas of lower contrast show the areas in the sample, which have less density or thickness, and thus more number of transmitted electrons are present. In the present study, TEM has been used for analyzing the shape and size of different sample of $CdWO_4$. We have done XRD analysis of our samples at under UGC-CSR Indore Center, Madhya Pradesh (figure 3.10).

Figure 3.10 TEM instrument at UGC-CSR, Indore Centre

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