Chapter 2

Synthesis and characterization techniques

This chapter includes the details of the cost-efficient and environment-friendly synthesis process used to synthesize the phosphors. The details of the characterization tools and the instruments used for characterization are also discussed in this chapter.

2.1 Overview

This chapter outlines the detailed sample preparation and experimental tools utilized for characterizing the prepared phosphors. In the present investigation, the phosphor compositions were synthesized by the urea-assisted auto-combustion and citrate sol-gel method. This chapter also describes the description of the apparatus and the procedure used for characterization. The chapter starts with the techniques and steps needed in the synthesis of doped $SrMoO_4$ and $Zn_3(VO_4)_2$ phosphors, followed by a discussion on the experimental techniques used for the measurement of structural and luminescence properties.

2.2 Synthesis of the composition

2.2.1 Doped $SrMoO_4$ compositions

The doped compositions of $SrMoO_4$ phosphors were prepared by urea assisted auto-combustion method. Fig. 2.1 explains the steps involved in the synthesis of the phosphors. Typically for the synthesis of doped $SrMoO_4$ phosphor, the stoichiometric quantity of rare-earth nitrates, strontium oxide, and precursors of other dopants were taken in a clean vessel with nitric acid in it. The solution was constantly stirred for 1 hour. To eliminate the surplus acid, the mixture was constantly heated. The stoichiometric quantity of ammonium molybdate (para) tetrahydrate was combined with double-distilled water in another beaker. For further 2 hours, the ammonium molybdate solution was constantly stirred. The Urea was then added to this solution with its mole ratio of metal nitrates as 2:1. The two solutions were combined, and the resulting solution was maintained at 100 °C until the surplus water is evaporated. After drying, the material was placed in a hot air oven set at 250 °C for 12 hours. The material was then powdered and put in a closed furnace for 4 hours of calcination at 1000 °C. The same process was used to make all of the phosphors. Fig. 2.1 depicts the schematic of the synthesis process.

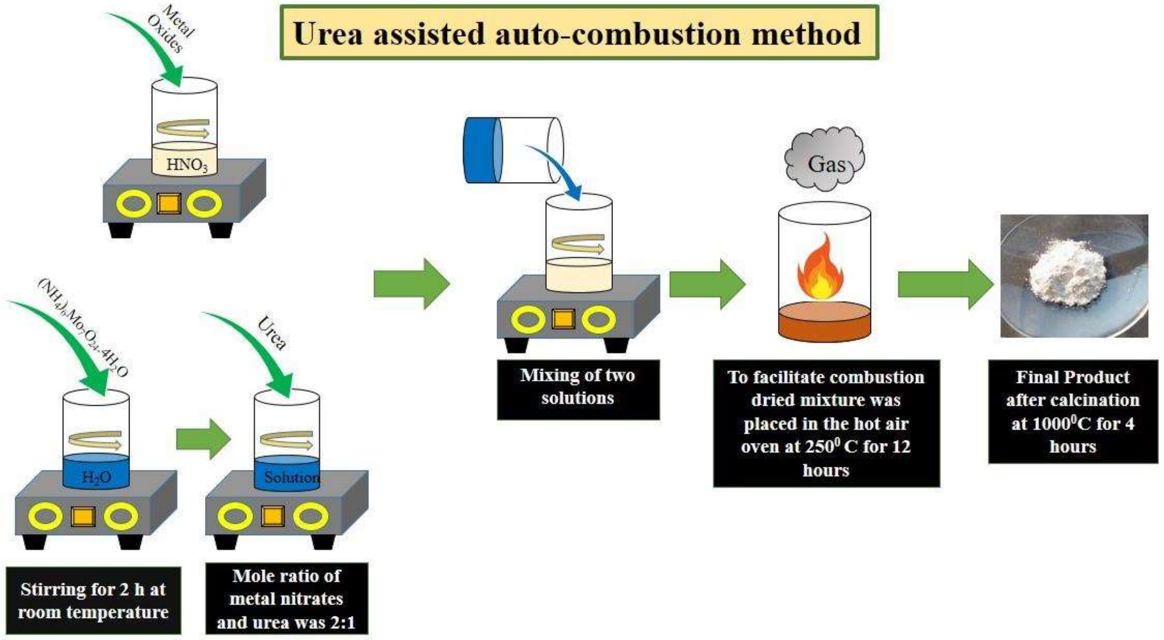

Fig. 2.1 Schematic of the auto-combustion synthesis process.

2.2.1 Doped $Zn_3(VO_4)_2$ compositions

The doped compositions of $Zn_3(VO_4)_2$ were prepared by the citrate sol-gel method. Fig. 2.2 explains the steps involved in the synthesis of the phosphors. At the start, the stoichiometric quantity of ammonium metavanadate and metal nitrates were mixed in a beaker containing distilled water (100 ml) for 1 h. After some time, the solution turns pale yellow and the temperature was raised to 80 °C. Later, citric acid in a molar ratio (metal ion/citric acid) 1:2, was added to the solution, which turns it yellow and transparent. After another 1 hour of stirring, the solution becomes blue, and the surplus water was evaporated. The dry gel was maintained at 250 °C for 12 hours before being annealed at 700 °C for 4 hours.

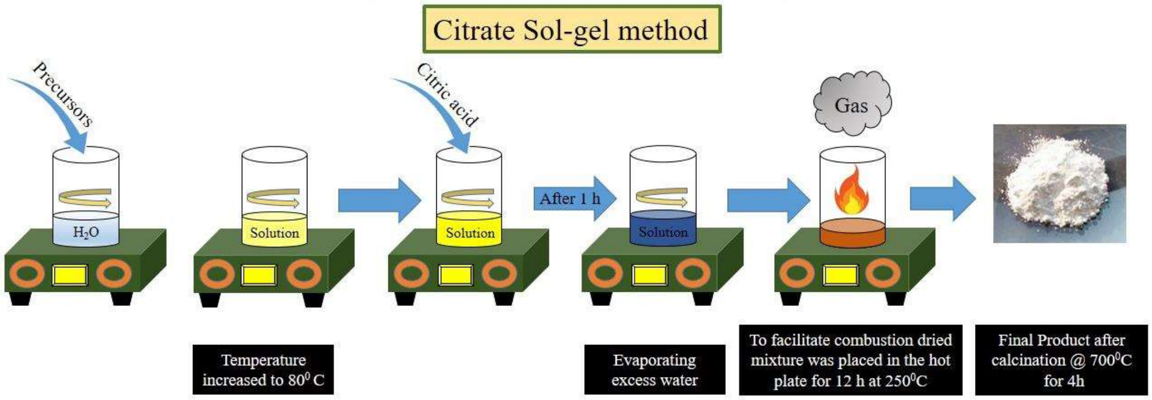

Fig. 2.2 Schematic of the citrate sol-gel synthesis method.

2.3 Characterizations techniques & their working principle

The techniques utilized to investigate the structural and luminescent characteristics of the materials are listed below and detailed descriptions in different sections.

- Structural properties: X-ray diffraction, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy.
- Elemental analysis: Energy dispersive X-ray spectroscopy.
- Surface morphology: Scanning electron microscopy.
- Absorption properties: UV-Vis spectroscopy.
- Photoluminescence properties: Photoluminescence excitation and emission spectroscopy, Photoluminescence decay analysis, Temperature-dependent photoluminescence properties.

2.3.1 X-ray diffraction:

X-ray diffraction (XRD) is a critical method for identifying and quantifying crystal structure and phase, as well as in determining crystallite size and microstrain. The XRD plots are also used to fetch refined atomic positions, lattice parameters, bond angles, and bond lengths after the Rietveld refinement. The Rigaku-MiniFlex 600 desktop x-ray diffraction system was used to record the XRD patterns of the powdered phosphors. The system is equipped with a 600 W Cu K_{α} radiation source (λ=1.5418 Å), NaI scintillation counter detector, and graphite monochromator. The X-ray diffractometer and the schematic representation of X-ray diffraction are presented in Fig. 2.3 (a) and (b), respectively.

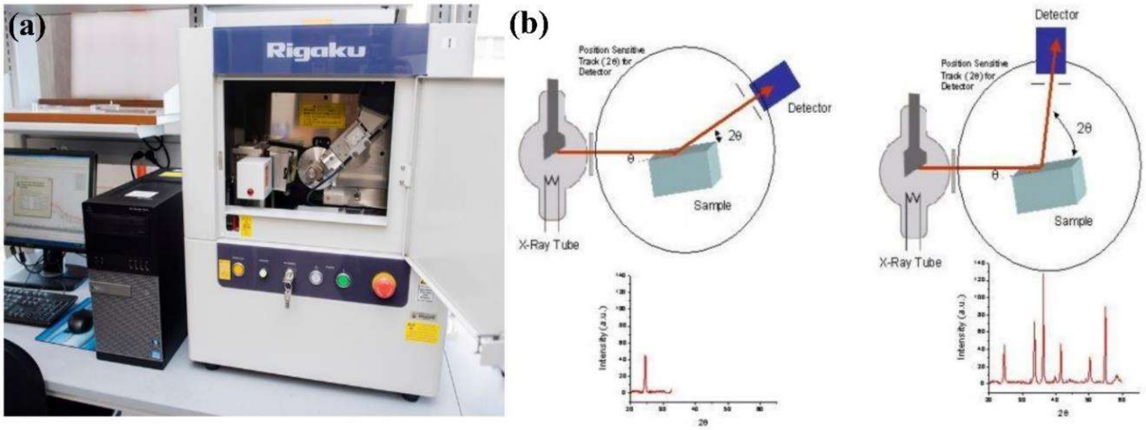

Fig. 2.3 (a) X-ray Diffractometer **(b)** Schematic representation of X-ray diffraction.

When an incoming beam contacts a powder sample, diffraction occurs in every conceivable direction of 2θ, as illustrated in Fig. 2.3 (b). A movable detector (NaI scintillation counter) linked to a chart recorder is used to detect the diffracted beam. In normal operation, the counter is configured to scan over a range of 2θ values at a constant angular velocity. Generally, a 2θ range of 10 to 90 degrees is enough to cover the important aspect of the specimen's crystal information. The identification of single or multiple phases aids in understanding the mechanism of sample formation.

The formulation of the XRD was first proposed by Sir Lawrence Bragg and Sir William Henry Bragg in 1913. They discovered that crystalline solids produce intense peaks of reflected radiation at specific wavelengths and incident angles. When a crystalline solid is bombarded with X-ray radiation of a wavelength comparable to the atomic spacing of the crystal lattice planes (d) and at a certain incident angle (θ), intense reflected X-rays are produced when the wavelength of the scattered X-rays (λ) interfere constructively. When the difference in the travel path is equal to the integral multiple of the wavelength, the scattered waves interfere constructively. When constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam. The condition for constructive interference is given by Bragg's law,

$$2dsin\theta \ = \ n\lambda$$

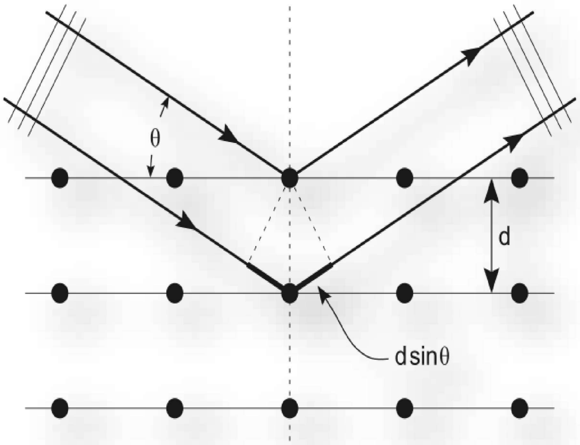

Fig. 2.4 Bragg's diffraction from atomic planes

2.3.2 Scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDS)

The SEM images are used to investigate the texture (morphology), crystallite structure, grain size, and orientation of the components that comprise the sample. The EDX was employed for both qualitative and quantitative examination of all elements that comprise the sample. The OXFORD Instrument SEM EVO 18 Research set up used for SEM and EDS analysis is shown in Fig. 2.5. The interaction of an electron beam with an atom at various depths within a sample generates different signals such as the secondary electrons, characteristic X-ray, backscattered electrons, cathodoluminescence, transmitted electrons, and absorbed current (specimen current). The signals are used by SEM to produce an image. Detecting all signals in an instrument is difficult. The standard equipment in all SEM is a secondary electron detector. Secondary electron imaging detects the secondary electrons that are released from the top surface of the specimen. SEM examination can be used to get very high-resolution images of a specimen's surface. Backscattered electrons are beam electrons that are reflected off a material due to elastic scattering. The resolution of backscattered electrons (BSE) is less than the secondary electron due to its origin from deeper locations within the specimen. The strength of the BSE signal is highly connected to the specimen's atomic number (Z), thus BSE pictures may be utilized to get information about the distribution of various elements in the sample. The sample in powder, as well as, palette form can be used for SEM analysis.

EDX spectroscopy is used to get information about the presence of an element as well as the atomic and weight percentage of an element in the sample. The energy-dispersive spectrometer measures the energy and amount of X-rays released by the material as a result of an energy difference between the higher and lower-energy shells. Since the energies of the X-rays are typical of the atomic structure of the emitting element and the energy difference between the two shells. Therefore, EDX may be used to determine the elemental makeup of the sample. The EDX is equipped with an SEM setup.

Fig. 2.5 SEM- EDS set up.

2.3.3 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectrum was utilized to learn about inter or intramolecular interaction, functional groups, and vibrational modes. FTIR spectroscopy is employed to collect an infrared spectrum of absorption, emission, and infrared inelastic scattering of a sample (solid, liquid, or gas). FTIR spectrometer obtains spectral data in a wide spectral range. This gives it a substantial edge over other spectrometers that measure intensity across a limited range of wavelengths at a time. The FTIR approach has eliminated the need for dispersive infrared spectrometers and opened up new possibilities for infrared spectroscopy. The phrase Fourier transform in FTIR spectroscopy refers to the process of converting raw data into an actual spectrum using a Fourier transform (a mathematical method). A schematic diagram for an FTIR spectrometer is shown in Fig 2.6 (a). The horizontal axis represents the mirror's location, while the vertical axis represents the amount of light measured. This is the "raw data" from which a spectrum can be generated.

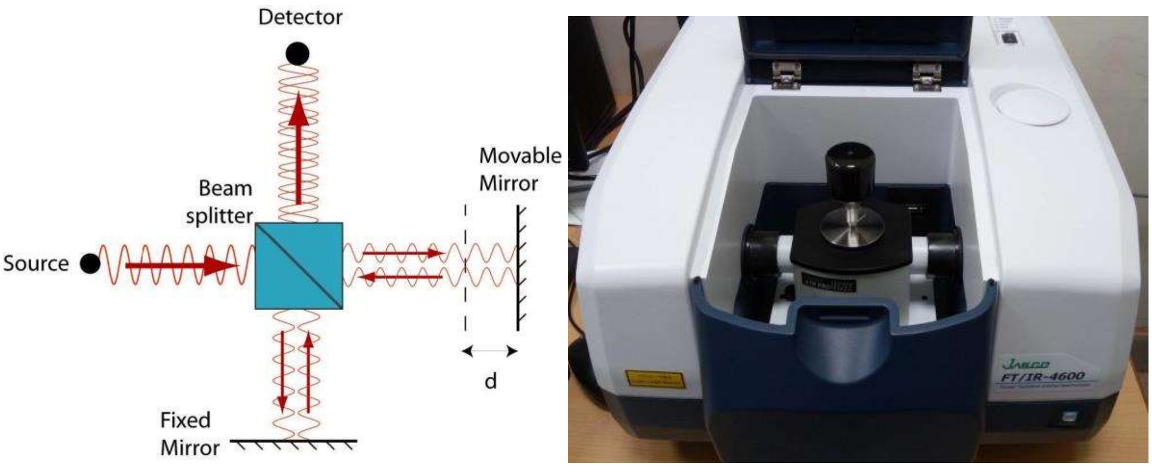

Fig. 2.6 (a) Working mechanism of a Michelson interferometer, configured for FTIR **(b)** JASCO 4600 FTIR spectrometer.

A light source produces the beam, which contains the whole range of wavelengths to be examined. The light is directed to a certain combination of mirrors known as a Michelson interferometer, which permits some wavelengths to pass through it. For each new data point, the beam is adjusted by changing one of the mirrors, which alters the set of wavelengths that pass through. Light from the source is collimated and routed to a beam splitter in a Michelson interferometer. Ideally, 50% of the light should be reflected and 50% should be sent to the moving mirror. The light is reflected back to the beam splitter by the two mirrors, and (ideally) 50% of the original light enters the sample compartment. Here the light is focused on the specimen. The light is refocused on the detector as it exits the sample chamber. The FTIR data for the thesis work was taken from the Jasco FT/IR-4600 spectrometer equipped with a 45^0 Michelson interferometer, High-intensity ceramic source, and DlaTGS detector. The sample measurement was performed using attenuated total reflectance (ATR) accessory equipped with a diamond ATR prism. The key advantage of the ATR-FTIR setup (Fig. 2.7) is that it requires no sample preparation before spectral measurement as the penetration depth of IR radiation in the sample with ATR measurements is independent of sample thickness. Another advantage is that because of the limited path length in the sample, the strong attenuation of the IR signal in highly absorbing media is avoided.

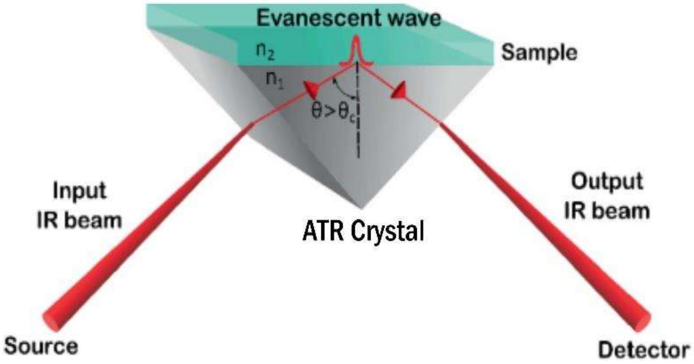

Fig. 2.7 Illustration of the mechanism behind ATR setup

2.3.3 X-ray photoelectron spectroscopy (XPS)

XPS is a quantitative spectroscopic and surface-sensitive technique. It is a powerful technique used to collect chemical information about the surfaces of solid materials viz., oxidation states, elemental composition, ligand coordination, etc. Insulators and conductors may both be examined in surface depths ranging from a few microns to a few millimeters. The XPS is used as a surface-sensitive tool since it mainly identifies those electrons produced near the surface. The kinetic energy of the photoelectrons is quite low. As a consequence of the inelastic collisions in the sample's atomic structure, photoelectrons producing more than 20 to 50 Å beneath the surface cannot escape with sufficient energy to be detected in this technique. The sample under investigation is kept inside an ultrahigh vacuum ambiance (typically ~10^{-10} torr) and then it is exposed to a monochromatic, low-energy X-ray source. The X-rays incident on the sample results in the ejection of core-level electrons from sample atoms. The energy of a core electron produced in such a photoemission process is a function of its binding energy and is a characteristic of the element from which it was emitted. The primary data used for XPS is the energy analysis of the photo-emitted electrons. An outer electron occupies the position of a core hole after the incoming X-ray ejects the core electron. By the emission of an Auger electron or a characteristic X-ray, these energies get compensated. Further, in XPS Auger electron’s energy can also be utilized along with the emitted photoelectrons. The Thermo scientific K- alpha XPS setup was employed to perform elemental analysis and chemical state of the compositions and is shown in Fig. 2.8. The X-ray source used in the setup is monochromatic Aluminium (Al) K-alpha X-ray.

Fig. 2.8 Thermo scientific K- alpha XPS setup

2.3.4 UV-Vis Spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is an analytical method that determines the wavelength of the incident photons that are transmitted through or absorbed by a specimen in contrast to a blank or reference. This feature is impacted by the sample composition, possibly giving information about the sample and its concentration. The application of the UV-Vis spectroscopy lies in the identification of the charge transfer transitions which results in the broad absorption spectrum, calculating the bandgap of the optical materials, validation of the defect trap states formed within the bandgap, photocatalysis, in the field of the pharmaceutical industry where absorbance peaks help to identify individual pharmaceutical compounds, beverage analysis, and many more.

2.3.4.1 UV-Vis spectrophotometer

The instrument used to record the absorption spectra of the sample is called the UV-Vis spectrophotometer. The absorption analysis of all the samples related to the thesis work is done with the help of the Jasco V-770 UV-Vis-NIR spectrophotometer. The spectrophotometer consists of four main components namely a radiation source, a sample holder compartment, a monochromator (diffraction grating), and a detector. The Jasco V-

770 spectrophotometer consists of two radiation sources, a deuterium lamp as a UV source and a Halogen lamp as a visible and NIR source. The detector fitted in the instrument is a photomultiplier tube (PMT) which detects UV and visible radiation. The absorption spectrum of powdered samples is measured with the help of a 60 mm UV-Vis integrating sphere. Barium sulfate is used to coat the inner surface of the integrating sphere as it reflects UV and visible radiation that are incident on it. The scanning monochromator "steps across" each wavelength, allowing the intensity to be measured as a function of wavelength.

2.3.4.2 UV-Vis spectroscopy analysis

The measurement of powdered samples is performed using an integrating sphere setup installed in the sample compartment of the spectrophotometer. The integrating sphere has an opening where the solid sample holder with the sample is kept for measurement and another opening for light to enter the sphere. Before the sample measurement, the baseline measurement is conducted by closing the opening of the integrating sphere with the barium sulfate chalk. After the baseline measurement, the sample is placed in a holder at the opening in the integrating sphere. The absorbance (A) is equated by taking the logarithm of a fraction involving the intensity of light before passing through the specimen (I_o) divided by the intensity of light after passing via the specimen (I). Transmittance (T) is defined as the fraction of I divided by I_o, which represents the amount of light passing via the specimen.

$$A = \log_{10}\left(\frac{I_0}{I}\right) = \log_{10}\left(\frac{1}{T}\right) = -\log_{10}(T)$$

Fig. 2.9 UV-Vis spectrophotometer (Jasco V-770) equipped with an integrating sphere setup.

2.3.5 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a non-destructive, non-contact, and powerful technique to probe the luminescence property of a specimen. Fundamentally, light is focused onto the specimen, followed by its absorption and the process is known as photo-excitation. The photo-excitation results in the compound jumping to the excited electronic state and eventually releasing photons (energy) when it relaxes and returns to a lower energy level. PL is the emission of photons or luminescence caused by this mechanism. Typically, the duration between absorption and emission is quite brief. The quantum mechanics rules are used to determine the allowed transitions between states. A fundamental principle is understood by examining the electron configurations and molecular orbital of basic molecules and atoms. Typical applications of the PL measurement include the determination of the luminescence phenomenon such as PL emission and excitation, bandgap determination, impurity levels, defect detection, molecular structure and crystallinity, recombination mechanism, and energy transfer processes.

2.3.5.1 PL spectrophotometer

The schematic diagram of the spectrophotometer employed in the thesis work is depicted in Fig 2.10 (a). The spectrophotometer used is Horiba fluorolog (Fig 2.10 (b)) which is fitted with a xenon arc lamp as an excitation source, two single grating monochromators at the excitation and emission ends, and a detector comprising a photomultiplier tube. The excitation monochromator consists of two gratings, which decrease stray light, that is, light with frequencies different from the selected one. To reduce stray light, these monochromators employ concave gratings created using holographic techniques. Both monochromators are motorized, allowing for automated wavelength scanning. Fluorescence is detected and measured using the proper electrical instruments. The output is often displayed graphically and digitally preserved.

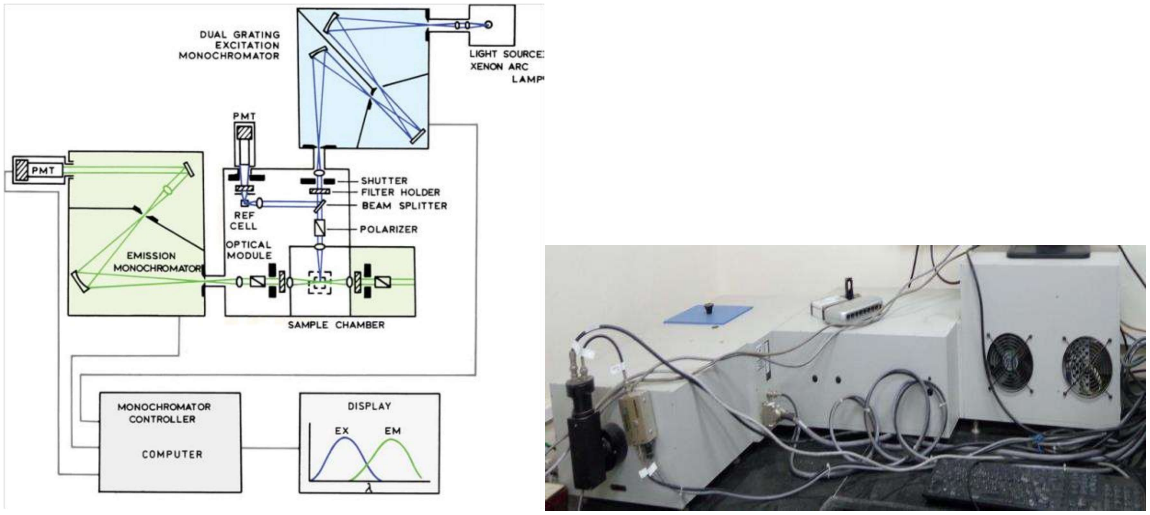

Fig. 2.10 (a) Components and working ray diagram of PL spectrophotometer setup **(b)** Horiba Photoluminescence spectrophotometer.

2.3.5.2 PL Lifetime measurement

The PL lifetime measurement is employed either in the frequency domain or time domain. The time domain approach includes illuminating a specimen with a short pulse of light and then measuring the intensity of the emission versus time. The slope of the decay curve is then used to calculate the PL lifespan. A fluorophore's PL lifespan is an inherent attribute.

Fluorophore concentration, specimen thickness, specimen absorption, method of measurement, photo-bleaching, fluorescence intensity, and/or excitation intensity do not affect PL lifespan. PL lifetime is sensitive to internal factors that are dependent on fluorophore structure.

2.3.5.3 Temperature-dependent PL measurement

The temperature-dependent PL analysis was performed using the same spectrophotometer. The sample was first prepared in pallet form and was then placed in the modified sample holder coupled with a heating element and temperature sensing device. The temperature was controlled by the external temperature controller. The temperature-dependent PL measurements of the samples in Chapters 5 and 7 were carried out using this setup. The samples in Chapter 4 were measured using a spectrophotometer (Ocean Optics) having a diode laser (405 nm) as an excitation source and an optical furnace as a heating element for the specimen.