Chapter 2
Synthesis process and Characterization tools

"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 Outline

In this chapter, the synthesis technique to prepare the samples and the experimental equipment used to assess the characteristics of the samples are mentioned. The $CaMoO_4$ host and doped all samples are prepared by a urea-based auto-combustion process, which is more useful than other processes due to its environment-friendly, simple technology and low cost. Moreover, the procedure used for device description and characterization is also described in this chapter. The synthesis technique and the steps for the doped $CaMoO_4$ samples are mentioned at the beginning of the chapter, followed by a discussion of the experimental techniques used for the measurement of structural and optical properties.

2.2 Synthesis process of undoped and doped $CaMoO_4$ samples

The urea-assisted auto-combustion approach has been used to prepare doped and undoped $CaMoO_4$ phosphor compositions. In this method, stoichiometric amounts of calcium carbonate ($CaCO_3$), rare-earth nitrates ($Re(NO_3)_3*xH_2O$), and other required dopants were taken in a clean vessel with nitric acid for the synthesis of doped $CaMoO_4$ phosphors. The solution was stirred continuously for one hour and the mixture was continuously heated to remove excess acid. In another beaker containing double distilled water, the required amount of ammonium molybdate (para) tetrahydrate was taken. The ammonium molybdate solution was stirred continuously for the next two hours. Then a 2:1 mole ratio of urea to metal nitrate was added to this solution. After mixing the two solutions, the new mixture was kept at 100 °C until the excess water evaporated. The material was dried, then heated to 250 °C for 12 h in a hot air oven. After grinding to powder form, the material was heated to 1000 °C in a sealed furnace for 4 h. All phosphors were produced using this same method. The flowchart of the synthesis process is shown in Fig. 2.1.

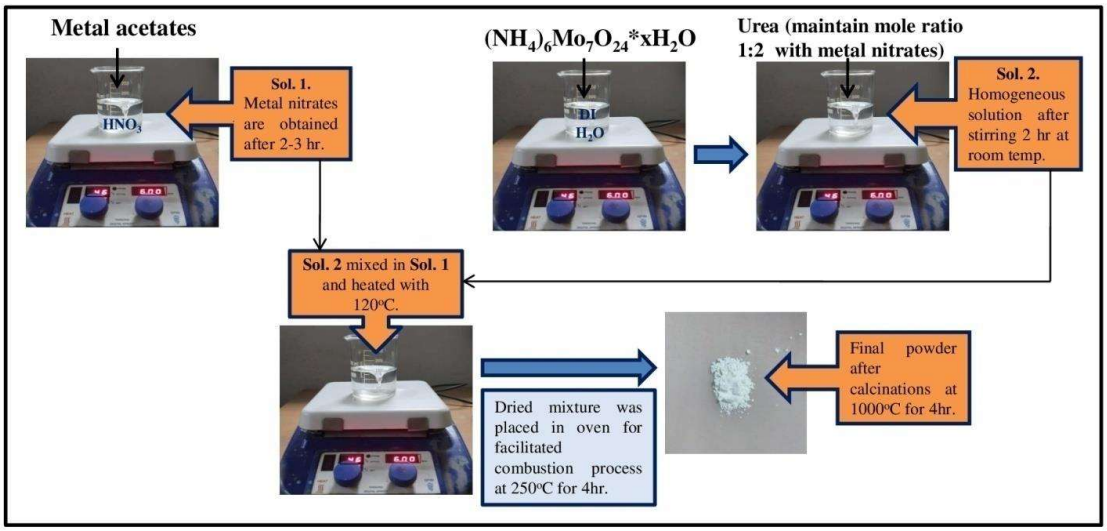

Fig. 2.1 Schematic diagram for synthesis process of $CaMoO_4$ phosphor.

2.3 Characterization tools

The structural study, surface morphology study, elemental study, absorption study and luminescence studies of all the materials prepared by the self-combustion technique have been analyzed by various techniques, which have been given detailed descriptions one by one in the following sections.

2.3.1 Structural study

2.3.1.1 X-ray diffraction (XRD) spectroscopy

The technique uses XRD to identify crystal structure and its phase, as well as to determine crystallite size and lattice strain. After Rietveld refinement, the modified atomic positions, lattice parameters, bond angles, and bond lengths are also obtained from the XRD plots. XRD patterns of the powdered phosphors were captured by a desktop Rigaku-Miniflex 600 XRD machine. The apparatus consists of a graphite monochromator, a NaI scintillation counter detector, and a 600 W Cu Kα radiation source (λ= 1.5418 Å). Fig. 2.2 (a) and (b) show a schematic illustration of the X-ray diffractometer and X-ray diffraction, respectively.

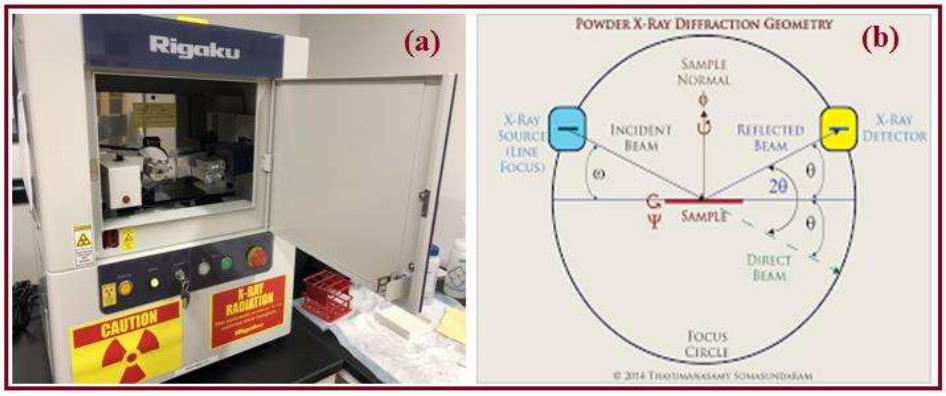

Fig. 2.2 (a) XRD instrument setup, and **(b)** Working principle of Poweder-XRD.

As shown in Fig. 2.2, X-rays are diffracted in all possible directions of 2θ when an incident beam is focused on a powder sample. The diffracted beam is detected using a mobile detector (a NaI scintillation counter) connected to a chart recorder. The counter is set up in typical operation to scan through a range of 2 values at a constant angular velocity. A significant portion of the crystal information of the sample can typically be covered within a 2° range of 10 to 90°, which makes identification of single or multiple phases easy.

Sir Lawrence and Sir William Henry Bragg initially formulated the XRD in 1913, which is as follows;

$$2dSin\theta = n\lambda \qquad 2.1$$

Bragg found that crystalline materials exhibit strong peaks of reflected radiation for a certain range of wavelengths and incident angles. When a crystalline solid is exposed to X-ray radiation having the same wavelength as the atomic spacing of the crystal lattice planes (d) and at a specific incidence angle (θ), powerful reflected X-rays are generated when the wavelength of the scattered X-rays (λ) interferes positively. Scattered waves interfere constructively when the difference in travel paths is equal to an integral multiple of the

wavelength. When constructive interference occurs, the diffracted X-ray beam will exit the crystal at an angle equal to the incident beam.

2.3.1.2 Fourier transform infrared (FTIR) spectroscopy

The Vibrational modes, functional groups, and inter- or intramolecular interactions have been studied using the FTIR spectrum. An infrared spectrum of absorption, emission, and inelastic scattering of a sample (solid, liquid, or gas) is obtained using FTIR spectroscopy. Thereby a wide range of spectrum data is collected. Thus it has a significant advantage over other spectrometers which only detect intensity at a small number of wavelengths at a time. In FTIR spectroscopy, the term "Fourier transform" refers to the process used to transform raw data into a real spectrum (a mathematical method). A Jasco FT/IR-4600 spectrometer, consisting of a 450 Michelson interferometer, a high-intensity ceramic source, and a DLA TGS detector, was used to collect the FTIR data. Fig. 2.3(a) shows the model of an FTIR spectrometer and Fig. 2.3(b) shows the working of FTIR spectroscopy.

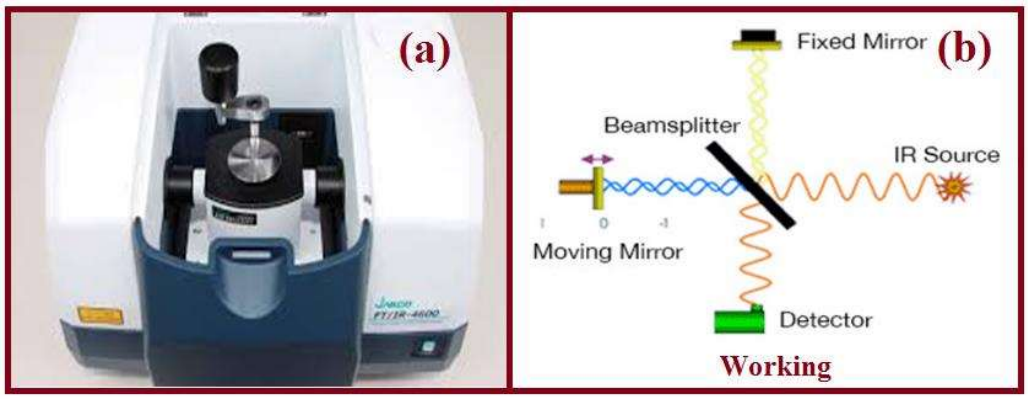

Fig. 2.3 (a) FTIR instrument setup, and **(b)** Working principle of FTIR.

In Fig. 2.3 (b), the vertical axis indicates the amount of light measured, while the horizontal axis represents the position of the mirror. The beam that will be studied is created by a light source and has all of the desired wavelengths. A Michelson interferometer, which consists of a certain set of mirrors, receives the light and allows some wavelengths to pass through.

One of the mirrors is changed to adapt the beam for each new data point, which changes the range of wavelengths that pass through. Collimated light from the source is sent to a beam splitter in a Michelson interferometer. In a perfect world, half of the light would be reflected and half would be directed toward the moving mirror. The two mirrors return the light to the beam splitter, and half of the original light now enters the sample chamber. Here, the specimen is the focal point of the light. As the light leaves the sample chamber, it is refocused onto the detector.

Attenuated total reflectance (ATR) equipment with a diamond ATR prism was used to measure the sample. The primary benefit of the ATR-FTIR system is that it eliminates the need for sample preparation before spectral measurement since ATR measurements can determine the depth to which IR radiation penetrates a sample regardless of sample thickness. Another benefit is that the sample's short travel length prevents the severe attenuation of the IR signal in the strongly absorbing material.

2.3.1.3 X-ray photoelectron spectroscopy (XPS)

The XPS is a surface-sensitive and quantitative method that provides chemical data on oxidation states, elemental composition, ligand coordination, and other characteristics of solid material surfaces. Surface depths ranging from a few microns to a few millimeters can be used to observe insulators and conductors, respectively. The elemental analysis and chemical characterization of the compositions were performed using a Thermo Scientific K-α XPS system, which is shown in Fig. 2.4(a). This system uses monochromatic Al-K-α X-rays as the X-ray source. The working of XPS is based on the emitted photoelectrons from the surface under incident X-rays on the sample, which are analyzed by studying their kinetic energy (Fig. 2.4(b)).

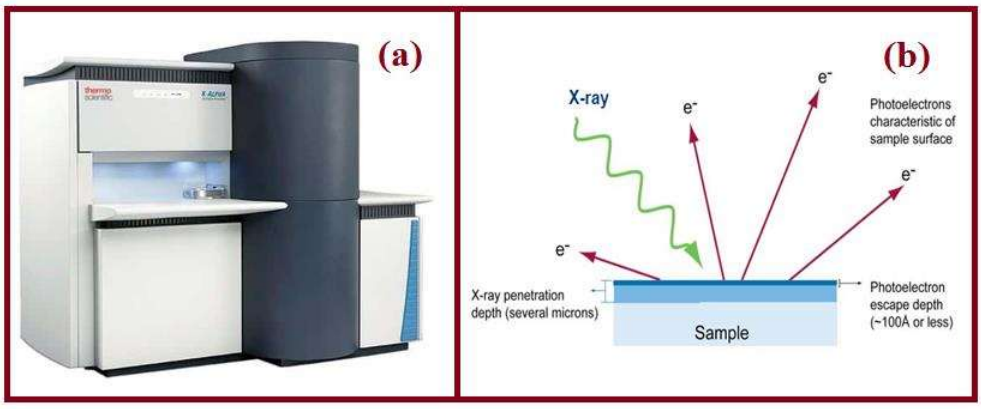

Fig. 2.4 (a) XPS instrument setup and **(b)** Mechanism of emitting photoelectrons.

It primarily isolates electrons generated close to the surface, making it known as a surface-sensitive device. The kinetic energy of photoelectrons is very small. Photoelectrons produced more than 20 to 50 below the surface may not escape with sufficient energy to be detected in this method because of inefficient collisions in the atomic structure of the sample. After being held in an ultrahigh vacuum environment (~10^{-10} Torr), the sample under investigation is subjected to a monochromatic, low-energy X-ray source. The incoming X-rays result in the atoms in the sample being ejected along with core-level electrons. In such a light emission process, the energy of the created core electron is a function of its binding energy and is a property of the element from which it was ejected. Energy analysis of photo-emitted electrons serves as the main source of information for XPS. After the incoming X-ray ejects the core electron, the core hole is filled by an outer electron. These energies are offset by the emission of an auger electron or a specific X-ray. Additionally, in XPS, the energy of the Auger electrons, in addition to the released photoelectrons, can be used to determine the oxidation states of the corresponding elements present in the sample, and the elemental composition of the sample.

2.3.2 Morphological study: Scanning electron microscope (SEM) and Transmitted electron microscope (TEM)

The SEM and TEM both images are used to study the morphology, grain size and crystalline structure. We used OXFORD Instrument SEM EVO 18 model to acquire SEM images and FEI company instrument Tecnai G2 20 TWIN model for TEM images, respectively. The models of both are shown in Fig. 2.5.

Fig. 2.5 Instrument setup of **(a)** Scanning Electron Microscope (SEM) and **(b)** Transmitted Electron Microscope (TEM).

The SEM, employs an electron beam that is directed at the sample. These electrons interact with the atoms on the sample's surface, resulting in a variety of signals that express the topography of the surface. These impulses are recorded by a detector, which creates an image.

The TEM short name refers to a transmitted electron microscope. An electron beam is sent through the material via this microscope. The interactions between the electrons and the sample's atoms result in the formation of an image. A luminous screen or photographic film is used to obtain the image. The device is capable of delivering high-resolution images.

Additionally, it can increase the magnification of a specimen by approximately 50 million times that of the original.

The difference between SEM and TEM is that whereas TEM creates images by detecting spontaneous electrons, SEM creates images by detecting reflected electrons. SEM examines a sample's surface, whereas TEM examines its interior structure. The limit of resolution of SEM images and TEM images is another distinction. SEM technology provides a maximum resolution of around 0.4 nm, whereas TEM technology provides 0.5 Å. As a result, the lattice spacing and crystal structure of the sample can also be detected by the high resolution of TEM images.

2.3.3 Elemental study: Energy dispersive x-ray (EDX) spectroscopy

All of the components of the sample were examined qualitatively and quantitatively using EDX. The EDS analysis was performed using the TEM and SEM research setups. An element's existence in a sample, as well as its atomic number and weight percentages, may all be determined using EDX spectroscopy. The energy and quantity of X-rays emitted by the substance as a result of a difference in energy between high- and low-energy shells are measured using energy-dispersive spectrometers. Since the energy of the X-rays depends on the atomic structure of the emitting element and the energy difference between the two shells. As a result, EDX may be used to ascertain a sample's elemental composition.

2.3.4 Absorbance study: UV-vis spectroscopy

The analytical study of the wavelengths of incident radiation absorbed or passed through a sample in comparison to a blank or reference is carried out by the technique of UV-vis spectroscopy. This property, which can provide details about the sample and its concentration, is affected by the amount of concentration of the sample. The charge transfer transition can be identified using UV-vis spectroscopy which is obtained as a broad

absorption spectrum, which results in the detection of the bandgap of the optical material. This confirms the existence of defect trap states formed within the bandgap absorption. Peaks obtained in the absorption spectrum are used for recognises of specific pharmaceutical compounds, beverage analysis, and many other applications.

Fig. 2.6 UV-Visible spectroscopy setup with the internal part.

UV-Vis spectrophotometer is the instrument used to capture the absorption spectra of a sample. We have used the setup of Jasco V-770 UV-Vis-NIR spectrophotometer for absorption analysis in our thesis work which is shown in Fig. 2.6. A radiation source, a sample holding compartment, a monochromator (diffraction grating), and a detector make up the four primary parts of the spectrophotometer. The JASCO V-770 spectrophotometer has two types of radiation sources for different visible regions: a deuterium lamp for UV light and a halogen lamp for visible and near-infrared light. Also inside its instrument is a photomultiplier tube detector, which can detect both UV and visible light. Using a 60 mm UV-vis integrating sphere, the absorption spectra of the powdered materials are studied. Since barium sulfate reflects incident UV and visible light, it is employed to cover the inner surface of the integrating sphere. Each wavelength is "stepped over" by the scanning monochromator, making it possible to determine the intensity as a function of wavelength.

2.3.4.1 Working principle

An integrating sphere arrangement placed in the sample chamber of the spectrophotometer is used to measure the powder content. The solid sample holder with the sample is placed inside the integrating sphere by one entrance, while light enters the sphere through another entrance. Before taking sample measurements, the aperture of the integrating sphere is sealed with barium sulfate chalk to take baseline measurements. The sample is placed in a holder over the opening of the integrating sphere after the baseline measurement. Absorbance (A) is calculated by multiplying the logarithm of the fraction involving the light intensity before passing through the sample (I_o) by the light intensity after passing through the sample (I).

$$A = log\left(\frac{I_o}{I}\right) \quad 2.2$$

Similarly, Transmittance (T) is equal to the logarithm of the intensity ratio of I and I_o.

$$T = log\left(\frac{I}{I_o}\right) = \log\left(\frac{1}{A}\right) = -logA \quad 2.3$$

2.3.5 Photoluminescence (PL) spectroscopy

A strong, non-contact, non-destructive method for examining a specimen's luminescence property is PL spectroscopy. The fundamental mechanism of photo-excitation involves focusing light onto the specimen, followed by its absorption. The photo-excitation causes the compound to move to the excited electronic state, where it stays until it relaxes and returns to a lower energy level, at which point it releases photons (energy). The luminescence or photon emission brought on by this process is known as PL. The time between absorption and emission is often relatively short. The permitted transitions between states are chosen based on the laws of quantum physics. By looking at the electron configurations and molecular orbitals of simple molecules and atoms, a fundamental

concept may be understood. The assessment of luminescence phenomena, such as PL emission and excitation, bandgap determination, impurity levels, defect detection, molecular structure and crystallinity, recombination mechanism, and energy transfer processes, are typical uses of the PL measurement.

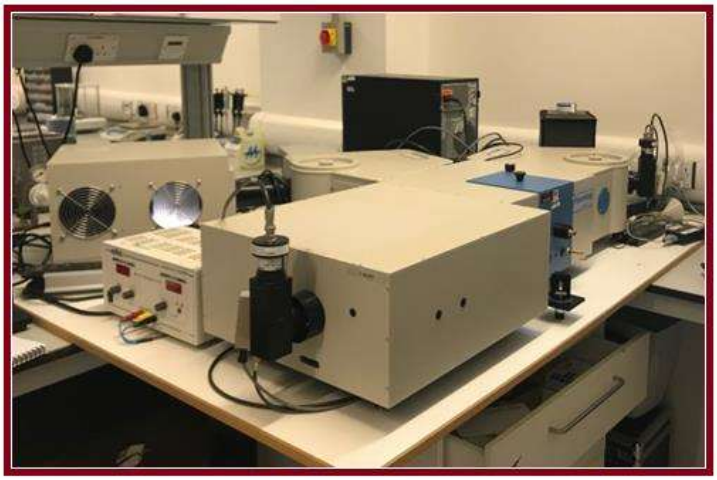

Fig. 2.7 Whole setup of Horiba PL spectroscopy.

PL spectrophotometer Horiba Fluorolog was used for luminescence analysis whose setup is shown in Fig. 2.7, consisting of two single grating monochromators at the excitation and emission ends and a xenon arc lamp as the excitation source as the detector. contains a photomultiplier tube. These gratings form the excitation monochromator, which attenuates stray light, or light with frequencies other than the chosen one. These monochromators use concave gratings made using holographic methods to reduce stray light. Due to the motorized nature of both monochromators, automatic wavelength scanning is possible. Using appropriate electrical equipment, the fluorescence is detected and quantified. The results of which are often visualized and stored digitally. PL spectroscopy is used in a variety of luminescence analyses.

This spectroscopy is used in PL lifetime frequency or time domain measurements. Using a brief light pulse to illuminate a sample, the emission intensity is measured as a function of

time using the time domain method. To determine the PL lifetime, the slope of the decay curve is employed. PL lifetime is a fundamental property of the fluorophore. The PL lifetime is unaffected by factors such as fluorophore concentration, sample thickness, sample absorbance, measuring technique, photo-bleaching, fluorescence intensity, and/or excitation intensity. Intrinsic variables that depend on the fluorophore structure can affect how long a photoluminescent particle stays.

The same spectrophotometer was used to study the temperature-dependent PL. It uses a modified sample holder, after being constructed in the form of a pallet, with a heating source and temperature measuring device. An external temperature controller is used to control the temperature. This setup was used to perform temperature-dependent PL measurements on samples in further chapters.