Chapter -2

Experimental Methods and Materials

2.1 Introduction

Nanostructured semiconductors are of great interest due to their excellent physicochemical properties, which differ from their bulk counterparts. Semiconductor nano crystals have been attracted during the past two decades. New devices with semiconductor nano crystals possess novel optical and electronic properties, which are potentially useful for technological applications. High surface area to volume ratio with the decrease of particle size leads to an increase in surface specific active sites for chemical reactions and photon absorptions. The size quantization effect leads to change in energy band gap between the conduction band electrons and valence band holes which leads to change in their optical properties [1, 2].

Zinc oxide, II–VI semiconductor finds applications in gas sensors, piezoelectric transducers, and solar cell windows. It has been used for applications in optoelectronics, short wavelength light emitting diode, photo detector, ultraviolet laser due to its wide band gap 3.37 eV at room temperature and large exciton binding energy (60meV) [3,4]. Fabrication of efficient devices based on semiconductor nanostructures requires in depth understanding of their optoelectronic behaviors, which depend on their shape, size, and impurity contents. On the other hand, luminescence properties of nanostructures also depend on their morphology, growth technique, synthesis conditions, and imperfections [5, 6].

Numbers of chemical methods have been applied to synthesize nanostructures viz hydrothermal [7], precipitation [8], sol–gel [9], solution combustion and thermal decomposition [10, 11] techniques, etc. Among these, combustion synthesis provides a molecular level mixing and high degree of homogeneity, short reaction time that leads to reduction in crystallization temperature and prevents from segregation during heating.
2.2 Synthesis of nanophosphors

2.2.1 Combustion synthesis

Solution combustion synthesis employs metal salts, including nitrates, sulfates and carbonates, as oxidants, and fuels as reducing reagents, such as urea, glycine, and sucrose, starch, based on the exothermicity of the redox reaction. The released heat of the combustion reaction fulfils the energy requirement for the formation of oxides. The most obvious advantage of SCS is its time and energy efficiency. Once the mixture of reagents is ignited, the high self-generated energy can convert precursors into the corresponding oxides without requirement of an additional external energy input [12-13].

The combustion process is performed in an electric muffle furnace (Delta power controls) operating on 240 V AC, 13.75A current. The heating element is Kanthal wire (ferritic iron-chromium-aluminium alloy) and heating rate is maintained at 10 K per minute. K type thermocouple (Chromel-Alumel) is used to measure the furnace temperature. Ventilating the flames from the combustion process is made by exhaust fan in the furnace. The operating current does not affect the process of combustion reaction.

Stoichiometry of the combustion

The oxidizer/fuel molar ratio (O/F) required for a stoichiometric mixture is determined by summing the total oxidizing and reducing valencies in the oxidizer compounds and dividing it by the sum of the total oxidizing and reducing valencies in the fuel compounds. In this type of calculation oxygen is the only oxidizing element; carbon, hydrogen, and metal cations are reducing elements and nitrogen is neutral. Oxidizing elements have positive valencies and reducing elements have negative valencies.

In solution combustion calculations, the valency of the oxidizing elements is modified and considered as negative, and the reducing elements as positive, similar to the oxidation number concept familiar to chemists. Accordingly, the elemental valency of C, Al, and H is +4, +3, and +1 respectively, and oxidizing valency of oxygen is taken as −2. The valency of nitrogen is considered to be zero.
The stoichiometry of the redox mixture for combustion is calculated based on the total oxidizing (O) and reducing (F) valencies of the oxidizer and the fuel, keeping O/F ratio unity, using the concepts of propellant chemistry [13].

\[
\sum \left( \text{Coefficient of oxidizing element in the specific formula} \times \text{Valency} \right) \div \sum \left( \text{Coefficient of reducing element in the specific formula} \times \text{Valency} \right) = \frac{O}{F}
\]

Table 1: Oxidizing (O) and reducing (F) valencies of the raw materials

<table>
<thead>
<tr>
<th>M (NO₃)₂, Where M is divalent metal</th>
<th>Total reducing valency of urea (CH₄N₂O)</th>
<th>Total reducing valency of sucrose (C₁₂H₂₂O₁₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M = +12</td>
<td>C = +4</td>
<td>12C = +48</td>
</tr>
<tr>
<td>6O = -12</td>
<td>4H = +4</td>
<td>22H = +22</td>
</tr>
<tr>
<td>2N = 0</td>
<td>2N = 0</td>
<td>11O = -22</td>
</tr>
<tr>
<td></td>
<td>O = -2</td>
<td></td>
</tr>
</tbody>
</table>

Nano crystalline zinc oxide (ZnO) synthesized via low temperature solution combustion method. The stoichiometric quantities of analytical grade Zn (NO₃) as oxidizer, urea CH₄N₂O and C₁₂H₂₂O₁₁ as fuels in separate reaction. All these are dissolved in minimum quantity of double distilled water keeping total oxidizing (O) and reducing (F) valencies of the components is unity (i.e. O/F=1). The petridish containing this solution was placed in a preheated muffle furnace set at 400°C. The mixture underwent dehydration at lower temperatures and decomposition resulting in simultaneous evolution of large amounts of gases. This exothermic reaction resulted into voluminous and fluffy product. The whole process lasted for 10 minutes. The dish was then taken out of the furnace, and the product was crushed into a fine powder. The stoichiometric balanced reaction as follows

\[
3 \text{ Zn (NO₃)₂} \cdot 6 \text{ H₂O} + 5 \text{ H₂NCONH₂} \rightarrow 3\text{ZnO} + 16\text{H₂O} + 5\text{CO₂} + 8\text{N₂}
\]

\[
3 \left[ (1-x) \text{ Zn (NO₃)₂} \cdot 6 \text{ H₂O} + x \text{ D (NO₃)₂} \right] + 5 \text{ H₂NCONH₂} \rightarrow 3\left[ \text{Zn (1-x) D } \cdot \text{O} \right] + 16\text{H₂O} + 5\text{CO₂} + 8\text{N₂}
\]

The obtained powders are annealed at 800 °C for two hours in order to remove carbon impurities. The flow chart of the combustion is shown in figure 2.1 as follows
Synthesis - Pure and doped ZnO: Combustion method

Figure 2.1 flow chart of the combustion synthesis.

Doped zinc oxide nanoparticles are synthesized by using zinc nitrate hexahydrate (Sigma Aldrich), M- nitrate (M: Cr³⁺, Co²⁺, Ni²⁺, Mn²⁺, Al³⁺, Mg²⁺, Sm³⁺, Ho³⁺) (Sigma Aldrich), urea or sucrose (Sigma Aldrich) are chosen as starting materials. Zinc nitrate hexa hydrate (oxidizer), M- nitrate (oxidizer), urea or sucrose (fuel) are dissolved using 45ml double distilled water in cylindrical petridish. The oxidizer to fuel ratio is chosen as unity. The detailed synthesis process followed as mentioned above.

2.2.2 Hydrothermal synthesis

Compared with other chemical methods, hydrothermal synthesis is adopted for the synthesis of undoped ZnO nanoparticles because it is carried at low temperature and allows the control on size, crystallinity and morphology by the altering experimental variables such as temperature, pressure, duration of process, concentration of chemical species and pH of solution [14-16]. Hydrothermal synthesis is an environment friendly, low temperature, low cost method and finds interesting material processing technique for practical applications. Hydrothermal synthesis is a process that utilizes single or heterogeneous phase reaction at elevated temperature and pressure to crystallize anhydrous ceramic materials or oxide materials directly from solutions. Reaction is
carried out in water at elevated temperature and pressure. Nucleation and particle growth that occur under these conditions can result in nanometer or sub-micron meter with controlled shape and size.

Hydrothermal synthesis of ZnO sample was carried out in Teflon lined stainless steel cylindrical chamber of 60ml capacity. All the reagents and solvents were of analytical grade point and are used without any further purification. The compound has been prepared using water as the solvent. 4.48 gm of KOH was mixed to 60ml water and stirred well till it gets dissolved completely. The pH level of the as prepared solution was 13.6. Then 2.7gm of solid Zinc nitrate hydrate (Zn [NO₃]₂ 6H₂O) is directly added to the above solution and stirring is continued till it gives white precipitate. The closed autoclave chamber is then placed inside a preheated box furnace maintained at a temperature 180 °C for 16 hrs. After the mixture is cooled to room temperature and the white precipitate obtained is collected and washed with water and ethanol for a several times to remove impurities if any and finally dried in air at room temperature [17]. Same procedure was carried to synthesize sample except the change in the solvent (mixture of ethanol + water). The obtained powders are annealed at 800 °C then used for the characterization.

2.3 Preparation of binder solution

Binder solution is prepared from polyvinyl alcohol (PVA) solution. The stoichiometric amount (4g) of PVA powder is added to the to100 ml of doubled distilled water. The above mixture is stirred using magnetic stirrer maintained 80 °C and the obtained clear transparent solution is used as binder for the preparation of pellets.

2.4 Preparation of pellets

Undoped and doped ZnO nano powders in pellet form are prepared using a homemade pellatizer. The pellatizer consists of a cylindrical pilot, pressure rod, knock out and the die set used for the preparation of pellets. The pilot, pressure pad and sample collector are prepared from a single block of high carbon steel. Undoped and doped ZnO doped nano powders are grounded with PVA binder and weighed using a microbalance (Sartorius BL 150S with an accuracy of 0.001g). 30 mg sample is transferred in to the cavity of the die supported by base disc having a projection of a cylindrical portion having the same diameter that of the rod. The piston disc is placed at the top of the die.
Then the whole set is placed exactly at the center of the pelletizer and the required pressure is applied for 10 seconds. The pellet of ~1mm thickness and 5 mm diameter is extracted from the pelletizer. These pellets are heat treated at 800 °C for 3 hours to remove binder impurity.

2.5 Gamma irradiation

Gamma irradiation is performed using \(^{60}\)Co source using GC 1200 chamber installed at IUAC, New Delhi. It consists of radiation source, a biological shield for the source, central drawer including the sample chamber, driving system, control panel and external cabinet. This compact unit enables the irradiation volume approximately 1000 cm\(^3\). The radiation field on the external surface of the unit is limited by shielding. The irradiation is done by setting up a program which can be operating using both manual and automatic dose and time scale. Built in timer provides accurate control of irradiation time from 6 seconds onwards. A stationary source pencil, symmetrically placed in a cylindrical cage ensures good uniformity of the radiation field in the sample chamber. The central drawer can be raised or lowered as required by a steel rope passing over a geared motor. This movement is controlled from the front control panel through an electrical circuit. The dose rate was 6.7 kGy per hour during irradiation.

2.6 Characterization techniques

2.6.1 X-ray Diffraction technique (XRD)

Phase purity of the prepared nanoparticles is characterized by powder X-ray diffraction (XRD) using Rigaku Miniflex II diffractometer with Cu Kα (\(λ = 1.541 \text{ Å}\)) radiation. X-ray diffraction is a non-destructive, versatile, technique used to determine the crystal structure of metals and alloys, minerals, inorganic compounds, polymers and organic materials. Also, this technique is applied to derive information on fine structure of materials like crystallite structure, lattice strain etc. Typical XRD pattern consists of a series of peaks, in which peak intensity is plotted on the Y-axis and diffraction angle (2θ) along X-axis. These peaks are called “reflections”. Each peak in the diffraction pattern corresponds to x-rays diffracted from a specific set of planes in the material. These peaks are of different intensities. The positions of the peaks in XRD pattern depend on the crystal structure of the material while intensities depend on many factors like incident intensity, atomic structure factors, slit width, number of grains etc [18, 19].
The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different crystal planes is an integral multiple of \( \lambda \). This condition is Bragg’s law \( 2d \sin \theta = n\lambda \). Here \( n \) is the order of diffraction, \( \lambda \) is the wavelength of X-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle. Experimentally obtained diffraction pattern of the material is compared with Joint Council Powder Diffraction (JCPDS) data for standards or International Centre for Diffraction Data (ICDD). This gives information of different crystallographic phases, relative abundance and preferred orientation. From the width of the diffraction peak, average grain size can also be estimated.

The average crystallite size (D) is calculated using Debye Scherrer equation

\[
D = \frac{k\lambda}{b\cos \theta}
\]  

(2.1)

Structural parameters such as lattice parameters and unit cell volumes for hexagonal Z particles are calculated from the lattice geometry equations [20].

\[
\frac{1}{d^2} = \frac{4}{3\left[\frac{h^2 +hk + k^2}{a^2}\right]} + \frac{1}{c^2}
\]  

(2.2)

\[
V = \frac{\sqrt{3}a^2c}{2} = 0.866a^2c
\]  

(2.3)

Where \( a \) and \( c \) are the lattice parameters and \( h, k, \) and \( l \) are the Miller indices and \( d_{hkl} \) is the inter planer spacing, which can be calculated from Bragg’s law:

\[
2d \sin \theta = n\lambda
\]  

(2.4)

Williamson and Hall (W–H) plots have been used to estimate the micro strain in ZnO samples annealed at different temperatures by using the relation:

\[
\beta \cos \theta = \frac{k\lambda}{D} + 4\varepsilon \sin \theta
\]  

(2.5)

Where \( \varepsilon \) is the strain associated with the nano crystals. Eqn 2.5 represents a straight line between \( 4\sin \theta \) (X-axis) and \( \beta \cos \theta \) (Y-axis). The slope of line gives the strain (\( \varepsilon \)) and intercept (\( k \lambda / D \)) of this line on Y-axis gives crystallite size (D).
2.6.2 Scanning Electron Microscopy (SEM)

Surface morphology of the undoped and doped ZnO powders is examined by scanning electron microscope (SEM) (Hitachi S-300N model). The scanning electron microscope is one of the most useful and versatile instruments for the investigation of surface topography, microstructure of the nano materials [21, 22]. Figure 2.2 shows a schematic representation of SEM.

![SEM Diagram](image)

Figure 2.2 Schematic representation of SEM.

The principle involved in imaging is to make use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the specimen. The electrons are produced by a thermal emission source, such as heated tungsten filament, or by using field emission cathode. To create SEM image, the incident electron beam is scanned in a raster pattern across the sample surface. Secondary electrons are produced due to the interaction of the primary electron beam. The emitted electrons are detected at each position in the scanned area by an electron detector. Intensity of the emitted electron signal is displayed as brightness on a cathode ray tube. There are two modes of imaging: one is by using Secondary Electrons and the other is by using
Backscattering Electrons. Secondary electron imaging provides high resolution imaging of fine surface morphology and the samples must be electrically conductive [21, 22].

SEM produces a magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down towards the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image. The scanned image is formed by point by point and scan is achieved by scan coils, they are electromagnetic coils and are organized by scan generator.

2.6.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera (figure 2.3) [23].

Transmission electron microscope (TEM) uses a high voltage electron beam to create an image. The electron beam is produced by an electron gun, commonly fitted with a tungsten filament cathode as the electron source. The electron beam is accelerated by an anode typically at 100 keV with respect to the cathode, focused by electrostatic and electromagnetic lenses, and transmitted through the specimen that is in part transparent to electrons and in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about the structure of the specimen that is magnified by the objective lens system of the microscope. The spatial variation in this information may be viewed by projecting the magnified electron image onto a fluorescent viewing screen coated with a phosphor or scintillator material. Alternatively, the image can be photographically recorded by exposing a photographic film or plate directly to the electron beam.
TEM uses high energy electrons (up to 400 kV accelerating voltage) which are much higher than SEM (2000-2700V). When an electron beam passes through a thin-section specimen of a material, electrons are scattered. A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum, depending on the mode of operation. Denser parts of the specimen absorb more electrons, making them look darker on the resulting image.

TEM technique operates in diffraction mode and image mode for the specimen observation. In diffraction mode, an electron diffraction pattern is obtained on the fluorescent screen, obtained from the sample area illuminated by the electron beam. The diffraction pattern is entirely equivalent to an X-ray diffraction pattern, a single crystal will produce a spot pattern on the screen, a polycrystalline or powder samples will produce a ring pattern and amorphous material will produce a series of diffused halos.

The image mode produces an image of the illuminated sample area. The image can contain contrast obtained by several mechanisms; mass contrast due to spatial separations between distinct atomic constituents and thickness contrast due to non uniformity in sample thickness; diffraction contrast which in the case of crystalline materials results from scattering of the incident electron wave by structural defects and phase contrast [23].
2. 6. 4 Fourier transforms infrared spectroscopy (FTIR)

Molecular purity and identification of molecular constituents in the samples are analyzed by fourier transform infrared spectroscopy. FTIR spectrum of a sample is made by passing a beam of infrared light through a sample or reflecting off of the surface of the sample. The infrared light is absorbed at specific frequencies representing the vibrations of bonds or groups in the molecule. For a vibrational mode in a molecule to be infrared active it must have a permanent dipole [24, 25]. The FTIR spectra of the samples are recorded using Perkin-Elmer spectrometer (Spectrum 1000) over a range of frequencies from 4000-400cm\(^{-1}\) using KBr pellet technique.

**KBr Pellet Method**

This method exploits the property that alkali halides become plastic when subjected to pressure and form a sheet that is transparent in the infrared region. Potassium bromide (KBr) is the common alkali halide used in the pellets. Approximately 0.1 to 1.0 % sample is well mixed into 200 to 250 mg fine alkali halide powder and then finely crushed and put into a pellet-forming die. A force of approximately 8 ton is applied under a vacuum of several mm Hg for several minutes form transparent pellets. Degassing is performed to eliminate air and moisture from the KBr powder, after drying the powder, store it in a desiccator. When performing measurements, the background can be measured with an empty pellet holder inserted into the sample chamber. However, background measurements on a pellet holder with a pellet of KBr only, that contains no sample, can correct for infrared light scattering losses in the pellet and for moisture adsorbed on the KBr.

2. 6. 5 Micro-Raman studies

Raman studies of doped and undoped ZnO nanoparticles are measured using ID Raman microscope from Ocean optics using 785nm laser excitation. The ID Raman micro from Ocean Optics (ID Raman micro-785) is optimizes Raman sampling by using the same focal plane for collecting images and Raman signals. This simplifies the often tedious and inexact process of acquiring data from a specific structure or location on a sample. Also, One Focus optimizes data collection for applications such as surface enhanced Raman spectroscopy (SERS), where only a single layer of material is applied to the surface.
Mechanism of Raman scattering lies in the change of the rotational or vibrational quantum states of the samples being illuminated. When light incident on a sample most of the scattering that takes place is elastic with no loss of energy, and therefore no frequency change, this is known as Rayleigh scattering. Raman scattering, however, is due to inelastic scattering of the incident photons whereby energy is transferred to or received from the sample due to changes in the vibrational or rotational modes of sample molecules, causing a change in the energy, and therefore the frequency of the scattered light. If the incident photon gives up energy to the sample it is scattered with a red shifted frequency and referred to as stokes shift. If the molecule is already in an exited energy state, and gives energy to the scattered photon, the output has a blue-shifted frequency, and is referred to as anti-stokes shift. Because the probability of a molecule being in an excited state is much lower than being in the ground state, the antistokes shift occurs much less frequently than the stokes-shift. In most cases, the Raman scattering photons collected and analyzed are the Stokes photons, referred to as Stokes lines. The selection rule governing Raman scattering is determined by changes in polarizibility during the vibration [26].

2.6.6 UV-visible absorption spectroscopy

UV-Visible absorption spectroscopy is a very useful technique to study, semiconductors and insulators in bulk, colloidal, thin film and nanostructure forms. Semiconducting as well as some insulating materials have an optical energy gap. When the energy of photons is insufficient to excite electrons from valence band to conduction band, no absorption takes place. At some critical photon energy, a sudden rise in absorption occurs as energy of photons is just sufficient to excite the electron to conduction band minimum. At still shorter wavelengths or higher energy photons continue to get absorbed. The absorbed (or reflected) intensity as a function of wavelength from ultraviolet to near infra red is useful to understand electronic structure and transitions between valence and conduction band of materials.

The optical energy gap ($E_g$) was estimated using the Tauc relation [27].

$$(ah\nu) \sim (h\nu - E_g)^{1/2}$$
Where $h\nu$ is the photon energy and $\alpha$ is the optical absorption coefficient near the fundamental absorption edge.

### 2.6.7 Diffused reflectance spectroscopy

Diffused reflectance is an effective spectroscopic tool to measure the band gap of the materials. Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials in the mid-IR and NIR spectral ranges. Diffuse reflectance relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material. The back reflected, diffusely scattered light is then collected by the accessory and directed to the detector optics. Only the part of the beam that is scattered within a sample and returned to the surface is considered to be diffuse reflection. Kubelka Munk theory gives the theoretic description of the diffused reflectance. Kubelka Munk equation given below [28].

$$k = \frac{(1-R)^2}{2R}$$

Where $R$ is reflectance, $k$ is absorption coefficient and $s$ is scattering coefficient. Band gap ($E_g$) is estimated from the graph of $[(k/s)\ h\nu]^2$ versus $h\nu$, by extrapolating graph to the X-axis. The diffused reflection of the phosphors recorded using the instrument Shimazdu (UV-1800).

### 2.6.8 Thermoluminescence (TL)

Thermoluminescence studies of all the samples measured using Harshaw 3500 TLD reader. The Harshaw 3500 TLD reader is a product of Harshaw Intruments, USA. This instrument is manually operated and has a sample drawer for a single element TLD dosimeter, a linear, programmable heating system and a cooled photomultiplier tube (PMT) with associated electronics to measure the TL signal output. It operates on WinREMS Software, which runs under Windows operating system on a dedicated computer, providing user friendly interface. It finds applications in medical Physics and dosimetry laboratories. The system is a PC-driven, table top instrument for TLD measurement. The external components of this reader include a front panel consisting of three LED status lights and a Read pushbutton, a sample drawer assembly that features an
interchangeable planchet and a built in test light for periodic monitoring of Reader performance, and a drawer for neutral density filters. The rear panel houses a voltage selectable power input module with fuse access, an instrument Reset button, a fitting for nitrogen gas tubing, an RS-232-C serial communication port, and a recessed pressure sensor adjusting screw. The dosimetry functions are divided between the Reader and the specialized. TLD shell software that runs on the PC. All dosimetric data storage instrument control, and operator inputs are performed on the PC; signal acquisition and conditioning are performed in the reader.

The Harshaw 3500 TLD reader uses contact heating with a closed loop feedback system that produces linearly sloped temperatures using a temperature controlled program. Its accuracy is within ±1 K. The standard one can go up to 673 K. The time temperature profile (TTP) is user-defined in three segments: Preheat Acquire and Anneal, each with independent times and temperatures. It also has the facility for flowing nitrogen around the planchet. By eliminating oxygen in the planchet area, the Nitrogen flow eliminating the unwanted oxygen induced TL signal. Nitrogen is also routed through the Photomultiplier Tube (PMT) chamber to eliminate moisture caused by condensation. Beside the recorded glow curve, this appears on the computer screen, the data could also be stored in the form of ASCII files for its utilization in further analysis [30].

Specifications

The HARSHAW TLD Model 3500 manual Reader includes a sample drawer for a single element TL detector, a linear, programmable heating system, and a cooled photomultiplier tube with associated electronics to measure the TL light output. Planchet heating incorporates a welded thermocouple for best temperature reproducibility. The operational software, ThermoScientific™ WinREMS™, which runs on a separate computer, provides the user interface, the reader control and the applications software [30].

Specifications

- Multiple, programmable, linear heating cycles such as pre-read anneal, acquire and post-read anneal cycles.
- Typical cycle time per detector: typically 30 seconds.
- Heating temperature capability up to 400°C (standard model) or 600°C (high-temperature version).
- Thermoelectric PMT cooler for maximum gain stability.
- Seven decade glow curve acquisition range.
- Options include glow curve deconvolution software (WinGCF Software), various types of neutral density filters to extend the high measurement range, and TL element specific planchets for best possible reproducibility.

- Easy to operate, service and maintain.
- Size: 31 × 32 × 47cm.
- Weight: 25kg.

2. 6. 9 Photoluminescence (PL)

Photoluminescence (PL) measurements of all the samples are performed using Hitachi F-2700 fluorescence spectrophotometer (Model F-2700) equipped with 150W Xenon lamp as an excitation source. The block diagram of the optical system of Hitachi F-2700 is shown in figure 2.4 and figure 2.5 shows an experimental setup for PL.

![Figure 2.4 Optical system of F-2700.](image)

The light emitted from the Xe lamp is condensed on entrance list of the excitation side monochromator via lenses L₁ and L₂. The light excitation light separated by excitation side diffraction grating enters the exit slit. The light coming from exit slit is reflected by concave mirror M₁, divided into two by beam splitter. Part of which
irradiates the monitor detector and this light quality is measured. A large part of the excitation light divided by the beam splitter is considered on the sample cell via lens L3. Fluorescence emitted from the sample is reduced and directed into entrance slit of the emission side monochromat via lenses L4 and L5. The fluorescence separated by emission side diffraction grating goes out through exit slit and is condensed onto photomultiplier by concave mirror where by its intensity is measured [31].

Solid sample cell is used to record the PL spectra. The sample cell consists of a round sample holder of diameter 1.5 cm, quartz disc and a threaded cap. The quartz disc is fixed into the sample holder and powder sample is spread on it. Then cap is fitted to hold the powder sample. The metal frame is put on the sample cell containing sample so that the front portion of the cell could fit into the metal frame aperture. When analyzing the sample, optical axis runs along the centerline of powder surface (quartz window). First the excitation (Ex) spectra are recorded by setting the emission (Em) wavelength at the zero order and keeping other parameters as specified in the manual. The Ex bands are identified from these spectra and the Em spectra are scanned for identified excitation wavelengths. This is necessary to know approximate nature of Ex and Em spectra. While, doing so the direct scattered light may super imposed on the excitation spectrum. So it is necessary to select a particular band in the emission for scanning the excitation. Therefore for proper excitation wavelengths, Em is set at the position as identified from the earlier emission spectrum. Again the same procedure is followed for identifying the proper Ex positions and Em is recorded for each Ex band separately.

In the ordinary measurements, a spectrum is affected by wavelength characteristics of the analysis system. In order to measure a spectrum of a sample free from influence due to wavelength characteristics of the analysis system, Ex spectrum correction is performed using Rhodamine B as a standard. Similarly Em spectrum is corrected by using diffuser and attenuator mentioned in the instrument manual. Both the spectra are correctable within 220 to 800 nm are scanned in the correct. Emission spectra are recorded with excitation band pass 5 nm and emission band pass 1.5 nm, while the excitation spectra are recorded with excitation band pass of 1.5 nm and emission band 5 nm.
Figure 2.5 Experimental setup of F-2700 fluorescence spectrophotometer.

**Specifications: Hitachi-F-2700 Fluorescence Spectrophotometer**

- Mono chromators: Large stigmatic concave grating having 900 lines/mm is used on both excitation and emission side with eagle mounting. Blaze wavelength is 300 nm on excitation side and 400 nm on emission side.

- Measuring Wavelength range: 220 to 800 nm and zero order light on both excitation and emission sides.

- Light source: 150W xenon lamp with ozone self dissociation function.

- Detector: Photomultiplier R372 F for measurements and photoelectric tube R518 for monitoring.

- Resolution: 1.5 nm (with minimum band pass)

- Wavelength accuracy: ±2 nm

- Wavelength scan speed: 60, 300, 1500, 3000, 12000 nm/min

- Excitation slit width: 2.5, 5, 10, and 20 nm

- Emission slit width: 2.5, 5, 10, and 20 nm

- PMT Voltage: 250, 400, 700 V
2.7 Conclusions

The solution combustion process is a potential technique for preparation of nano powders of oxide materials. Combustion synthesis is an important powder processing technique generally used to prepare oxide materials. It involves several advantages like fast heating, short reaction time, besides producing foamy, homogeneous and high surface area nano crystalline products. It has also the advantage of doping desired amount of ions in solution medium and low processing temperature leading to uniform crystallite size. The combustion-synthesized powders have high surface area and can be sintered to high densities at lower sintering temperatures. The samples prepared from combustion technique. The various powder properties can be systematically tuned, by altering the oxidant-to-fuel ratio. Whereas, other techniques require long processing time, expensive chemicals, special experimental set up and long sintering or annealing time to get the desired product. The nano-crystalline undoped and doped ZnO powders are synthesized by solution combustion method.

Structural and luminescent properties by using various techniques such as powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), Raman, UV–Vis, photoluminescence (PL) and thermoluminescence (TL) techniques.

Phase purity of the nanoparticles is characterized by powder X-ray diffraction (XRD) using Rigaku Miniflex II diffractometer with Cu Kα (λ = 1.541 Å) radiation. Surface morphology of the powders is examined by scanning electron microscope (SEM) (Hitachi S-300N model). Diffused reflectance is recorded using Shimadzu (UV-1800). Raman studies are carried by Jov Raman micro-785 Ocean Optics microscope. The UV–Vis absorption of the samples is recorded on SL 159 ELICO UV–Vis Spectrophotometer. Photoluminescence (PL) measurements are performed using Hitachi Spectrofluorimeter (Model F-2700) equipped with 150W Xenon lamp as an excitation source. For TL measurements, 40 mg of nanophosphor are exposed to γ- rays (60Co) 0. TL measurements are carried out on a TL Reader (model: TL1009I; Nucleonix Systems Pvt Ltd, Hyderabad, India) in the temperature range 325-750 K and Harshaw 3500 TLD reader.
2.8 References

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