Chapter 2
Experimental (methodology and materials)
2.1. Materials

In this chapter a brief description of the experimental techniques used to synthesise and characterization of the Yttrium silicate ($Y_2SiO_5$) nano phosphors is presented. The combustion method was used to synthesize the Yttrium silicate nano phosphors using organic and plant based fuels. Chemicals used for preparing $Y_2SiO_5$ nano phosphors is given in the below Table 2.1.

**Table 2.1.** List of chemicals / extracts used for the preparation of undoped and doped $Y_2SiO_5$ nanophosphors.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemical Name</th>
<th>Chemical formula</th>
<th>Manufacture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Yttrium (III) Nitrate, Hexahydrate</td>
<td>$Y(NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>2</td>
<td>Praseodymium (III) Nitrate, Hexahydrate</td>
<td>$Pr(NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>3</td>
<td>Dysprosium (III) Nitrate, hydrate</td>
<td>$Dy(NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>4</td>
<td>Samarium (III) Nitrate, Hexahydrate</td>
<td>$Sm(NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>5</td>
<td>Europium (III) Nitrate, Hexahydrate</td>
<td>$Eu(NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>6</td>
<td>Cerium (III) Nitrate, Hexahydrate</td>
<td>$Ce NO_3)_3.6H_2O$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>7</td>
<td>Urea</td>
<td>$NH_2CONH_2$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>8</td>
<td>Sugar</td>
<td>$C_{12}H_{22}O_{11}$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>9</td>
<td>Diformyl Hydrazine (DFH)</td>
<td>$C_2H_4N_2O_2$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>10</td>
<td>Fumed silica</td>
<td>$SiO_2$</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>11</td>
<td>Sodium Chloride</td>
<td>$NaCl$</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>12</td>
<td>Potassium Iodide</td>
<td>$KI$</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>13</td>
<td>Ammonium Fluoride</td>
<td>$NH_4F$</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>14</td>
<td>Ammonium Chloride</td>
<td>$NH_4Cl$</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>15</td>
<td>Ammonium Bromide</td>
<td>$NH_4Br$</td>
<td>SD Fine Chemicals</td>
</tr>
<tr>
<td>16</td>
<td>Latex of <em>Calotropis gigantea</em></td>
<td>-</td>
<td>Collected from plant</td>
</tr>
</tbody>
</table>
The obtained product was calcined at 1000 °C for 3 hrs and used for characterisation. The powder X-ray diffraction (PXRD) and scanning electron microscope (SEM) coupled with the energy dispersive X-ray (EDX) spectrometer were used to investigate the crystalline structure, particle morphology and elemental composition of the phosphor powders, respectively. Transmission Electron Microscopy (TEM) was also used to examine the crystalline structure of the phosphors. A 325 nm He-Cd laser fitted with a Horiba spectrometer and a photomultiplier detector was used to collect photoluminescence data in air at room temperature.

2.2. Combustion chamber

The combustion process was performed in an electric muffle furnace (Tempo Instruments and Equipment, Bombay) is shown in Fig 2.1. It operates on 240 Volts AC, 13.75 Amps current. It has power rating of 3.3 KW and an operating volume of 35x15x15 cm$^3$. The heating element is Kanthal wire (Fe-67 %, Cr-25 %, Al-5 % and Co-3 %) of 18 SWG. The average heating rate is maintained at 10 °C per minute. Chromel–Alumel thermocouple (Cr-Al: 1200 °C, HIMA) is used to measure the furnace temperature. An exhaust fan for ventilating the fumes emanating from the combustion process is positioned approximately at 6 feet above the furnace such that the convection current does not affect the combustion process.

![Muffle furnace used for combustion synthesis](image)

**Fig.2.1.** Muffle furnace used for combustion synthesis
2.2.1. Preparation of Diformyl hydrazine (C$_2$H$_4$N$_2$O$_2$; DFH)

Formic acid (2 mol %) and hydrazine hydrate (1 mol %) are used for the preparation of DFH fuel. For preparation 150 ml of formic acid, 50 ml of hydrazine hydrate were mixed well and heated on the steam bath overnight. The solvent obtained is then removed by heating under reduced pressure for which 100 ml of ethanol was added to separate the solid DFH which was then collected and then dried in air (MP 160 oC). The yield obtained was ~60%. The equation for the preparation of DFH is given below

\[
2\text{HCOOH} + \text{N}_2\text{H}_4.\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{N}_2\text{O}_2 (s) + 3\text{H}_2\text{O} (l) \quad \text{------(2.0)}
\]

2.2.2. Collection of latex of Calotropis Gigantea fuel

*Calotropis gigantea* (Crown flower) is a species of *Calotropis* native to Cambodia, Indonesia, Malaysia, Philippines, Thailand, Sri Lanka, India, China and Pakistan.

![Calotropis gigantea latex](image)

*Fig.2.2. Calotropis gigantea* latex used for the preparation of nanophosphors (Inset: milky extract collected from the plant)
It is a large shrub growing to 4 m (13 ft) tall. It has clusters of waxy flowers that are either white or lavender in colour. Each flower consists of five pointed petals and a small, elegant "crown" rising from the centre, which holds the stamens. The calotropis has only two species namely *Calotropis gigantea* and the *Calotropis procera*. Both the species are found throughout the world, but the *calotropis procera* is more common which has purple flower while the *Calotropis gigantia* has whitish flower. Physically the main difference between the two species that are easily differentiated is their flowers color while in bud or bloomed condition. So, it is difficult to recognize the species if the plant is not having flower. A brief account of the properties of latex of both species was presented by Verma and Verma [1]. Further Murti and Sheshadri studied some properties of calotropis gigantia [2], Dhar and Singh published a paper on the chemistry of calotropis procera [3], Gupta et. al [4] reported the presence of two pentacyclic triterpenes. Edeoga et. al studied a few chemical constituents [5] of calotropis gigantea.

The *Calotropis* has several uses from the ancient time. Tannin used as dyestuff. A macerated bark extract can be used for de-hairing hides and tanning. The bark and the latex are widely used as arrow and spear poisons. The latex is cardio toxic with the active ingredient being calotropin. Latex of Calotropis procera is 80 % effective in inhibiting the activity of the tobacco mosaic virus. The leafy branches are said to deter ants. In medicine compounds derived from the plant have been found to have emeto-cathartic and digitalic properties. The principal active medicines are asclepin and mudarin. Other compounds have been found to have bactericidal and vermicidal properties. The latex contains a proteolytic enzyme called caloptropaine. An infusion of bark powder is used in the treatment and cure of leprosy and elephantiasis. It is inadvisable to use bark that has been kept for more than a year. The root bark is an emetic, the flower a digestive, and a tonic is used for asthma. Bark and wood stimulate lactation in cattle. Roots (extremely poisonous) are applied for snakebite. The milky sap is used as a rubefacient and is also strongly purgative and caustic.

The latex is used for treating ringworm, guinea worm blisters, scorpion stings, venereal sores and ophthalmic disorders. It’s use in the treatment of skin diseases has caused severe bullous dermatitis leading sometimes to hypertrophic scars. The local
The effect of the latex on the conjunctiva is congestion, epiphora and local anaesthesia. The twigs are applied for the preparation of diuretics, stomach tonic and anti-diarrhoeics and for asthma. It is also used in abortion, as an anthelmintic, for colic, cough, whooping cough, dysentery, headache, lice treatment, jaundice, sore gums and mouth, toothache, sterility, swellings and ulcer.

In the present work *Calotropis gigantea* milky latex is collected at Tumkur University campus, Tumkur, Karnataka, India, which is shown in Fig 2.2. The milky plant latex was collected in the early morning by cutting the stems of the plant and directly used for synthesis of the samples.

### 2.3. Calculation of stoichiometry of redox mixture

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 [6]. Carbon and hydrogen are considered as reducing elements with the values +4 and +1 respectively. Oxygen was considered as oxidizing element with the value of –2. The valence of nitrogen is considered to be zero because of its conversion to molecular nitrogen during combustion. Oxidizing elements have positive valencies and reducing elements have negative valencies.

Accordingly, the oxidizing (O) and reducing (F) valences for M (NO₃)₃ and fuels can be calculated as follows. The total oxidizing valency of metal nitrates can be calculated by arithmetic summation of oxidizing and reducing valencies of elements present in oxidizer. Similarly, the total reducing valency of a reducer (fuel) can also be obtained by arithmetic summation of oxidizing and reducing valencies of elements present in it.

\[
\frac{Oxidizer}{fuel} = \frac{\sum \text{all oxidizing and reducing elements in oxidizer}}{\sum \text{oxidizing and reducing elements in fuel}} \quad (2.1)
\]

Accordingly, the oxidizing (O) and reducing (F) valencies for different compounds can be calculated as follows:
Oxidiser valence for metal nitrates: \( M(\text{NO}_3)_3 \) where \( M = \text{Y, Sm, Dy, Eu, Ce, Pr} \)

\[
\begin{align*}
1 \ M &= 1 \times (+3) = 03 \\
9 \ O &= 9 \times (-2) = -18 \\
3 \ N &= 3 \times (0) = 00 \\
\text{Total oxidiser valence} &= -15
\end{align*}
\]

Reducer valence for fuels

a) Urea \((\text{NH}_2\text{CONH}_2)\):

\[
\begin{align*}
2 \ N &= 2 \times (00) = 00 \\
4 \ H &= 4 \times (+1) = +04 \\
1 \ C &= 1 \times (+4) = +04 \\
1 \ O &= 1 \times (-2) = -02 \\
\text{Total reducer valence} &= -06
\end{align*}
\]

b) Sugar \((\text{C}_{12}\text{H}_{22}\text{O}_{11})\):

\[
\begin{align*}
12 \ C &= 12 \times (+4) = +48 \\
22 \ H &= 22 \times (+1) = +22 \\
11 \ O &= 11 \times (-2) = -22 \\
\text{Total reducer valence} &= 48
\end{align*}
\]

c) DFH \((\text{C}_2\text{H}_4\text{N}_2)\):

\[
\begin{align*}
2 \ C &= 2 \times (+4) = +04 \\
4 \ H &= 4 \times (+1) = +00 \\
2 \ N &= 2 \times (0) = -04 \\
2 \ O &= 2 \times (-2) = +08 \\
\text{Total reducer valence} &= +08
\end{align*}
\]
(i) Preparation of pure $\text{Y}_2\text{SiO}_5$ with different fuels

**Table 2.2. (a).** The stoichiometry of the redox mixture for combustion process to synthesise pure $\text{Y}_2\text{SiO}_5$ with different fuels

<table>
<thead>
<tr>
<th>Y(NO$_3$)$_3$ (gms)</th>
<th>Fumed Silica (gms)</th>
<th>Urea (gms)</th>
<th>Sugar (gms)</th>
<th>DFH (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8301</td>
<td>0.6008</td>
<td>1.5</td>
<td>1.0696</td>
<td>1.7715</td>
</tr>
</tbody>
</table>

(ii) Preparation of the Sample $\text{Y}_2\text{SiO}_5$:M$^{3+}$

Where M = dopants (Rare earth ions) Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$, Ce$^{3+}$ & Pr$^{3+}$

(iii) Preparation of the Sample $\text{Y}_2\text{SiO}_5$: M$_X$.N$_Y$

Where M = dopants Dy$^{3+}$ (3 mol %) and Ce$^{3+}$(1 mol %)

N = Co- dopants Eu$^{3+}$, Sm$^{3+}$, Y = 0.25, 0.50, 0.75, 1.0, 1.5, 2.5, 3.5, 4.5 and 5.5 mol %.

**Table 2.2 (b).** The stoichiometry of the redox mixture for combustion process to synthesise of doped and codoped $\text{Y}_2\text{SiO}_5$ nano phosphors

<table>
<thead>
<tr>
<th>X (mol %)</th>
<th>Y(NO$_3$)$_3$ (gms)</th>
<th>SiO$_2$ (gms)</th>
<th>Eu (NO$_3$)$_3$ (gms)</th>
<th>Dy (NO$_3$)$_3$ (gms)</th>
<th>Sm (NO$_3$)$_3$ (gms)</th>
<th>Ce (NO$_3$)$_3$ (gms)</th>
<th>Pr (NO$_3$)$_3$ (gms)</th>
<th>Urea (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.8301</td>
<td>0.6008</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>0.01</td>
<td>3.8158</td>
<td>0.6008</td>
<td>0.0338</td>
<td>0.0348</td>
<td>0.0444</td>
<td>0.04342</td>
<td>0.04349</td>
<td>1.5</td>
</tr>
<tr>
<td>0.03</td>
<td>3.7774</td>
<td>0.6008</td>
<td>0.1014</td>
<td>0.1045</td>
<td>0.1333</td>
<td>0.1302</td>
<td>0.1304</td>
<td>1.5</td>
</tr>
<tr>
<td>0.05</td>
<td>3.7391</td>
<td>0.6008</td>
<td>0.1690</td>
<td>0.1742</td>
<td>0.2221</td>
<td>0.2171</td>
<td>0.2174</td>
<td>1.5</td>
</tr>
<tr>
<td>0.07</td>
<td>3.7007</td>
<td>0.6008</td>
<td>0.2366</td>
<td>0.2439</td>
<td>0.3110</td>
<td>0.3039</td>
<td>0.3044</td>
<td>1.5</td>
</tr>
<tr>
<td>0.09</td>
<td>3.6624</td>
<td>0.6008</td>
<td>-</td>
<td>0.3136</td>
<td>0.3999</td>
<td>0.3907</td>
<td>0.3714</td>
<td>1.5</td>
</tr>
<tr>
<td>0.11</td>
<td>3.6240</td>
<td>0.6008</td>
<td>-</td>
<td>0.3833</td>
<td>0.4888</td>
<td>0.4776</td>
<td>0.4783</td>
<td>1.5</td>
</tr>
</tbody>
</table>
2.4 Synthesis

2.4.1. Preparation of pure $Y_2\text{SiO}_5$ nanopowders with different organic fuels

$Y_2\text{SiO}_5$ nanopowder was synthesized by solution combustion technique using urea, sugar and DFH as fuels. The starting materials used were yttrium nitrate and fumed silica. An aqueous solution containing stochiometric amounts of yttrium nitrite \( \text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \); Silica fumes (\( \text{SiO}_2 \): surface area \( \sim 200 \text{ m}^2 \text{ g}^{-1} \)) and fuel were taken in a cylindrical Pyrex dish of 300 ml capacity and dissolved in double distilled water. The stoichiometry of composition was calculated based on the total oxidizing and reducing valences of oxidizer and the fuel [7]. The excess water was allowed to evaporate by heating over a hot plate until a wet powder was left out. Then the crystalline Pyrex dish was introduced into a pre-heated muffle furnace maintained at \( 400 \pm 10 ^\circ \text{C} \). The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products (nitrogen and carbon). Flow chart for the synthesis of $Y_2\text{SiO}_5$ nanophosphors by green synthesis method and chemical method is show in Fig. 2.3(a) and 2.3(b). The obtained sample was calcined at 1200, 1300 and 1400 \(^\circ\text{C}\) for 2 hr. The complete reaction can be written as

\[
2\text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}+\text{SiO}_2+\text{C}_1\text{H}_2\text{H}_2\text{O}_{11} \text{(Sugar)} \rightarrow \text{Y}_2\text{SiO}_5+3\text{N}_2+23\text{H}_2\text{O}+6\text{CO}_2 \quad \text{------- (2.2)}
\]
\[
2\text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}+\text{SiO}_2+\text{C}_2\text{H}_4\text{N}_2\text{O}_2 \text{(DFH)} \rightarrow \text{Y}_2\text{SiO}_5+4\text{N}_2+14\text{H}_2\text{O}+2\text{CO}_2 \quad \text{------- (2.3)}
\]
\[
2\text{Y(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}+\text{SiO}_2+\text{CO(NH}_2\text{)}_2 \text{(Urea)} \rightarrow \text{Y}_2\text{SiO}_5+4\text{N}_2+14\text{H}_2\text{O}+\text{CO}_2 \quad \text{------- (2.4)}
\]
Fig. 2.3(b). Flow chart for the synthesis of $Y_2SiO_5$ nanophosphor
2.4.2. Synthesis Y$_2$SiO$_5$ nanophosphors by chemical and green synthesis route

2.4.2.1 Preparation of Y$_2$SiO$_5$:Sm$^{3+}$ (1-9 mol %) nanophosphor with different fluxes by chemical route

Y$_2$SiO$_5$:Sm$^{3+}$ (1-9 mol %) nanophosphors were synthesized by solution combustion technique using Urea as a fuel. The stoichiometrically calculated quantity of Yttrium nitrate Y(NO$_3$)$_3$.6H$_2$O, Silica fumes (SiO$_2$), Samarium nitrate Sm(NO$_3$)$_3$.6H$_2$O, and urea (NH$_2$CONH$_2$) were taken in a cylindrical Pyrex dish of 300 ml capacity and dissolved in double distilled water and after that required amount of fluxes (NaCl, KI, NH$_4$Br, NH$_4$Cl and NH$_4$F) were introduced in to the reaction mixture and stirred well for 5 – 10 min. Then the crystalline Pyrex dish was introduced into a pre-heated muffle furnace maintained at 400 ± 10 °C. The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products (nitrogen and carbon dioxide). The obtained product Y$_2$SiO$_5$:Sm$^{3+}$ (1-9 mol %) show fluffy and voluminous. The obtained product was calcined at 1200 °C and used for characterization. The complete reaction can be written as

$$2Y(NO_3)_3.6H_2O(aq)+SiO_2(s)+Sm(NO_3)_3+CO(NH_2)_2\text{(Urea)}\rightarrow Y_2SiO_5:Sm^{3+}(s)$$

$$+4N_2(g)+14H_2O(g)+CO_2(g)$$

--- (2.5)

2.4.2.2 Preparation of Y$_2$SiO$_5$:Dy$^{3+}$ (1-9 mol%) nano phosphor via chemical route

Yttrium nitrate Y(NO$_3$)$_3$.6H$_2$O(Sigma Aldrich), Dysprosium nitrate Dy(NO$_3$)$_3$.6H$_2$O (Sigma Aldrich), the fuel urea (Sigma Aldrich), Silica fumes (Aldrich, surface area 200 m$^2$ g$^{-1}$) and flux NaCl were taken as starting materials. Appropriately weighed and thoroughly mixed batches of these raw materials in a petridish. The proper amount of NaCl flux was dissolved in double distilled water and well stirred for 10 min. Then the crystalline Pyrex dish is introduced into a pre-heated muffle furnace maintained at 400 ± 10 °C. The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products (nitrogen and carbon dioxide). The obtained product of Y$_2$SiO$_5$:Dy$^{3+}$ show fluffy and voluminous. Series of powders which have the compositions of Y$_2$SiO$_5$:Dy$^{3+}$ (1-9 mol %) were synthesized and the samples were calcined at 1000 °C for 3 hrs.
2.4.2.3 Preparation of $Y_2SiO_5: Dy^{3+} (3 \text{ mol} \%) : Eu^{3+} (0.5 - 5.5 \text{ mol} \%)$ nano phosphor via chemical route

Yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$, Dysprosium nitrate $Dy(NO_3)_3 \cdot 6H_2O$, Europium nitrate $Eu(NO_3)_3 \cdot 6H_2O$, Silica fumes, the fuel urea and flux NaCl were taken as starting materials. Appropriately weighed and thoroughly mixed batches of these raw materials in a petridish. The proper amount of NaCl flux was dissolved in double distilled water and well stirred for 10 min. The excess water was allowed to evaporate by heating over a hot plate until a wet powder is left out. Then the crystalline Pyrex dish is introduced into a pre-heated muffle furnace maintained at $400 \pm 10^\circ \text{C}$. The reaction mixture undergoes thermal dehydration and ignites at one spot with liberation of gaseous products (nitrogen and carbon dioxide). Series of samples which have the compositions $Y_2SiO_5 : Dy^{3+} (3 \text{ mol} \%) : Eu^{3+} (0.5 - 4.5 \text{ mol} \%)$ were synthesized and the samples were calcined at $1000^\circ \text{C}$ for 3 hrs.

2.4.2.4 Preparation of $Y_2SiO_5: Ce^{3+} (0.5 - 7 \text{ mol} \%)$ nano phosphors via bio mediated route

In a typical synthesis of $Y_2SiO_5: Ce^{3+} (0.5 \text{ mol} \%)$, Stoichiometrically calculated amount of Yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich), Cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich), Silica fumes, NaCl as flux and $10 \text{ ml}$ of Calotropis gigantea latex as fuel were dissolved in double distilled water, taken in a cylindrical pyrex dish of 300 ml capacity. Then the cylindrical pyrex dish was introduced into a pre-heated muffle furnace maintained at $400 \pm 10^\circ \text{C}$. The reaction mixture undergoes thermal dehydration and ignites at several spots with liberation of gaseous products. The obtained sample was calcined at $1000^\circ \text{C}$ for 3 hrs. Similar procedure was adopted for the preparation of $Y_2SiO_5$ for other concentrations of $Ce^{3+} (1 - 7 \text{ mol} \%)$ nanophosphors.

2.4.2.5. Preparation of $Y_2SiO_5: Ce^{3+} (1 \text{ mol} \%): Sm^{3+} (0.2 - 1 \text{ mol} \%)$ nanophosphor via bio-mediated route

$Y_2SiO_5: Ce^{3+}_{1 \text{ mol} \%}: Sm^{3+} (0.2, 0.4, 0.6, 0.8, 1 \text{ mol} \%)$ nanophosphors was prepared by using Calotropis gigantea (latex) as a fuel and NaCl as a flux in solution combustion technique. Stoichiometrically calculated amount of Yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich), Cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich), Samarium nitrate $Sm(NO_3)_3 \cdot 6H_2O$ (Sigma Aldrich), Silica fumes, flux NaCl and latex of Calotropis
*gigantea* (natural plant) as a fuel were dissolved in double distilled water, taken in a cylindrical Pyrex dish of 300 ml capacity. The stoichiometry of composition was calculated based on the total oxidizing and reducing valencies of oxidizer and the fuel. Then the cylindrical Pyrex dish was introduced into a pre-heated muffle furnace maintained at 400 ± 10 °C. The reaction mixture underwent thermal dehydration and ignites at several spots with liberation of gaseous products (nitrogen and carbon dioxide). The obtained product $\text{Y}_2\text{SiO}_5$:Ce$^{3+}$Sm$^{3+}$ (0.2, 0.4, 0.6, 0.8, 1 mol %) and it was calcined at 1000 °C for 3 hrs.

**2.4.2.6. Preparation of $\text{Y}_2\text{SiO}_5$:Pr$^{3+}$ (1-9mol%) nanophosphor by bio-mediated route**

$\text{Y}_2\text{SiO}_5$:Pr$^{3+}$ (1-9 mol%) nanopowders are synthesized by solution combustion technique using *calotropis gigantea* as a fuel and NaCl as flux. Yttrium nitrate Y(NO$_3$)$_3$.6H$_2$O, Pr(VO)$_3$.6H$_2$O, Silica fumes (SiO$_2$), and calotropis gigantea (natural plant latex) were dissolved in double distilled water and taken in a cylindrical Pyrex dish of 300 ml capacity. Then the cylindrical Pyrex dish was introduced into a pre-heated muffle furnace maintained at 400 ± 10 °C. The reaction mixture underwent thermal dehydration and ignites at several spots with liberation of gaseous products (nitrogen and carbon dioxide). The obtained product $\text{Y}_2\text{SiO}_5$:Pr$^{3+}$ (1-9 mol%) was fluffy and voluminous and it was calcined at 1000 °C for 3 hrs.

**2.4.2.7. Preparation of $\text{Y}_2\text{SiO}_5$:Eu$^{3+}$(1-7 mol %) nano phosphor by bio-mediated route**

In a typical synthesis of $\text{Y}_2\text{SiO}_5$:Eu$^{3+}$ (1 mol %), stoichiometrically calculated amount of Yttrium nitrate Y(NO$_3$)$_3$.6H$_2$O; Europium nitrate Eu(NO$_3$)$_3$. 6H$_2$O, NaCl as flux and 10 ml of *Calotropis gigantea* latex as fuel were dissolved in double distilled water, taken in a cylindrical pyrex dish of 300 ml capacity. Then the cylindrical pyrex dish was introduced into a pre-heated muffle furnace maintained at 400 ± 10 °C. The reaction mixture undergoes thermal dehydration and ignites at several spots with liberation of gaseous products. The obtained product $\text{Y}_2\text{SiO}_5$:Eu$^{3+}$ was calcined at 1000 °C for 3 hrs.. Similar procedure was adopted for the preparation of $\text{Y}_2\text{SiO}_5$ for other concentrations of Eu$^{3+}$ (3, 5 and 7 mol %) nanophosphors.
2.5. Characterization techniques

2.5.1 Powder X-Ray diffraction (PXRD)

X-ray diffraction technique was one of the most useful in the characterization of crystalline materials, such as metals, inter metallics, ceramics, minerals, polymers, plastics, or other inorganic or organic compounds. X-ray diffraction techniques can be used to identify the phases present in samples from raw starting materials to finished product and to provide information on the physical state of the sample, such as grain size, texture, and crystal perfection. Most of X-ray diffraction techniques are rapid and non-destructive. The sample may be as small as an airborne dust particle or as large as an airplane wing. In general, X-ray analysis is restricted to crystalline materials, although some information may be obtained on amorphous solids and liquids. XRD samples are acceptable in many forms, depending on the availability of the material and the type of analysis to be performed. Single crystals from a few microns to a few inches in diameter or loose or consolidated aggregate of many small crystals can be used. Although the overall size of the sample may be large, the actual area of the sample examined in a given experiment rarely exceeds 1 cm$^2$. The type of information obtained from X-ray diffraction studies ranges from sample composition to details of the crystal structure or the state of orientation of the crystallites. Phase identification can be conducted on virtually all single crystal or powder samples.

2.5.2 Crystallite size measurement from the line broadening in PXRD X-ray Powder Diffraction.

X-ray powder diffraction technique was used to characterize the samples in the form of loose powders or aggregates of finely divided material. These techniques cover various investigations, including qualitative and quantitative phase identification and analysis, determination of crystallinity, micro identification, lattice-parameter determinations, high-temperature studies, thin film characterization, and, in some cases, crystal structure analysis. The powder diffraction method is perhaps best known for its use as a phase characterization tool partly because it can routinely differentiate between phases having the same chemical composition but different crystal structures.
When a beam of monochromatic X-radiation is directed at a crystalline material, the scattering of X-rays by the atoms in a crystalline material produces two distinct results. When the X-rays scattered by atoms in different crystal planes (Figure 2.4) are in-phase, then constructive interference occurs and a strong diffraction signal is observed. The intensity of this diffraction signal depends on the number of atoms within the crystal planes.

![Bragg's Law Diagram](image)

**Fig. 2.4. Scattering of X-rays by atoms of different crystal planes**

For example, scattered X-rays in the above figure, even though they have different path lengths are completely in phase and therefore reinforce one another to produce a strong diffraction peak. In contrast, when the two scattered rays are out-of-phase, they destructively interfere and result in no scattering intensity. X-ray diffraction from a crystalline material arises according to Bragg’s law

$$2d_{hkl} \sin \theta = n \lambda \quad \text{--------} \quad (2.6)$$

where $n$ is an integer, $\lambda$ the wavelength of the x-ray source, $d_{hkl}$ the lattice spacing between the crystallographic planes (hkl) in the crystal (defined by the Miller indices, h, k and l ), and $\theta$ the angle between the x-ray beam and the crystallographic planes. Each crystalline phase has a set of characteristic $d$-values. Each X-ray peak can be characterised by its intensity (height or area) and its width. The intensity depends on the reflecting properties of the particular crystal plane.
From the experimentally obtained d-values major features of the material can be deduced. Firstly, the experimentally obtained values may be compared with the JCPDS standard crystallographic data base so that the diffracting crystallite is identified if the crystal structures were known, as well as providing a measure of sample purity. The d-value and its corresponding hkl values may also be utilised to calculate the lattice parameters accurately. Lattice parameters are the magnitude of the unit vectors a, b and c and α, β, γ which represent the angles between a, b, c, which define the unit cell of the crystal. Calculating the lattice parameters allows for changes in the unit cell, such as expansion or distortion arising due to atomic substitution, to be observed. Secondly, if a combination of phases is present within the XRD patterns, indexing of the unit cell parameters allows for the identification of the individual phases that have contributed to the combined spectra.

The average crystallite size of the nano powders were estimated from the full width at half maximum (FWHM) of the intense peak in the XRD pattern using the Scherrer’s formula, which is given by \( D = \frac{k \lambda}{\beta \cos \theta} \); Where D is the crystallite size (in angstroms), \( \lambda \) the X-ray wavelength and \( \theta \) the Bragg angle. The line broadening, \( \beta \), is measured from the extra peak width at half the peak height and is obtained from the Warren formula

\[
\beta = \beta_M - \beta_S
\]

Where \( \beta_M \) is the measured peak width in radians at half maxima and \( \beta_S \) is the measured peak width in radians at half maxima of the peak corresponding to standard material (silicon). In the present study, shimatzu 7000 diffractometer based on the Bragg-Brentano reflection geometry, was used for the characterization of all the samples. The Cu-Kα from sealed tube was used as the incident beam. A Ni foil was used as a filter and the diffracted beam was mono chromatised with a curved graphite single crystal. The shimatzu 7000 diffractometer was attached with a proportional counter (Argon filled) for the detection of X rays. The X-ray tube rating was maintained at 30 kV and 20 mA. The goniometer was calibrated for correct zero position using silicon standard. Samples were well grounded and made in the form of a slide. As all the micro crystals were randomly oriented, at any point on the sample different planes from crystals will be exposed to X-rays.
Various factors may affect the broadening of diffraction peaks namely (i) crystalline domain size (ii) domain size distribution (iii) crystalline facets (external defects) and micro strain (deformation of the lattice), etc.

The crystalline size (d) was estimated from the broad PXRD peaks using the Scherer’s method [8].

\[ d = \frac{K \lambda}{\beta \cos \theta} \]  \hspace{1cm} (2.8)

where \( d \) the average grain size of the crystallites, \( \lambda \) the wavelength of the CuK_α (1.54 Å), \( \theta \) the angle between the incident beam and the reflection lattice planes and \( \beta \) is the full width at half maxima (FWHM) of the diffraction peak in radian. \( K \) a constant (shape factor) depends on the grain shape. The value of \( K \) can vary 0.7 to 0.9 depending on the crystalline shape. Klug and Alexander suggest the use of 0.9 for calculating average crystallite diameter for circular shaped particles.

Further the broadening of PXRD peaks are due to microstrain, which is proportional to the \( \tan \theta \). Thus, we can obtain the Williamson-Hall (W-H) formula [9] by combining the effect on powder X-ray diffraction patterns for broadening

\[ \beta \cos \theta = \frac{0.9 \lambda}{D} + 4 \varepsilon \sin \theta \]  \hspace{1cm} (2.9)

where \( \varepsilon \) the strain associated with the nanomaterials. Equation (2.9) 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 (0.9\( \lambda \)/D) of this line on Y-axis gives grain size (D).

(i) X-ray Powder Diffraction (XRD) Instrumentation

X-ray diffractometers shown in Fig. 2.5 consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being \( K_\alpha \) and \( K_\beta \). \( K_\alpha \) consists, in part, of \( K_{\alpha 1} \) and \( K_{\alpha 2} \). \( K_{\alpha 1} \) has a slightly shorter wavelength and twice the intensity as \( K_{\alpha 2} \). The specific
wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kα1 and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

![Fig.2.5. Shimadzu X-ray diffractometer (PXRD-7000) used for analysis (Inset: Sample holder)](image)

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed as goniometer. For typical powder patterns, data is collected at 2θ from 5° - 70°, angles that are present in the X-ray scan.
(ii) Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).

Other applications include:

(a) characterization of crystalline materials
(b) identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
(c) determination of unit cell dimensions
(d) measurement of sample purity

With specialized techniques, XRD can also be used to:

a) determine crystal structures using Rietveld refinement
b) determine of modal amounts of minerals (quantitative analysis)
c) characterization of thin films samples.

2.6. Scanning electron microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The schematic view of scanning electron microscope is shown in Fig. 2.6.
The electrons interact with atoms in the sample producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures. The most common (Hitachi-TM 3000 model) SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam as shown in Fig. 2.7.
Transmission electron microscopy (TEM) is used to obtain information from samples that are thin enough to transmit electrons. The schematic view for Transmission electron microscopy as shown in Fig 2.8. In TEM the whole area of interest is illuminated simultaneously. An electron source is required which can produce large total current, so that whole region of interest is illuminated at a useful intensity, even when examining at magnifications of 100 times or less. The transmitted electrons are generally used to from either an image or a diffraction pattern of the specimen. The diffraction lens (The lens immediately after the objective lens) is focused on the plane where image is formed by the objective lens. Subsequent lenses are used to magnify this further and hence a highly magnified image can be formed on the final screen. In the diffraction lens is focused on the plane where the objective lens forms a diffraction pattern. Again the lenses below the diffraction lens are used to magnify further the diffraction pattern. There are two different ways of obtaining images of sample in TEM: (a) conventional imaging and (b) high resolution imaging. First method involves the use of an aperture in the back focal plane, which allows only one electron beam to contribute to the image.
Fig. 2.8. The schematic view for Transmission electron microscopy

This method of obtaining image information therefore exclude the possibility of observing the periodicity of crystalline samples, since interference of at least two beams are required in the image plane to obtain such periodic information and
contrast arises either from diffraction contrast or phase contrast. The second method of obtaining an image also involves the use of an aperture, but in this case the direct beam and a number of diffracted beams are allowed to contribute to the image. When using the microscope in the conventional image mode, the objective aperture is used to select only one electron beam to form the image. A bright field image is formed in directly transmitted beam is selected and a dark field image is formed if a diffracted beam is selected. If the crystal has been set up in such a way that only one strong diffraction beam is excited, then this beam is selected for imaging. This technique is usually used when crystal defects are imaged. A diffraction pattern is formed in the back focal plane of the objective lens. Hence if the diffraction lens is focused onto the back plane of the objective lens, rather that on to the first image plane and objective aperture is removed, the diffraction pattern will be visible on final screen. There are two methods which are commonly available a) selected area electron diffraction (SAED) using an aperture to select the area b) selected area diffraction using a focused electron probe to define the selected area.

The first method is used in conjunction with a defocused electron beam so that a large area of the sample is illuminated with electron and hence this large area is contributing to the generation of diffraction of beams. The technique involves inserting an aperture in the first image plane so that only those electrons generated from the area defined by the aperture will be able to contribute to the diffraction pattern. The other technique simply involves condensing the electron probe to the area of interest, so that the probe position uniquely define the region from where the diffraction beam originates. The electron probe mode is the most common method of obtaining the diffraction pattern.

In the present study the Hitachi H-8100 (accelerating voltage up to 200 kV LaB6 filament) shown in Fig 2.9 equipped with an ultra high resolution objective pole piece in the top entry configuration was used. The cleaved samples are examined under the transmission electron microscope in order to study the nature of the defect (dislocation) structure and the inter planar spacing. The SAED patterns are also obtained in certain cases.
Fig. 2.9. Hitachi H-8100, Transmission electron microscopy used for TEM studies

2.8. UV-Visible absorption spectroscopy

UV-Visible absorption spectroscopy investigates the interactions between ultraviolet or visible electromagnetic radiation and matter. UV-Visible spectroscopic measurements provide precise information about molecular species present in the sample. The UV-Vis spectral range is approximately 190 - 900 nm, as defined by the working range of typical commercial UV-Vis spectrophotometers. The short-wavelength limit for simple UV-Vis spectrometers is the absorption of ultraviolet wavelengths less than 180 nm by atmospheric gases. Purging a spectrometer with nitrogen gas extends this limit to 175 nm. Working beyond 175 nm requires a vacuum spectrometer and a suitable UV light source. The long-wavelength limit is usually determined by the wavelength response of the detector in the spectrometer. High-end commercial UV-Vis spectrophotometers extend the measurable spectral range into the NIR region as far as 3300 nm. The light source is usually a deuterium discharge lamp for UV measurements and a tungsten-halogen lamp for visible and NIR measurements. The instruments automatically swap lamps when scanning between the UV and visible regions. The wavelengths of these continuous light sources are
typically dispersed by a holographic grating in a single or double monochromator or spectrograph. The spectral band pass is then determined by the monochromator slit width or by the array-element width in array-detector spectrometers. Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements. The detector in single-detector instruments is a photodiode, phototube, or photomultiplier tube (PMT). UV-Vis-NIR spectrometers utilize a combination of a PMT and a Peltier-cooled PbS IR detector. The light beam is redirected automatically to the appropriate detector when scanning between the visible and NIR regions. The diffraction grating and instrument parameters such as slit width can also be changed. The schematic view for UV-Vis measurements is shown in Fig. 2.10. UV-Vis absorption instrument (Lambda 35 UV, WinLab V6.0) was used to record the absorption was shon in Fig. 2.11.

![Schematic View](image)

**Fig. 2.10.** The schematic view for UV-Vis measurements

![Perkin Elmer Lambda-35 Spectrophotometer](image)

**Fig 2.11.** Perkin Elmer Lambda-35 Spectrophotometer used for UV-Vis studies.
2.9. Fourier Transform Infrared (FT-IR) spectroscopy

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. The schematic view of Fourier Transform Infrared (FT-IR) spectrometer is shown in Fig 2.12.

![FTIR interferometer diagram](image)

**Fig 2.12.** The schematic view of Fourier Transform Infrared (FT-IR) spectrometry

The normal instrumental process is as follows:

(i) The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector). (ii) The Interferometer: The
beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer. (iii) The Sample: The 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. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed. (iv) The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. (v) The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

Fig 2.13. Perkin Elmer (1000) Spectrophotometer used for FTIR studies.

In the present work Perkin Elmer (1000) Spectrophotometer used for FTIR studies which is shown in Fig 2.13.
2.10 Creation of defects

2.10.1 Gamma (γ) irradiation

The energy associated with gamma radiation (gamma rays emitted by cobalt-60) is high enough to break the molecular bonds and ionize atoms, but not high enough to affect structure of the atomic nucleus. Gamma radiation may modify chemical, physical or biological properties of the irradiated material, however, the irradiated product does not become radioactive.

Cobalt-60 ($^{60}\text{Co}$) decays (disintegrates) into a stable (non-radioactive) nickel isotope ($^{60}\text{Ni}$) principally emitting one negative beta particle (of maximum energy 0.313 MeV) with a half-life of about 5.27 years. It is produced artificially by neutron activation of the isotope $^{59}\text{Co}$. The activated nickel nucleus emits two gamma rays with energies of 1.17 and 1.33 MeV, hence the overall nuclear equation of the reaction is

$$^{59}_{27}\text{Co} + n \rightarrow ^{60}_{28}\text{Ni} + e^- + \text{gamma rays} \quad \text{(2.10)}$$

In order to create defects in silicate nanophosphors equal amount of sample powder were measured and covered with a black cardboard to avoid external radiations present in the surroundings. Then placed in the gamma chamber (shown in Fig. 2.14) of energy 1.17 to 1.33 MeV at ISRO, ISAC, Bangalore supplied by Board of Radiation and Isotope Technology, Mumbai. The dose rate of the gamma source used is 37 rad s$^{-1}$. In the present studies the dose range used was 1-6 kGy exposed at room temperature.

Calculations: The gamma radiation chamber dose rate = 37 rad/s,

In terms of kGy (1 Gy = 100 rad)

For 1 kGy time, \( \text{time} = \frac{10^5}{37 \times 60} = 45\ \text{min} \) \quad \text{(2.11)}
Fig. 2.14. Schematic diagram of gamma chamber - 900 used to irradiate the powdered/pellet sample

2.10.2 UV irradiation

UV radiation covers a small part of the electromagnetic spectrum. Other regions of the electromagnetic spectrum include radio waves, microwaves, infrared radiation, visible light, X-rays, and γ radiation. The feature that characterizes the properties of any particular region of the spectrum is the wavelength of the radiation. UV radiation spans the wavelength region from 400 to 100 nm. Even in the UV portion of the spectrum the biological effects of the radiation vary enormously with wavelength and for this reason the UV spectrum is further subdivided into three regions.

( i ) UVA (near UV) 315 - 400 nm
( ii ) UVB (middle UV) 280 - 315 nm
( iii ) UVC (far UV) 180 - 280 nm

The division between UVB and UVC is chosen as 290 nm since UV radiation at shorter wavelengths is unlikely to be present in terrestrial sunlight, except at high altitudes. The choice of 320 nm as the division between UVB and UVA is perhaps
more arbitrary. Although radiation at wavelengths shorter than 320 nm is generally more photobiologically active than longer wavelength UV radiation, advances in molecular photobiology indicate that a subdivision at 330–340 nm may be more appropriate and for this reason the UVA region has been divided into UVAI (340–400 nm) and UVAII (320–340 nm). The defects can be easily created by exposing phosphor material to UV radiations. The instruments used for UV exposure is shown in Fig.2.15. For UV exposure the phosphor material were equally measured and placed under UV source of fluorescent lamp 15 W and wavelength 254 nm, provided by Nucleonix instruments, Hyderabad by spreading uniformly for required time period in the range 1-60 min. Then the exposed samples were directly used for TL measurements.

![Fig.2.15. UV source for UV-irradiation](image)

### 2.11. Thermoluminescence (TL)

Significant advancements have been made in thermoluminescence experiments during last couple of decades on bulk materials. With the advent of nanotechnology, there is still a considerable amount of research for new nanophosphor materials with better TL and dosimetric properties. The importance of nanomaterials has increased tremendously because of the enhanced optical, electronic and structural properties than their bulk counterparts due to quantum size effect and an increased surface to volume ratio. In order to use information about luminescence process of phosphors in various applications, the knowledge of defect centres and their distribution in the band gap of solids is very important. Further, it is also important for basic study to
understand defects and reorganization of energy levels in nanostructured materials and related phenomena. One of the most sensitive methods of studying radiation induced defects is TL. It is well known that the defect centres created by ionizing radiations are intimately related to the process of TL. Thermoluminescence studies of nanocrystalline phosphors are important not only from application point of view, TL efficiency increases due to increase in the surface states which also increase on increasing the particle size. Accordingly, as the contents of the surface states increase, the particles may provide more accessible carriers (holes and electrons) for the TL recombination proportional to the surface states. As the surface states increase rapidly, the TL efficiency can be enhanced.

Thermostimulated luminescence (TSL) is a phenomenon of light emission from a previously energy absorbed material when heated. This is quite different from light emission from a substance when it is heated to incandescence. In the case of TSL, when once the light is emitted during heating it cannot be made to emit light again by simply cooling the specimen and reheating. The TSL is a simple, very sensitive and reliable technique and has wide applications in personal monitoring, archeological age determination of pottery, geological dating etc.

In the present study, pure and rare earth doped nanosilicates irradiated with gamma rays at room temperature has been studied. The TSL measurements were carried out using TSL set up assembled with the components supplied by Nucleonix systems[10] private Ltd (Fig.2.16).

![Fig. 2.16. Experimental setup used for TL studies](image)
2.12. Photoluminescence (PL) studies

A schematic diagram of a general purpose spectrofluorometer has a xenon lamp as a source of exciting light as shown in Fig. 2.17. The instrument shown is equipped with monochromators to select both the excitation and emission wavelengths. The excitation monochromator in this schematic contains two gratings, which decreases stray light, that is, light with wavelengths different from the chosen one. In addition, these monochromators use concave gratings, produced by holographic means to further decrease stray light. The fluorescence is detected with photomultiplier tubes and quantified with the appropriate electronic devices. The output is usually presented in graphical form and stored digitally.

The instrument schematic also shows the components of the optical module that surrounds the sample holder contains a number of convenient features that are useful on a research instrument. Shutters are provided to eliminate the exciting light or to close off the emission channel. A beam splitter is provided in the excitation light path. This splitter reflects part of the excitation light to a reference cell, which generally contains a stable reference fluorophore. The beam splitter consists of a thin piece of clear quartz, which reflects about 4% of the incident light. This amount is generally adequate for a reference channel that frequently contains a highly fluorescent quantum counter. The intensity from the standard solution is typically isolated with a band pass filter, and is proportional to the intensity of the exciting light. Changes in the intensity of the arc lamp may be corrected for by division of the intensity from the sample by that of the reference fluorophore. Polarizers are present in both the excitation and emission light paths. Generally, the polarizers are removable so that they can be inserted only for measurements of fluorescence anisotropy, or when it is necessary to select for particular polarized components of the emission and/or excitation. Accurate measurement of fluorescence anisotropies requires accurate angular positioning of the polarizers. The polarizer mounts must be accurately indexed to determine the angular orientation. The optical module shown in Fig. 2.17 has an additional optical path on the right side of the sample holder.

The present trend is toward small compact spectrofluorometers, with all the optical components in a single enclosure. Such instruments are easy to maintain because there is little opportunity to alter the configuration. In the present study
Horiba Fluorolog-3 Spectrofluorimeter used for PL studies which is shown in Fig. 2.18.

**Fig. 2.17.** Schematic diagram of spectrofluorimeter

**Fig. 2.18.** Horiba Fluorolog-3 Spectrofluorimeter used for PL studies (Inset: sample holder)
2.13 Raman spectroscopy

Raman spectroscopic studies were performed using a Renishaw In-via Raman spectrophotometer equipped with a CCD (charge coupled device) with 633 nm (He–Cd laser power set at 30 mW) and a Leica DMLM optical microscope equipped with 50x objective providing a laser spot of 2 mm in diameter. The schematic diagram of Raman spectrophotometer is shown in Fig. 2.19. The system also includes a monochromator and a filter system. The Raman spectra are taken from different places of the implanted samples in the range 100-2500 cm\(^{-1}\) to verify the reproducibility and consistency of the data. Three accumulations for each position with an accumulation time of 10 s was maintained for all the measurements. The spectra are calibrated using 520 cm\(^{-1}\) line of silicon wafer. The data acquisition and analysis are carried out using *WIRE 2.0* software [11].

![Schematic diagram of the Raman Spectrophotometer.](image)

*Fig. 2.19. Schematic diagram of the Raman Spectrophotometer.*
References


