Chapter 2

Experimental Studies
Different experimental procedures used by the author in the preparation of certain rare-earth ions doped powder phosphors are described. Measurements concerning the X-ray diffractograms, thermal analysis, scanning electron microscopy (SEM) and fluorescence spectra of powder phosphor materials are also given here. The following five different types (I-V) of phosphors are prepared.

**Type – I (Chapter-III (A, B, C))**

a) (La, Zn)OF: \( \text{Sm}^{3+} \) Under an inert (\( N_2 \) gas) atmosphere with fixed dopant (0.05 mol) and varied (La, Zn) ion concentrations.

b) (Ln, Zn)OF: \( \text{Eu}^{3+} \) (Ln=Y, La, Gd) Varied (Ln, Zn) and fixed dopant, \( \text{Eu}^{3+} \) (0.05 mol) ion concentrations.

c) (Gd, Zn)OF: \( \text{Ce}^{3+} \) Varied (Gd, Zn) and fixed dopant, \( \text{Ce}^{3+} \) (0.05 mol) ion concentrations.

**Type – II (Chapter-IV (A, B, C))**

a) LnOBr : \( \text{Eu}^{3+} \) (Ln=Y, La, Gd) Under an inert (\( N_2 \) gas) atmosphere with a varied Ln and a fixed dopant (\( \text{Eu}^{3+} \)) (0.05 mol).

b) (Gd, Y)OBr : \( \text{Sm}^{3+} \) Varied hosts (Gd, Y) and having a fixed dopant \( \text{Sm}^{3+} \) (0.05 mol).

c) LnOBr: \( \text{Tb}^{5+} \) (Ln=Y, La, Gd) With a varied host (Ln) and a fixed dopant \( \text{Tb}^{5+} \) (0.05 mol).

d) (Gd, Y)OBr: \( \text{Ce}^{3+} \) With a varied host (Gd, Y) and a fixed dopant (\( \text{Ce}^{3+} \)) (0.05 mol).
Type-III (Chapter – V(A,B,C))

a) \((\text{La, Gd})\text{OCl} : \text{Sm}^{3+}\)
   Ambient atmosphere with different hosts (La, Gd) and a fixed dopant Sm\(^{3+}\) (0.1 wt%)

b) \(\text{LnOCl} : \text{Dy}^{3+}\)
   With a varied host Ln and a fixed dopant Dy\(^{3+}\), Ho\(^{3+}\) (0.1 wt %)

c) \(\text{LnOCl} : \text{Eu}^{3+}\)
   With a varied host Ln and fixed dopant Eu\(^{3+}\), Tb\(^{3+}\) (0.1 wt%)

Type – IV (Chapter – VI (A, B, C & D))

a) \(\text{GdPO}_4 : \text{Eu}^{3+}\)
   Inert (\(\text{N}_2\) gas) atmosphere with a varied dopant ion (Eu\(^{3+}\)) i.e. 0.001, 0.005, 0.01, 0.05 & 0.1 mol.

LaPO\(_4\) : Tb\(^{3+}\)
   With a varied dopant (Tb\(^{3+}\)) (in mol) i.e. 0.005, 0.01, 0.05, 0.1 & 0.5

LaPO\(_4\) : Ce\(^{3+}\)
   With a varied dopant (Ce\(^{3+}\)) (in mol) i.e. 0.005, 0.01, 0.05, 0.1 & 0.4

b) \(\text{LnPO}_4 : \text{Tb}^{3+}(\text{Ln} = \text{Y, La, Gd})\)
   With a varied host (Ln) and a fixed dopant (Tb\(^{3+}\)) (0.05 mol)

c) \(\text{LnPO}_4 : \text{Eu}^{3+}(\text{Ln} = \text{Y, La, Gd})\)
   With varied host Ln with fixed dopant (Eu\(^{3+}\)) (0.05 mol)

d) \((\text{La, Y})\text{PO}_4 : \text{Sm}^{3+}\)
   With a varied host (La,Y) and a fixed dopant (Sm\(^{3+}\)) (0.05 mol)
Type -V (Chapter-VII)

\((\text{La, Y})\text{V}_0_4 : \text{Eu}^{3+}\) Under an inert \((\text{N}_2 \text{ gas})\) atmosphere with a varied host \((\text{La, Y})\) and a fixed dopant \((\text{Eu}^{3+})\) 

\((0.05 \text{ mol})\)

**Synthesis of Lanthanide oxyfluoride and oxybromide based powder phosphors:** X-ray phosphors were mostly synthesized by certain solid state reactions at the temperature higher than \(800^\circ\text{C}\) by a flux method. Here, a flux is defined as a material which melts at lower temperature than the solid state reaction temperature, dissolving one or more of the components and allowing the material to transport to the reaction zone without entering into the solid state reaction. The synthesis of these phosphors has been a little difficult process when compared with the other phosphors due to the sensitivity nature of bromide and fluorides to the moisture and also because of the volatization at higher temperatures. Highly pure chemicals have been used in the preparation of lanthanide oxyfluorides and oxybromides:

- \(\text{Y}_2\text{O}_3, \text{La}_2\text{O}_3, \text{Gd}_2\text{O}_3, (\text{CH}_3\text{ COO})_2 \text{Zn, H}_2\text{O} \) (host chemicals)
- \(\text{NH}_4\text{F, NH}_4\text{Br} \) (fluorinating, brominating agents)
- \(\text{KBr} \) (flux)
- \(\text{Sm}_2\text{O}_3, \text{Eu}_2\text{O}_3, \text{Tb}_4\text{O}_7, \text{CeO}_2 \) (dopant salts)

Here a fixed \((0.05 \text{ mol})\) dopant \((\text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{5+} \& \text{Ce}^{3+})\) ion concentration has been chosen and synthesized different powder phosphors as follows:

**Chapter – III (A)**

a) \(\text{LaOF : Sm}^{3+}\)
b) \((\text{La}_{0.75}, \text{Zn}_{0.25})\text{OF} : \text{Sm}^{3+}\)
c) \((\text{La}_{0.5}, \text{Zn}_{0.5})\text{OF} : \text{Sm}^{3+}\)
d) \((\text{La}_{0.25}, \text{Zn}_{0.75})\text{OF} : \text{Sm}^{3+}\)
e) \(\text{ZnOF : Sm}^{3+}\)
Chapter III (B)

a) YOF : Eu$^{3+}$

b) $(Y_{0.75}, Zn_{0.25})$OF : Eu$^{3+}$

c) $(Y_{0.5}, Zn_{0.5})$OF : Eu$^{3+}$

d) $(Y_{0.25}, Zn_{0.75})$OF : Eu$^{3+}$

e) ZnOF : Eu$^{3+}$

(g) $(La_{0.75}, Zn_{0.25})$OF : Eu$^{3+}$

(h) $(La_{0.5}, Zn_{0.5})$OF : Eu$^{3+}$

(i) $(La_{0.25}, Zn_{0.75})$OF : Eu$^{3+}$

(j) GdOF : Eu$^{3+}$

(k) $(Gd_{0.75}, Zn_{0.25})$OF : Eu$^{3+}$

(l) $(Gd_{0.5}, Zn_{0.5})$OF : Eu$^{3+}$

(m) $(Gd_{0.25}, Zn_{0.75})$OF : Eu$^{3+}$

Chapter III (C)

a) GdOF : Ce$^{3+}$

b) $(Gd_{0.75}, Zn_{0.25})$OF : Ce$^{3+}$

c) $(Gd_{0.5}, Zn_{0.5})$OF : Ce$^{3+}$

d) $(Gd_{0.25}, Zn_{0.75})$OF : Ce$^{3+}$

e) ZnOF : Ce$^{3+}$

Chapter IV (A)

a) LaOBr : Eu$^{3+}$

b) GdOBr : Eu$^{3+}$

c) YOBr : Eu$^{3+}$

d) $(Gd_{0.8}, Y_{0.2})$OBr : Eu$^{3+}$

f) $(Gd_{0.8}, Y_{0.2})$OBr : Eu$^{3+}$

g) $(Gd_{0.8}, La_{0.2})$OBr : Eu

h) $(Gd_{0.8}, La_{0.4})$OBr : Eu

i) $(Gd_{0.8}, La_{0.6})$OBr : Eu$^{3+}$

Chapter IV (C)

a) GdOBr : Sm$^{3+}$

b) $(Gd_{0.9}, Y_{0.1})$OBr : Sm

c) $(Gd_{0.6}, Y_{0.4})$OBr : Sm

d) $(Gd_{0.3}, Y_{0.7})$OBr : Sm
Chapter -IV (C)

a) GdOBr : Tb$^{3+}$
b) LaOBr : Tb$^{3+}$
c) YOBr : Tb$^{3+}$
d) (Gd$_{0.9}$, La$_{0.1}$)OBr: Tb$^{3+}$
e) (Gd$_{0.6}$, La$_{0.4}$)OBr: Tb$^{3+}$
f) (Gd$_{0.3}$, La$_{0.7}$)OBr: Tb$^{3+}$
g) (Gd$_{0.9}$, Y$_{0.1}$)OBr: Tb$^{3+}$
h) (Gd$_{0.6}$, Y$_{0.4}$)OBr: Tb$^{3+}$
i) (Gd$_{0.3}$, Y$_{0.7}$)OBr: Tb$^{3+}$

The above chemical compositions were thoroughly powered in an agate mortar and pestle by a slurry method with the acetone as the solvent. The solid state reaction process is as follows:

800°C, flux

$$\text{Ln}_2\text{O}_3 + \text{RE}_2\text{O}_3 + \text{NH}_4\text{X} \rightarrow 2\text{LnO}x: \text{RE}^{3+} + \text{NH}_3 + \text{H}_2\text{O}$$

1000°C (N$_2$ atmosphere)

$$\text{(Ln= Y, La, Gd; RE= Sm, Eu, Tb, Ce; X= F, Br)}$$

Each of the dried mixtures was collected into the quartz boat and fired in a silica tube at the central zone of the high temperature furnace for an hour at 800°C under N$_2$ gas atmosphere. The obtained powder was cooled in a desiccator and powdered again by adding an additional amount of NH$_4$F and NH$_4$Br, a second firing was also performed at 1000°C for an hour with N$_2$ atmosphere. The experimental set up used for the synthesis of these powder phosphors has shown in Fig.1. In the preparation of lanthanide oxyfluorides and oxybromides, NH$_4$F and NH$_4$Br would act as fluorinating and brominating agents, while KBr functions as a flux for the proper crystallization of these powder phosphors, respectively [1]. A second firing was carried out because lanthanides are rather non-reactive at relatively low temperatures [2]. Soon after the completion of the synthesis of the phosphors and found them as red (Eu$^{3+}$), orangish-red (Sm$^{3+}$), green (Tb$^{3+}$), blue (Ce$^{3+}$) color emitting phosphors (UV- emission from Ce$^{3+}$-
Fig. 1: Experimental set-up for the synthesis of powder phosphors in an inert ($\text{N}_2$) atmosphere

Fig. 2: Experimental set-up for the preparation of lanthanide oxychloride based powder phosphors
phosphors) under UV-lamp. Such synthesized powder phosphors have been preserved in Borosil containers.

**Preparation of lanthanide oxychloride powder phosphors**

Lanthanide oxychloride powder phosphors have been prepared following a method reported earlier by Fidancev et al. [3,4]. Pure chemicals have been used for the preparation of lanthanide oxychloride powder phosphors as given below:

- YCl₃, LaCl₃, GdCl₃ (host chemicals)
- CaCl₂ (flux)
- SmCl₃, DyCl₃, HoCl₃, TbCl₃ (dopant salts)

The concentration of the dopant rare earth ions was fixed as 0.1 wt% based on the reported results [5]. The weight percentage of the starting chemicals used for the synthesis of the lanthanide oxychloride phosphors are as follows:

**Chapter V (A)**

a) LaOCl : Sm³⁺

b) GdOCl : Sm³⁺

c) YOCl : Sm³⁺

d) (La₀.₇, Gd₀.₃)OCl : Sm³⁺

e) (La₀.₆, Y₀.₄)OCl : Sm³⁺

**Chapter V (B)**

a) (La₀.₇, Gd₀.₃)OCl : Dy³⁺

b) (La₀.₆, Y₀.₄)OCl : Dy³⁺

c) (Gd₀.₅, Y₀.₅)OCl : Dy³⁺

d) (La₀.₇, Gd₀.₃)OCl : Ho³⁺

e) (La₀.₆, Y₀.₄)OCl : Ho³⁺

**Chapter V (C)**

For labelling purpose, the red color emitting europium phosphors are abbreviated as RP and green-color emitting terbium phosphors as G.P.
Each of the above compositional chemical mixtures was collected into small silica crucibles and fixed at 700°C in an electric tubular furnace in ambient atmosphere. This solid state reaction has been carried out for an hour. The experimental set-up has been shown in the Fig. 2. These phosphors are again powdered finely and transferred into the Borosil containers and further analysis was carried out on them.

**Synthesis of Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$ and Ce$^{2+}$ doped lanthanide Phosphate powder phosphors:** In 1986, Kim et. al [6] have suggested that the emission spectra intensity varies with the change in the dopant rare earth ion concentration significantly. To have the satisfactory fluorescence intensity with the dopant rare earth ions (Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, & Ce$^{2+}$) first the lanthanide phosphate phosphors were synthesized with varying dopant ion concentration and 0.05 mol is the optimum dopant ion concentration. Here, we have adopted a precipitation technique involving a direct and clean reaction process between lanthanide oxides and phosphoric acid without formation of any by-products except water [7].

For the synthesis of these phosphors high purity:

- Gd$_2$O$_3$, La$_2$O$_3$, Y$_2$O$_3$, H$_3$PO$_4$ (host chemical)
- Eu$_2$O$_3$, Tb$_2$O$_3$, Sm$_2$O$_3$, CeO$_2$ (dopant salts)

were taken as the starting chemicals. Due to the hygroscopic nature of the lanthanide oxides, the starting oxides were calcined at 700°C [8]. Following compositions in moles were mixed thoroughly by using acetone:
Chapter VI (A)

a) \( \text{Gd}_{0.999}\text{PO}_4 : \text{Eu}^{3+}_{0.001} \)
b) \( \text{Gd}_{0.999}\text{PO}_4 : \text{Eu}^{3+}_{0.005} \)
c) \( \text{Gd}_{0.99}\text{PO}_4 : \text{Eu}^{3+}_{0.01} \)
d) \( \text{Gd}_{0.96}\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
e) \( \text{Gd}_{0.9}\text{PO}_4 : \text{Eu}^{3+}_{0.01} \)

a) \( \text{La}_{0.999}\text{PO}_4 : \text{Tb}^{3+}_{0.005} \)
b) \( \text{La}_{0.99}\text{PO}_4 : \text{Tb}^{3+}_{0.01} \)
c) \( \text{La}_{0.96}\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
d) \( \text{La}_{0.9}\text{PO}_4 : \text{Tb}^{3+}_{0.1} \)
e) \( \text{La}_{0.3}\text{PO}_4 : \text{Tb}^{3+}_{0.5} \)

Chapter VI (B)

a) \( \text{GdPO}_4 : \text{Tb}^{3+}_{0.05} \)
b) \( (\text{Gd}_{0.25}, \text{La}_{0.75})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
c) \( (\text{Gd}_{0.5}, \text{La}_{0.5})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
d) \( (\text{Gd}_{0.75}, \text{La}_{0.25})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
e) \( (\text{Gd}_{0.75}, \text{Y}_{0.25})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
f) \( (\text{Gd}_{0.5}, \text{Y}_{0.5})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
g) \( (\text{Gd}_{0.25}, \text{Y}_{0.75})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
h) \( \text{YPO}_4 : \text{Tb}^{3+}_{0.05} \)
i) \( \text{LaPO}_4 : \text{Tb}^{3+}_{0.05} \)
j) \( (\text{La}_{0.75}, \text{Y}_{0.25})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
k) \( (\text{La}_{0.5}, \text{Y}_{0.5})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)
l) \( (\text{La}_{0.25}, \text{Y}_{0.75})\text{PO}_4 : \text{Tb}^{3+}_{0.05} \)

Chapter VI (C)

a) \( \text{GdPO}_4 : \text{Eu}^{3+}_{0.05} \)
b) \( (\text{Gd}_{0.25}, \text{La}_{0.75})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
c) \( (\text{Gd}_{0.5}, \text{La}_{0.5})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
d) \( (\text{Gd}_{0.75}, \text{La}_{0.25})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
e) \( \text{LaPO}_4 : \text{Eu}^{3+}_{0.05} \)
f) \( (\text{La}_{0.75}, \text{Y}_{0.25})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
g) \( (\text{La}_{0.5}, \text{Y}_{0.5})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
h) \( (\text{La}_{0.25}, \text{Y}_{0.75})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
i) \( \text{YPO}_4 : \text{Eu}^{3+}_{0.05} \)
j) \( (\text{Gd}_{0.75}, \text{Y}_{0.25})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
k) \( (\text{Gd}_{0.5}, \text{Y}_{0.5})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)
l) \( (\text{Gd}_{0.25}, \text{Y}_{0.75})\text{PO}_4 : \text{Eu}^{3+}_{0.05} \)

Chapter – VI (D)

a) \( \text{LaPO}_4 : \text{Sm}^{3+}_{0.05} \)
b) \( (\text{La}_{0.75}, \text{Y}_{0.25})\text{PO}_4 : \text{Sm}^{3+}_{0.05} \)
c) \( (\text{La}_{0.5}, \text{Y}_{0.5})\text{PO}_4 : \text{Sm}^{3+}_{0.05} \)
d) \( (\text{La}_{0.25}, \text{Y}_{0.75})\text{PO}_4 : \text{Sm}^{3+}_{0.05} \)
e) \( \text{YPO}_4 : \text{Sm}^{3+}_{0.05} \)
The dried lanthanide oxide powders were slowly added to a 85% phosphoric acid. The reaction was vigorous and exothermic in nature. Large precipitates were immediately formed at the reaction site causing the formation of fine particles. The solution was dense and stable and did not separate for a long period of time. The solution was later stirred for thirty minutes and then separated by centrifuging. Traces of excess phosphoric acid were removed by washing the samples several times with a deionized water. The chemical reaction involved in the present synthesis is as follows:

\[
\text{Ln}_2\text{O}_3 + \text{RE}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{LnP}_2\text{O}_7 + 3\text{H}_2\text{O} \quad (\text{Ln}=\text{Y,La,Gd}; \text{RE}=\text{Eu,Tb,Sm & Ce}).
\]

The obtained white powders have been collected into quartz boats and fired in a silica tube in the central zone of a high temperature furnace for three hours at 950°C in an inert (N₂ gas) atmosphere. Soon after the completion of the synthesis, these phosphors are found to white in color, emitting red (Eu³⁺: Phosphors), green (Tb³⁺: phosphors), orangish - red (Sm³⁺: phosphors) and UV-radiation (Ce³⁺: phosphors) under an UV - source. The phase purity for each of the synthesized powder phosphors was checked by X-ray diffractometry (XRD).

**Preparation of Eu³⁺-doped lanthanide vanadate powder phosphors:** These phosphors were prepared by solid state reactions and through wet routes under different gas atmospheres. Erdei et al have synthesized these lanthanide vanadate phosphors in a hydrolized colloidal reaction [9,10]. Solid state reaction method in an inert (N₂ gas) atmosphere has been employed for the synthesis of these lanthanide vanadate phosphors [11,12]. High purity lanthanum oxide, yttrium oxide (Y₂O₃), europium oxide (Eu₂O₃) and ammonium vanadate (NH₄VO₃) were taken as the starting chemicals. Due to the hygrosopic nature of the lanthanide oxides, initially these oxides were calcined at 700°C before weighing [8]. In the present studies, a fixed dopant europium (0.05 mol)
concentration \((\text{Eu}_2\text{O}_3)\) was maintained. The following chemicals were mixed thoroughly with the acetone.

Chapter - VII

a) \(\text{LaVO}_4 : \text{Eu}^{3+}\)  

b) \((\text{La}_{0.75}, \text{Y}_{0.25})\text{VO}_4 : \text{Eu}^{3+}\)  
c) \((\text{La}_{0.5}, \text{Y}_{0.5})\text{VO}_4 : \text{Eu}^{3+}\)  
d) \((\text{La}_{0.25}, \text{Y}_{0.75})\text{VO}_4 : \text{Eu}^{3+}\)  
e) \(\text{YVO}_4 : \text{Eu}^{3+}\)

These compositions as dried powders were collected into quartz boats and fired in a silica tube by using high temperature furnace at \(600^\circ\text{C}\) for an hour in an inert \((\text{N}_2)\) atmosphere. The samples were later pulverized and fired at \(1100^\circ\text{C}\) for an hour in an inert \((\text{N}_2)\) atmosphere. The phase purity of the synthesized phosphors were checked by a Philips, PW 18140, X-ray diffractometer and preserved in Borosil containers.

Characterization

Both the excitation and fluorescence spectra of the powder phosphors reported in this thesis were recorded at the laboratories of Central Electrochemical Research Institute (CECRI), Karaikudi, Central University, Hyderabad and University of Pune, Pune on HITACHI 650-10S, Fluorescence spectrophotometer and Perkin-Elmer LS-50, luminescence spectrometer. The excitation and fluorescence spectra are recorded using a Hamamatsu R 928F photomultiplier tube on a 150W xenon arc lamp as a excitation source. The block diagram of the spectrophotometer (Hitachi 650-10S model) and the lamp mounting arrangements are shown in the Figs. (3-5). Table 1, gives the data regarding the lines of excitation used for recording the fluorescence spectra and the range of spectral measurements of the phosphors studied.
Fig. 3: Functional block diagram of Hitachi 650-10S Fluorescence spectrophotometer
Fig. 4: Schematic diagram of the Hitachi 650-10S Fluorescence Spectrophotometer

Fig. 5: 150W xenon arc lamp mounting in Hitachi 650-10S Fluorescence spectrophotometer.
Table 1: The selected lines of excitation for the measurement of the emission spectra of Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Ho$^{3+}$ and Ce$^{3+}$-powder phosphors

<table>
<thead>
<tr>
<th>Phosphor host matrix</th>
<th>Dopant ion</th>
<th>Excitation Wavelength $\lambda_{exc}$ (nm)</th>
<th>Emission spectral Wavelength range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Type - I</strong></td>
<td></td>
</tr>
<tr>
<td>a. (La,Zn)OF</td>
<td>Sm$^{3+}$</td>
<td>402</td>
<td>500-700</td>
</tr>
<tr>
<td>b. (La,Zn)OF</td>
<td>Eu$^{3+}$</td>
<td>240</td>
<td>500-720</td>
</tr>
<tr>
<td>c. (Gd,Zn)OF</td>
<td>Ce$^{3+}$</td>
<td>237</td>
<td>250-600</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Type - II</strong></td>
<td></td>
</tr>
<tr>
<td>a. LnOBr</td>
<td>Eu$^{3+}$</td>
<td>395</td>
<td>550-720</td>
</tr>
<tr>
<td>b. LnOBr</td>
<td>Sm$^{3+}$</td>
<td>410</td>
<td>540-670</td>
</tr>
<tr>
<td>c. LnOBr</td>
<td>Tb$^{3+}$</td>
<td>352</td>
<td>450-650</td>
</tr>
<tr>
<td>d. LnOBr</td>
<td>Ce$^{3+}$</td>
<td>366</td>
<td>380-560</td>
</tr>
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<td></td>
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<td><strong>Table - III</strong></td>
<td></td>
</tr>
<tr>
<td>a. LnOCl</td>
<td>Sm$^{3+}$</td>
<td>408</td>
<td>500-680</td>
</tr>
<tr>
<td>b. LnOCl</td>
<td>Ho$^{3+}$</td>
<td>384</td>
<td>440-640</td>
</tr>
<tr>
<td>c. LnOCl</td>
<td>Dy$^{3+}$</td>
<td>356</td>
<td>440-600</td>
</tr>
<tr>
<td>d. LnOCl</td>
<td>Eu$^{3+}$</td>
<td>396</td>
<td>550-720</td>
</tr>
<tr>
<td>e. LnOCl</td>
<td>Tb$^{3+}$</td>
<td>240</td>
<td>440-640</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Type-IV</strong></td>
<td></td>
</tr>
<tr>
<td>a. GdPO$_4$</td>
<td>Eu$^{3+}$</td>
<td>398</td>
<td>540-720</td>
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<tr>
<td>b. LaPO$_4$</td>
<td>Tb$^{3+}$</td>
<td>370</td>
<td>440-640</td>
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<td>c. LaPO$_4$</td>
<td>Ce$^{3+}$</td>
<td>258</td>
<td>300-480</td>
</tr>
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<td>d. LaPO$_4$</td>
<td>Sm$^{3+}$</td>
<td>400</td>
<td>500-680</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>Type - V</strong></td>
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<tr>
<td>a. LnVO$_4$</td>
<td>Eu$^{3+}$</td>
<td>247</td>
<td>540-720</td>
</tr>
</tbody>
</table>

Where Ln = Y, La & Gd

**X-ray diffractometry (XRD):** The phase purity of the synthesized powder phosphors has been checked from a Philips PW 18140, X-ray diffractometer fitted with a PM 8203A on line recorder. All diffractograms were recorded with CuK$_\alpha$(\(\lambda=0.1542\) nm) radiation.
**Scanning electron microscope (SEM):** The surface morphological features (shape and grain size) of the powder phosphors synthesized were studied by using Leica Stereoscan 440, scanning electron microscope. For the SEM analysis, the samples were pre-coated with a thin layer of gold in a polaran E5000 coating unit in order to prevent the charging of the sample particles. For a comparative study the electron beam parameters such as accelerating voltage ($V_{acc}$), working distance (WD), magnification and 25PA beam current were fixed as constant and shown on the SEM photographs. For type - III phosphors, SEM studies have not been carried out because those are more hygroscopic in nature.

**Thermal analysis:** It refers to the group of methods in which some physical property of the sample is continuously measured as a function of temperature, whilst the sample is subjected to a controlled temperature range. Thermogravimetric (TGA/DTA) investigations were carried out for the synthesized powder phosphors with a Metler Toledo, TGA/SDTA 851®. The samples were heated in different temperature regions in a dynamic inert ($N_2$) atmosphere, at a heating rate of $10^6$C/minute. From the thermal analysis the weight loss of the powder phosphors have been studied and data are reported in respective chapters. Thermal analysis has not been carried out for all the types of samples, because of the difficult accessibility of the instrument.

**FT-IR Spectral measurements:** The synthesized lanthanide phosphate and vanadate powder phosphors were also characterized by recording the FT-IR spectra. Absorption and transmittance spectra of these samples were carried out on a Perkin-Elmer spectrometer (Spectrum 2000) with KBr pellets in the wavenumber range 1400-370 cm$^{-1}$, typical FT-IR spectra has been given in respective chapters.
**Emission transition lifetimes:** Measurements on the lifetimes of the fluorescent transition $^5D_0 \rightarrow ^7F_{1,2}$ (LaPO$_4$: Eu$^{3+}$) and $^5D_4 \rightarrow ^7F_{6,5,4,3,2,1}$ (LaPO$_4$:Tb$^{3+}$) powder phosphors were carried out on a Spex Fluorolog-3, Spectrofluorimeter coupled with a 1934D3 phosphorimeter. These measurements were carried out only for certain samples at Nanyang Technological University, Photonics Laboratory, Singapore. As we could establish collaboration, just very recently, hence, lifetimes data for all samples could not be presented.
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