Synthesis and characterization of $\text{Eu}^{3+}/\text{Ce}^{3+}$ co-doped $\text{Na}_3\text{Gd}(\text{PO}_4)_2$ phosphors
4.1. Introduction

In the recent times, extensive research work has been carried out on light-emitting diodes (LEDs) and phosphor materials to generate white light [1]. Solid state lighting technology has more advantages over the conventional fluorescent lamps, due to its low energy consumption, environmental protection and efficient light output. White light-emitting diodes (W-LEDs) save 70% of the energy, when compared with the conventional light sources of incandescent lamps and thus the white light emitting diodes can be considered as the next generation solid state light sources [2]. Rare earth doped phosphate based host matrices have been extensively investigated for the development of laser materials, optical amplifiers, and display devices because of their low cost and thermal stability [3]. Moreover, phosphates doped with rare earth ions have thought to be ideal for the charge stabilization, excellent thermal stability and tetrahedral rigid three-dimensional network [4-5].

Ce$^{3+}$ ions exhibit the emission spectrum in the near ultraviolet (UV) region owing to the 4f-5d transitions [6]. The energy levels are due to the parity allowed electric dipole transitions having larger oscillator strengths along with efficient broadband luminescence and also they strongly depend on the host lattice. Due to the extended radial wavefunctions of 5d state, the Ce$^{3+}$ ions exhibit larger Stokes shift, when compared with the other rare earth ions. Cerium activated host materials have received great attention because of their practical applications in thermoluminescence lighting and scintillators. In addition, the Eu$^{3+}$ ion is widely used as the luminescent center in many phosphors due to the characteristic red emission (620 nm) corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. Phosphors doped with Eu$^{3+}$ ions exhibit higher absorption coefficient and excellent luminescence efficiency [7]. However, phosphors co-doped with Ce$^{3+}$ and Eu$^{3+}$ ions are normally used to produce the blue and red emissions, respectively [8]. Co-doped rare earth ions emit wide variety of colors which are used very effectively in display technology.

4.2. Experimental

A series of singly doped Ce$^{3+}$, Eu$^{3+}$ and co-doped Eu$^{3+}$/Ce$^{3+}$ ions in Na$_3$Gd(PO$_4$)$_2$ phosphors were prepared by the solid state reaction method by keeping the
Eu\(^{3+}\) ions concentration constant (0.5 mol\%) and varying the Ce\(^{3+}\) ions concentrations as 0.5, 1.0, 2.0 and 5.0 mol\%. The preparation of these phosphors is explained in Chapter 2.

4.3. RESULTS AND DISCUSSION

4.3.1. Photoluminescence studies

Fig. 4.1 shows the excitation spectrum of singly doped Na\(_3\)Gd(PO\(_4\))\(_2\):0.5Eu\(^{3+}\) phosphor obtained by monitoring the emission at 596 nm. The spectrum exhibits characteristic bands of Eu\(^{3+}\) ion in the region 300-550 nm, corresponding to the 4f-4f transitions of 

\[
\begin{align*}
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{H}_6 (307 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{H}_5 (312 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{H}_4 (318 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{D}_4 (363 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{G}_4 (382 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{L}_6 (394 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{D}_3 (417 \text{ nm}), \\
\text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{D}_2 (466 \text{ nm}) \text{ and } \text{7}^2\text{F}_0 & \rightarrow \text{5}^2\text{D}_1 (527 \text{ nm}).
\end{align*}
\]

The emission spectrum shown in Fig.4.2, reveals five bands at 560, 595, 620, 655 and 700 nm corresponding \(\text{5}^2\text{D}_0 \rightarrow \text{7}^2\text{F}_0, 1, 2, 3, 4\) transitions, respectively.

**Fig.4.1.** Excitation spectrum of Na\(_3\)Gd(PO\(_4\))\(_2\):Eu\(^{3+}\) phosphor (\(\lambda_{em} = 596\) nm).

**Fig.4.2.** Emission spectrum of Na\(_3\)Gd(PO\(_4\))\(_2\):Eu\(^{3+}\) phosphor (\(\lambda_{ex} = 394\) nm).
Among all the emission transitions, the $^5D_0 \rightarrow ^7F_{2,4}$ transitions are electric dipole (ED) forced by the crystal field environment in the vicinity of the Eu$^{3+}$ ions and the $^5D_0 \rightarrow ^7F_1$ transition is allowed magnetic dipole (MD) and independent of host matrix, whereas the $^5D_0 \rightarrow ^7F_{0,3}$ transitions are forbidden by the selection rules [9]. Fig.4.3 shows the excitation spectrum singly doped of Na$_3$Gd(PO$_4$)$_2$:0.5Ce$^{3+}$ phosphor, which exhibits an intense band at 380 nm and a weak band at 275 nm. Fig.4.4 shows the emission spectrum of Ce$^{3+}$ ions in Na$_3$Gd(PO$_4$)$_2$ phosphor obtained with the 380 nm excitation wavelength. The two broad emission peaks observed in the region 410-450 nm are assigned to the 5d$\rightarrow$4f transitions of Ce$^{3+}$ ions. The two broad emission peaks at 420 and 440 nm are due to the 5d (1) $\rightarrow ^2F_{7/2}$ and 5d (1) $\rightarrow ^2F_{5/2}$ transitions respectively.

![Excitation spectrum of Na$_3$Gd(PO$_4$)$_2$:Ce$^{3+}$ phosphor](image)

**Fig.4.3. Excitation spectrum of Na$_3$Gd(PO$_4$)$_2$:Ce$^{3+}$ phosphor**

The Ce$^{3+}$ ion acts as activator as well as sensitizer, depending on the splitting of 5d excited levels by the crystal field symmetry. It is well-know that the f-d transitions of Ce$^{3+}$ ions exhibit splitting due to the influence of crystal field and spin-orbit coupling [10]. From the spectral profiles of Fig.4.3, it is evident that these transitions are sensitive to the crystal field environment due to the nearest excited state of Ce$^{3+}$ ions that lies in the d-shell. Generally, the emission spectrum of Ce$^{3+}$ ions in the ultra violet (UV) region posses doublet structure due to the spin-orbit splitting of ground state under 380 nm excitation as observed in Fig.4.4.
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Fig. 4.4. Emission spectrum of Na$_3$Gd(PO$_4$)$_2$:Ce$^{3+}$ phosphor

The excitation spectrum of Eu$^{3+}$/Ce$^{3+}$ co-doped Na$_3$Gd(PO$_4$)$_2$ phosphor obtained by monitoring the emission at 596 nm corresponding to the $^5$D$_0$→$^7$F$_1$ transition is shown Fig. 4.5. The spectrum exhibits seven bands at 363 nm ($^7$F$_0$→$^5$D$_4$), 382 nm ($^7$F$_0$→$^5$G$_4$), 394 nm ($^7$F$_0$→$^5$L$_6$), 417 nm ($^7$F$_0$→$^5$D$_3$), 466 nm ($^7$F$_0$→$^5$D$_2$), 527 nm ($^7$F$_0$→$^5$D$_1$) and 535 nm ($^7$F$_1$→$^5$D$_1$). Among these bands, the band at 394 nm ($^7$F$_0$→$^5$L$_6$) is the most intense one. Fig. 4.6 shows the emission spectra of Na$_3$Gd(PO$_4$)$_2$:0.5Eu$^{3+}$ phosphors co-doped with 0.5, 1.0, 2.0 and 5.0 mol% of Ce$^{3+}$ ions. The emission spectra exhibited

![Excitation spectrum of Na$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$/Ce$^{3+}$ phosphor](image)

Fig. 4.5. Excitation spectrum of Na$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$/Ce$^{3+}$ phosphor
characteristic bands at 410, 440, 595, 612, 655 and 702 nm corresponding to the Ce\(^{3+}\): 5d (1) \(\rightarrow\) \(^2\!F_{7/2}\), 5d (1) \(\rightarrow\) \(^2\!F_{5/2}\); Eu\(^{3+}\): 5\(^D_0\) \(\rightarrow\) \(^7\!F_1\), 5\(^D_0\) \(\rightarrow\) \(^7\!F_2\), 5\(^D_0\) \(\rightarrow\) \(^7\!F_3\) and 5\(^D_0\) \(\rightarrow\) \(^7\!F_4\) transitions respectively. It is observed that the intensities of emission bands of Eu\(^{3+}\) ions decrease with the increase of Ce\(^{3+}\) ions concentration indicating the energy transfer (ET) from Eu\(^{3+}\) to Ce\(^{3+}\) ions [11].

![Emission spectra of Na\(_3\)Gd(PO\(_4\))\(_2\):Eu\(^{3+}\)/Ce\(^{3+}\) phosphor (\(\lambda_{\text{exi}} = 380\) nm).]

4.3.3. Color Coordinates

Fig.4.7 shows the location of color coordinates (x, y) for the A: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\), B: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Ce\(^{3+}\), C: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Ce\(^{3+}\)/0.5Eu\(^{3+}\), D: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/1.0Ce\(^{3+}\), E: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/2.0Ce\(^{3+}\) and F: Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/5.0Ce\(^{3+}\) phosphors in the CIE chromaticity diagram. The Na\(_3\)Gd(PO\(_4\))\(_2\):0.5Eu\(^{3+}\) phosphor exhibited red color with chromaticity co-ordinates of (0.54, 0.32), while the Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Ce\(^{3+}\) phosphor exhibited blue color with chromaticity coordinates of (0.19, 0.20). The evaluated chromaticity coordinates are (0.46, 0.16), (0.36, 0.28), (0.29, 0.22) and (0.22, 0.14) respectively for the co-doped Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Ce\(^{3+}\)/0.5Eu\(^{3+}\), Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/1.0Ce\(^{3+}\), Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/2.0Ce\(^{3+}\) and Na\(_3\)Gd(PO\(_4\))\(_2\): 0.5Eu\(^{3+}\)/5.0Ce\(^{3+}\) phosphors. Table 4.1 presents the calculated CIE coordinates for the Eu\(^{3+}\)/Ce\(^{3+}\) co-doped Na\(_3\)Gd(PO\(_4\))\(_2\) phosphors.
Fig. 4.7. CIE color coordinates for the Na$_3$Gd(PO$_4$)$_2$ singly doped (Ce$^{3+}$, Eu$^{3+}$) and co-doped (Eu$^{3+}$/Ce$^{3+}$) phosphors excited at 380 nm.

Table 4.1. CIE chromaticity coordinates (x, y) of Na$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$/Ce$^{3+}$ phosphors for different dopant concentrations (mol%).

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>$\lambda_{\text{exi}}$: 380 nm</th>
<th>(x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Na$_3$Gd(PO$_4$)$_2$: 0.5Eu$^{3+}$</td>
<td>0.54, 0.32</td>
<td></td>
</tr>
<tr>
<td>B: Na$_3$Gd(PO$_4$)$_2$: 0.5Ce$^{3+}$</td>
<td>0.19, 0.20</td>
<td></td>
</tr>
<tr>
<td>C: Na$_3$Gd(PO$_4$)$_2$: 0.5Eu$^{3+}$/0.5Ce$^{3+}$</td>
<td>0.46, 0.16</td>
<td></td>
</tr>
<tr>
<td>D: Na$_3$Gd(PO$_4$)$_2$: 0.5Eu$^{3+}$/1.0Ce$^{3+}$</td>
<td>0.36, 0.28</td>
<td></td>
</tr>
<tr>
<td>E: Na$_3$Gd(PO$_4$)$_2$: 0.5Eu$^{3+}$/2.0Ce$^{3+}$</td>
<td>0.29, 0.22</td>
<td></td>
</tr>
<tr>
<td>F: Na$_3$Gd(PO$_4$)$_2$: 0.5Eu$^{3+}$/5.0Ce$^{3+}$</td>
<td>0.22, 0.14</td>
<td></td>
</tr>
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</table>
4.4. Conclusions

The co-doped Na$_3$Gd(PO$_4$)$_2$:Eu$^{3+}$/Ce$^{3+}$ phosphors were synthesized by solid state reaction method. It is observed that with the increase Ce$^{3+}$ ions concentration, the emission associated with the Eu$^{3+}$ ions decreases greatly due to the energy transfer from Eu$^{3+}$ to Ce$^{3+}$ ions. The luminescent colors of co-doped Na$_3$Gd(PO$_4$)$_2$: Ce$^{3+}$/Eu$^{3+}$ phosphors were changed from red to blue with the increase of Ce$^{3+}$ ions concentration. The calculated chromaticity coordinates of (0.36, 0.28) and (0.29, 0.22) pertaining to the co-doped with Na$_3$Gd(PO$_4$)$_2$:1.0Ce$^{3+}$/0.5Eu$^{3+}$ and Na$_3$Gd(PO$_4$)$_2$:2.0Ce$^{3+}$/0.5Eu$^{3+}$ phosphors under an excitation of 380 nm fall in the white light region of the CIE chromaticity diagram.
References