Chapter - IV

Photoluminescence Spectra of Ln₂O₂S:RE³⁺ Powder Phosphors (Ln=Y,La,Gd; RE=Eu,Tb)
Introduction

In recent times, a greater importance has been attached to certain rare-earth doped lanthanide oxysulfide (Ln$_2$O$_2$S, Ln=Y,La,Gd) phosphors because of their significant commercial applications in TVs and display devices [1-10]. Therefore, in the present Chapter of this thesis an attempt has been made to prepare and characterise such useful and important powder phosphor materials. By employing a flux method, these phosphor materials have been prepared and the related experimental details are earlier described in the second Chapter. The main interest in the present work is to study the photoluminescence spectra of both Eu$^{3+}$ and Tb$^{3+}$ ions doped lanthanide oxysulfide (Ln$_2$O$_2$S, Ln Y,La,Gd) powder phosphors to understand their colour emitting performance.

Results and Discussion

Part-A: Luminescence Spectra of Eu$^{3+}$: Ln$_2$O$_2$S Powder Phosphors:

Both the excitation and the photoluminescence spectra of Ln$_2$O$_2$S (Ln=Y,La,Gd) powder phosphors have been recorded on a Hitachi 650-10S Spectrophotometer fitted with a Hamamatsu R-928F photomultiplier tube and a 150W xenon arc lamp. The excitation spectra of the Eu$^{3+}$ doped Y$_2$O$_2$S, La$_2$O$_2$S, Gd$_2$O$_2$S powder phosphors are shown in Figs. 1(a,b,c). From the recorded excitation spectra the line of excitation for each phosphor has been selected for recording their photoluminescence spectra as shown in Figs. 2(a,b,c). The photoluminescence spectra of these Eu$^{3+}$ phosphors have shown the following emission transitions.
Fig. 1(a): Excitation Spectrum of $Y_2O_2S:Eu^{3+}$ Powder Phosphor
Fig. 1(b): Excitation Spectrum of La$_2$O$_2$S:Eu$^{3+}$ Powder Phosphor
Fig. 1(c): Excitation Spectrum of Gd$_2$O$_2$S:Eu$^{3+}$ Powder Phosphor
Fig. 2(a): Photoluminescence Spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ Powder Phosphor
Fig 2(b): Photoluminescence Spectrum of La$_2$O$_2$S:Eu$^{3+}$ Powder Phosphor

Relative fluorescence intensity

5D$_0$ $\rightarrow$ 7F$_4$

5D$_0$ $\rightarrow$ 7F$_1$

5D$_0$ $\rightarrow$ 7F$_0$

5D$_1$ $\rightarrow$ 7F$_2$

$\lambda_m$: 335 nm
Fig. 2(c): Photoluminescence Spectrum of Gd₂O₂S:Eu³⁺ Powder Phosphor
\[
\begin{align*}
^5D_1 &\rightarrow ^7F_2 \quad (553 \text{ nm}) \\
^5D_0 &\rightarrow ^7F_0 \quad (582 \text{ nm}) \\
&\rightarrow ^7F_1 \quad (592 \text{ nm}) \\
&\rightarrow ^7F_2 \quad (625 \text{ nm}) \\
&\rightarrow ^7F_4 \quad (705 \text{ nm})
\end{align*}
\]

Of these, the emission transition (\(^5D_0 \rightarrow ^7F_2\)) has been found to be more intense (at \(\lambda_{\text{em}} = 625 \text{ nm}\)) peak in all the phosphors examined. The stronger emission at \(\lambda_{\text{em}} = 625 \text{ nm}\) confirms the formation of the oxysulfide host [1]. If there had been a stronger emission at \(\lambda_{\text{em}} = 610 \text{ nm}\), it would have been due to a \(Y_2O_3\) host.

In order to compare the fluorescence efficiencies the relative fluorescence intensity ratios (\(R\)) for these \(Eu^{3+}\) powder phosphors have been computed and the results are presented in Table 1. Following the standard procedures of the CIE (France), the colour co-ordinates \((x', y')\) have been evaluated and are given in Table 2. These colour co-ordinates are very well in agreement with the standard values that are reported earlier in the literature [11,12] for certain commercial red phosphors. The computed values of the stimulated emission cross section \((\sigma_p^E)\) of the emission transition \((^5D_0 \rightarrow ^7F_2\)) are given in the Table 2 itself. In Fig.3, the CIE chromaticity diagram with three primary colours (blue, green & red) has been described. In that diagram, the measured colour co-ordinates \((x', y')\) are superimposed in order to verify the validity of our results with those values recommended values of the colour co-ordinates. The Fig.3 shows that the investigated phosphors are in the red region of the colour co-ordinates (the blackened portion) from the measurement of their emission spectra.
### Table 1

Relative Fluorescence Intensity Ratios (R) of the Emission Transitions \((^5D_0 \rightarrow \ ^7F_4, \ ^7F_2, \ ^7F_1, \ ^7F_0, \ ^5D_1 \rightarrow \ ^7F_2)\) of Eu\(^{3+}\): Ln\(_2\)O\(_2\)S Powder Phosphors

<table>
<thead>
<tr>
<th>Ratios between the transition</th>
<th>(Y_2O_2S) Tb(^{3+})</th>
<th>(La_2O_2S) Tb(^{3+})</th>
<th>(Gd_2O_2S) Tb(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_4)</td>
<td>0.988</td>
<td>0.833</td>
<td>0.960</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_1)</td>
<td>5.930</td>
<td>5.897</td>
<td>5.64</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_2)</td>
<td>2.250</td>
<td>2.638</td>
<td>2.16</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_1)</td>
<td>0.31</td>
<td>1.66</td>
<td>0.24</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_{-1})</td>
<td>0.238</td>
<td>0.166</td>
<td>0.240</td>
</tr>
<tr>
<td>(^5D_0 \rightarrow \ ^7F_{-2})</td>
<td>0.107</td>
<td>0.472</td>
<td>0.080</td>
</tr>
</tbody>
</table>

### Table 2

Colour Co-ordinates \((\bar{x}, \bar{y})\) of Eu\(^{3+}\): Ln\(_2\)O\(_2\)S Powder Phosphors, Emission Level Peak Wavelength \((\lambda_p \text{ nm})\) and Stimulated Emission Cross-section \((\sigma_p^E \times 10^{22} \text{ cm}^2)\) for the Transition \(^5D_0 \rightarrow \ ^7F_2\) of Eu\(^{3+}\) ion

<table>
<thead>
<tr>
<th>Powder Phosphor</th>
<th>(\bar{x})</th>
<th>(\bar{y})</th>
<th>(\lambda_p \text{ nm})</th>
<th>(\sigma_p^E \times 10^{22} \text{ cm}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Y_2O_2S): Eu(^{3+})</td>
<td>0.665</td>
<td>0.334</td>
<td>625</td>
<td>10.02</td>
</tr>
<tr>
<td>(La_2O_2S): Eu(^{3+})</td>
<td>0.641</td>
<td>0.358</td>
<td>623</td>
<td>8.16</td>
</tr>
<tr>
<td>(Gd_2O_2S): Eu(^{3+})</td>
<td>0.647</td>
<td>0.352</td>
<td>623</td>
<td>8.63</td>
</tr>
</tbody>
</table>
Fig. 3: CIE Chromaticity Diagram showing the Colour Points for the Red (Eu$^{3+}$) and Green (Tb$^{3+}$) Emitting Ln$_2$O$_2$S Powder Phosphors
Part-B: Luminescence Spectra of Tb$^{3+}$:Ln$_2$O$_2$S Powder Phosphors:

The measured excitation spectra of a Tb$^{3+}$:Ln$_2$O$_2$S (Ln=Y,La,Gd) powder phosphors are shown in Figs. 4(a,b,c) and the photoluminescence spectra in Figs 5(a,b,c). From the recorded photoluminescence spectra, the following emission transitions have been identified:

\[ ^{5}D_{4} \rightarrow ^{7}F_{4} \quad (590 \text{ nm}) \]
\[ \rightarrow ^{7}F_{5} \quad (545 \text{ nm}) \]
\[ \rightarrow ^{7}F_{6} \quad (490 \text{ nm}) \]

Of these a transition \((^{5}D_{4} \rightarrow ^{7}F_{5})\) has been responsible for the strong green emission in all Tb$^{3+}$:Ln$_2$O$_2$S powder phosphors. The green colour emission was confirmed and analyzed from the computation of the colour co-ordinates \((x'\bar{y})\) by following the standard procedures recommended by CIE (France). The computed values of the colour co-ordinates \((x'\bar{y})\) and the stimulated emission cross-section (\(\sigma_p^E\)) of the transition \(^{5}D_{4} \rightarrow ^{7}F_{5}\) and the results are presented in Table 3. The computed colour co-ordinates \((x'\bar{y})\) have been found to fit well in the green colour region of the chromaticity diagram [(Fig 3) a shaded region] and the co-ordinates are in good agreement.

### Table 3

<table>
<thead>
<tr>
<th>Phosphors</th>
<th>(x')</th>
<th>(\bar{y})</th>
<th>(\lambda_p)</th>
<th>(\sigma_p^E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_2$S : Tb$^{3+}$</td>
<td>0.2918</td>
<td>0.5805</td>
<td>545</td>
<td>52.39</td>
</tr>
<tr>
<td>La$_2$O$_2$S : Tb$^{3+}$</td>
<td>0.3055</td>
<td>0.5725</td>
<td>545</td>
<td>56.14</td>
</tr>
<tr>
<td>Gd$_2$O$_2$S : Tb$^{3+}$</td>
<td>0.2629</td>
<td>0.5975</td>
<td>545</td>
<td>62.87</td>
</tr>
</tbody>
</table>
Fig. 4(a): Excitation Spectrum of $\text{Y}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ Powder Phosphor
Fig. 4(b): Excitation Spectrum of $\text{La}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ Powder Phosphor
Fig. 4(c): Excitation Spectrum of $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ Powder Phosphor
$\lambda_{\text{exc}} = 290$ nm

Fig. 5(a): Photoluminescence Spectrum of Y$_2$O$_2$S:Tb$^{3+}$ Powder Phosphor
Fig. 5(b): Photoluminescence Spectrum of La$_2$O$_2$S:Tb$^{3+}$ Powder Phosphor
Fig. 5(c): Photoluminescence Spectrum of Gd₂O₂S: Tb³⁺ Powder Phosphor
agreement with the standard values [11]. In order to compare the fluorescence efficiencies, the relative fluorescence intensity ratios (R) have been estimated and these are given Table 4.

Table 4

| Relative Fluorescence Intensity Ratios of Tb$^{3+}$: Ln$_2$O$_2$S Powder Phosphors (Ln = Y, La and Gd) |
|-------------------------------------------------|------------------------------|-------------------------------|------------------|
| Ratios between the transition | Y$_2$O$_2$S Tb$^{3+}$ | La$_2$O$_2$S Tb$^{3+}$ | Gd$_2$O$_2$S Tb$^{3+}$ |
| $^7$D$_4$ , $^7$F$_5$ | 0.305 | 0.375 | 0.326 |
| $^7$D$_4$ , $^7$F$_2$ | 0.583 | 0.750 | 0.6309 |
| $^7$D$_4$ , $^7$F$_3$ | 0.194 | 0.250 | 0.195 |
| $^7$D$_4$ , $^7$F$_4$ | 1.833 | 2.000 | 1.956 |
| $^7$D$_4$ , $^7$F$_5$ | 0.611 | 5.062 | 4.195 |
| $^7$D$_4$ , $^7$F$_6$ | 0.722 | 0.875 | 0.804 |
| $^7$D$_4$ , $^7$F$_7$ | 1 | 1 | 1 |

Based on the fluorescence spectral features Figs. (2 & 5) and also from computed data given in Tables (1-4), it could be concluded that between the two kinds of phosphors investigated, one in the composition of Y$_2$O$_2$S: Eu$^{3+}$ for the bright red and two hosts of La$_2$O$_2$S and Gd$_2$O$_2$S: Tb$^{3+}$ for an attractive green emission and thus there are three in total as the ideal fluorescence phosphor materials for their use in certain image forming systems.
References


J. Appl. Phys. 72 (1992) 5416


New Trends in Professional Colour Multilayered CRT’s
Thomson CSF, St Egreve, France

J. Electrochem. Soc. 123 (1976) 75

J. Electrochem. Soc. 122 (1975) 152

[8] H. Yamamoto and T. Kano
J. Electrochem. Soc. 126 (1979) 305

[9] P.N. Yocom
US Pat. 3,418,247 (1968)

