Chapter 7

Fluorescence spectra of LnVO$_4$:Eu$^{3+}$ (Ln=La,Y) powder phosphors
Introduction

This final chapter summarises the preparation and fluorescence properties of Eu³⁺-doped LaVO₄, (La₀.₇₅, Y₀.₂₅)VO₄, (La₀.₅, Y₀.₅)VO₄, (La₀.₂₅, Y₀.₇₅)VO₄ and YVO₄ powder phosphors. Luminescence spectra of RE³⁺-doped phosphates and vanadates of Y, Gd, Lu and La-have been studied for applications as the coating materials in CRTs, monitors of color TVs, etc. [1,2]. Erdei et al. have reported that YVO₄:Eu³⁺ phosphor as a novel material (displaying luminescence even at temperatures around 300°C) and also investigated the influence of powder preparation based on thermoluminescence spectra [3]. In general, lanthanide vanadates have either xenotime (tetragonal) or a monazite (monoclinic) structure at ordinary pressures. Scheelite structures are also found in the rare earth vanadates and arsenates at high pressure [4]. YVO₄ crystallizes in the D¹⁹₄₉ structure of zircon. This structure is tetragonal with a c/a ratio of 0.833 and is not optically active [5]. In the present work, we have fixed up the dopant europium concentration (Eu₂O₃) as 0.05 moles and investigated the effects of dual lanthanides on the fluorescence behaviours.

Results and Discussion

The phase purity of the synthesized phosphors was checked by XRD patterns from a Philips PW 18140 X-ray diffractometer fitted with a PM 820 3A on line recorder using CuKα (λ=0.1542 nm) target (Fig.1). Both excitation (Fig.2) and fluorescence spectra Figs. 3(a-e) of these phosphors were recorded on a Perkin-Elmer LS 50 luminescence spectrophotometer using a 150W xenon arc lamp as the excitation source. From the recorded XRD spectrum of YVO₄:Eu³⁺, it was observed that no peaks other than those of phosphors as were detected [6] (Fig.1). From the FT-IR transmittance spectra (Fig. 4(a-e)) of five Eu³⁺: phosphors, two prominent IR peaks were observed due to VO₄³⁻ vibrations [5]. Besides this, the I.R. peak positions were significantly changed in the range 435.7- 449.6 cm⁻¹ and 804.8 - 831.4 cm⁻¹.
Fig. 1: XRD pattern of YVO$_4$: Eu$^{3+}$ powder phosphor

Fig. 2: Excitation spectrum of YVO$_4$: Eu$^{3+}$ powder phosphor

Fig. 3: Fluorescence spectra of Eu$^{3+}$-doped (a) LaVO$_4$, (b)(La$_{0.75}$, Y$_{0.25}$)VO, (c)(La$_{0.5}$, V$_{0.5}$)VO$_4$ (d)(La$_{0.25}$, Y$_{0.75}$)VO$_4$ and (e) YVO$_4$ powder phosphors
Fig. 4: FT-IR spectra of Eu$^{3+}$-doped (a) LaVO$_4$, (b) (La$_{0.75}$, Y$_{0.25}$)VO$_4$ (c) (La$_{0.5}$, Y$_{0.5}$)VO$_4$, (d) (La$_{0.25}$, Y$_{0.75}$)VO$_4$ and (e) YVO$_4$ powder phosphors.
depending upon the chemical composition of the phosphors. The measured excitation spectrum of YVO₄:Eu³⁺(Fig.2) was in fair agreement with the literature [7]. The profiles of the fluorescence spectra of all Eu³⁺:phosphors (Fig.3) show the following emission transitions [6,7].

\[ ^{5}D_{0} \rightarrow ^{7}F_{4}, \quad ^{7}F_{3}, \quad ^{7}F_{2}, \quad ^{7}F_{1}, \quad \text{&} \quad ^{7}F_{0} \]

The main emission peaks were located at 614.6 - 619.3 nm (\(^{5}D_{0} \rightarrow ^{7}F_{2}\)). Since it is a hypersensitive transition it was found to split into same number of components in all the fluorescence spectra recorded. The transition (\(^{5}D_{0} \rightarrow ^{7}F_{1}\)) with a magnetic dipole character was split into two components. The presence of the sensitive forbidden transition (\(^{5}D_{0} \rightarrow ^{7}F_{0}\)) was identified in all the phosphors. Similarly, the transitions \(^{5}D_{0} \rightarrow ^{7}F_{3}\) and \(^{5}D_{0} \rightarrow ^{7}F_{4}\) were found to be present as singlet and doublet peaks, respectively. The fluorescence spectra of all the five Eu³⁺:phosphors were overlayed in Figs. 3(a-e). From Fig. 3, it was noticed that the intensity of the transition \(^{5}D_{0} \rightarrow ^{7}F_{2}\) was increasing with an increase in the yttrium concentration. Additionally, the peak positions were also found to be shifted by 5nm towards the higher wavelength side. The relative fluorescence intensity ratios (R) values were calculated and observed to increase as a function of yttrium concentration (Fig. 5) (Table 1).

Table 1: Relative fluorescence intensity ratios (R) for the measured emission levels of Eu³⁺-doped LnVO₄ (Ln=La&Y) powder phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>(^{5}D_{0} \rightarrow ^{7}F_{0})</th>
<th>(^{5}D_{0} \rightarrow ^{7}F_{1})</th>
<th>(^{5}D_{0} \rightarrow ^{7}F_{2})</th>
<th>(^{5}D_{0} \rightarrow ^{7}F_{3})</th>
<th>(^{5}D_{0} \rightarrow ^{7}F_{4})</th>
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<tbody>
<tr>
<td>LaVO₄:Eu³⁺</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>(La₀.₇₅₀,Y₀.₂₅₀)VO₄:Eu³⁺</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>(La₀.₅₀,Y₀.₅₀)VO₄:Eu³⁺</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>(La₀.₂₅₀,Y₀.₇₅₀)VO₄:Eu³⁺</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>YVO₄:Eu³⁺</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
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Fig. 5: Relative fluorescence intensity ratio ($R$) as a function of yttrium concentration of all LnVO$_4$:Eu$^{3+}$(Ln = La & Y) Powder Phosphors

Fig. 6: TGA/DTA curves of Eu$^{3+}$-doped (a$_1$/b$_1$) LaVO$_4$, (a$_2$/b$_2$) (La$_{0.75}$Y$_{0.25}$)VO$_4$, and (a$_3$/b$_3$) YVO$_4$ powder phosphors
The stimulated emission cross sections ($\sigma^E_p$, cm$^2$) (Table 2) values for the transition $^5D_0 \rightarrow ^7F_2$ have been evaluated and found to vary with the host matrix.

Table 2: The emission peak positions ($\lambda_p$, nm) and stimulated emission cross sections ($\sigma^E_p \times 10^{-23}$ cm$^2$) values for $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$- doped LnVO$_4$ (Ln = La & Y) powder phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>$\lambda_p$</th>
<th>$\sigma^E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaVO$_4$:Eu$^{3+}$</td>
<td>614.6</td>
<td>1.00</td>
</tr>
<tr>
<td>(La$<em>{0.75}$,Y$</em>{0.25}$)VO$_4$:Eu$^{3+}$</td>
<td>618.9</td>
<td>1.375</td>
</tr>
<tr>
<td>(La$<em>{0.5}$,Y$</em>{0.5}$)VO$_4$:Eu$^{3+}$</td>
<td>618.9</td>
<td>1.375</td>
</tr>
<tr>
<td>(La$<em>{0.25}$,Y$</em>{0.75}$)VO$_4$:Eu$^{3+}$</td>
<td>619.3</td>
<td>1.378</td>
</tr>
<tr>
<td>YVO$_4$:Eu$^{3+}$</td>
<td>619.3</td>
<td>1.504</td>
</tr>
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Table 3: Color coordinates ($X$, $Y$) of LnVO$_4$ : Eu$^{3+}$ (Ln=La & Y) powder phosphors

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>$X$</th>
<th>$Y$</th>
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<tbody>
<tr>
<td>LaVO$_4$:Eu$^{3+}$</td>
<td>0.6070</td>
<td>0.3915</td>
</tr>
<tr>
<td>(La$<em>{0.75}$,Y$</em>{0.25}$)VO$_4$:Eu$^{3+}$</td>
<td>0.6385</td>
<td>0.3605</td>
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<tr>
<td>(La$<em>{0.5}$,Y$</em>{0.5}$)VO$_4$:Eu$^{3+}$</td>
<td>0.6453</td>
<td>0.3537</td>
</tr>
<tr>
<td>(La$<em>{0.25}$,Y$</em>{0.75}$)VO$_4$:Eu$^{3+}$</td>
<td>0.6456</td>
<td>0.3534</td>
</tr>
<tr>
<td>YVO$_4$:Eu$^{3+}$</td>
<td>0.6486</td>
<td>0.3503</td>
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The color coordinates ($X$, $Y$) were computed based on the standard formulations made available by the CIE (Commission International de l'Eclairage, France). From the computed color coordinates (Table 3) it has been found that $X$ - coordinate value has been increasing with an increase in the yttrium concentration. Thermogravimetric (TGA/DTA) investigations were carried out on the phosphor samples YVO$_4$:Eu$^{3+}$, LaVO$_4$:Eu$^{3+}$ and (La$_{0.75}$,Y$_{0.25}$)VO$_4$:Eu$^{3+}$ (Fig. 6) by using Metler Toledo, TGA/SDTA 851$^c$, which indicates the total 0.513%, 0.367% and 0.394% weight loss, respectively. No
Fig. 7: SEM images of Eu$^{3+}$ doped (a) YVO$_4$, (b) LaVO$_4$ and (c) (La$_{0.5}$, Y$_{0.5}$)VO$_4$ powder phosphors
appreciable weight loss in TGA (Fig.6 (a, b, & a,) and absence of any noticeable peak in DTA (Fig.6 (b, b, & b,) mode indicates thermal stability with respect to chemical as well as crystalline phase transformation changes in a covered temperature range. The scanning electron microscopic images of the samples YVO₄:Eu³⁺, LaVO₄:Eu³⁺ and (La₀.₅₃ Y₀.₇)VO₄:Eu³⁺ were recorded by using Leica Stereoscan 440 (Figs 7(a-c)) with 10 KV EHT, 7 mm working distance (WD), 5.00 KX magnification and 25 PA beam current, with 35 mm camera attached on the high resolution recording unit. From the SEM image of YVO₄:Eu³⁺ phosphor (Fig.7(a)), it is noticed that agglomerated particles, size variation from 500 nm to 2 µm with pebble shape exist in the system. In the case of LaVO₄:Eu³⁺ (Fig.7(b)) and (La₀.₅₃ Y₀.₇)VO₄:Eu³⁺ (Fig.7(c)), the morphological features with particles in 2-3 µm size with loosely bound, spinel shaped porous agglomerations are predominantly seen [6]. From this study, we conclude, that depending upon the relative fluorescence intensity ratios (R), color coordinates (X, Y) and SEM images, the phosphor YVO₄:Eu³⁺ could be suggested as a promising material for its application in certain electronic display systems.
REFERENCES


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    L.E. Cross

Thus the present thesis summarizes comprehensively, the results based on the investigation made on the fluorescence properties of Eu$^{3+}$, Tb$^{3+}$, Ce$^{3+}$, Sm$^{3+}$, Dy$^{3+}$ and Ho$^{3+}$-doped in certain phosphor host matrices of LnOX (X= F, Cl, Br), LnPO$_4$ and LnVO$_4$ (Ln= Y, La, Gd) powder phosphors. In each section a few phosphor systems have been identified as good materials for their applications in certain electronic display systems.