

Synthesis and characterization of $Y_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ and $La_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ complexes for solid state lighting

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Abstract

Binuclear complexes $Y_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ and $La_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ were synthesized by solution technique, where ($x = 0.2, 0.4, 0.5, 0.6$ and 0.8). Y = Yttrium, La – Lanthanum, Eu = Europium DBM – dibenzoylmethane, phen = 1, 10 phenanthroline. The doping of Y^{3+} and La^{3+} with europium has been carried out stochiometrically by mole %. Thin films of these binuclear complexes with thickness of 1000 \AA have been made under high vacuum (1×10^{-6} Torr). Among all Y-doped and La doped Eu complexes, thermal stability and melting point was found to be maximum for $La_{0.6}Eu_{0.4}Eu(DBM)_3(Phen)$ (231.4°C) and for $La_{0.8}Eu_{0.2}Eu(DBM)_3(Phen)$ (189.55°C), respectively. λ_{max} of all Y and La doped Eu complexes were found at 360 nm with no much variation or shifting in absorbance wavelength. However, change in absorption intensity in both Y and La series was observed, indicating that the absorption spectrum depends on the aromatic compound (DBM) in the complexes. Photoluminescence spectra displays sharp red light emission with very narrow full width half maxima (FWHM) at $580, 611, 617, 620$ and 626 nm due to ${}^5D_0 \rightarrow {}^7F_j$ ($j = 1, 2, 3$) transition. Maximum PL emission intensity was observed for $Y_{0.6}Eu_{0.4}(DBM)_3(Phen)$ and $La_{0.4}Eu_{0.6}(DBM)_3(Phen)$ in their respective series. As these binuclear complexes are thermally stable and emit intense red light emission, these complexes can be employed as red emissive material for organic light emitting diodes, flat panel displays, solid state lighting and as laser host material.

Key words: laser, OLED, thin films, thermal stability, photoluminescence

1. Introduction

Rare earth metal complexes have favorable characteristics, such as extremely narrow emission bands and high internal quantum efficiencies, which are suitable for use as the emission material in OLEDs [1-5]. Efficient and bright luminescent complexes have been obtained by i) selection of proper ligand and ii) the introduction of metal ion into the complexes [6]. Binuclear complexes as an emitter were used in lasers and OLEDs, in which there is an efficient energy transfer process between ligand and metal ions when operated at low voltages. Organic light emitting diode have been studied extensively because of their potential application in flat panel display since the first device with high quantum efficiency and luminescence was fabricated by C. W. Tang et al [7-8] With the

commercialization of OLEDs and for the development of low cost devices, binuclear complexes may be useful for the organic OLEDs or other optical devices such as lasers, where red color emission is required.

Rare earth (RE) ions, such as Nd, Er and Eu, find important applications in Opto electronic, including solid state lasers and phosphors because of partially filled 4f shell shielded by completely filled outer 5s and 5p levels, which results in very sharp optical emissions due to 4f-4f electron transitions with energies largely independent of the host material [9]. Europium has the second lowest melting point and the lowest density of all lanthanides, hence widely used [10]. Europium is used in the production of phosphors for the creation of small lasers, dopant in some types of glass in lasers and other

optoelectronic devices [11-13]. Europium oxide (Eu_2O_3) is widely used as a red phosphor in TVs and fluorescent lamps, and as an activator for yttrium-based phosphors. [14-16]. Eu^{3+} ion has a sharp red emission and its complexes are used as an emitter in OLEDs [17-18]. The luminescence enhancement of Eu(III) or Tb(III) complexes with organic ligand was observed by the addition of Y, La, Gd and Lu in a Micelle solution where concentration of each component was the same. In this report, synthesis and characterization of Europium doped Yttrium and Lanthanum complexes for laser and OLED applications are described.

2. Experimental

2.1. Synthesis of $\text{Y}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ and $\text{La}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$

2.1.1. Reagents and solvents

Starting materials for the synthesis of this Yttrium/lanthanum-doped europium complexes are EuCl_3 purity 99.5 %, Yttrium chloride (YCl_3) purity 99.5 %, Lanthanum chloride (LaCl_3) purity 99.5 %, Tris-(1, 3 -Diphenyl 1, 3 - Propanedions) $\text{C}_{15}\text{H}_{12}\text{O}_2$ M.wt. = 224.26 gm/mole. purity 99.5 %, 1-10 Phenanthroline (monohydrate) Redox Indicator, $\text{C}_{12}\text{H}_8\text{N}_2\text{H}_2\text{O}$, M.wt. = 180.0784 – purity 99.5 %, Ethanol absolute ($\text{C}_2\text{H}_5\text{OH}$), purity 99.98 % 1 litre = 0.79 Kg, M.wt = 46.07 g/mol., KOH – purity 99.98 % .For the synthesis of these complexes, the proportion of $\text{Y}^{3+}/\text{La}^{3+}-\text{Eu}^{3+}$ have been adjusted stichiometrically as shown in Table 1.

Table 1: Chemicals composition of $\text{Y}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ and $\text{La}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$

Complexes	DBM (gm)	phen (gm)	EuCl_3 (gm)	YCl_3 (gm)
$\text{Y}_8\text{Eu}_2(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.413	0.078
$\text{Y}_6\text{Eu}_4(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.309	0.156
$\text{Y}_5\text{Eu}_5(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.258	0.195
$\text{Y}_4\text{Eu}_6(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.206	0.234
$\text{Y}_2\text{Eu}_8(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.103	0.312
$\text{La}_8\text{Eu}_2(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.413	0.130
$\text{La}_6\text{Eu}_4(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.309	0.260

$\text{La}_8\text{Eu}_2(\text{DBM})_3(\text{Phen})$	1.345	0.396	0.258	0.325
$\text{La}_4\text{Eu}_6(\text{DBM})_3(\text{Phen})$	1.345	0.39	0.206	0.39
$\text{La}_2\text{Eu}_8(\text{DBM})_3(\text{Phen})$	1.345	0.39	0.103	0.52

2.1.2. Synthesis procedure

In 20 ml of hot ethanol (60°C), 6 mmol of dibenzoylmethane and 2 mmol of neutral ligand (phen – 1, 10 – phenanthroline) were dissolved and then 6 ml of 1 N potassium hydroxide solution was added to this solution. The complete hot mixture was stirred well and 2 mmol of rare earth salt solution, $[(\text{EuCl}_3)_x$ and $(\text{YCl}_3)_{(1-x)} / (\text{LaCl}_3)_{(1-x)}]$ was added drop wise. This hot mixture was allowed to cool for 15 min. and recrystallise from 95 % ethanol [19]. This mixture was filtered out and the resulting precipitate was dried for 2 hrs at 80°C in oven to remove the moisture. Synthesis method of $\text{La}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ is same as described above, but instead of YCl_3 , Lanthanum Nitrate ($\text{La}(\text{NO}_3)_3$) has been used. Chemical structure of $\text{Y}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ and $\text{La}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ are shown in Fig. 1.

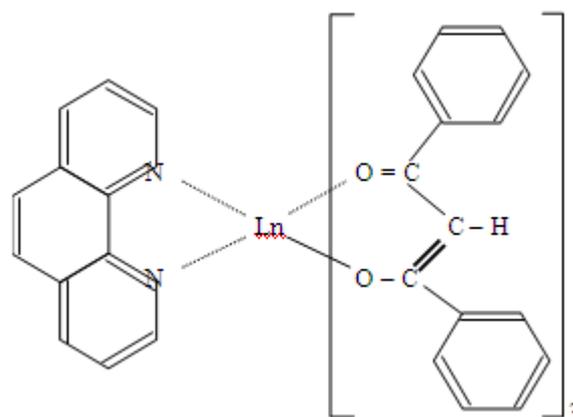


Fig.1: Chemical structure of $\text{Ln}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$, where $\text{Ln}=\text{Y/La}$ ($x=0.8,0.6,0.4,0.2$)

2.2. Preparation of thin film

Thin films of Y/La doped Eu binuclear complexes were prepared on a 14mm x 14mm glass substrate by vacuum evaporation technique. Initially, they were cleaned in methanol, alternatively in ether. The vacuum chamber was cleaned very carefully so that no particles remain inside the chamber. $\text{Y}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})/\text{La}_{(1-x)}\text{Eu}_x(\text{DBM})_3(\text{Phen})$ powder was kept in a boat made up of

molybdenum, which have high melting point (1400 °C). The boat was placed on the coil, which is connected to the electrode. After attaining the vacuum of 1×10^{-6} Torr, the current was increased very slowly until counter start counting. Quartz crystal and the glass substrate were placed at the same height from the boat. After a measurement of fixed count by the frequency counter, the current was decreased slowly and finally to zero value. Later, vacuum chamber cock was closed. The films with glass substrate were taken away and kept in the decicator. The thickness of the thin film was 1000 \AA .

3. Results and discussion

3.1. TGA and DTA Measurement

In order to confirm the sublimation temperature, thermal stability and melting point (phase transition) of the synthesized complexes, TGA and DTA measurements were carried out on Mettler Toledo Star System in nitrogen atmosphere. TGA / DTA measurement of $Y_{(1-x)}Eu_x(\text{DBM})_3(\text{Phen})$ and $La_{(1-x)}Eu_x(\text{DBM})_3(\text{Phen})$ are depicted in Fig. 2 and 3, respectively. The horizontal portion AB in the TGA curve indicated no weight change, specifying the ability of the synthesized binuclear complexes to maintain the properties unchanged on heating (thermal stability) and T_i at point B represents the decomposition temperature, of the respective complexes. Thermal stability in $Y_{(1-x)}Eu_x$ and $La_{(1-x)}Eu_x$ series of complexes were in the range of 225.37 – 229.48 °C and 222.31 – 231.4 °C respectively. The curved portion BC indicates the weight loss by heating the sample to a given temperature. The temperature T_f on the TGA curve indicates the final temperature at which cumulative weight change first reaches its maximum value, corresponding to the complete reaction time, which lies between 420-430°C for all Y/Ln doped Eu complexes. The reaction interval is taken as the difference between the final and initial temperature $T_f - T_i$.

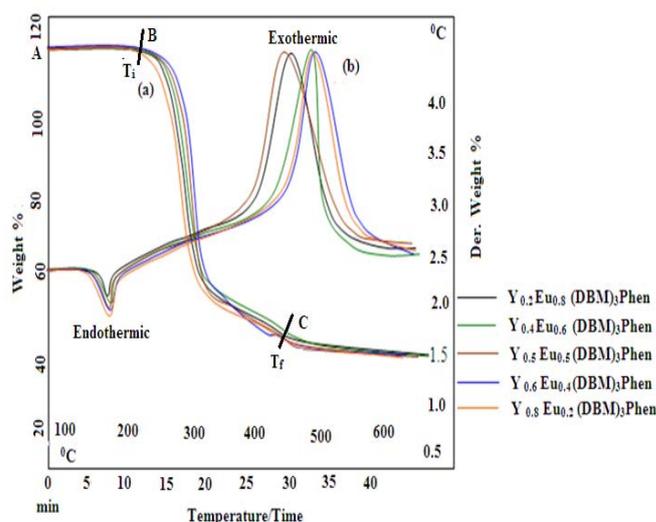


Fig. 2: (a) TGA and (b) DTA of $Y_{(1-x)}Eu_x(\text{DBM})_3(\text{Phen})$

DTA curve was found to be parallel to the temperature axis till 200°C, this suggests that all the synthesized samples undergo physical or chemical change of state after this temperature. At low temperatures, ranging between 185-190°C, the reactions associated with the heat absorptions are endothermic, characterized by negative peaks, revealing chemical changes in the synthesized complexes. As the temperature increases above 320°C, the reactions associated with liberation of heat are exothermic, characterized by positive peaks, revealing the physical changes in the sample in the range of 400-550°C. Sublimation temperature, thermal stability and melting point of $Y_{(1-x)}Eu_x(\text{DBM})_3(\text{Phen})$ and $La_{(1-x)}Eu_x(\text{DBM})_3(\text{Phen})$ are included in Table 2. Among all Y-doped and La doped Eu complexes, thermal stability and melting point was found to be maximum for $La_{0.6}Eu_{0.4}Eu(\text{DBM})_3(\text{Phen})$ (231.4°C) and for $La_{0.8}Eu_{0.2}Eu(\text{DBM})_3(\text{Phen})$ (189.55 °C), respectively.

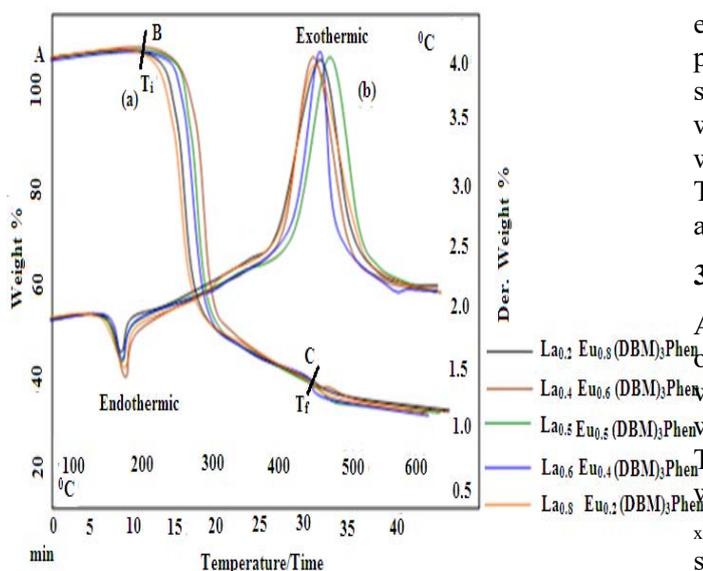


Fig. 3: (a) TGA and (b) DTA of $La_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$

Table 2: Sublimation temperature, thermal stability and melting point of $Y_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ and $La_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$

Complex	Sublimation temperature ($^{\circ}C$)	Thermal stability ($^{\circ}C$)	Melting point ($^{\circ}C$)
$Y_{.8}Eu_{.2}(DBM)_3(Phen)$	261.40	229	188.20
$Y_{.6}Eu_{.4}(DBM)_3(Phen)$	262.47	229.48	186.45
$Y_{.5}Eu_{.5}(DBM)_3(Phen)$	263.68	228.01	187.21
$Y_{.4}Eu_{.6}(DBM)_3(Phen)$	265.70	226.2	189.41
$Y_{.2}Eu_{.8}(DBM)_3(Phen)$	264.21	225.37	187.39
$La_{.8}Eu_{.2}Eu(DBM)_3(Phen)$	266.32	222.31	189.55
$La_{.6}Eu_{.4}Eu(DBM)_3(Phen)$	267.10	231.40	186.42
$La_{.5}Eu_{.5}Eu(DBM)_3(Phen)$	260.0	230.10	185.02
$La_{.4}Eu_{.6}Eu(DBM)_3(Phen)$	255.9	226.40	185.67
$La_{.2}Eu_{.8}Eu(DBM)_3(Phen)$	263.60	228.60	186.20

3.2. Optical Measurements

UV-visible absorption spectra was carried out to probe the accurate measurements of light absorption at different wavelengths in and near VIS range of the electromagnetic spectrum. When the sample is exposed to UV-Visible light having an energy that matches a possible electronic

transition within the molecule, some of the light energy will be absorbed and the electron is promoted to higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance verses wavelength.

3.2.1. Absorption spectra

Absorption on the vertical scale is just a measure of amount of light absorbed (absorbance) and the wavelength on horizontal scale indicates the wavelength at which light is absorbed [20-21]. The presence of chromophores in a molecule is well documented by the absorption spectra of $Y_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ and $La_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$ as shown in Fig. 4 and 5, respectively. λ_{max} of all Y and La doped Eu complexes were found at 360 nm without much variation or shifting in absorption wavelength. However, change in absorption intensity in both Y and La series was observed, indicating that the absorption spectrum depends on the aromatic compound (DBM) in the complexes.

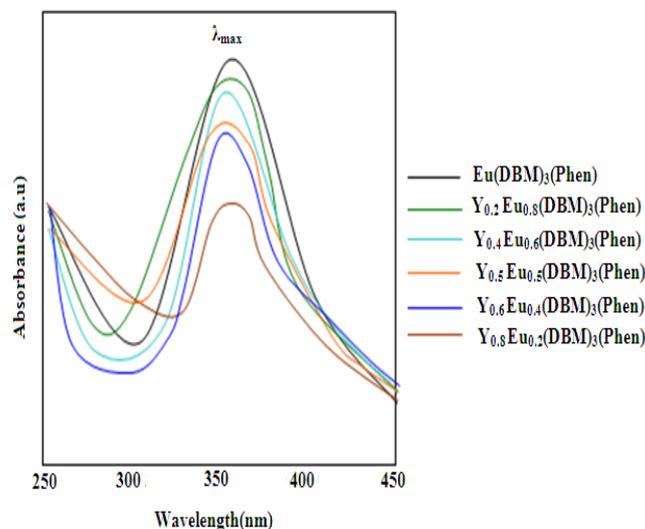


Fig. 4: Absorption spectrum of thin film of $Y_{(1-x)}Eu_{(x)}(DBM)_3(Phen)$.

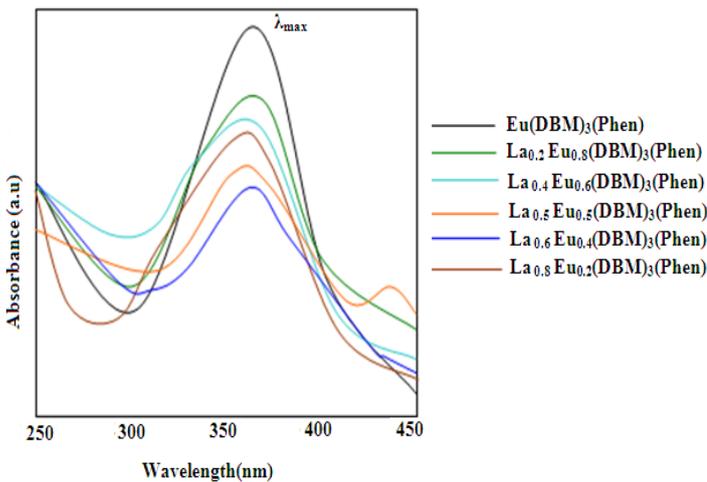


Fig. 5: Absorption spectrum of thin film of $\text{La}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$

3.2.2. Photoluminescence spectra

Fig. 6 and 7 shows the excitation measurement of doped $\text{Y}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$ and $\text{La}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$, when excited in the range 250 nm – 500 nm, monitored at 611 nm. PL excitation peak occurred at 380 nm for all these doped complexes. There is a variation in the PL intensity among the series as the number of europium ions varied from complex to complex in these series.

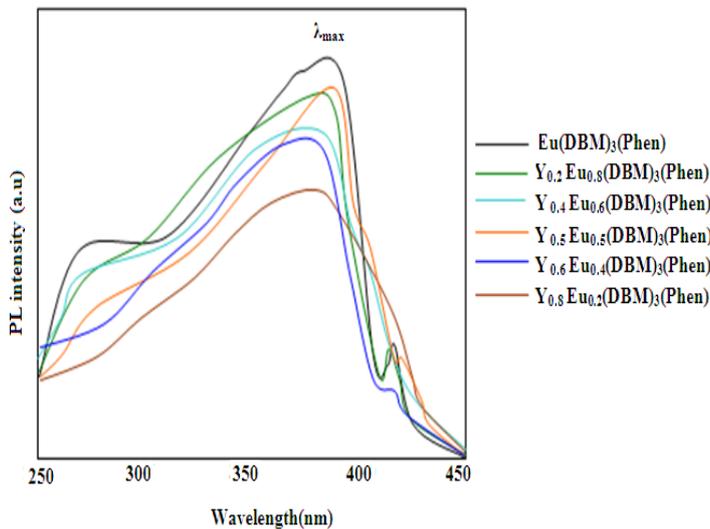


Figure 6: Excitation spectrum of thin film of $\text{Y}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$.

A very sharp spectral line is observed in the emission spectrum at 611 nm, which falls in the red region of the visible region. This may be due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, when excited at 360 nm as shown in Fig. 8 for $\text{Y}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$

complexes. The emission spectrum consists of peaks at 580, 611, 617, 620 and 626 nm due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 1, 2, 3$) transitions. When these emission spectra are compared within a series and with the pure $\text{Eu}(\text{DBM})_3(\text{Phen})$, continuous decrease in PL intensity is observed as the concentration of Y^{3+} ion increases in Y – Eu series [22-23].

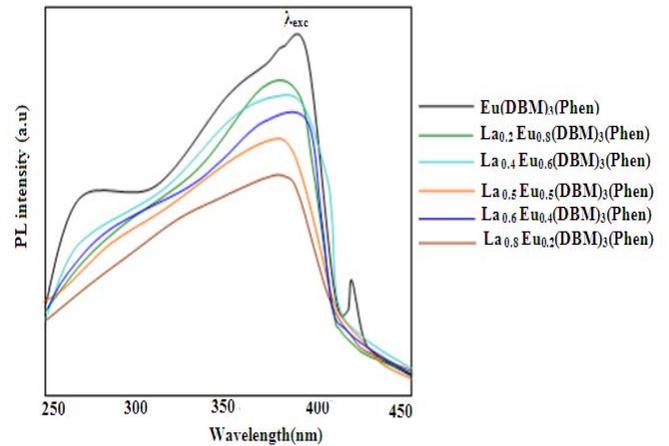


Fig.7: Excitation spectrum of thin film of $\text{La}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$

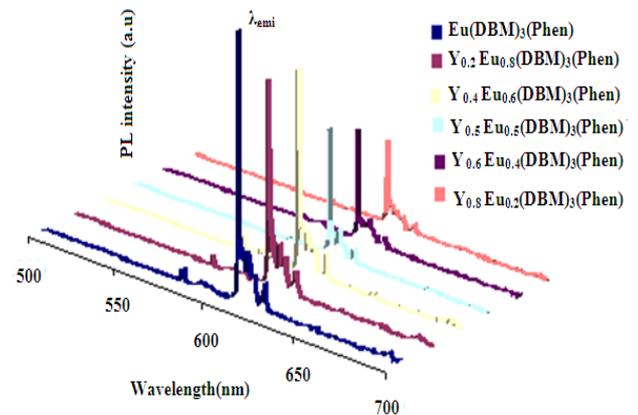


Figure 8: Emission spectrum of thin film of $\text{Y}_{(1-x)}\text{Eu}_{(x)}(\text{DBM})_3(\text{Phen})$, ($x = 0.2, 0.4, 0.5, 0.6, 0.8$)

Similarly, the PL intensity decreased in La – Eu series as the concentration of La^{3+} ion increased, this may be due to concentration quenching. It may be possible that, even though the Y^{3+} and La^{3+} are luminescence enhancing ions in micelle's solution but in powder complex, excitation energy of Y^{3+} and La^{3+} can not transferred to Eu^{3+} through DBM ligand. Hence, as number of Eu^{3+} ion decreases, the PL

intensity decreases accordingly. Maximum PL emission intensity was observed for $Y_4Eu_6(DBM)_3(Phen)$ in Y series. Similarly, sharp spectral line was observed in the emission spectrum of $La_{(1-x)}Eu_x(DBM)_3(Phen)$, at 611 nm due to $^5D_0 \rightarrow ^7F_2$ transition, when excited at 380 nm, as shown in Fig. 9. The emission spectra consist of peaks at 580, 611, 617, 620 and 626 nm due to $^5D_0 \rightarrow ^7F_j$ ($j = 1, 2, 3$) transition. Minimum PL emission intensity observed for $La_4Eu_6(DBM)_3(Phen)$ in La series. As the cost of $EuCl_3$ is more as compared to $La(NO_3)_3$, as synthesized complexes found to be more economical.

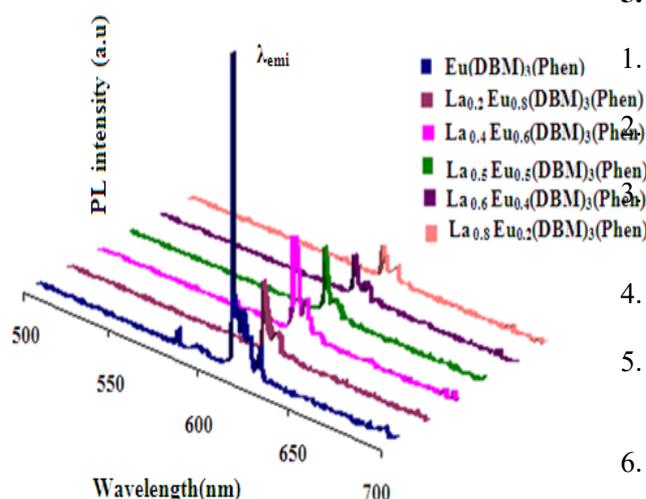


Fig. 9: Emission spectrum of thin film of $La_{(1-x)}Eu_x(DBM)_3(Phen)$, ($x = 0.2, 0.4, 0.5, 0.6, 0.8$)

4. Conclusions

Binuclear complexes $Y_{(1-x)}Eu_x(DBM)_3(Phen)$ and $La_{(1-x)}Eu_x(DBM)_3(Phen)$ red light emitting complexes were synthesized by solution technique by maintaining stoichiometric ratio. Among Y-doped and La doped Eu complexes, thermal stability and melting point was found to be maximum for $La_6Eu_4Eu(DBM)_3(Phen)$ ($231.4^\circ C$) and for $La_8Eu_2Eu(DBM)_3(Phen)$ ($189.55^\circ C$), respectively. λ_{max} of all Y and La doped Eu complexes were found at 360 nm with no much variation or shifting in absorbance wavelength. However, change in absorption intensity in both Y and La series was observed, indicating that the absorption spectrum depends on the aromatic compound (DBM) in the complexes. A very sharp spectral line is observed

in the emission spectra with sharp red light emission with very narrow full width half maxima (FWHM) at 611 nm, which falls in the red region of the visible region. This may be due to $^5D_0 \rightarrow ^7F_2$ transition, when excited at 360 nm. The emission spectrum consists of peaks at 580, 611, 617, 620 and 626 nm due to $^5D_0 \rightarrow ^7F_j$ ($j = 1, 2, 3$) transition. Maximum PL emission intensity was observed for $Y_6Eu_4(DBM)_3(Phen)$ and $La_4Eu_6(DBM)_3(Phen)$ in their respective series. As these binuclear complexes are thermally stable and emit intense red light emission, they can be employed as emissive materials in optoelectronic devices.

5. References

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