

RESEARCH ARTICLE

Improvement of quantum efficiency through Gd³⁺ to Eu³⁺ energy transfer in YF₃ phosphor

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Abstract

This paper reports the energy transfer from Gd³⁺ to Eu³⁺ in YF₃ and the consequent downconversion luminescence for the YF₃:Gd³⁺, Eu³⁺ fluoride phosphor. The phosphor was synthesized using a soft chemical route, followed by a reactive atmosphere process. Because of the wide band gap in YF₃ and the correct energy site for ⁸S_{7/2}–⁶G_J transitions of Gd³⁺ ions, fluoride YF₃ doped with Gd³⁺–Eu³⁺ were studied in their vacuum-ultraviolet (VUV) spectral regions. Powder X-ray diffraction (XRD) analysis showed the structural purity of YF₃. VUV excitation and emission properties were explored using a VUV synchrotron radiation beam line. Downconversion of energy from VUV (157 nm) to visible light with quantum efficiency c. 189% was seen. This YF₃:Gd³⁺, Eu³⁺ phosphor would be an option for mercury-free fluorescence lamps.

KEYWORDS

downconversion luminescence, mercury-free fluorescence lighting, quantum cutting (QC), VUV spectroscopy

1 | INTRODUCTION

Downconversion luminescence is the phenomenon through which it is possible to obtain two or more visible photons for each VUV photon absorbed by the phosphor. Consequently, it will lead to luminescence quantum efficiency (QE) larger than 100% and better energy efficiency in lighting or display devices.^[1] This cognition was first projected by Dexter and later on verified in YF₃:Pr³⁺ with VUV excitation at 185 nm and QE of c. 140%.^[2–4] In subsequent research, some rare-earth ions, such as Pr³⁺, Tm³⁺ or Gd³⁺, showed a quantum-cutting phenomenon.^[5,6] It was concluded from the experimental results and prediction of Judd–Ofelt theory that further improvement in the efficiency of quantum-cutting phosphors using the single ion system was impossible.^[5] Further investigations^[7,8] have suggested that the ion pair Gd³⁺ and Eu³⁺ in a suitable host lattice results in QE greater than 100% under VUV excitation. The use of energy transfer (ET) between the sensitizer and activator in phosphors is well established and is one way to tune emission colour.^[9–12]

In the current report, results of downconversion luminescence for YF₃:Gd³⁺, Eu³⁺ synthesized using a soft chemical route and subsequent heating in a reactive atmosphere are presented. The resulting fine powder was tested for phase purity using an XRD technique. VUV excitation and emission properties were investigated through remote access of 4B8 VUV spectroscopy beam lines at the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics in Beijing, China.

2 | EXPERIMENTAL

Yttrium fluoride (YF₃) doped with Gd³⁺, Eu³⁺ was synthesized using a soft chemical route and subsequent heating in a reactive atmosphere. During synthesis, analytical grade oxide (Y₂O₃) was used as a precursor. The mixture of stoichiometric amounts of

nitrates of yttrium, gadolinium and europium was obtained by dissolving the respective oxides (AR grade) in the least amount of HNO_3 . A small amount of double-distilled water was added to the mixture, which was stirred for 30 min. Hydrofluoric acid (HF) was added dropwise to the mixture to obtain a white precipitate. The precipitate was washed, filtered and then dried under an infrared (IR) lamp.

The powder was then heated in the reactive atmosphere created by a suitable amount of ammonium fluoride in the sealed glass tube. It was further heated for 1 h in a graphite crucible at suitable temperature and then suddenly quenched to room temperature.^[13,14] The synthesis process is illustrated in a flow chart (Figure 1).

3 | RESULTS AND DISCUSSION

3.1 | XRD analysis

The resulting fine powders of doped and undoped YF_3 were tested for phase purity using the XRD technique. The XRD pattern for both was consistent with the corresponding ICDD file (01-070-1935) for YF_3 . The XRD pattern confirmed that the YF_3 lattice had an orthorhombic structure [space group: Pnma (62)] with unit cell parameters, $a = 6.3537\text{\AA}$, $b = 6.8545\text{\AA}$, $c = 4.3953\text{\AA}$ and $\alpha = \beta = \gamma = 90^\circ$. XRD patterns are shown in Figure 2. Diffraction peaks in all cases were indexed to a pure

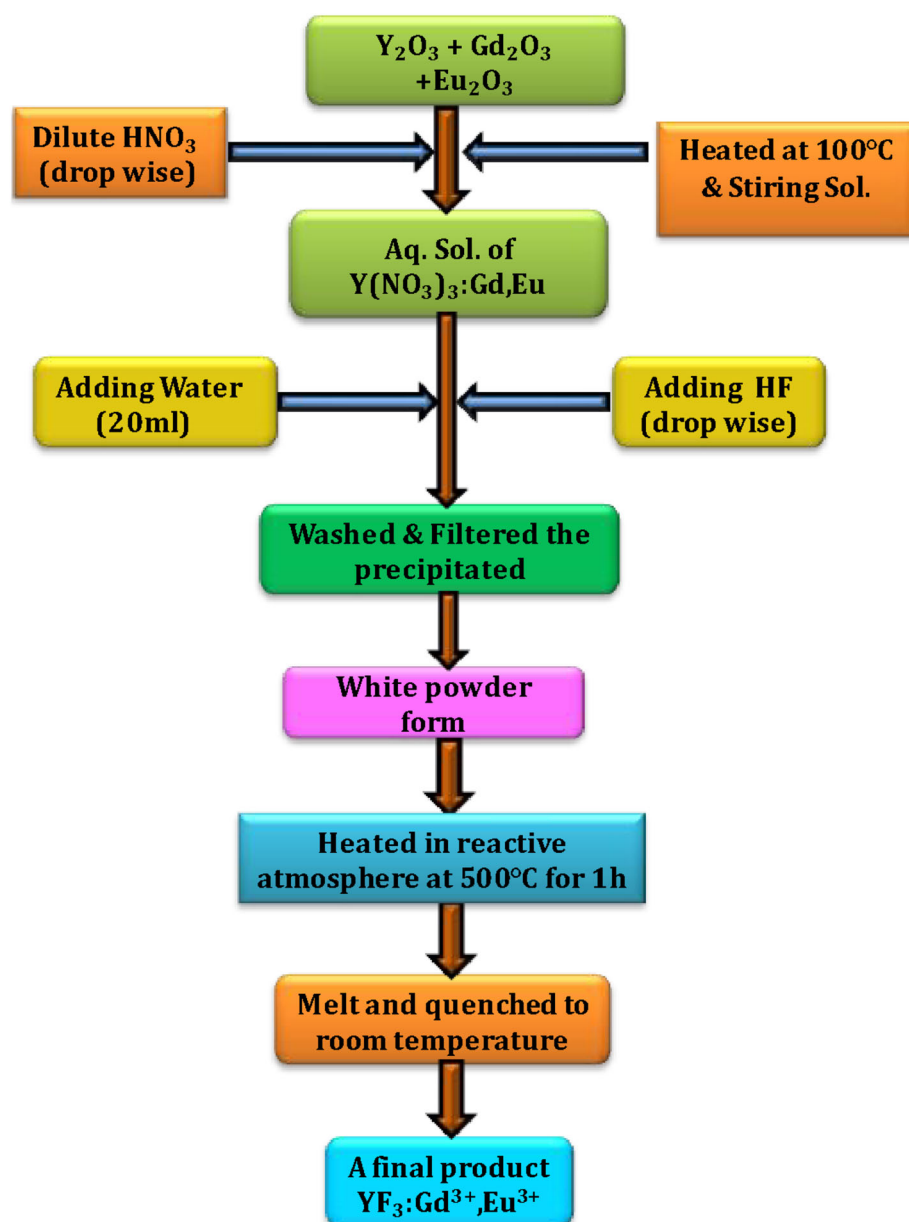


FIGURE 1 Flow chart of the synthesis process for $\text{YF}_3:\text{Gd}^{3+}, \text{Eu}^{3+}$

FIGURE 2 XRD patterns for undoped, singly doped, and co-doped YF_3

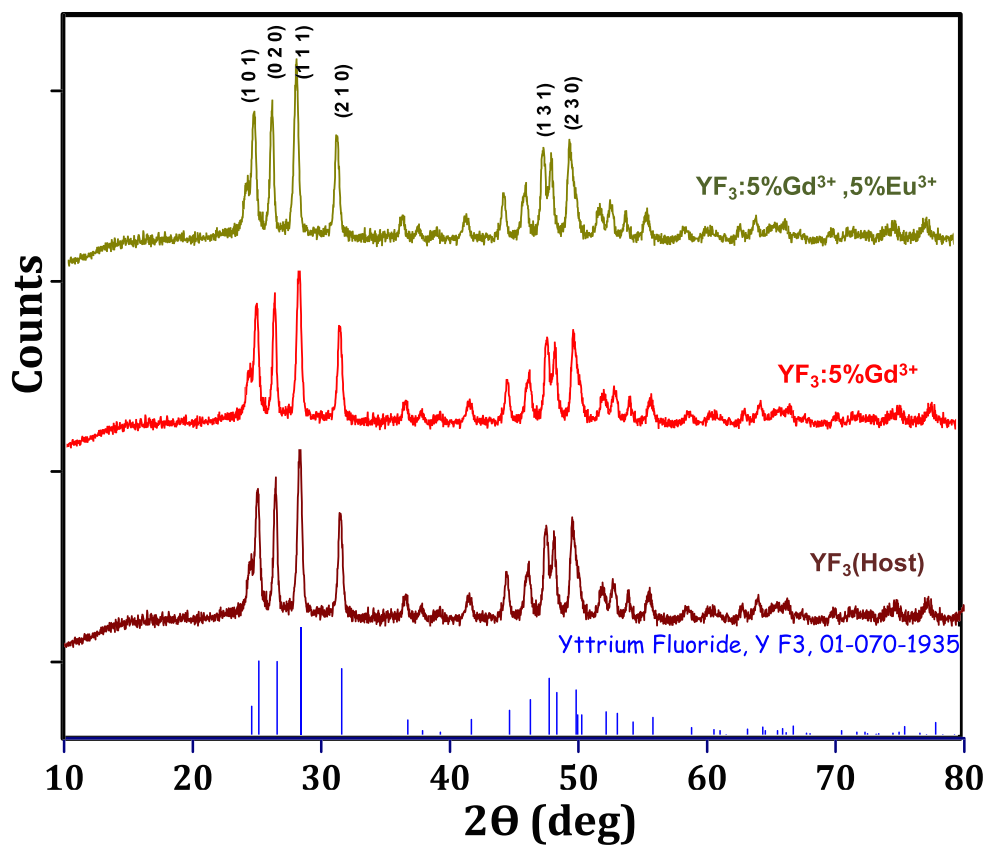
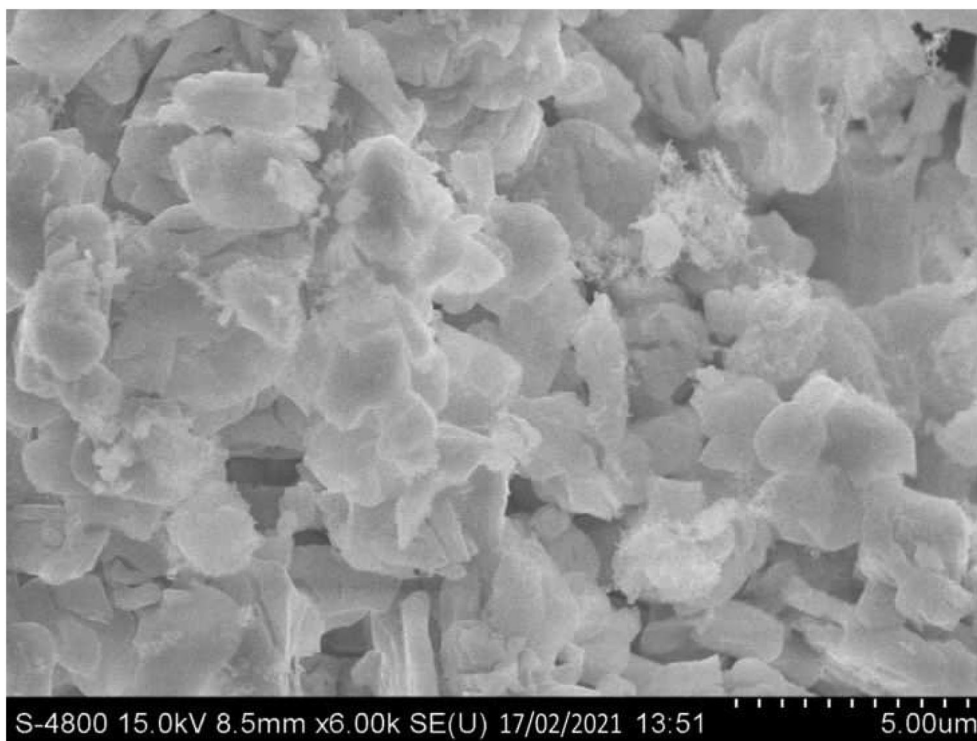


FIGURE 3 SEM micrograph of the synthesized $\text{YF}_3:\text{Gd}-\text{Eu}$ phosphor



orthorhombic structure of YF_3 without the presence of any spare phases.

3.2 | Scanning electron micrograph (SEM) analysis

The SEM micrograph of the synthesized $\text{YF}_3:\text{Gd}-\text{Eu}$ phosphor is given in Figure 3, which shows the formation of crystal grains with individual grain size in the order of a few microns or less.

3.3 | VUV photoluminescence studies

It can be seen from Figure 4 that at 5 mol% of Gd^{3+} in YF_3 there is maximum intensity of photoluminescence (PL) emission and a prominent PL emission peak was located at 311 nm under VUV (273 nm) excitation. Therefore Gd^{3+} showed concentration quenching as a sensitizer in the YF_3 host at higher concentrations. Figure 5 shows the excitation spectrum of $\text{YF}_3:\text{Gd}^{3+}$ monitored at 311 nm emission. Three major excitation bands corresponded to transitions $^8\text{S}_{7/2} \rightarrow ^6\text{G}_J$, $^6\text{D}_J$, $^6\text{I}_J$ of Gd^{3+} .

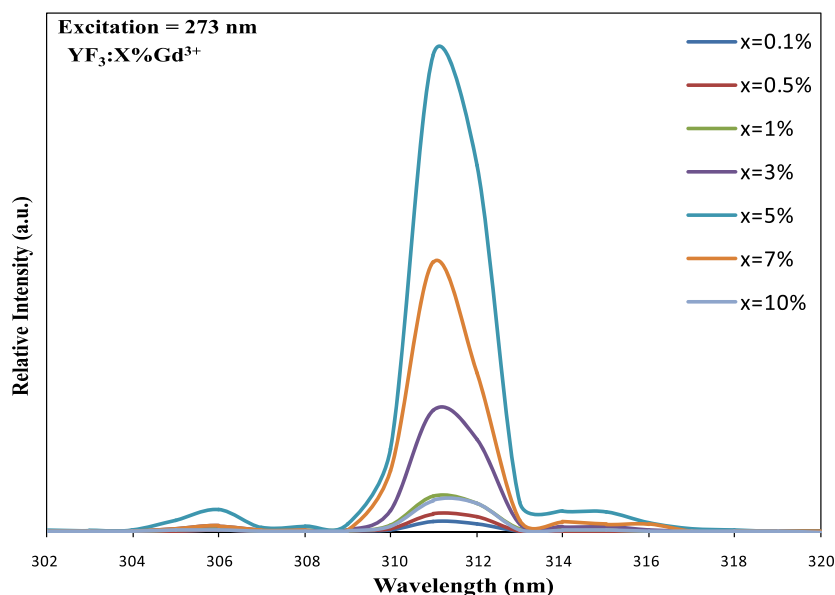


FIGURE 4 Emission spectra of $\text{YF}_3:\text{Gd}^{3+}$ under 273 nm excitation

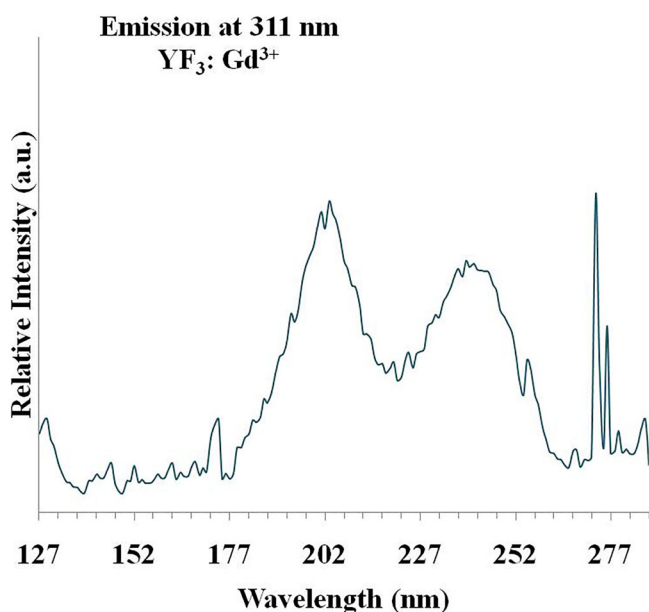


FIGURE 5 Excitation spectra of $\text{YF}_3:\text{Gd}^{3+}$ monitored at 311 nm emission

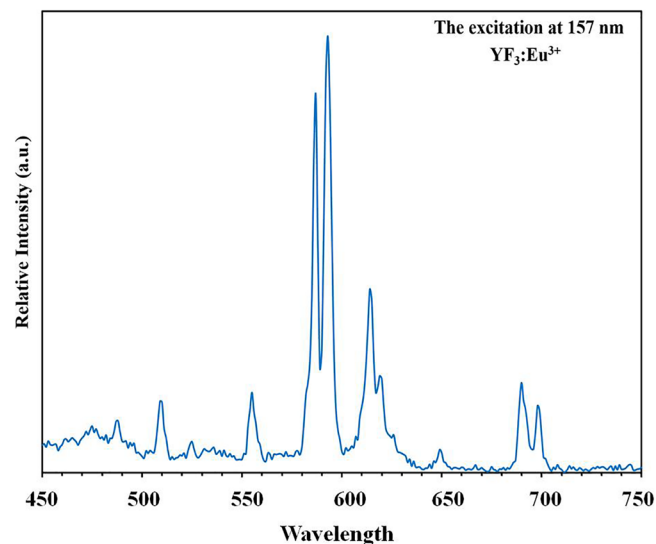


FIGURE 6 Emission spectra of $\text{YF}_3:\text{Eu}^{3+}$ under the excitation of 157 nm

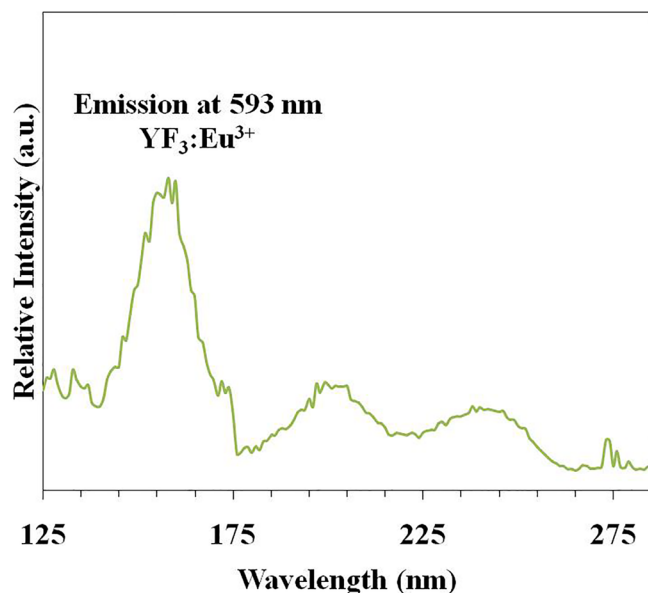


FIGURE 7 Excitation spectra of $\text{YF}_3:\text{Eu}^{3+}$ monitored at 593 nm emission

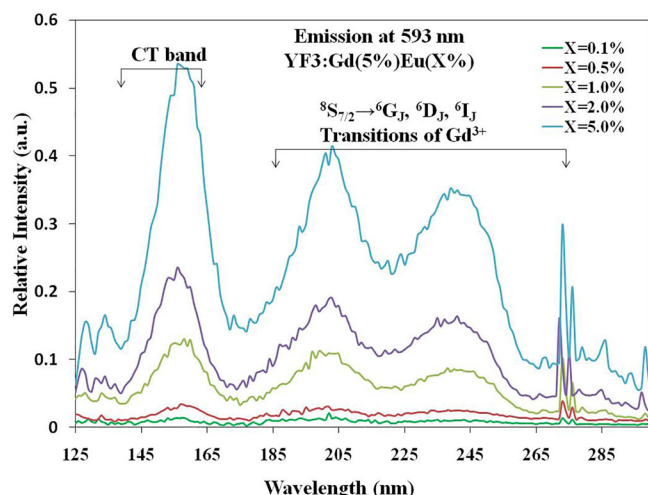


FIGURE 8 Excitation spectrum of $\text{YF}_3:5\%\text{Gd}^{3+}, X\%\text{Eu}^{3+}$ monitored at 593 nm emission

Figures 6 and 7 depict, respectively, the emission and excitation spectra of Eu^{3+} singly doped YF_3 . The prominent emission bands (Figure 6) of Eu^{3+} that peaked at 593, 613, 650 and 700 nm corresponded to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 1, 2, 3, 4$) transitions. The excitation spectra consisted of a broad excitation band c. 157 nm that was attributed to charge transfer absorption.^[15]

In further investigations, the PL emission and excitation spectra of $\text{YF}_3:\text{Gd}^{3+}, \text{Eu}^{3+}$ were studied for 0.1, 0.5, 1, 2 and 5 mol% of

Eu^{3+} , keeping the Gd^{3+} concentration constant at 5 mol%. Figure 8 depicts the excitation spectrum monitored for the 593 nm Eu^{3+} emission band and Figure 9 depicts the PL emission spectrum monitored at the 157 nm excitation wavelength. From Figures 6 and 7, it is seen that, with increase in Eu^{3+} concentration, the intensities of emission and excitation bands also increased.

Excitation peaks (Figure 8) at 157 nm were attributed to the charge transfer band,^[15] but this was absent from the excitation spectra (Figure 5) of Gd^{3+} singly doped YF_3 and peaks at 201, 236 and 273 nm may be attributed to transitions ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J, {}^6\text{D}_J, {}^6\text{I}_J$ of Gd^{3+} . Emission bands (Figure 9) for Eu^{3+} peaking at 593, 613, 650 and 700 nm corresponded to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 1, 2, 3, 4$) transitions. ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transitions were comparatively much more intense than those for ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$ transitions.

The combination of Gd^{3+} and Eu^{3+} ions in YF_3 plays a vital role in bringing the luminescence QE of the phosphor beyond 100%. The process of absorption of the VUV photon through the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$ transition of Gd^{3+} ion, transfer of energy to two Eu^{3+} ions leading to ${}^7\text{F}_J \rightarrow {}^5\text{D}_0$ transitions and emission of two visible photons through ${}^5\text{D}_J \rightarrow {}^7\text{F}_J$ transitions of Eu^{3+} ions is described in the energy level diagram (Figure 10).

As illustrated in Figure 10, cross-relaxation ET (step 1) can bring only the Eu^{3+} ion into the ${}^5\text{D}_0$ excited state, therefore emissions due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ transition are only probable. However in direct ET (step 2), all excited states ${}^5\text{D}_J$ ($J = 0, 1, 2, 3$) of Eu^{3+} are probable, so emission bands corresponded to all the ${}^5\text{D}_J$ ($J = 0, 1, 2, 3$) $\rightarrow {}^7\text{F}_J$ transitions.^[16,17]

Figure 11 depicts the PL emission spectra of $\text{YF}_3:5\text{ mol}\% \text{Gd}^{3+}, 5\text{ mol}\% \text{Eu}^{3+}$ across the entire visible range of wavelengths monitored at 157 and 273 nm excitations, to authenticate the ET process and quantum cutting.

The 157 nm excitation converts Gd^{3+} to ${}^6\text{G}_J$ states, while 273 nm excitation converts Gd^{3+} to ${}^6\text{I}_J$ states. The two-step relaxation process of Gd^{3+} and therefore quantum cutting was impossible due to excitation at the ${}^6\text{I}_J$ states. So emissions corresponding to ${}^5\text{D}_J \rightarrow {}^7\text{F}_J$ transitions (step 2 in Figure 10) of Eu^{3+} showed a typical branching ratio between ${}^5\text{D}_0$ and other ${}^5\text{D}_J$ states. Conversely, with the 157 nm excitation to ${}^6\text{G}_J$ states, quantum cutting can occur by two-step ET. This results in an increase in ${}^5\text{D}_0$ emissions over the typical branching ratio between ${}^5\text{D}_0$ and other ${}^5\text{D}_J$ states. This fact was used to calculate the luminescence QE of the phosphor with a formula proposed in previous publications.^[14,18–22]

$$\frac{P_1}{P_1 + P_2} = \frac{R({}^5\text{D}_0/{}^5\text{D}_{1,2,3})_{e_{G_J}} - R({}^5\text{D}_0/{}^5\text{D}_{1,2,3})_{e_{I_J}}}{1 + R({}^5\text{D}_0/{}^5\text{D}_{1,2,3})_{e_{I_J}}}$$

where P_1 and P_2 are the probabilities of ET from Gd^{3+} to Eu^{3+} through cross-relaxation and direct transfer, respectively, R

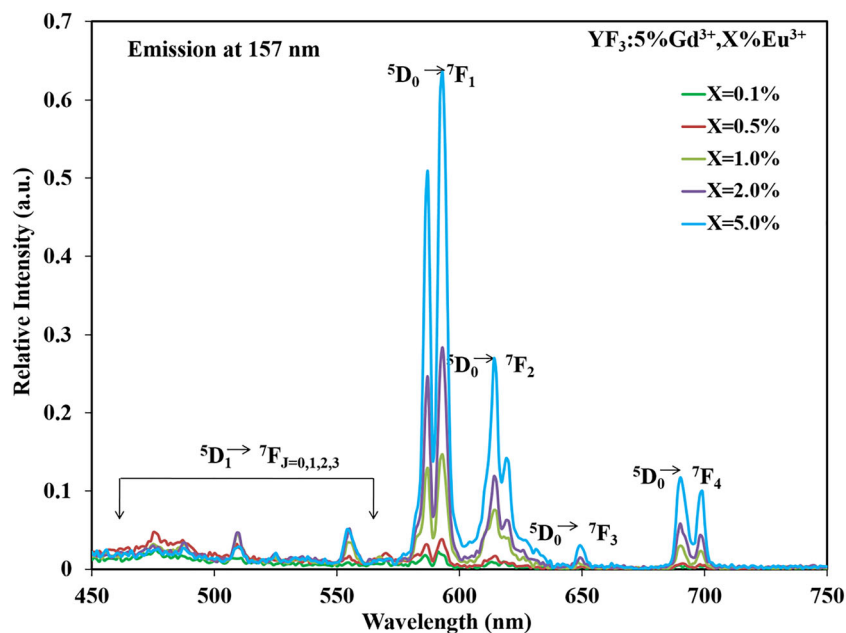


FIGURE 9 Emission spectra of $\text{YF}_3:5\%\text{Gd}^{3+}, X\%\text{Eu}^{3+}$ at 157 nm excitation wavelength

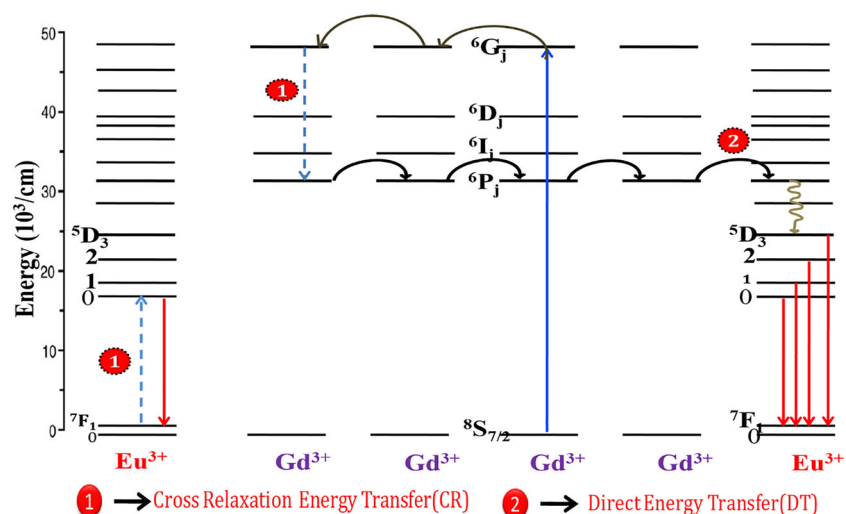


FIGURE 10 Energy level diagrams of Eu^{3+} and Gd^{3+} showing the cross-relaxation energy transfer process

$(^5D_0/^5D_{1,2,3})$ is the ratio of the 5D_0 and $^5D_{1,2,3}$ emission integral intensities. The subscript (6G_j or 6I_j) represents the excitation level for which the ratio is observed.

From the emission spectra (Figure 9), the values of R ($^5D_0/^5D_{1,2,3}$) and R ($^6D_0/^6D_{1,2,3}$) were found to be 4.3 and 1.8 respectively. Therefore, the value of $\frac{P_1}{P_1+P_2}$ obtained was 0.89. This means that there were 89 out of 100 Gd^{3+} ions in the 6G_j excited state that returned through a two-step ET

by emitting two visible photons by Eu^{3+} transitions. Therefore, 89 out of 100 Gd^{3+} ions emitted 178 visible photons and the remaining 11 Gd^{3+} ions emitted 11 visible photons by Eu^{3+} . Therefore for 100 absorbed VUV photons, the total number of emitted visible photons was 189. So, the overall QE of the phosphor was 189%. Here should be noted that the incident VUV photon absorption efficiency was taken into consideration and some nonradiative losses at defects and impurities were disregarded.

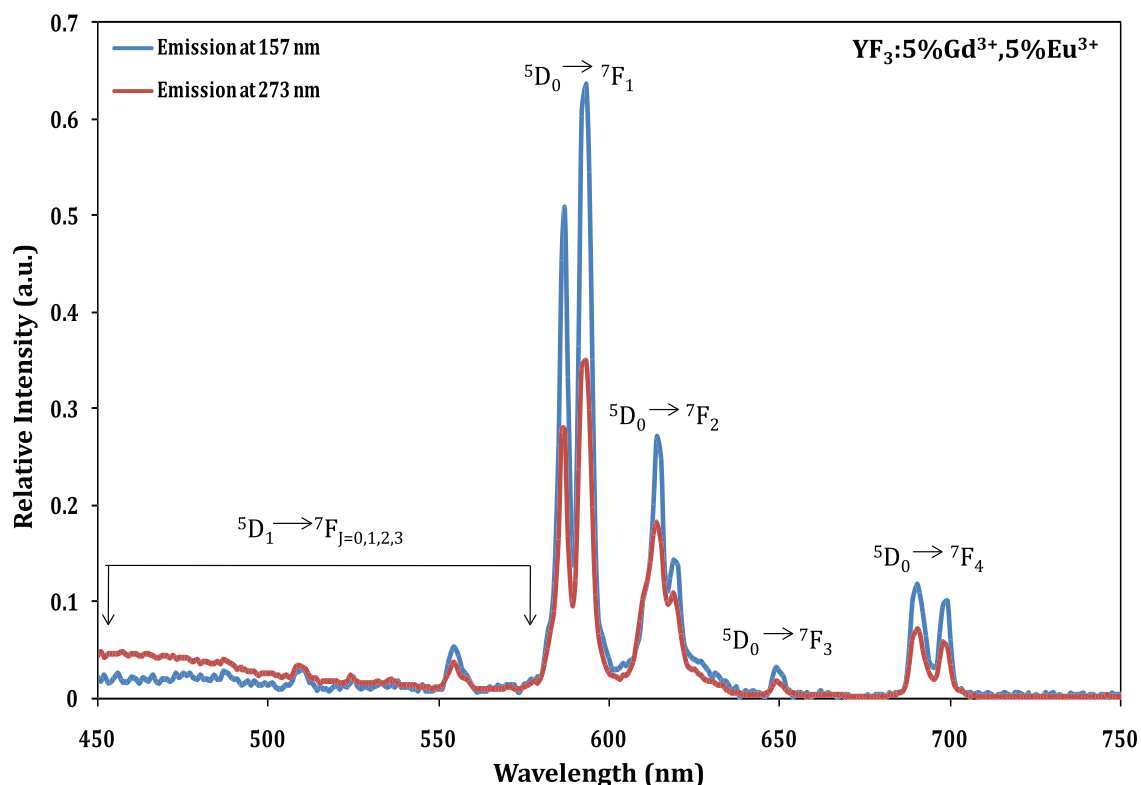


FIGURE 11 Emission spectra of $\text{YF}_3:5\%\text{Gd}^{3+}, X\%\text{Eu}^{3+}$ at 157 and 273 nm excitation wavelengths

4 | CONCLUSION

The inorganic material $\text{YF}_3:\text{Gd}^{3+}, \text{Eu}^{3+}$ successfully prepared through a soft chemical route and subsequent heating in a reactive atmosphere. The XRD pattern confirmed the orthorhombic structure of YF_3 . The study recognized visible quantum cutting and the optimum ET from Gd^{3+} to Eu^{3+} in YF_3 . The QE was found to be c. 189%, which advocates that $\text{YF}_3:\text{Gd}^{3+}, \text{Eu}^{3+}$ would be a probable phosphor for mercury-free fluorescence lamps.

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