

# Vacuum Ultraviolet Spectroscopic Properties in $Gd^{3+}$ - $Eu^{3+}$ Ions Pair Doped $MYF_4$ ( $M = Li, Na, \text{ and } K$ )

S. R. Jaiswal<sup>\*1</sup>, U. T. Bhati<sup>2</sup>, P.A. Nagpure<sup>3</sup>, S. K. Omanwar<sup>4</sup>

<sup>1</sup>Department of Physics, Shri R. L. T. College of Science, Akola. 444001 (INDIA)

**E-Mail:** [srjaiswal07@gmail.com](mailto:srjaiswal07@gmail.com)

<sup>2</sup>Department of Physics, Shri Shivaji Arts, Comm. & Sci. College Akot. 444101 (INDIA)

<sup>3</sup>Department of Physics, Shri Shivaji Science College, Amravati. 444602 (INDIA)

<sup>4</sup>Department of Physics, Sant Gadge Baba Amravati University, Amravati. 444602 (INDIA)

**Abstract.**  $LiYF_4$ ,  $NaYF_4$ , and  $KYF_4$  doped with  $Gd^{3+}$ - $Eu^{3+}$  ion pairs synthesised by soft route (wet) chemical technique tracked by Reactive Atmosphere Process (RAP). The phase purity of every synthesized material is verified using the X-ray Diffraction (XRD) method. The photoluminescence excitation (PLE) and photoluminescence emission (PL) properties are examined in ultra-violet (UV) and vacuum ultraviolet (VUV) regions. A new type of photon harvesting (cutting) process is studied in the synthesized phosphors. The Quantum Cutting (QC) is observed only in host  $LiYF_4$  doped with  $Gd^{3+}$ - $Eu^{3+}$  Phosphor.

**Keywords:** Visible Quantum Cutting, Down-Conversion (DC), Mercury-Free Fluorescent Lamps (MFFL), Quantum Efficiency (QE)

## 1. Introduction

Visible QC through DC is the process in which gain more than one visible photon for respectively absorbed VUV Photon by the materials. Subsequently, it results to luminescence QE larger than unity (100%) and recover energy proficiency in illumination devices or 3D display [1]. The Dexter was projected primary possibility and far ahead on confirmed in  $YF_3:Pr^{3+}$  with absorption at 185 nm wavelength in the VUV region and QE around 140% [2-4]. In the succeeding research, the Quantum-Cutting (QC) phenomenon was found in case of luminescent materials doped by rare-earth ions such as  $Gd^{3+}$ ,  $Tm^{3+}$ , or  $Pr^{3+}$  [5-6]. According to the prediction of Judd–Ofelt theory and experimental results it has also been concluded that utilizing a single ion activator system cannot further improve the efficiency of the QC phosphors [5]. In further surveys, it was found that the  $Gd^{3+}$  -  $Eu^{3+}$  pair in the appropriate host matrix results QE larger than unity under the excitation of VUV [7–8]. Jaiswal et al also showed the visible QC in  $Gd^{3+}$ ,  $Eu^{3+}$  doped  $YF_3$  phosphor synthesised by the wet chemical method trailed by RAP [9].

In this research report, possibility of visible QC with  $Gd^{3+}$  -  $Eu^{3+}$  pair in the yttrium fluoride host matrix with alkali metal ions is explored. This paper presents, for the first time, an analysis of the quantum harvesting and energy transfer process in the  $MYF_4:Gd^{3+}$ ,  $Eu^{3+}$  ( $Li, Na, K$ ) phosphor.

## 2. Experimental

The  $MYF_4$  phosphor (where  $M = Li, Na, K$ ) doped with  $Gd^{3+}$  and  $Eu^{3+}$  ions were synthesised via the soft route (wet) chemical, followed by heating in a RAP. In the preparation, A. R. grade precursors such as Oxide ( $Y_2O_3$ ) and nitrates  $MNO_3$  ( $M=Li, Na, K$ ) were used. In the least amount of  $HNO_3$  the combination of stoichiometric quantities of nitrates of Y, Gd, and Eu were got by liquifying the corresponding oxides. The stoichiometric quantity of lithium nitrate ( $LiNO_3$ ) was added to the combination. A small quantity of double distilled (DD) water was introduced into a complete nitrate mixture and stirred for 30 minutes. The dropwise hydrofluoric acid (HF) was added to the mixture to get a whitish paste. The paste undertook washing, filtered, and subsequent drying using under the filament/IR light. After the dried, the powder was heated at 500 °C for 1 hour in the wrapped/sealed glass test tube under reactive gas environment which was formed by appropriate quantity of ammonium



fluoride ( $\text{NH}_4\text{F}$ ). It was then heated for 4 hours in the pre-heated graphite crucible at  $800^\circ\text{C}$  temperature and then abruptly quenched to normal ( $25^\circ\text{C}$ ) temperature [9-11]. After cooling the sample was crushed in a mortar pestle to make a white fine powder of  $\text{LiYF}_4:\text{Gd}^{3+}, \text{Eu}^{3+}$  Phosphor.

The identical procedure was replicated for the  $\text{Gd}^{3+}, \text{Eu}^{3+}$ -doped  $\text{NaYF}_4$  and  $\text{KYF}_4$  phosphors. The fig.1 shows the flow map of the synthesis process.

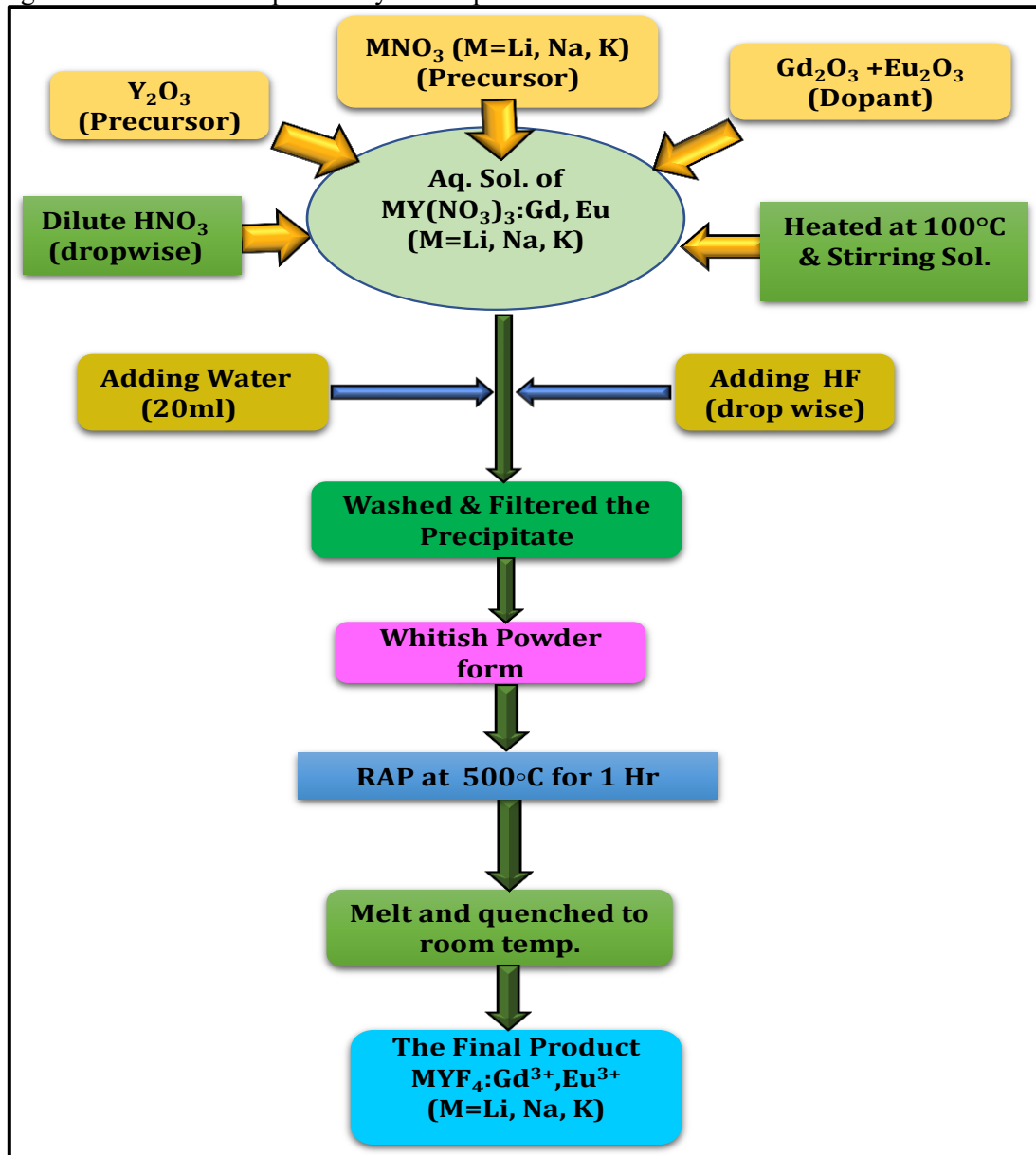
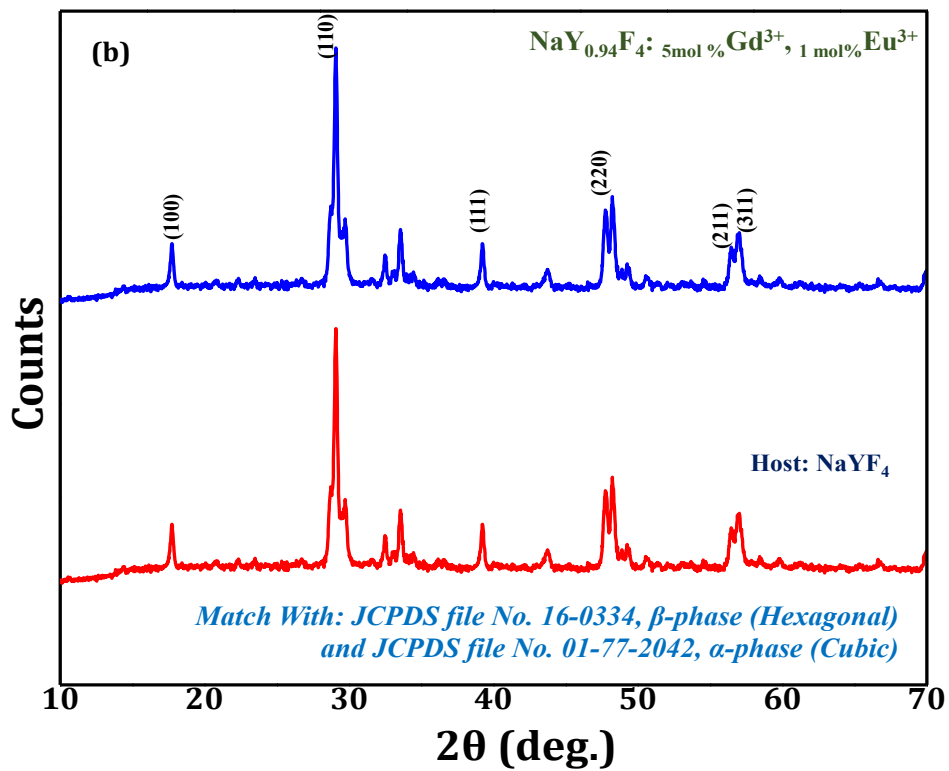
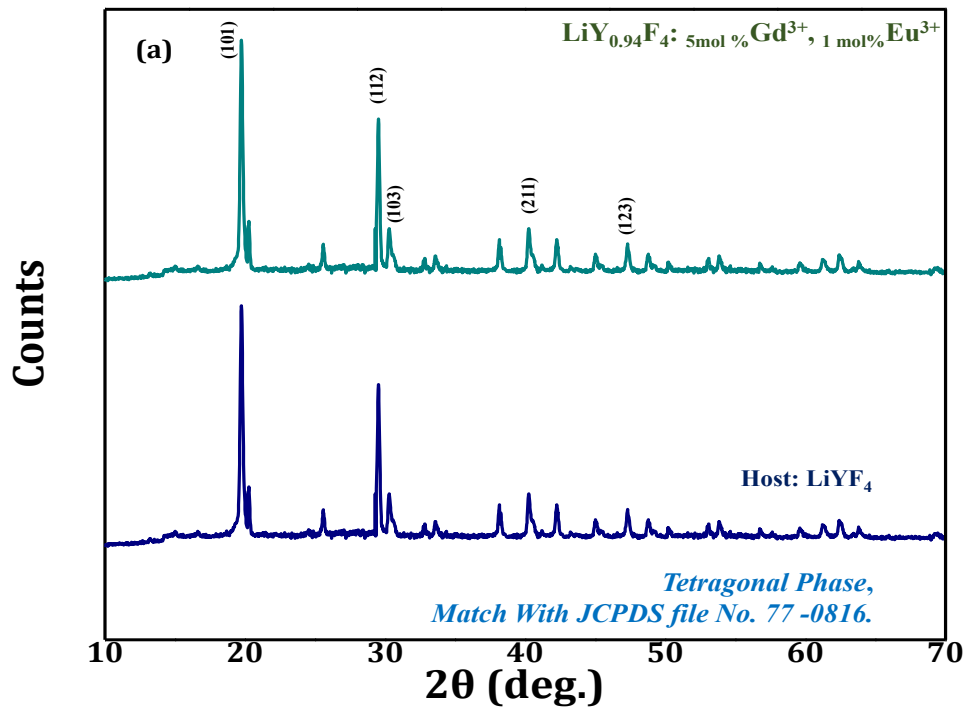


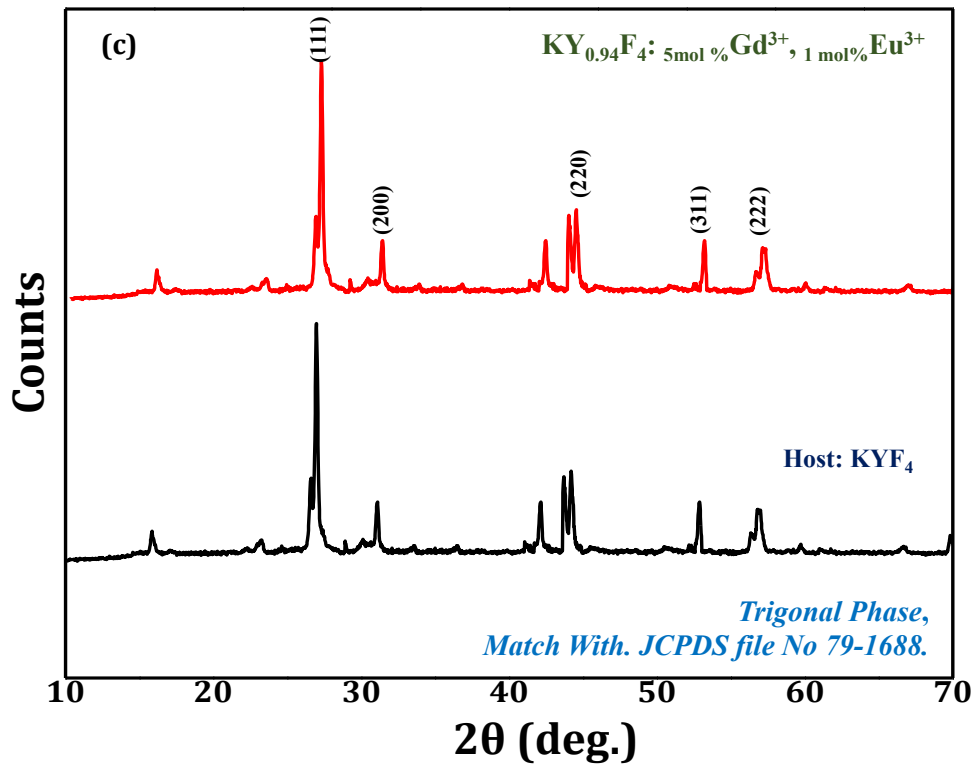
Figure 1. Flow map of the complete synthesis procedure

### 3. Outcomes & Argument

#### 3.1 The study of XRD

The fig. 2 represents detailed XRD pattern of doped-undoped  $\text{MYF}_4$  (M= Li, Na, K) phosphor.



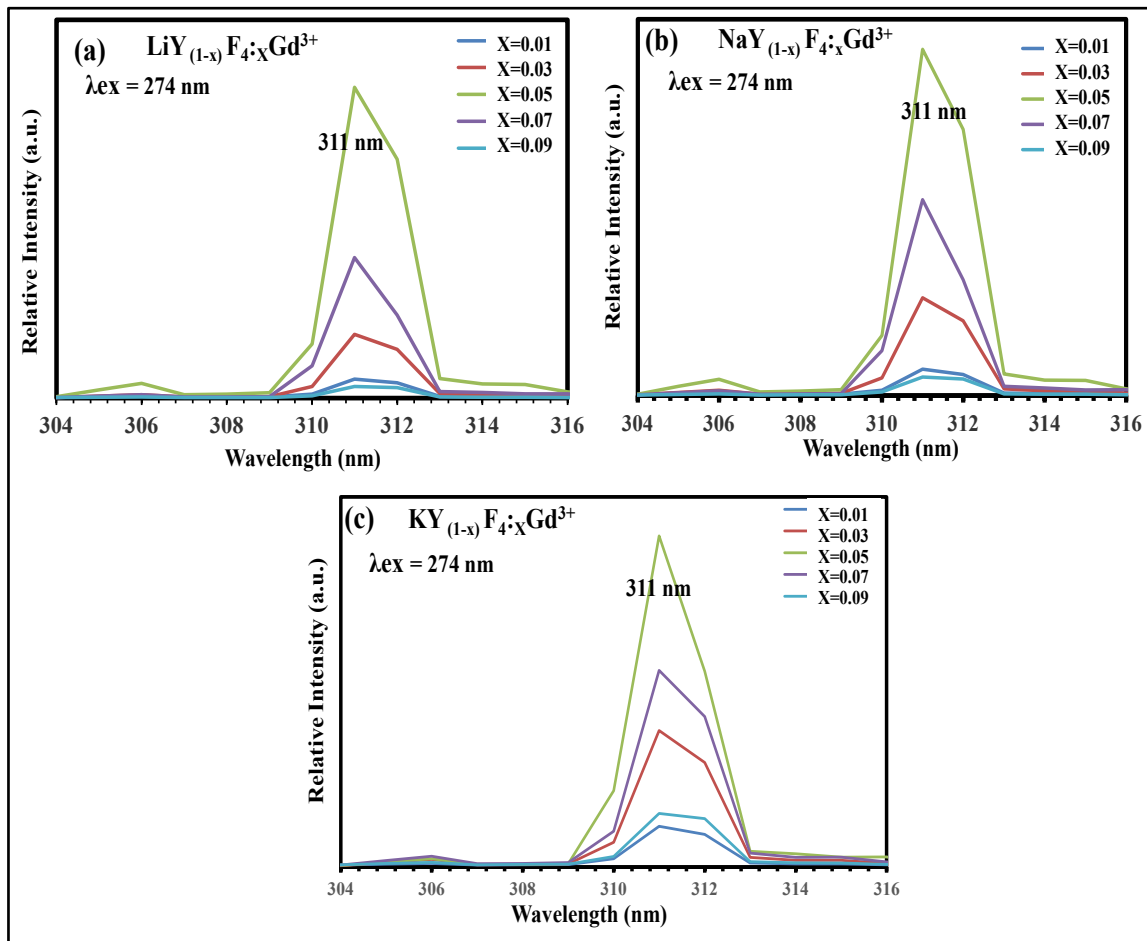


**Figure 2.** (a), (b), and (c): XRD pattern of doped-undoped  $\text{MYF}_4$  ( $M = \text{Li, Na and K}$ ) phosphors

The purity of phase of resulting synthesized products doped and undoped  $\text{MYF}_4$  ( $M = \text{Li, Na, K}$ ) were verified by XRD on a Rigaku D/max-2400 powder diffractometer with CuK $\alpha$  radiation. In the XRD pattern, all major diffraction peaks for doped and undoped  $\text{LiYF}_4$  match well with the JCPDS file No. 77-0816 [12] and has a tetragonal structure. The XRD pattern of  $\text{NaYF}_4$  doped and undoped shows the hexagonal phase match with the  $\beta$ -phase of JCPDS file no.16-0334 [13], while quite a few puny scattered crests correspond to the cubic phase match with  $\alpha$ -phase of JCPDS file no. 01-77-2042 [14]. The XRD pattern of the doped and undoped  $\text{KYF}_4$  phosphors proves a close match between all diffraction peaks of the standard PDF card no. 79-1688, confirming that the synthesised  $\text{KYF}_4$  samples exhibit a hexagonal structure [15].

### 3.2 Photoluminescence Analysis:

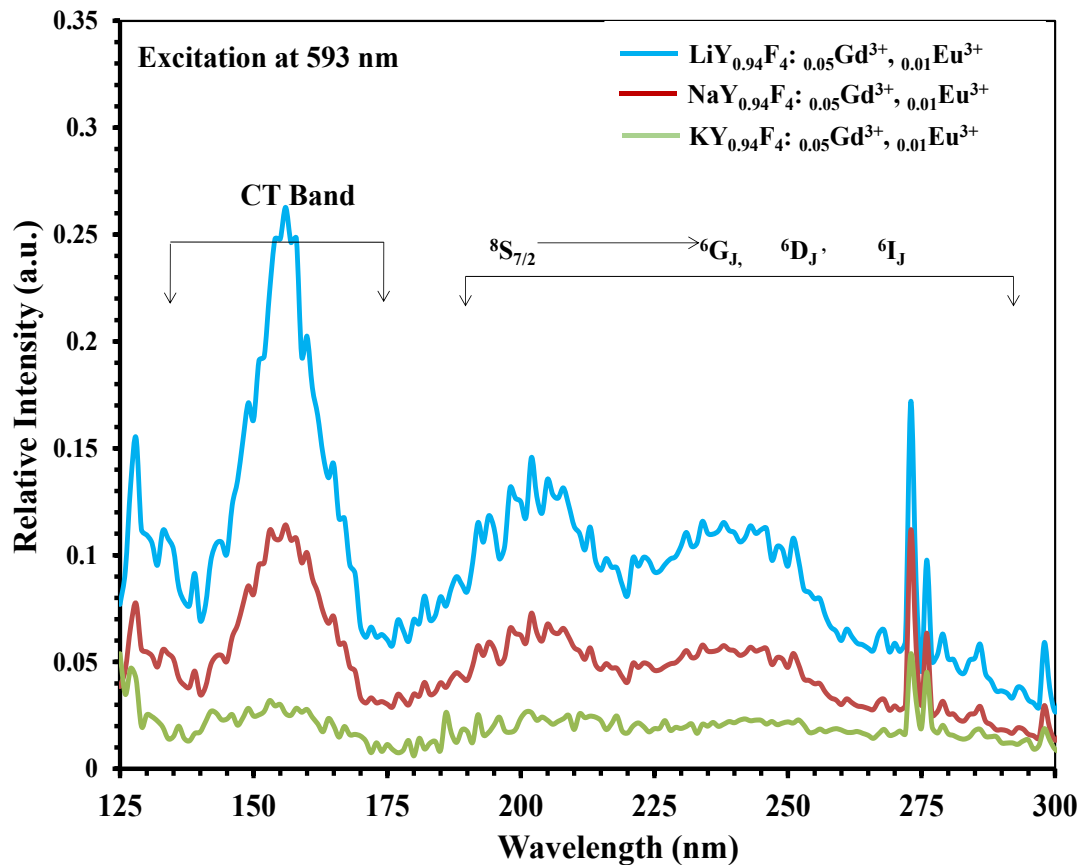
The concentration quenching of sensitizer  $\text{Gd}^{3+}$  in the  $\text{MYF}_4$  ( $M = \text{Li, Na, K}$ ) i.e.,  $\text{Li Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$ ,  $\text{Na Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$ , and  $\text{K Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$  ( $0.01 \leq x \leq 0.09$ ) host related was unbendable. The largest energy difference amongst the ground level  $^8\text{S}_{7/2}$  and the first excited level  $^6\text{P}_{7/2}$  was found in  $\text{Gd}^{3+}$  ion among trivalent RE ions. The luminescent intensity rises with an intensification in the concentration of  $\text{Gd}^{3+}$  ions lacking concentration quenching up to  $x = 0.05$  at 311 nm. The quenching starts when there is an adequate drop in the average distance among activators due to increase in its concentration in the host lattice to favour nonradiative energy transfer (ET). In this case concentration quenching starts when concentration of  $\text{Gd}^{3+}$  exceeds over 0.05. In the PL emission spectrum, we got a sharp peak at 311 nm is attributed to the  $^6\text{P}_{7/2}$  to  $^8\text{S}_{7/2}$  transitions of  $\text{Gd}^{3+}$  ions. Apart from that, a small peak at 306 nm is ascribed to the  $^6\text{P}_{5/2}$  to  $^8\text{S}_{7/2}$  transitions of  $\text{Gd}^{3+}$  ions [16]. From Fig.3 (a), 3 (b), and 3 (c) it can be encounter that at 0.05 moles of  $\text{Gd}^{3+}$  ions in the  $\text{MYF}_4$  host illustrate the bigger intensity peak at 311 nm under the excitation of 274 nm.



**Figure 3 (a), 3 (b), and 3 (c)** are emission spectra of  $\text{Li Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$ ,  $\text{Na Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$ , and  $\text{K Y}_{(1-x)}\text{F}_4: x\text{Gd}^{3+}$  ( $0.005 \leq x \leq 0.07$ ) shows maximum intensity peak (311 nm)

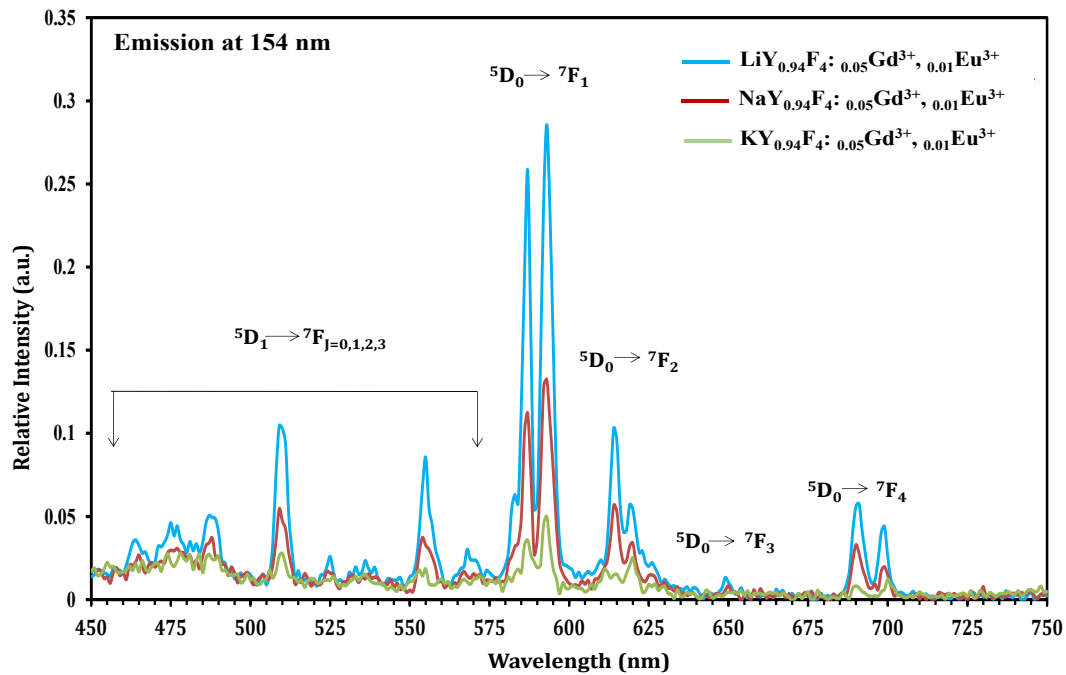
### 3.3 PL Excitation and Emission Spectra:

Excitation spectra of  $\text{MY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) phosphor monitor at 593 nm emission wavelength shown in fig. 4. The excitation lines peak maximum at about 154 is accredited to the charge transfer band [17] and peaks at 273, 236 and 201 nm might be attributed to the transitions  $^8\text{S}_{7/2} \rightarrow ^6\text{I}_j, ^6\text{D}_j$  and  $^6\text{G}_j$  of  $\text{Gd}^{3+}$  respectively. As we have seen in the excitation spectra, here we compare the intensity peaks at 154 nm of the CT band and the peak at 273 nm of  $^8\text{S}_{7/2} \rightarrow ^6\text{I}_j$  shift of  $\text{Gd}^{3+}$ . The excitation spectra show the intensity peaks at 154 nm are decreasing and the peaks at 273/274 nm are increasing while we replace Li, Na, K in the host lattice. The intensity of peak at 154 nm in  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  phosphor is optimum as compared to  $\text{NaY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  and  $\text{KY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  phosphor.



**Figure 4.** Excitation spectra of  $MY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  ( $M = Li, Na, K$ ) phosphor monitor at 593 nm.

The fig. 5 illustrates the spectra of PL emission of  $MY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  ( $M = Li, Na, K$ ) phosphors monitored in the series of 450 to 750 nm at 154 nm excitation wavelength. The PL emission lines of  $Eu^{3+}$  peak at about 593, 614, 649, 691, and 701 nm conforming to  ${}^5D_0 \rightarrow {}^7F_{J=1,2,3,4}$  transitions respectively, and the  ${}^5D_{J=0,1,2,3} \rightarrow {}^7F_J$  conversion peaks of  $Eu^{3+}$  are far punier than those of  ${}^5D_0 \rightarrow {}^7F_J$  transition are shown in the fig 5. The figure express that the intensities of emission spectra vary with the replacement of Li, Na, K in the crystal lattice. It was found to be optimum in the  $LiY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  phosphor. No additional change was detected in both the PL emission and excitation spectra excepting the intensity. The inorganic luminescent phosphors are normally exaggerated by the factors such as lattice faults, crystal filed, and charge disparity. Due to the point defects in the crystal, growths the non- radiative process resulting in the decrease of the PL emission intensity [18,19]. To improve the PL intensity of the phosphors, the alkaline metal ions such as Li, Na and K are combined in the phosphors. These alkali metal ions are univalent cations which interim as a charge compensator. From the emission intensity outline, it was noted that the PL intensity amplified ( $K^+ < Na^+ < Li^+$ ). It may occur due to the unalike ionic radii of Li, Na, and K. So that host lattice which may reason a consequence on luminescence intensity.



**Figure 5.** PL emission spectrum of MY<sub>0.94</sub>F<sub>4</sub>: 0.05Gd<sup>3+</sup>, 0.01Eu<sup>3+</sup> (M = Li, Na, K) phosphors monitored at 154 nm.

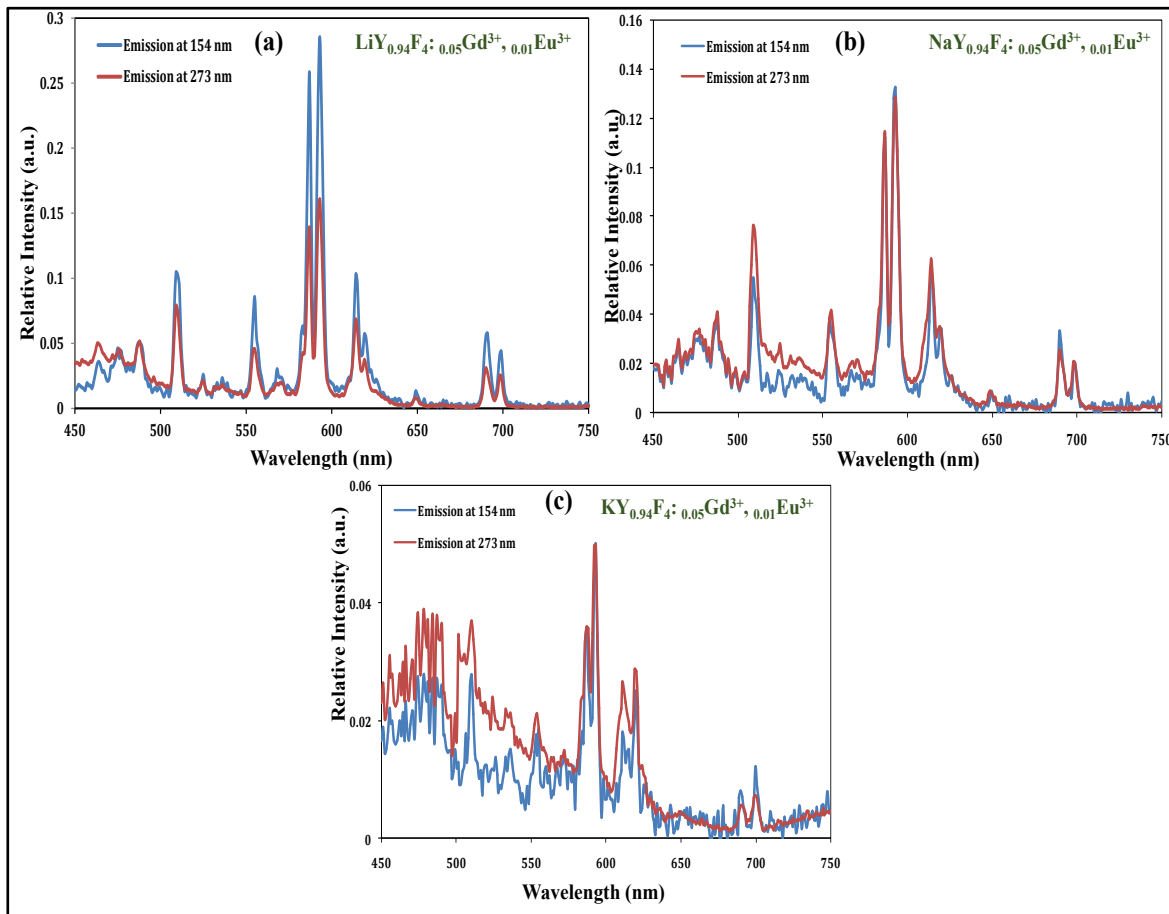
**4. Study of ET and QC Process**

Blend of Gd<sup>3+</sup>- Eu<sup>3+</sup> ion pairs in the host lattice plays an energetic role in delivering the luminescence QE of the phosphor greater than 100%. In the process of ET, the one high energy VUV photon absorb by the Gd<sup>3+</sup> ion in the host crystal, transmission of energy to two Eu<sup>3+</sup> ions leading to <sup>7</sup>F<sub>J</sub> to <sup>5</sup>D<sub>0</sub> shifts, and got two visible photons emissions via <sup>5</sup>D<sub>J</sub> to <sup>7</sup>F<sub>J</sub> transition of Eu<sup>3+</sup> ions. Fig. 7 represent Cross Relaxation Energy Transfer (CRET) process via energy level diagram of Eu<sup>3+</sup> and Gd<sup>3+</sup>. The figures 6(a), (b), and (c) represent PL emission spectra of LiY<sub>0.94</sub>F<sub>4</sub>: 0.05Gd<sup>3+</sup>, 0.01Eu<sup>3+</sup>, NaY<sub>0.94</sub>F<sub>4</sub>: 0.05Gd<sup>3+</sup>, 0.01Eu<sup>3+</sup>, and KY<sub>0.94</sub>F<sub>4</sub>: 0.05Gd<sup>3+</sup>, 0.01Eu<sup>3+</sup> in the wavelength of visible range observed at 154 and 274 nm excitation, to confirm an ET process and QC.

The 154 and 273 nm excitations of Gd<sup>3+</sup> corresponds to <sup>6</sup>G<sub>J</sub> and <sup>6</sup>I<sub>J</sub> states respectively. The QC is intolerable due to the excitation at <sup>6</sup>I<sub>J</sub> states. So, the emission corresponds to <sup>5</sup>D<sub>J</sub> to <sup>7</sup>F<sub>J</sub> transitions of Eu<sup>3+</sup> have a characteristic branching ratio between <sup>5</sup>D<sub>0</sub> and others <sup>5</sup>D<sub>J</sub> states. The QC can happen via two-step energy transfer at 154 nm excitation wavelength of <sup>6</sup>G<sub>J</sub> states. Its growths <sup>5</sup>D<sub>0</sub> emissions over the typical branching ratio between <sup>5</sup>D<sub>0</sub> and other <sup>5</sup>D<sub>J</sub> states. This circumstance is utilised to determine the luminescence QE of the phosphor using the equation (1) projected by Wegh [20-30] as follows:

$$\frac{P_{CR}}{P_{CR} + P_{DT}} = \frac{R(^5D_0 / ^5D_{1,2,3})_{^6G_J} - R(^5D_0 / ^5D_{1,2,3})_{^6I_J}}{R(^5D_0 / ^5D_{1,2,3})_{^6I_J} + 1} \dots\dots\dots (1)$$

Where, P<sub>CR</sub> = possibility for cross-relaxation, P<sub>DT</sub> = possibility for the direct energy transfer from Gd<sup>3+</sup> to Eu<sup>3+</sup>. R(<sup>5</sup>D<sub>0</sub>/<sup>5</sup>D<sub>1,2,3</sub>) is the proportion of the <sup>5</sup>D<sub>0</sub> and <sup>5</sup>D<sub>1,2,3</sub> emission integral intensities. The subscript <sup>6</sup>G<sub>J</sub> and <sup>6</sup>I<sub>J</sub> denotes the level of excitation for which the ratio is observed.



**Figure 6 (a), 6 (b), and 6 (c):** PL emission spectra of  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$ ,  $\text{NaY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$ , and  $\text{KY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  monitored at 154 and 273 nm

From the emission spectra of  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  shown in fig. 6 (a), the values of intensity ratio of  ${}^5\text{D}_0/{}^5\text{D}_{1,2,3}$  of  ${}^6\text{G}_J$  state and the ratio of  ${}^5\text{D}_0/{}^5\text{D}_{1,2,3}$  of  ${}^6\text{I}_J$  state are found to be 1.24 and 0.76 respectively. Therefore, the value CRET attained is 0.27. So, the inclusive QE of the phosphor comes out to be **127%**.

From the emission spectra of  $\text{NaY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  and  $\text{KY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$  shown in fig. 6 (b) and (c), we can say that the phenomenon of the quantum cutting process has not possible in these synthesized phosphors. The reason behind that is the emission strength at 273 nm excitation wavelength of  ${}^6\text{I}_J$  states is comparable to or greater than the emission strength at excitation wavelength 154 nm of  ${}^6\text{G}_J$  states. Hence QC is unbearable due to excitation at  ${}^6\text{I}_J$  states.



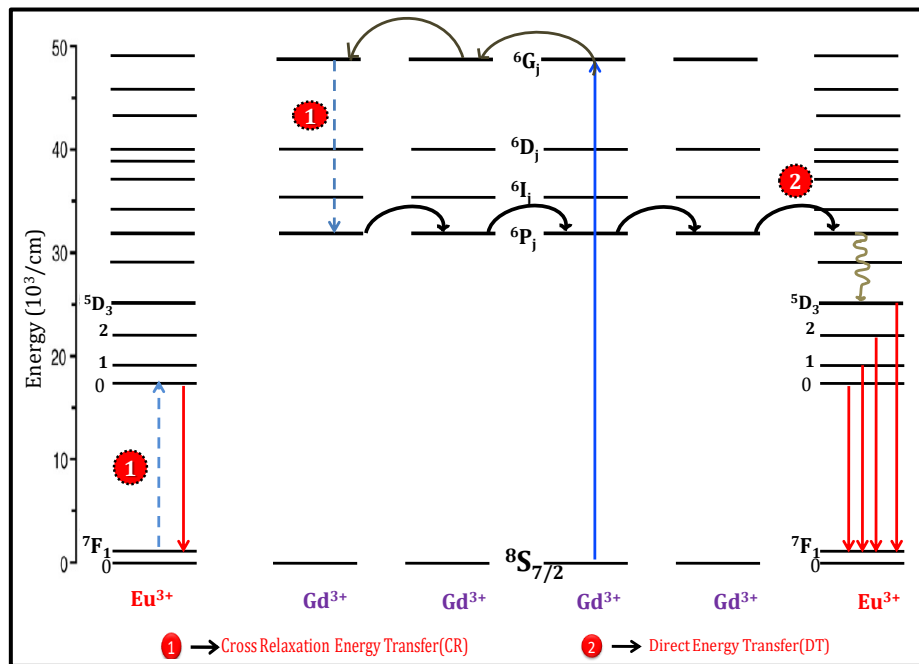


Figure 7. Energy states illustrations of  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  present the CRET process.

### 5. The SPD Spectrum and CIE Co-ordinates

The colour excellence of the phosphor will be generally measure by CIE chromaticity synchronize (X, Y). As per the PL emission spectra of  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$ , the chromaticity coordinates of the material are found to be (0.434 and 0.4041). The fig. 8 shows Spectral Power Distribution (SPD) input spectra of  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$ , tailored to the CIE 1931 chromaticity diagram.

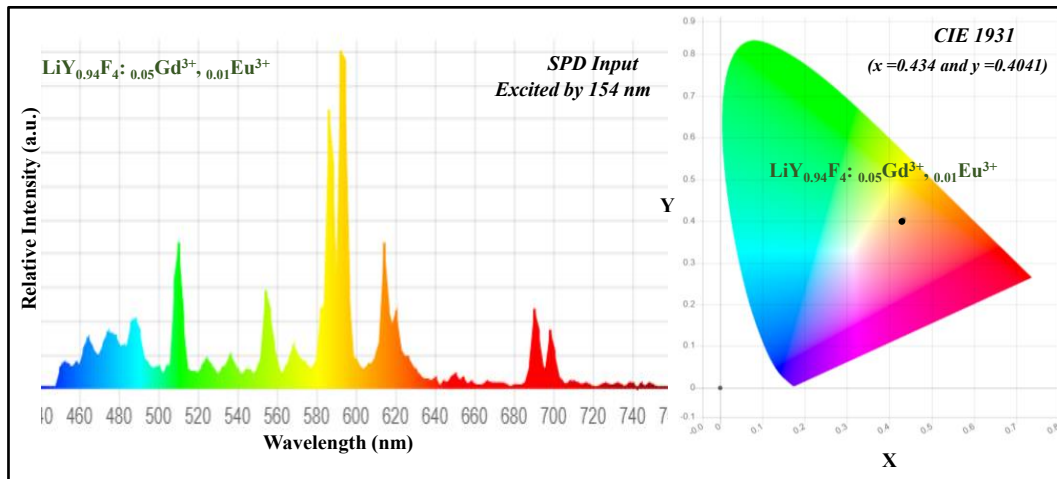


Figure 8. SPD input and CIE chromaticity coordinates of the phosphor  $\text{LiY}_{0.94}\text{F}_4: 0.05\text{Gd}^{3+}, 0.01\text{Eu}^{3+}$

### 6. Conclusions

The inorganic phosphor materials  $\text{MYF}_4:\text{Gd}^{3+}, \text{Eu}^{3+}$  (where M = Li, Na, K) doped with  $\text{Gd}^{3+}-\text{Eu}^{3+}$  ion pairs are successfully synthesized through a soft chemical route (wet chemical) and succeeding heating in reactive atmosphere. The  $\text{LiYF}_4$  doped and undoped XRD pattern shows a tetragonal structure and matches well with JCPDS file No. 77-0816. The XRD pattern of  $\text{NaYF}_4$  doped and undoped shows mixed phases of hexagonal and cubic that resembles with JCPDS file no. 16-0334 (called  $\beta$ -phase) and

JCPDS file no. 01-77-2042 (called  $\alpha$ -phase) respectively. From the emission spectra it is clear that, the PL intensity improved when the alkali metal ions are incorporated in the subsequent order  $K^+ < Na^+ < Li^+$  in the phosphors. The visible QC and ET through DC is observed only in  $LiY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  and the QE was intended to be around 127% under the excitation of 154 nm wavelength. No quantum cutting is observed in  $NaY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  and  $KY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  phosphor under the 154 nm excitation wavelength. Hence  $LiY_{0.94}F_4: 0.05Gd^{3+}, 0.01Eu^{3+}$  phosphor may be potential candidate for MFFL.

### Acknowledgments

The one of the authors is grateful to the scientist at Beijing Synchrotron Radiation Facility [BSRF], China for providing remote access to record the VUV PL and PLE spectrum using 4B8 window of synchrotron radiation.

### References:

- [1] Ronda C R 1995 *Journal of Alloys & Compounds* **225** 534.
- [2] Dexter D L 1957 *Physical Review* **108** 630.
- [3] Sommerdijk J L *et al* 1974 *Journal of Luminescence* **9** 288
- [4] Piper W W *et al* *Journal of Luminescence* **8** 344
- [5] Xiao S, Yang X and Ding J 2010 *Applied Physics B* **99** 769
- [6] Wegh R T, Donker H, Oskam K D and Meijerink A 1999 *Science* **283** 663
- [7] Wegh R T 1997 *Phys. Rev. B* **56** 13841
- [8] Wegh R T, Van Loef E and Meijerink A 2000 *Journal of Luminescence* **90** 111
- [9] Jaiswal S R, Nagpure P A, and Omanwar S K 2021 *Luminescence* **36** 1395
- [10] Belsare P D *et al* 2006 *Journal of Alloys & Compounds* **450** 468
- [11] Omanwar S K *et al* 2017 *St. Peterburg polytechnical university Journal: Physics and mathematics* **3** 218
- [12] Janani K *et al* 2018 *Optik* **169** 147
- [13] Sobolev B P, Mineev D A and V P Pashutin 1963 *Doklady Akademii Nauk SSSR* **150** 791.
- [14] Roy D M and Roy R 1964 *Journal of the Electrochemical Society* **111** 421
- [15] Zheng B *et al* 2021 *Results in Physics* **28** 104595
- [16] Sytsma J, Van Schaik W and Blasse G 1991 *J. Phys. Chem.* **52** 419
- [17] Sobolev B P, Mineev D A, and Pashutin 1963 *Doklady Akademii Nauk SSSR* **150** 791
- [18] Yan Y, Cao F B, Tian Y W, and Li L S 2011 *J. Lumin.* **131** 1140
- [19] Liu H *et al* 2011 *J. Lumin.* **131** 2422
- [20] Kodama N and Watanabe Y 2004 *Applied Physics Letters* **4141** 84
- [21] Kodama N and Oishi S 2005 *Journal of Applied Physics* **98** 3515
- [22] Hua R *et al* 2006 *Nanotechnology* **1642** 17
- [23] Zhou Y 2008 *Physical Review* **77** 075129
- [24] Karbowski M, Mech A and Romanowski W 2005 *Journal of Luminescence* **65** 114
- [25] Liu B *et al* 2003 *Journal of Luminescence* **101** 155
- [26] Jaiswal S R, Sawala N S, Nagpure P A, Bhatkar V B and Omanwar S K 2017 *J. Materials Sci: Materials in Electronics* **28** 2407
- [27] Jaiswal S R, Sawala N S, Koparkar K A, Bhatkar V B and Omanwar S K 2017 *Materials Discovery* **7** 15
- [28] Jaiswal S R, Sawala N S, Nagpure P A, Barde W S and Omanwar S K *Advanced Materials Research* **1171** 17
- [29] Jaiswal S R, Nagpure P A and Omanwar S K 2021 *Int." J. Sci. Res. Science & Technology* **8** 272
- [30] Jaiswal S R, Sawala N S, Nagpure P A and Omanwar S K 2022 *Journal of Emerging Technologies & Innovative Research* **9** 75