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Synthesis and VUV Spectral Properties of Red-Emitting $K_2Gd_{0.97}Zr(PO_4)_3$:3mol%Eu^{3+} Phosphor via Down-Conversion

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Abstract: $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} were prepared by the solid-state diffusion method and under a vacuum ultra-violet (VUV) region, photoluminescence properties of the phosphor were examined. The phenomenon of visible quantum harvesting via DC was observed in synthesized phosphor for the Gd^{3+}–Eu^{3+} pair. In the process of quantum harvesting, the two visible light photons are emitted per absorbed VUV photon. This phenomenon occurred upon the 190 nm excitation of Gd^{3+} at the ^6G_J level through a two-step energy transfer from Gd^{3+} to Eu^{3+} by cross-relaxation and sequential transfer of the remaining excitation energy. The consequences are that the quantum efficiency of the $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor in the energy transfer process from Gd^{3+} to Eu^{3+} could reach 233%. The quantum efficiency goes to more than 200% (i.e., 233%) at just low concentration Eu^{3+} ions (i.e. 3% only). This novelty was found in the prepared phosphor. Therefore, the phosphor $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} was a potential quantum harvester and potential candidate for mercury free fluorescent lamp and plasma display panel.

1. Introduction

Light is essential for humanoid strength and well-being. As we spend more time indoors, we are progressively exposed to artificial light. The development of artificial lighting has allowed us to control the brightness, colour, and timing of our light exposure [1]. Over recent years, a technological revolution has taken place in which conventional lighting has been replaced by light emitting diodes (LEDs). Some studies have shown the possibility that blue light from these artificial sources could have deleterious effects on the retina [2]. We have the alternative called mercury free fluorescent light (MFFL). Recently, for the development of mercury-free fluorescent lightning technology, new quantum harvesting phosphors are mandatory for the study of highly efficient luminescent materials under VUV excitation [3]. Visible quantum harvesting via down-conversion has been reported in many fluoride-based phosphors such as GdF_3, $LiGdF_4$, $LiGdF_4$, etc. doped with the rare earth ($Gd^{3+}$and Eu^{3+}/ Tb^{3+}) with great quantum efficiency [4-12]. These researches show that Gd^{3+} – Eu^{3+} ions pair is ideal that can implement quantum cutting. However, fluoride compounds were found to be unstable. Therefore, the oxide-based phosphors that had a wide range of absorption in the VUV region were more easily applied than the fluoride system [13].

Therefore, present research interests have been concentrating on the oxide-based phosphors such as $GdPO_4$, $GdBO_3$, and Gd_2O_3 doped with rare-earth ions (Eu^{3+}/Tb^{3+}) to implement quantum cutting in more applied [13-15].

The impact of the intensity and position of the Eu^{3+}–O^{2-} charge transfer (CT) band is prejudiced by the oxygen coordination number of Eu^{3+} on the efficiency of quantum harvesting reported [13]. Also reported that with an increase in oxygen coordination number, the energy of the CT band decreases therefore it is beneficial to the occurrence of quantum cutting. In short, we said that $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor is a promising host for quantum harvesting.

In the current work, the solid-state diffusion method successfully synthesized $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+}. The photoluminescence (PL) characteristics under VUV excitations and quantum harvesting process between the Gd^{3+} to Eu^{3+} pair were studied.

2. Experimental

In this method, starting materials were first measure with the Mettler Toledo AB 204 balance and taken in an appropriate stoichiometric ratio and mixed in the china basin with the help of double-distilled water (DDW) to obtain a clear solution. This mixture was heated on a hot plate at 70-100°C for 30-60 minutes. Then, the sample was kept in a muffle furnace (Ceramic Muffle (h × w × d): 14 cm × 14 cm × 25 cm and Max. Temp. 1200 °C) with the cycle of heating and intermediate grinding; finally, the sample was quenched at room temperature. The samples are ready to analysis. The X-ray diffraction analysis was carried out on Rigaku Miniflex II X-ray Diffractometer. The general flow chart of the SSD method is shown in Fig. 1

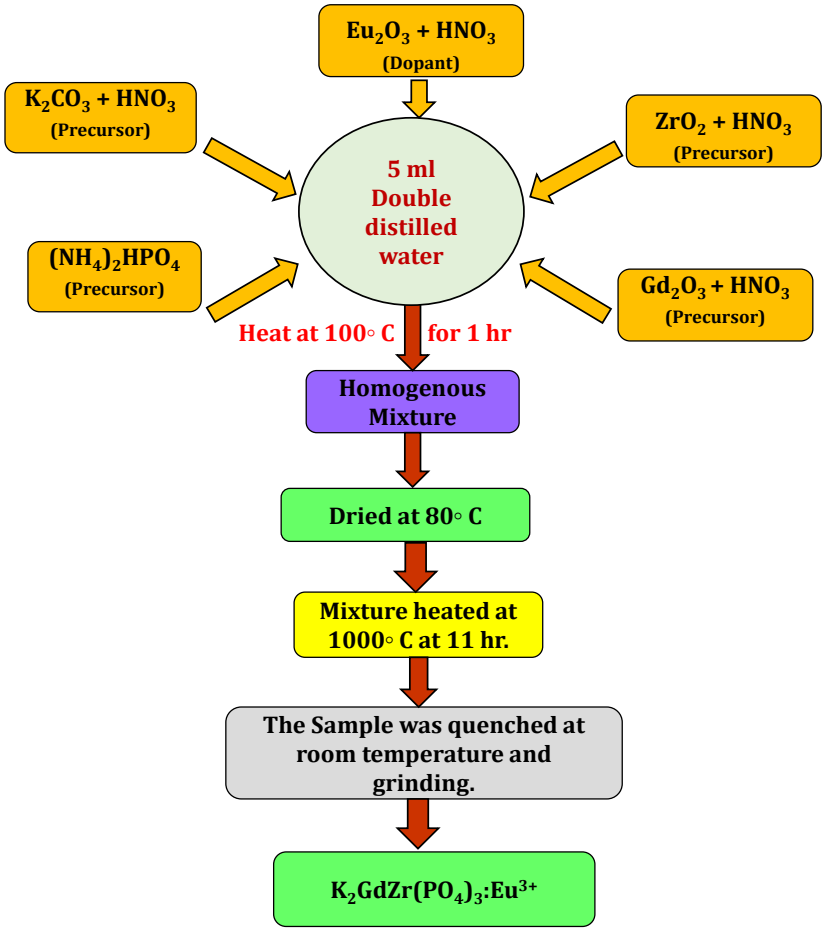

Figure 1. Flow chart of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} synthesized by the solid-state diffusion method.

3. Results and Discussion

3.1 XRD characterization

The XRD patterns of the host material and with doped are shown in Fig. 2 The samples are indexed to the phase of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} (JCPDS No. 49-0634) with the space group $P2_13$ and there are negligible minuscule extra peaks corresponding to any other phases. From the XRD pattern, the high intensity peaks were observed at 15.26, 19.54, 27.70, 32.84 and 45.16 which are corresponding to Miller indices (1 1 1), (1 2 0), (1 3 0), (3 2 1) and (4 2 1) respectively.

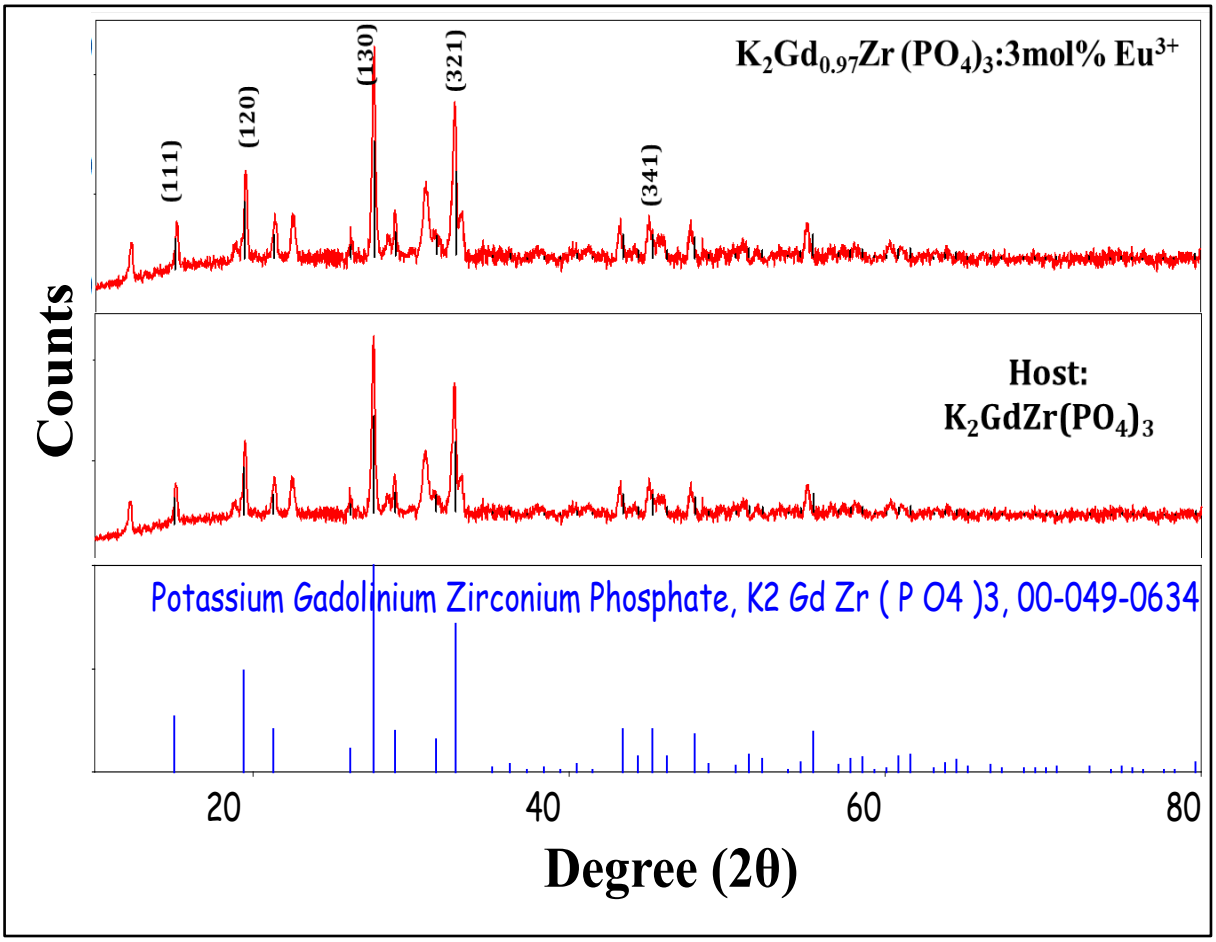

Figure 2. XRD pattern of the host material and $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} synthesized by the solid-state diffusion method.

3.2 VUV PL properties

The VUV absorption spectrum for monitoring the $^5D_0 \rightarrow {}^7F_1$ (593 nm) and $^5D_0 \rightarrow {}^7F_2$ (610 nm) transitions of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} is shown in Fig. 3. Both the peaks were found to be same in nature but different in intensities.

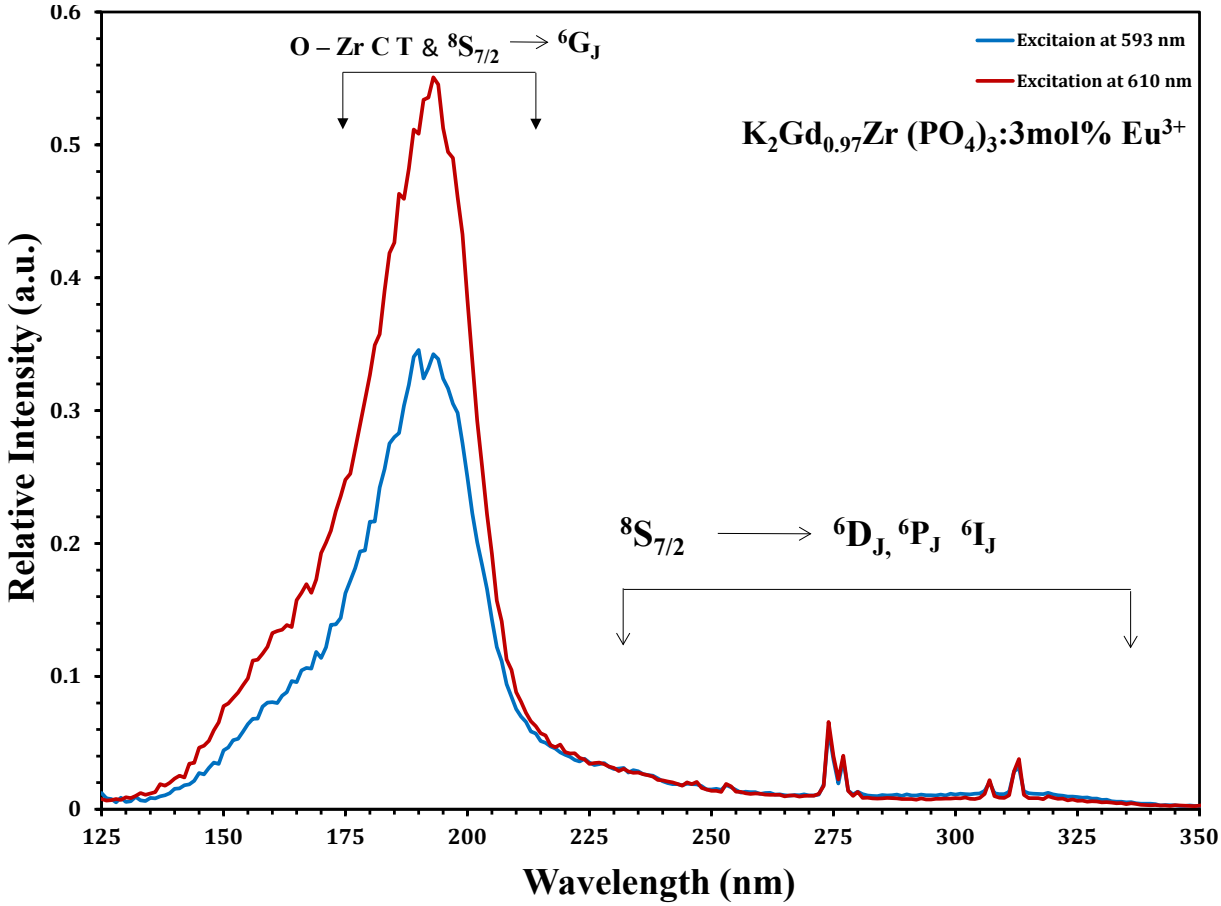

Figure 3. Excitation spectra of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} were monitored at of 593 and 610 nm.

The broadband excitation peaks from 134 nm to 240 nm with the extreme at around 190 nm can be attributed to the mixing of the host lattice absorption i.e., O–Zr CT band [17] and the $^8S_{7/2} \rightarrow {}^6G_J$ transition of Gd^{3+} were observed. In addition, three-week intensities excitation peaks corresponded to the transitions $^8S_{7/2} \rightarrow {}^6D_J$ (254 nm), $^8S_{7/2} \rightarrow {}^6I_J$ (274, 277 nm), and $^8S_{7/2} \rightarrow {}^6P_J$ (307, 313 nm) of Gd^{3+} were also observed. At the 190 nm wavelength, the intensity peak was found to be very high as compared to the 274 nm, which is very effective and beneficial to energy transfer and quantum harvesting occurring between the Gd^{3+} and Eu^{3+} in $K_2GdZr(PO_4)_3$ Phosphor.

Fig. 4 depicts the PLE spectra of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} in the range of 400-750 nm monitored by 190 and 274 nm respectively for the study of quantum efficiency and energy transfer process. In the emission spectra monitored at 190 nm, the emission lines of Eu^{3+} peaked at about 593, 610, 653, and 704 nm corresponding to $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) transitions respectively, and the ^5D_J (J=0, 1, 2, 3) $\rightarrow {}^7F_J$ transition peaks of Eu^{3+} are much weaker than those of $^5D_0 \rightarrow {}^7F_J$ transition. But in emission spectra monitored at 274 nm, the intensities of $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 3, 4) transitions are comparable with the ^5D_J (J=0, 1, 2, 3) $\rightarrow {}^7F_J$ transition of Eu^{3+} peaks. Therefore, the energy transfer from Gd^{3+} to Eu^{3+} in synthesized phosphor is very effective. This also suggests that quantum harvesting has happened in $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} system.

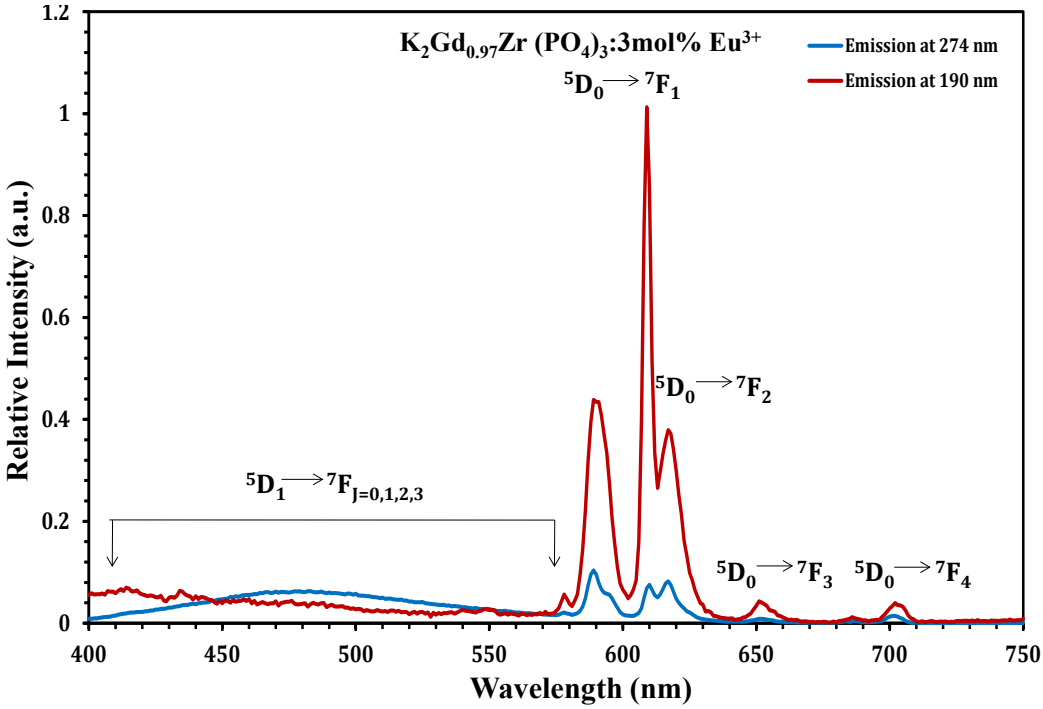

Figure 4. PL emission spectra under the excited at 274 and 190 nm of the of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor.

Fig. 5 shows the emission spectra of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor in the range of 400-750 nm monitored by 147 and 172 nm respectively.

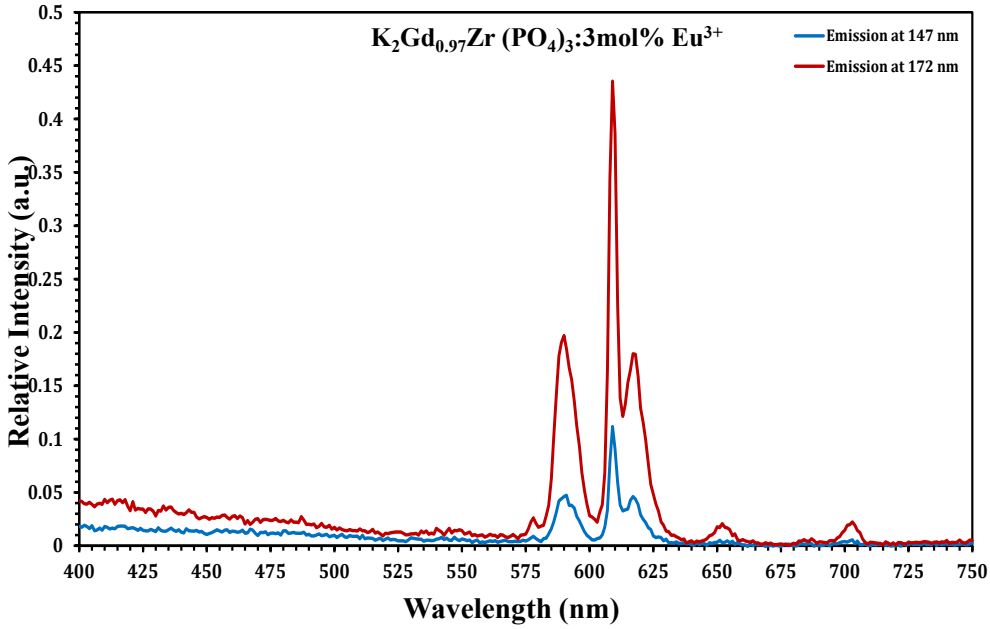

Figure 5. PL emission spectra under the excited at 147 and 172 nm of the of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor.

Now evaluate the existence of the quantum harvesting process by comparing the emission spectra for excitation at the ^6G_J levels of Gd^{3+} (190 nm) and the ^6I_J levels of Gd^{3+} (274 nm). As per the previous survey, we can use the equation (1) proposed by Wegh [1, 2, 4, 5, 7, 8] to determine the quantum efficiency of the cross-relaxation in Gd^{3+}– Eu^{3+} systems as follow:

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

Where PCR is the probability for cross-relaxation, PDT is the probability for the direct transfer from Gd^{3+} to Eu^{3+}. R ($^5D_0/^5D_{1,2,3}$) is the $^5D_0$ and $^5D_{1,2,3}$ emission integral intensities ratio. The subscript (^6G_J or ^6I_J) represents the excitation level for which the ratio is observed. From the emission spectra, the value of R ($^5D_0/^5D_{1,2,3}$) ^6G_J and R ($^5D_0/^5D_{1,2,3}$) ^6I_J can be calculated at 2.185 and 0.365, respectively. Therefore, the value of $P_{CR}/P_{CR} + P_{DT}$ is 1.33. It means that 133% Gd3+ ions in the 6GJ excited state settle down through a two-step energy transfer emitting two visible photons in this method. So, a quantum cutting efficiency of 233% can be obtained. Therefore, the visible quantum harvesting process in the Gd^{3+}–Eu^{3+} couple of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} effectively occurred, and the synthesized material would be a promising material for mercury-free fluorescent lighting [18-23].

3.3 SPD Spectra and CIE Color Coordinates

The color quality of the prepared phosphor will be mostly measured by the CIE chromaticity coordinate (x, y). According to the emission spectrum of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol%Eu^{3+} at 190 nm, the chromaticity coordinates of this sample are found to be (0.5061 and 0.3221). The SPD input spectra of $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} fitted to the CIE 1931 chromaticity diagram are shown in Fig 6.

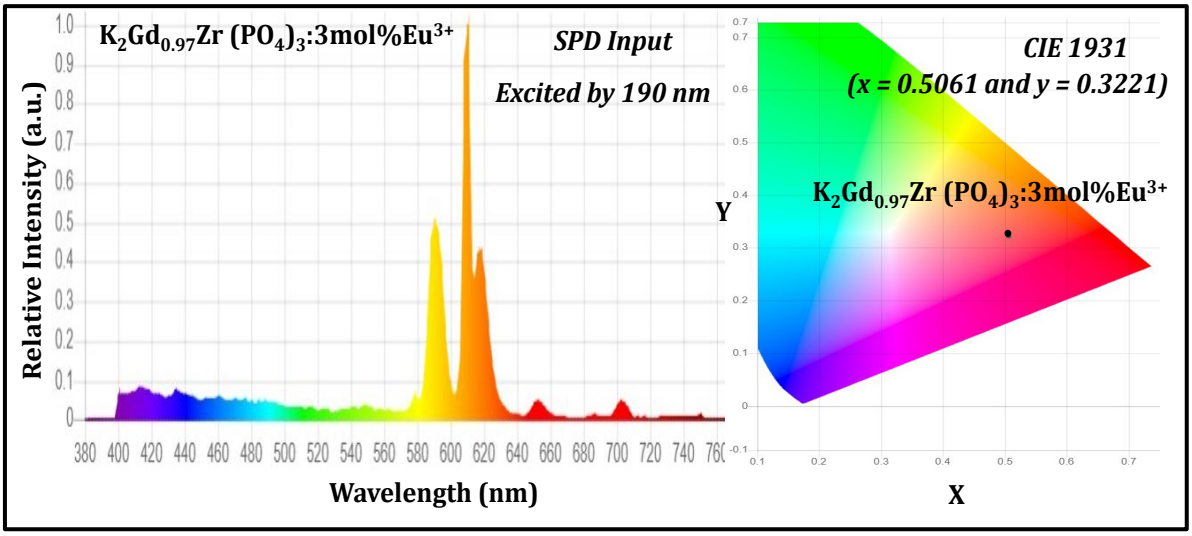

Figure 6. CIE 1931 XY Coordinates from Spectral Power Distribution (SPD) under the excitation of 190 nm wavelength.

4. Conclusion

Visible quantum harvesting via DC was detected for the Gd^{3+}–Eu^{3+} ions pair in Eu^{3+} doped $K_2GdZr(PO_4)_3$Phosphor. The investigation of their PL properties in the VUV range showed that the energy transfers from Gd^{3+} to Eu^{3+} are very effective. The quantum efficiency of the $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} phosphor in the energy transfer process from Gd^{3+} to Eu^{3+} could reach 233%. The quantum efficiency goes to more than 200% (i.e., 233%) at just low concentration Eu^{3+} ions (i.e., 3% only). The chromaticity coordinates of this sample are found to be (0.5061 and 0.3221). The phosphor emits yellowish red radiation. This novelty was found in the prepared phosphor. Therefore, the phosphor $K_2Gd_{0.97}Zr(PO_4)_3$:3mol% Eu^{3+} has a potential quantum harvester and Mercury free fluorescent lamps.

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