



VUV Photoluminescence properties of quantum harvester $\text{GdPO}_4:\text{Tb}^{3+}$

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Abstract

The luminescence phosphor $\text{GdPO}_4:\text{Tb}^{3+}$ with a single-phase monoclinic crystal structure has been successfully synthesized via the co-precipitation method by varying molar concentration of Tb^{3+} ions. Gadolinium phosphate singly doped terbium compound was first time reported with the co-precipitation method. This paper explores the photoluminescence properties of $\text{Gd}_{(1-x)}\text{PO}_4: x\% \text{Tb}^{3+}$ under VUV excitation. The energy transfer process between host matrix (GdPO_4) and dopant (Tb^{3+}) was investigated successfully. The extreme quantum efficiencies were found to be 168 and 163 %, under the VUV excitation of 205 and 155 nm respectively. The emission of green color ($\lambda = 543$ nm) was observed under the excitation of 147 and 172 nm. Therefore, this compound may be a potential candidate for mercury-free fluorescent lighting (MFFL) application.

Keywords: Quantum Cutting (QC), Vacuum Ultraviolet (VUV), Quantum Efficiency (QE), Mercury Free Fluorescent Lamps (MFFL).

1. INTRODUCTION

In the lamp phosphors industries, research has been enthused due to the need for new luminescent material suitable for mercury (Hg) free fluorescent lamps (MFFL). In Hg free fluorescent lamp, phosphor powder is excited by VUV photons (140-190 nm), which are usually generated from the Xe resonance emission line (147 nm) or by the Xe_2 molecular emission band (172 nm) and get a visible photon. The greater energy of the VUV photons intrinsically confines the energy efficiency of a phosphor if only one visible photon is generated per VUV photon in the discharge. If compare between Hg discharge & Xe discharge, it has been observed that more energy losses in Xe discharge. Therefore, new phosphors with quantum efficiency greater than 100% are mandatory for this purpose. The host materials must possess a large bandgap so that materials are capable to absorb high-energy photons ($\lambda < 200$ nm). It is one of the necessary conditions for attaining QE of more than 100 % by QC [1, 2].

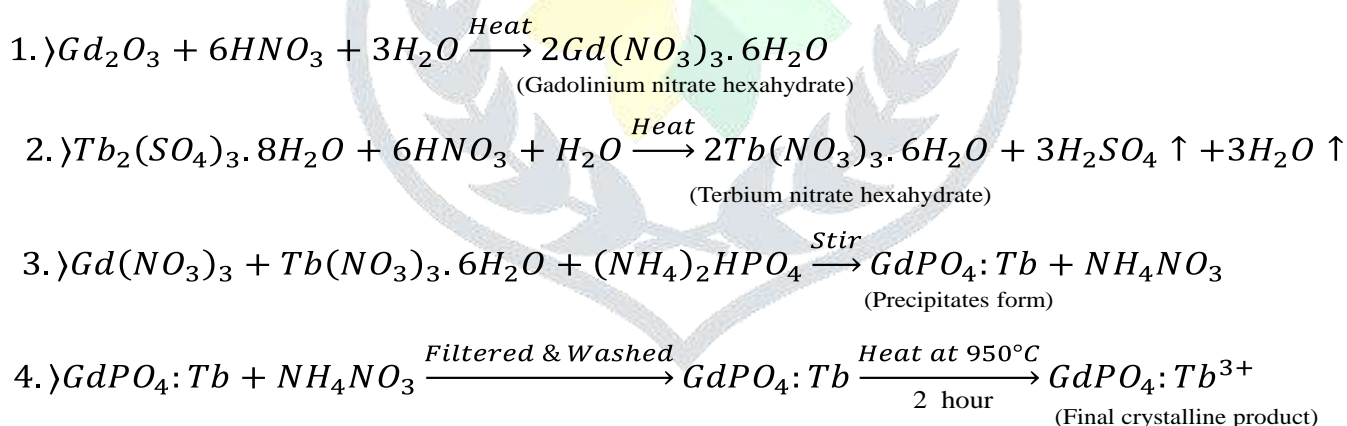
QC is a process that happens in materials that emit two or more photons per photon absorbed [3]. Theoretically, it is possible because a VUV photon has two times larger the energy of a visible photon. The quantum cutting phenomenon can be understood via photon cascade emission and cross-relaxation energy transfer (CRET); the process involved in CRET is also known as down-conversion [4-6].

Many researchers have discussed the energy transfer process between Gd^{3+} and Tb^{3+} ions in different host materials [1,2,10,14] and concluded that Gd^{3+} (acts as a sensitizer) transferred the excitation energy from its 6P_J level to a neighboring Tb^{3+} (acts as an activator) in the host materials. However, there is petite deliberation about the quantum cutting process between Tb^{3+} to Tb^{3+} in the host materials

Inspired by the above reviews, here we proposed to study the visible QC process via down-conversion (CRET) under the VUV excitation in $GdPO_4:Tb^{3+}$ phosphor. In this work, phosphor was synthesized via the co-precipitation method, which had been first-time used by varying the Tb^{3+} concentration. The method is more efficient, low cost, low temperature, does not require any other agent for initiation of the process of synthesis, and necessarily requires soluble precursors. However, the main significance of the method is magnificent luminescent intensity even at a low concentration of activator with a good quantum efficiency (QE) in $GdPO_4:Tb^{3+}$ phosphor, which is the main achievement of the present work. The vacuum ultraviolet (VUV) excitation and emission spectrum are deliberate via remote access to the 4B8 VUV spectroscopy beamline of BSRF, the Institute of High Energy Physics in Beijing, China.

2. EXPERIMENTAL

The Gadolinium Phosphate [$Gd_{(1-x)}PO_4: x\%Tb^{3+}$ ($0.5\% \leq x \leq 7.0\%$)] were synthesised by co-precipitation method. In the synthesis, analytical grade Oxide (Gd_2O_3) was used as a precursor. The mixture of stoichiometric amounts of nitrates of Gadolinium and Terbium was obtained by dissolving the respective oxide and sulfate (AR grade) in the least amount of HNO_3 . A small amount of double-distilled (DD) water adds to the mixture. The mixture was heated gradually at $80^\circ C$ until the whole paste dissolved. To boil off excess acid, the solution was further heated for a few minutes. A small amount of DD water was added again to the solution. The resulting solution was considered as a $Gd(NO_3)_3:Tb$. The homogeneous solution of $(NH_4)HPO_4$ (A. R.) was taken in the burette and then added to the resulting solution drop-by-drop to get precipitates. The precipitate was filtered and then washed multiple times to remove the excess acid and impurities & then dried under an IR lamp. The dried powder was finally crushed and heated at $950^\circ C$ for 2 hours in the crucible to obtain a white crystalline powder of $GdPO_4:Tb^{3+}$ [2]. The complete process shows in the reaction and is also represented in a flow chart in Fig. 1.



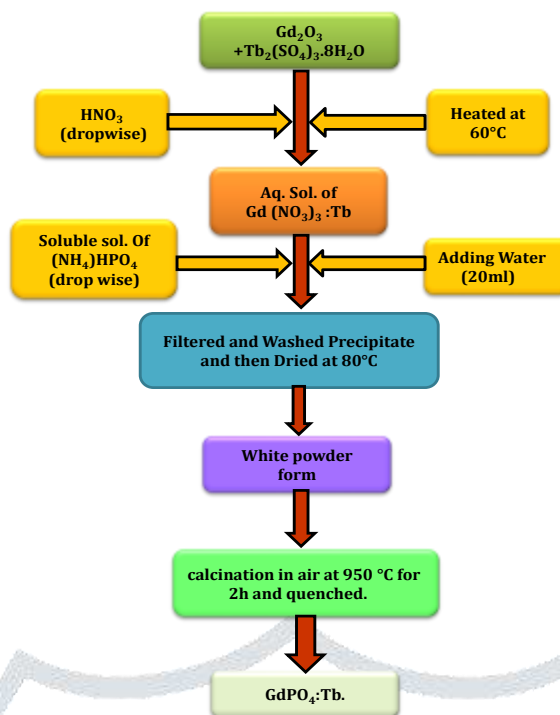


Fig. 1. Flow chart of $\text{GdPO}_4:\text{Tb}^{3+}$ phosphor synthesis by co-precipitation.

The phase purity of the phosphors was checked by powder XRD technique using a Rigaku mini flex II. The vacuum ultraviolet (VUV) excitation and emission spectrum are deliberate via remote access to the 4B8 VUV spectroscopy beamline of BSRF, the Institute of High Energy Physics in Beijing, China. Complete experiments were executed at room temperature.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The resulting crystalline powder of un-doped and doped GdPO_4 was checked by powder XRD technique as shown in Fig.2. The XRD pattern of both is consistent with the corresponding JCPDS file with card no. 84-0920 [7]. From the XRD pattern, it is confirmed that the GdPO_4 host matrix has a monoclinic structure and the higher intensity peaks were observed at 22.11, 27.94, 29.99, 30.06, 42.68, and 49.66 which are corresponding to diffracting planes (expressed by Miller indices) (1 1 1), (2 0 0), (1 2 0), (012), (311), and (3 2 0) respectively.

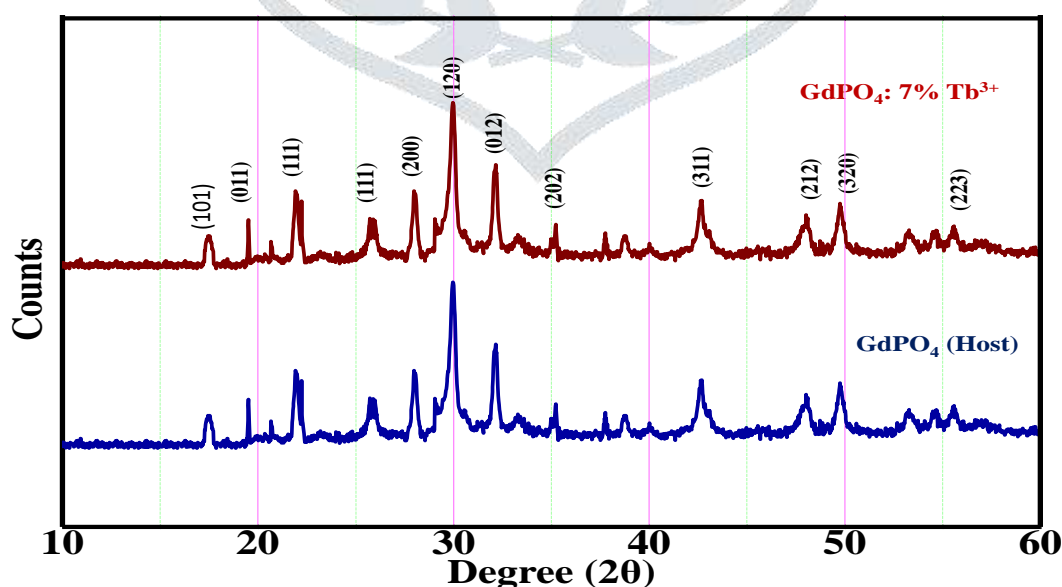


Fig. 2. XRD pattern of un-doped and doped GdPO_4 phosphor

3.2 VUV photoluminescence properties and quantum cutting

The Fig.3 shows VUV excitation spectra of $\text{Gd}_{(1-x)}\text{PO}_4: x\% \text{Tb}^{3+}$ ($0.5\% \leq x \leq 7.0\%$). The entire excitation spectra consist of several bands and have comparable but their intensities are different. These

excitation spectra were obtained by monitoring the ${}^5D_4 \rightarrow {}^7F_5$ emission (543 nm) line of the Tb^{3+} ion. The band in the region from 130 to 165 nm with a peak value of 155 nm is due to the host absorption, which may be connected to the intramolecular transition of the PO_4^{3-} group [8]. The spectral range from 170 to 225 nm (second broadband) is allocated to the intra configuration $4f^8-4f^7 5d^1$ transition of Tb^{3+} [8-10]. Some of the sharp and weak bands near 275 nm are attributed to the ${}^8S_{7/2} \rightarrow {}^6I_1$ transition of Gd^{3+} . When one electron of Tb^{3+} is stimulated from the ground states $4f^8$ to the $4f^7 5d^1$ excited state, it can harvest two types of $4f^8 - 4f^7 5d^1$ transitions: spin-allowed (more energetic) and spin-forbidden transitions [10].

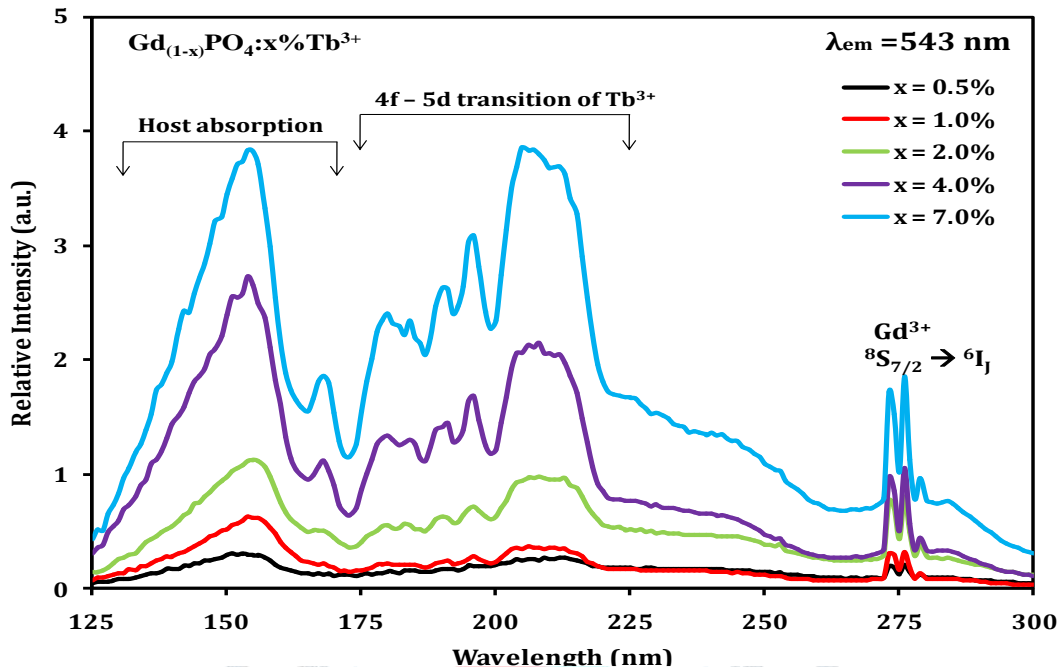


Fig. 3. VUV excitation spectra of $Gd_{(1-x)}PO_4:x\%Tb^{3+}$ ($0.5\% \leq x \leq 7.0\%$) monitored by the emission of Tb^{3+} at 543 nm.

The emission spectra of $Gd_{(1-x)}PO_4:x\%Tb^{3+}$ ($0.5\% \leq x \leq 7.0\%$) were measured at 147, 172 and 155, 205, 273 nm as shown in Figs. 4 a, b and 5a-d respectively. The higher intensity overlay emission spectra (monitored at $\lambda = 273, 205,$ and 155 nm) of the phosphor at $x = 7\%$ Tb^{3+} concentration which was used for the determination of the area under the curve for the investigation of the quantum cutting process as shown in Fig. 5d.

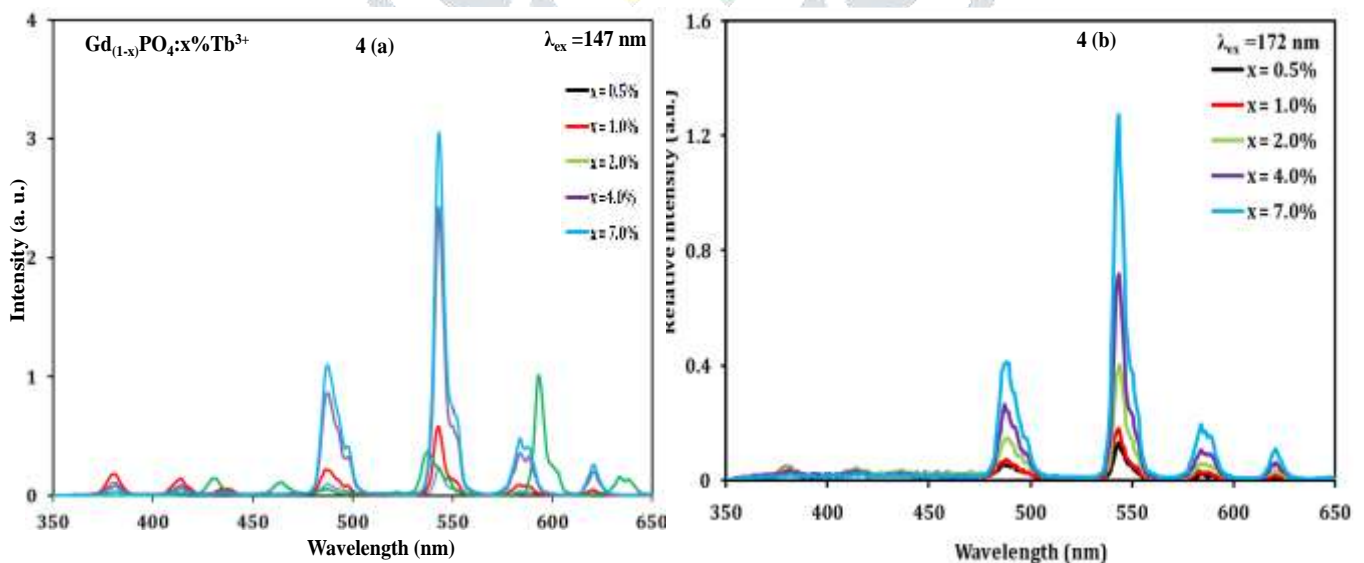


Fig. 4 Emission spectra of $Gd_{(1-x)}PO_4:x\%Tb^{3+}$ ($0.5\% \leq x \leq 7.0\%$) excited at (a) 147 nm and (b) 172 nm

The emissions could be attributed to 5D_3 to 7F_J ($J = 2, 3, 4, 5, 6$) and 5D_4 to 7F_J ($J = 3, 4, 5, 6$) transitions of Tb^{3+} ions among which the transition 5D_4 to 7F_5 is most significant to green emission at 543 nm. Due to the cross-relaxation between the 5D_3 to 5D_4 transition and 7F_6 to 7F_0 transition of Tb^{3+} , the 5D_4 emission of Tb^{3+} amplified while the 5D_3 emission de amplified with an increase in the Tb^{3+} content [11–13]. The 5D_4 emission of Tb^{3+} increased quickly with an increase in the concentration of Tb^{3+} . This is due to many factors in concern

with the cross-relaxation among the 5D_3 and 5D_4 levels since luminescence centers increase with the attentiveness of Tb^{3+} ions in the host lattice.

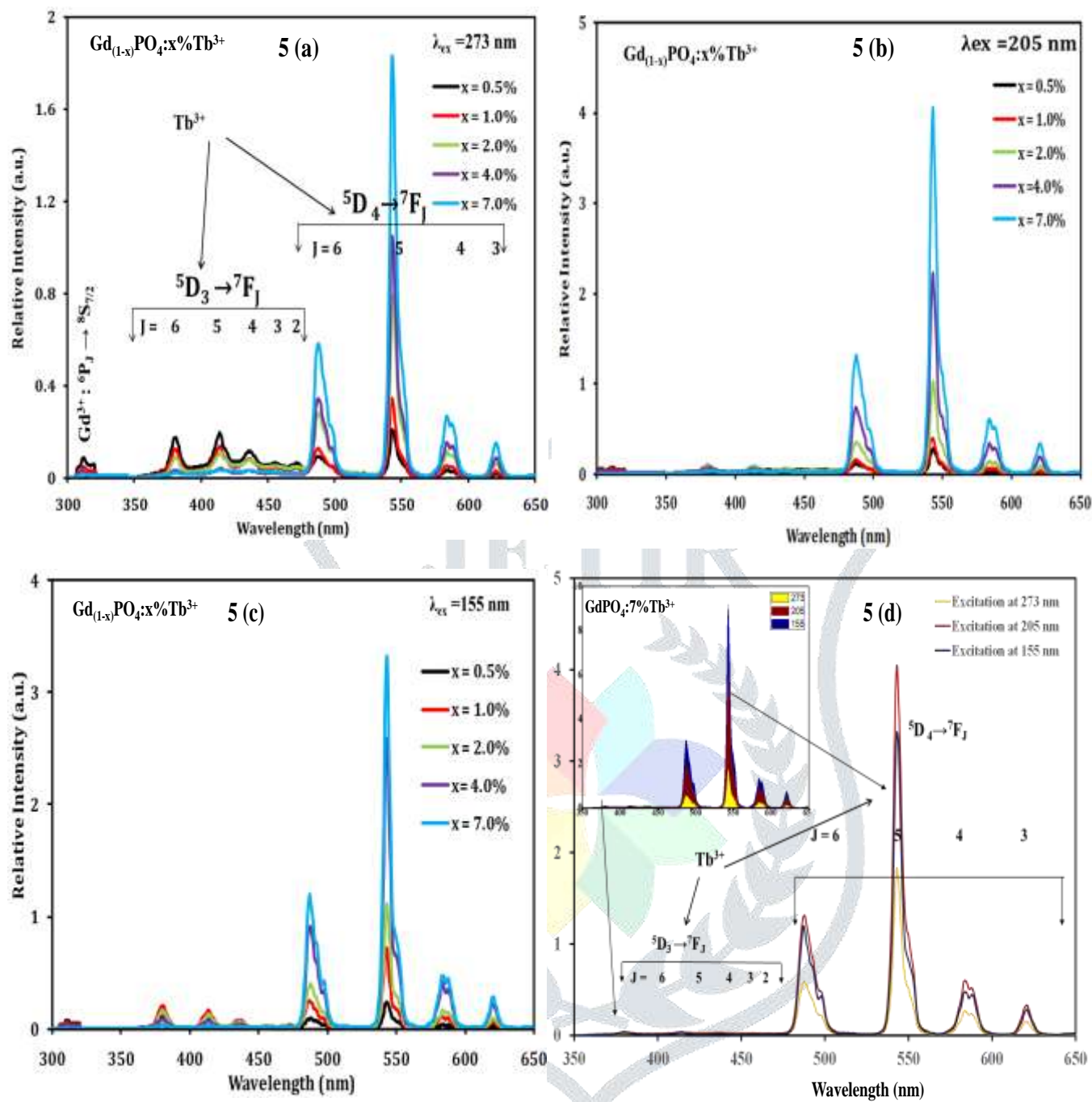


Fig. 5. Photoluminescence emission spectra $Gd_{(1-x)}PO_4:x\%Tb^{3+}$ ($0.5\% \leq x \leq 7.0\%$) excited at (a) 273nm, (b) 205nm & (c) 155 nm. The Fig. 5 (d) shows comparative spectra of $GdPO_4:7\%Tb^{3+}$ phosphor.

Investigate the phenomenon of quantum cutting in $GdPO_4:7\%Tb^{3+}$ phosphor by comparing the emission spectra excited at the 6I_1 level of Gd^{3+} (273nm) with that excited at the other two wavelengths (205 and 155 nm) as already shown in Fig. 5d. The combination of Gd and Tb ions plays a vital role in bringing luminescence quantum efficiency of the phosphor beyond 100%. We find that the percentage of emission from 5D_4 is higher than that excited by 273 nm radiation, representing that quantum cutting occurs in $GdPO_4: 7\%Tb^{3+}$. No quantum cutting occurs in $GdPO_4:Tb^{3+}$ with excitation of the 6I_1 level of Gd^{3+} (273nm). When Tb^{3+} ions are excited to their $^4F_7-^5d_1$ states, the quantum cutting can be explained by a two-step route: cross-relaxation (CR) energy transfer (step-1) and directed energy transfer (DT) (step-2) illustrate in Fig. 6. We have already discussed regarding quantum cutting with $Tb^{3+} - Tb^{3+}$ and $Gd^{3+} - Tb^{3+}$ pairs in our literature [1, 2, and 14]. Many researchers have also explained very well regarding the cross-relaxation energy transfer and direct energy transfer process in Gd to Tb & Tb to Tb pairs in their literature [5-8].

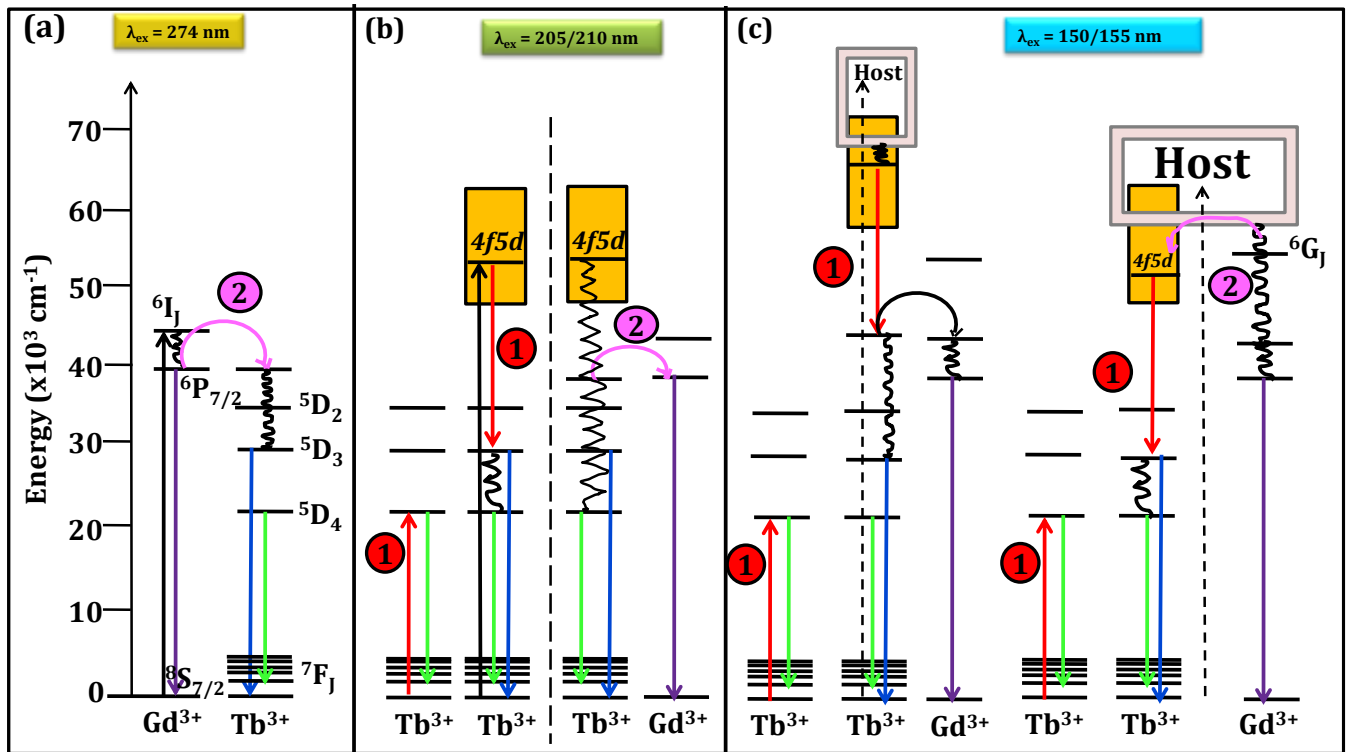


Fig. 6. Energy level diagrams of Gd³⁺ and Tb³⁺ show cross relaxations energy transfer process [2]

If the quantum efficiency of the phosphor via DET (step-2) is considered to be 100%, the calculated CR efficiency (step-1) by using equation (eq.-2) proposed in the literature [3, 15-17] for GdPO₄:7%Tb³⁺ phosphor was found to be more than 100%. Equations as follow were used for calculating the CR efficiency (η).

$$\eta_{QC} = \eta + \eta_{DT} \quad \text{----- (1)}$$

$$\eta = \frac{P_1}{P_1 + P_2} = \frac{R_2 - R_1}{R_2 + 1} \quad \text{----- (2)}$$

Here P1 and P2 are the probabilities of energy transfer from Gd³⁺ to Tb³⁺ through cross-relaxation and the direct transfer respectively.

Here $R_1 = ({}^5D_4 / \text{rest})_{Gd^{3+}}$

(⁵D₄/rest) is the ratio of PL intensity of ⁵D₄ to that attributed to ⁵D₃ of Tb³⁺ and ⁶P_{7/2} of Gd³⁺ where the subscript designates the excitation is from Tb³⁺ or Gd³⁺.

The CR efficiency were found to be very small for low concentration of Tb³⁺ (x = 0.5%, 1%, 2% and 4%) and it is increases with increasing Tb³⁺ concentration in the host matrix. The maximum calculated value of cross-relaxation efficiency from eq.-2 for GdPO₄:7%Tb³⁺ excited at 205 and 155 nm were found to be 0.68 and 0.63 respectively. Therefore, the resulting quantum efficiency value was calculated as 168% and 163% at the excitation of 205 and 155 nm, respectively. Here should be noted that the incident VUV photon absorption efficiency has been taken into consideration also some non-radiative losses at defects and impurities are disregarded.

4. CONCLUSION

The inorganic material Gd_(1-x)PO₄: x %Tb³⁺ (0.5 % ≤ x ≤ 7.0 %) successfully prepared via co-precipitation method. The XRD pattern confirmed the monoclinic structure of GdPO₄. Gadolinium phosphate singly doped terbium compound was first time reported with the co-precipitation method. The study recognized visible quantum cutting and the optimum energy transfer from Gd³⁺ to Tb³⁺ in GdPO₄:Tb³⁺ Phosphor. The extreme quantum efficiencies were found to be 168% and 163 % which advocates this compound would be one of the probable phosphors for Hg-free applications.

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