Pr^{3+} luminescence in a $GdTaO_4$ host

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Abstract. A red glowing $GdTaO_4$ doped with Pr^{3+} phosphor with major emission coming from the $^1D_2 \rightarrow {}^3H_4$ and $^3P_0 \rightarrow {}^3F_2$ transitions, was prepared via the solid state route at 1200 ^oC. The X-ray diffraction pattern confirmed that the phosphor crystallized and formed a well known fergusonite structure phase of $GdTaO_4$ corresponding to the ICSD 415433 standard file. The diffuse reflectance spectrum showed the absorption peaks corresponding to TaO_4 charge transfer, and direct excitation of Pr^{3+} and Gd^{3+}. The photoluminescence emission spectrum consisted only with peaks from Pr^{3+}, suggesting that there was energy transfer from TaO_4 and Gd^{3+} to Pr^{3+}. The phosphorescence life time of the phosphor was estimated from the phosphorescence decay curve to be approximately 10 min.

Keywords: Red emitting phosphor, Pr^{3+}emission, long afterglow phosphor

1. Introduction

The $GdTaO_4$ compound exhibits a fergusonite structure, and it is classified under the distorted scheelites [1]. The $LnTaO_4$ (Ln = Ce, Gd, La, Y and Lu) group can absorb X-ray photons in the absence of a dopant ion, and re-emit a broad emission that is in the blue region of the electromagnetic spectrum. The broad emission is attributed to the TaO^{4-} group charge transfer [1,2]. The photoluminescence (PL) of Tb^{3+} and Eu^{3+} doped $GdTaO_4$ has been reported by Blasse at el. [1]. This achievement opens up a research opportunity to investigate the properties of other rare earth ions doped in $GdTaO_4$, to prepare a variety of phosphors that can be used in light emitting devices of different types. Since one of the major pursuit in phosphor research is to develop red phosphors that is close to that of an ideal red color with CIE coordinates (0.63, 0.33), Pr^{3+} doped $GdTaO_4$ has emerged as a potential red light emitting phosphor. Pr^{3+} was chosen because it emits red light with CIE color coordinates (0.68, 0.31) that are close to that of an ideal red color, as reported for $CaTiO_3:Pr^{3+}$ [3,4]. The luminescent dynamics of trivalent Pr^{3+} ion were previously studied in several other host materials, such as $LiYF_4$ [5], $YAlO_3$ [6], etc. In such materials the emission is a result of electron transition from the lowest manifold of the 4f5d state to the 4f ($^3H_4$ level) states, and thus leading to an up conversion process. The pumping of carriers to the 4f5d state in $YAlO_3$ is aided by the wide band gap of the material and its strong crystal field. These lead to the 4f5d state to be well positioned in the energy band gap of the material [6]. Noto et al [7] reported a single red emission from Pr^{3+} doped in $CaTiO_3$ at 613 nm wavelength due to the $^1D_2 \rightarrow {}^3H_4$ transition. They attributed the single red emission to metal-to-metal charge transfer (*Intervalence charge transfer*), which leads to a complete depopulation of carriers in the $^3P_0$ level by crossing it over to the $^1D_2$ level.

Pr^{3+} doped $GdTaO_4$ is a potential long persistent red emitting phosphor because it is chemically stable [1] and it can therefore be used in fabrication of devices that can be used in medical diagnostics, emergency and traffic signage at night [8]. The long afterglow observed in these materials is aided by the existence of defect levels that have the capacity to temporally store the energy of the excited carriers and liberate it after a certain period of time which may last for more than ten hours [8,9] after stopping the excitation.

The role of red phosphors with a persistent afterglow seems crucial in the modern world, and it becomes necessary for researchers in luminescent studies to thrive to develop such phosphors. In our laboratory we are studying the preparation and optical properties of red glowing phosphors with the view of increasing their intensity and enhancing their afterglow. In the present paper, we report luminescent dynamics of Pr^{3+} doped $GdTaO_4$ phosphor and its decay characteristics. In addition, we present a possible mechanism of energy transfer from TaO_4 and Gd^{3+} to enhance red emission of Pr^{3+}.

2. Experiments

$GdTaO_4$ doped with 0.5 mol% of Pr^{3+} was prepared by solid state chemical reaction route at 1200 °C for 4 h. The compound was prepared in the presence of Li_2SO_4 that was acting as a fluxing agent, as suggested by Hristea at al [10], in order to achieve complete reaction. The phosphor was prepared by stoichiometrically mixing Gd_2O_3, Ta_2O_5 and $PrCl_3$ into a slurry using ethanol, in the presence of 30 wt% of Li_2SO_4. This was then dried in an oven at 120 °C for 10 h. The dried mixture was baked in a furnace at 1200 °C for 4 h, and the final product ($Gd_{0.995}TaO_4$:$0.005Pr^{3+}$) was cooled to room temperature and washed with distilled water to remove the excess Li_2SO_4.

The phase purity and structure of $GdTaO_4$:Pr^{3+} were analysed using the X-ray diffractometer (AXS D8 Advance X-ray diffractometer (XRD)), and the morphology of the particles was analysed using Scanning Electron Microscopy (SEM) (Shimadzu SSX-550, Kyoto, Japan). The photoluminescent (PL) properties of the phosphor were measured using the Varian Carry-Eclipse fluorescence spectrometer, and the diffuse reflectance was measured using the PerkinElmer Lambda 950 UV/VIS absorption spectrometer. The phosphorescence lifetime measurements were conducted using the Thermoluminescence (TL) spectrometer TL 10091, Nucleonix spectrometer.

3. Results and Discussion

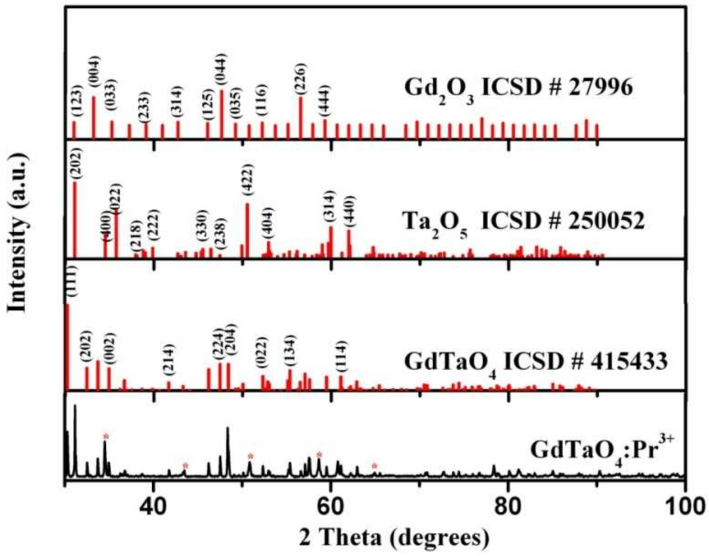

Figure 1: XRD patterns of $GdTaO_4$:Pr^{3+}

The state of the phase purity illustrated with the XRD pattern (fig. 1) of the prepared $GdTaO_4$ compound doped with Pr^{3+} matches closely with that of the fergusonite structure of the $GdTaO_4$ standard file (ICSD 415433). The impurity phases (arising from incomplete reaction of precursors) are marked with asterisks in figure 1. The particle morphology of the compound suggests that the particles are of different irregular shapes and have different sizes. Distinguishably are the sharp edges of the particles shown in the SEM image (fig. 2),

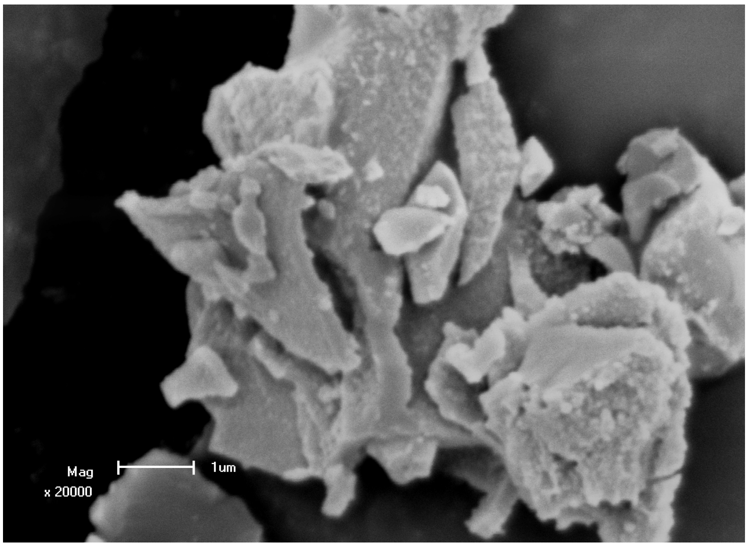

Figure 2: The SEM image of $GdTaO_4:Pr^{3+}$

The diffuse reflectance spectrum of $GdTaO_4:Pr^{3+}$ (fig. 3) shows that the major absorption of the phosphor material comes from band to band excitation at 245 nm. At lower wavelengths are 4f → 4f5d state excitations. There are also 4f → 4f absorptions that correspond to $^3H_4 \rightarrow {}^3P_{2,1}$, $^1I_6$, $^3P_0$ transitions of Pr^{3+} around 450 to 490 nm, and also the $^3H_4 \rightarrow {}^1D_2$ transition of Pr^{3+} around 600 nm [11,12]. There is a prominent charge transfer to the TaO_4 group at 285 nm [1,10] and there are absorptions at 272 and 279 nm which correspond to the $^8S \rightarrow {}^6I_j$, ^6P_j transitions of Gd^{3+} absorption centers [1].

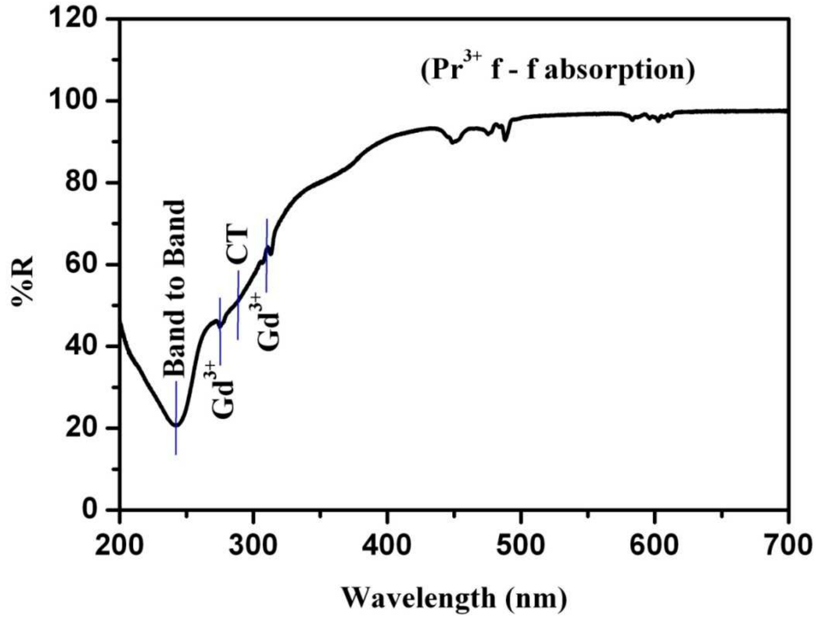

Figure 3: Diffuse reflectance spectrum of $GdTaO_4:Pr^{3+}$

The PL spectrum (fig. 4) of the phosphor was recorded using a Varian Cary Eclipse Fluorescence spectrometer at room temperature by exciting with a 245 nm wavelength using a monochromated xenon lamp as an excitation source. This excitation wavelength according to the diffuse reflectance spectrum should give maximum electron excitation to the conduction band [11]. From the spectrum, the blue and red emissions are observed, and the red emission is more intense than the blue emission. The blue emission peaks at 490 and 511 nm correspond to $^3P_0 \rightarrow {}^3H_{4,5}$ transitions of Pr^+ respectively. The red emission peaks at 610 and 630 nm corresponds to the $^1D_2 \rightarrow {}^3H_4$ transitions of Pr^{3+} [11].

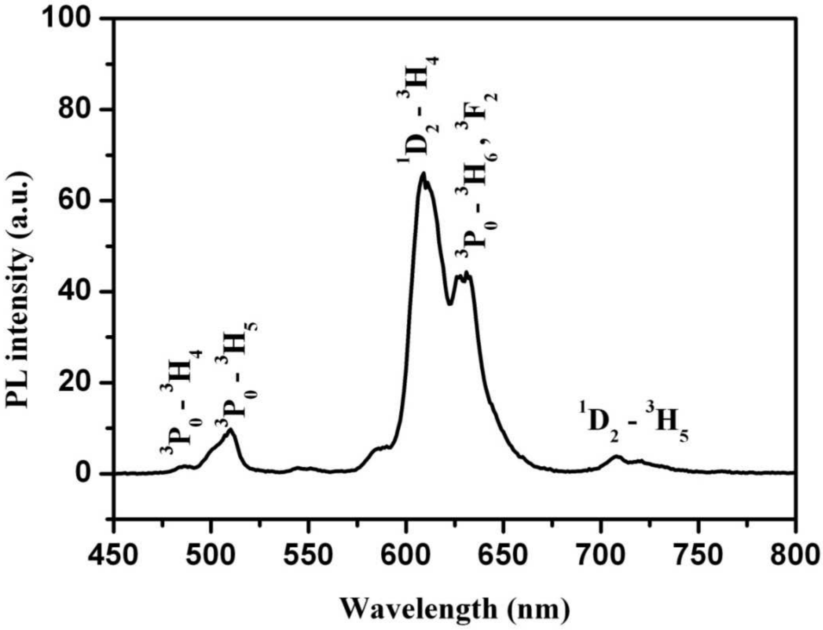

Figure 4: The photoluminescence spectrum measured at room temperature

The phosphorescence lifetime measurements were carried out using a TL spectrometer system by clamping the temperature at 30 °C, and pumping the carriers to the conduction band from the valence band for 5 minutes. The phosphorescent decay curve is composed of two exponential components that can be fitted using the second order exponential equation (eq. 1) [12]:

$$I(t) = Ae^{-t/\tau 1} + Be^{-t/\tau 2} \qquad \mathbf{[1]}$$

where $I(t)$ is the luminescence intensity, A and B are constants and t is the time [12]. The first term (eq. 1) describes the fast component (fig. 5) that is attributed to the lifetime of Pr^{3+} emission with a lifetime (τ_1) equal to 64 ± 1 secs. The second term describes (eq. 1) the slow component (fig. 5) and is attributed to the lifetime of the emission coming from the electron trap levels, and its lifetime (τ_2) is 620 ± 63 secs. [12]

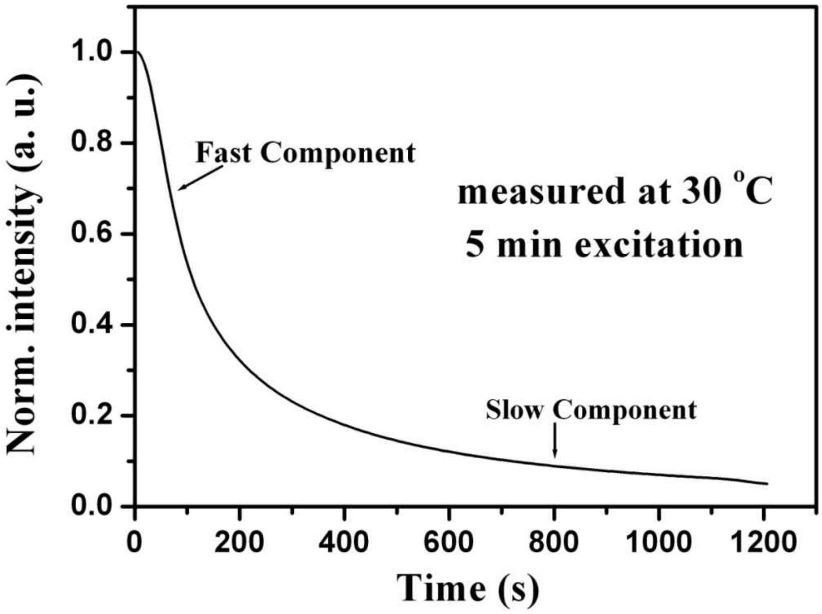

Figure 5: The phosphorescence lifetime spectrum measure at 30 °C

An explanation leading to the energy transfer and the phosphorescence decay time is illustrated using the mechanism of luminescence in figure 6. As observed from the diffuse reflectance spectra (fig. 3), there is a charge transfer to the TaO_4 group of GdTaO4 and absorption by Gd^{3+} upon exciting the material [1, 10]. However from the PL spectrum (fig. 4) there is only an emission coming from Pr^{3+}. From these results we speculate that the absorbed energy by the TaO_4 group is transferred to the Gd^{3+} because the absorption of Gd^{3+} overlaps with the emission of the TaO_4 group [1]. The energy captured by Gd^{3+} states is then transferred to Pr^{3+} luminescent state and hence we only observe the emission from Pr^{3+} (fig. 5).

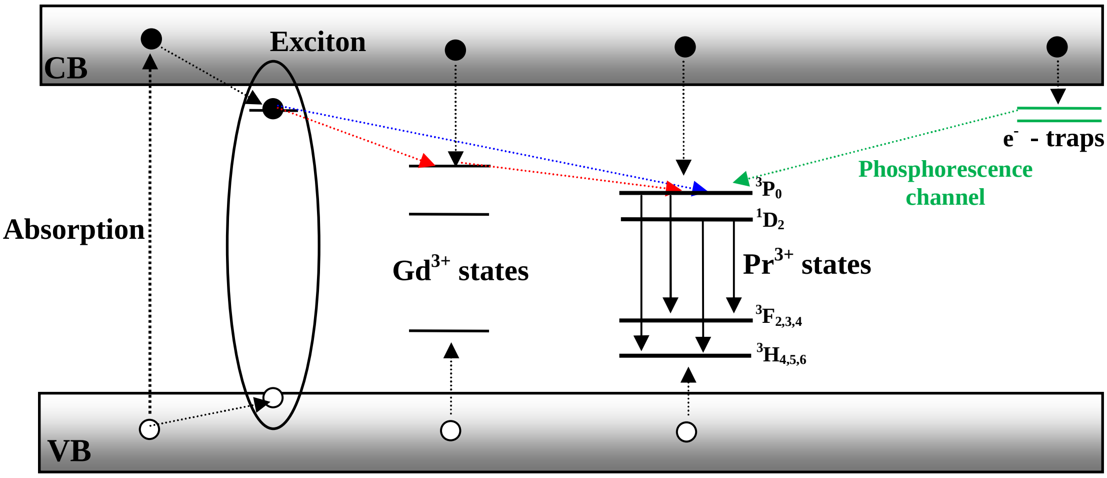

Figure 6: The phosphorescence and energy transfer mechanism

The oxide compounds in general have oxygen defects and amongst them are oxygen vacancies with different orientations. The different orientations result different trap energy distributions [13,16,17].

The shallow electron traps (fig. 6) in the material are responsible for the long afterglow luminescence, and the emission lifetime resulting from the electrons that were trapped is represented in figure 5. The electrons trapped within deeper traps are suitable to reveal the energy distribution of the traps using thermoluminescence spectroscopy [14–17].

4. Conclusion

$GdTaO_4$ doped with Pr^{3+} phosphor was prepared via the solid state route at 1200 ^oC for 4 hours. The XRD pattern of the final compound matched with the standard (ISCD 415433) file and it showed the presence of the unreacted reagent phases. Upon excitation, the diffuse reflectance shows absorption by TaO_4 and Pr^{3+} and Gd^{3+} and the PL shows emission only corresponding to Pr^{3+} transitions and thus we speculate that there was energy transfer from TaO_4 and Gd^{3+} to Pr^{3+}. The phosphorescence life time of the phosphor was estimated to be 10 min.

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