Blue-green luminescence in Hg free excited Sr$_2$P$_2$O$_7$:$Tb^{3+}$ pyrophosphate phosphor for NUV excited LEDs

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Abstract. Tb$^{3+}$ activated Sr$_2$P$_2$O$_7$ phosphor was prepared by modified solid state diffusion technique at 700°C. The XRD pattern of Sr$_2$P$_2$O$_7$ is in well argument with the standard ICDD File (24-1011) available. Surface morphology of the present phosphor has been studied by scanning electron microscope (SEM). In photoluminescence investigation, the excitation spectra of the phosphor extends from 200 to 400 nm gives optimum absorption at 352 nm, which is mercury free excitation and characteristics of NUV excited LED. Under the excitation of 352 nm, Sr$_2$P$_2$O$_7$ doped with trivalent terbium ions produces weak blue emission between 400–500 nm owing to the $^5D_3$ to $^7F_J$ transitions of Tb$^{3+}$ and strong green emission in 500–650 nm region of the visible spectrum due to the 4f–4f transitions from the $^5D_4$ to $^7F_J$ ($J=6, 5, 4, 3$) states of Tb$^{3+}$. The entire study reveals that the present phosphor have promising applications in the lamp industry especially for solid state lighting (mercury free excited lamp phosphor) and NUV LEDs.

Keywords: Photoluminescence; Phosphor; Pyrophosphate; XRD.

1. Introduction
In the recent era of solid-state lighting the demand for mercury free excited phosphor-converted LEDs has significantly increased. Literature study authenticates that phosphate base phosphors are renowned for their thermal and chemical stability [1]. Since, they are extensively used as hosts doped with different rare earth ions to obtain phosphors for verity of lighting applications. Consequently the research on phosphors suitable for fabricating NUV excited light-emitting diodes has attracted more attention. Compared to the conventional incandescent lamps, LEDs have numerous advantages such as less energy consumption, optimum luminosity, and extended lifetime [2]. They have been used mainly for LCD backlighting, traffic lights, and information boards. In sight of green emission at around 545 nm trivalent terbium ions based phosphors play a vital role in the field of displays and enlightenment. Particular phosphors such as GdMgB$_2$O$_{10}$, Y$_2$SiO$_5$ and LaPO$_4$ based on energy transfer from Ce$^{3+}$ to Tb$^{3+}$ found diversified applications for their green emission in lamps [3]. Herein, the main objective of this work is to develop an efficient pyrophosphate phosphor that absorbs energy in the near-UV range and emit in the visible range and to examine the photoluminescence and structural properties of the newly synthesized Sr$_2$P$_2$O$_7$ pyrophosphate phosphor. The prepared phosphor has been characterized by XRD and SEM. The photoluminescence investigations are performed to explore the luminescence characteristics of trivalent terbium doped strontium pyrophosphate. The observed blue and intense green emission from Sr$_2$P$_2$O$_7$:$Tb^{3+}$ with 352 nm (mercury free) excitation suggests a possibility of applying the newly synthesized phosphors for phosphor- converted NUV-LEDs and solid state lighting.
2. Experimental

The powder samples of Sr₂P₂O₇:Tb³⁺ pyrophosphor were prepared by high temperature modified solid state diffusion. The starting materials used in the preparation were high purity strontium carbonate SrCO₃ (Merck, 99.995%), ammonium dihydrogen phosphate NH₄H₂PO₄ (Merck 99.99% pure) and the molar ratio of rare earth, terbium oxide Tb₂O₃ (Aldrich, 99.999%) was varied from 0.1 to 1 mol% in Sr₂P₂O₇ phosphor with respect to Sr ions. After being ground thoroughly in stoichiometric ratios by using an agate mortar, to ensure the best homogeneity and reactivity, powder was transferred to silica crucible, and corresponding mixtures were initially heated in a muffle furnace at 350 °C for 1 hr in order to decompose NH₄H₂PO₄. Afterwards, the mixture was reground for 30 min before heating at higher temperatures and then heated in furnace at 700 °C for 12 hrs. The temperature was cooled to 500°C and air-quenched to room temperature. All samples were found out to be purely white and various techniques were used to characterize the synthesized phosphor. The prepared phosphor was characterized by XRD, SEM and PL.

The basic chemical reaction for Sr₂P₂O₇ pyrophosphor can be described as follows:

\[ \text{Sr(CO}_3\text{)} + 2(\text{NH}_4\text{H}_2\text{PO}_4) \rightarrow \text{Sr}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + 3\text{H}_2\text{O} + 3\text{CO}_2. \]

3. Results and discussion

3.1. XRD of Sr₂P₂O₇:Tb³⁺ pyrophosphate phosphor. The phase purities of the sample was checked by powder X-ray diffraction using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.010, continue time 20s, in the 2θ range from 10° to 60°. Figure 1 illustrates the XRD pattern for Sr₂P₂O₇:Tb³⁺ prepared at 700 °C.

![XRD pattern](image)

**Figure 1.** XRD of Sr₂P₂O₇:Tb³⁺ pyrophosphate phosphor.

The above sample was heated in air and the obtained XRD pattern is similar to that reported for the compound strontium pyrophosphate Sr₂P₂O₇ (ICDD file No.24-1011), indicating the formation of the crystalline phases. XRD pattern (Figure 1) reveals that the trivalent terbium ions (dopant) have no noticeable influence on the crystalline structure of the host Sr₂P₂O₇ [4]. Considering the effect of ionic sizes of the cations, it is predictable that Tb³⁺ can effectively occupy Sr²⁺ sites, since the ionic radii of Tb³⁺ (1.04 Å) and Sr²⁺ (1.12 Å) are in the close vicinity with one another. [5]. This shows solid state reaction of the mixtures took place well and final product acquires crystalline phases.

3.2. SEM of Sr₂P₂O₇:Tb³⁺ pyrophosphate phosphor. The particle morphology of the present pyrophosphate was studied by (SEM, JEOL 6380A). An average crystallite size is in sub-micrometer range seen in SEM images. The microstructure of the phosphor prepared at 700°C reveals an average size of about 5 to 10 μm. Particles possess foamy like morphology formed from extremely
agglomerated crystallites and sample Sr₂P₂O₇:Tb³⁺ shows formation of porous structure. The sample revealed sintered structures in which individual particles could barely be recognized. However the particles were attached with each other all the way through necking and possibly they may be crushed to obtain separate particles. Most particles showed smoothed rounded surfaces and sizes of a few micrometers. All these characteristics were beneficial when considering their application as phosphor powders for fabrication of NUV-LEDs (coating purpose) [6]. The typical morphological images are represented in Figure 2.

Figure 2. SEM photographs of Sr₂P₂O₇:Tb³⁺ pyrophosphate.

3.3 Photoluminescence (PL) spectra of Sr₂P₂O₇:Tb³⁺ pyrophosphate phosphor. The photoluminescence (PL) investigations were performed on a Shimadzu RF5301PC spectrofluorophotometer using a spectral slit width of 1.5 nm. The equal amount of powder sample was used (i.e. 2 g, each) for the measurement of emission and excitation spectra. Figure 3(a), demonstrates the PL excitation and emission spectra of Sr₂P₂O₇:Tb³⁺ pyrophosphate phosphor. The excitation peak observed at 352 nm is highly intense amongst other excitation peaks which are observed at 262 nm to 280 nm shown in Figure 3(a). The energy level transitions of Tb³⁺ ions are represented in Figure 3(b).

Figure 3(a). PL excitation and emission spectra for Sr₂P₂O₇ doped with Tb³⁺ activators. Figure 3(b). Energy level transitions of Tb³⁺ ions.

Only the emission intensity is variable with respect to all excitation wavelengths; however there is no effect on the emission wavelengths. In this framework, we select 352 nm wavelengths for
our study since it is more suitable for Hg free excited lamp phosphors and NUV excited LEDs. In the PL emission spectrum Sr₃P₂O₇:Tb³⁺, the broad emission lines are observed at 413, 438, 469, 484, 545 and 590 nm. The weak emission peaks at 413, 438 nm are due to the transition from excited level ⁵D₃ to ⁷F₃ and ⁷F₄ levels of Tb³⁺ ions, respectively. The emission peaks observed at 469 nm is due to ⁵D₃ → ⁷F₂ and peak at 484 nm is ascribed to the ⁵D₄ → ⁷F₆ transitions of Tb³⁺ [7]. The small peak observed at 590 nm arise due to the ⁵D₄ → ⁷F₄ transitions. Sample showed intense green emission of light at 545 nm wavelength corresponding to the strongest ⁵D₄ → ⁷F₅ transition of Tb³⁺ ions stimulated probably from both electric-dipole and magnetic-dipole transitions [8].

In general at lower doping concentrations of Tb³⁺ ions, it shows more intense emission in blue region, as a result the emission around 380 - 385 nm due to ⁵D₃ → ⁷F₆ transition can also observe in the Near UV region, however with increasing concentrations of Tb³⁺ ions, the green emission becomes most intense because of cross relaxation. A series of Sr₃P₂O₇:Tb³⁺ pyrophosphate phosphors have been synthesized with the dopant concentration ranging from 0.1 to 1 mol % and an optimum doped molar concentration of Tb³⁺ ions is 0.5 mol % attained in our study.

4. Conclusions
In conclusion, the Sr₃P₂O₇:Tb³⁺ pyrophosphate phosphor prepared by the conventional high temperature modified solid state diffusion. The formation of crystalline phases was confirmed by the X-ray diffraction technique (XRD). In the SEM study, an average crystallite size is found out to be 5 to 10 μm range with foam-like morphology. The photoluminescence (PL) spectra exhibit intense green light emission at 545 nm wavelength when excited by NUV lights at 352 nm (mercury free excitation). In view of the extended excitation band and admirable luminescent properties, Tb³⁺ activated Sr₃P₂O₇ pyrophosphate phosphor can be utilized as blue-green phosphors in tricolor lamps for solid state lighting and useful for NUV excited LEDs because of its uncomplicated synthesis, lower manufacturing cost, unhygroscopic nature and mercury free excitation.

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