

# Emission spectra of $\text{LnPO}_4:\text{RE}^{3+}$ ( $\text{Ln} = \text{La}, \text{Gd}$ ; $\text{RE} = \text{Eu}, \text{Tb}$ and $\text{Ce}$ ) powder phosphors

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## Abstract

This paper reports the emission spectra at room temperature and presents an optimum concentration for each of the dopants in  $\text{GdPO}_4:\text{Eu}^{3+}$ ,  $\text{LaPO}_4:\text{Tb}^{3+}$  and  $\text{LaPO}_4:\text{Ce}^{3+}$  powder phosphors for the observation of bright reddish-orange, green and UV emission, respectively. FT-IR and a thermal analysis of these phosphor materials have been carried out. Scanning electron microscopic investigations were also conducted to understand surface morphological features (shape) and the grain size in the powder phosphor systems.

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**Keywords:** Lanthanide phosphates;  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$  dopants; Optimum concentration

## 1. Introduction

Fluorescence spectra of rare earth activated materials have potential industrial applications, for example, in solid state lasers (YAG:Nd), in color TV monitors ( $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ ) and in X-ray intensifying screens ( $\text{LaOBr}:\text{Tb}$ ) [1,2]. Lanthanide orthophosphates ( $\text{LnPO}_4$ ) crystallize in two polymorphic types, the monoclinic monazite type (for  $\text{Ln} = \text{La}$  to  $\text{Gd}$ ) and the quadratic xenotime type (for  $\text{Ln} = \text{Tb}$  to  $\text{Lu}$ ). The emission spectrum of  $\text{Eu}^{3+}$  in  $\text{LnPO}_4$  was reported for the first time by Ropp [3] who compared the emission intensities of the rare earth phosphates and rare earth oxide phosphors. The highly efficient  $\text{Tb}^{3+}$ -doped monazite phase ( $\text{La}_x\text{Tb}_y\text{Ce}_z$ )  $\text{PO}_4$  has been a green phosphor in fluorescent lamps [4–6]. Ropp who reported that  $\text{Ce}^{3+}$ -activated rare earth phosphates have lifetimes in the nanosecond range [7].  $\text{YPO}_4:\text{Ce}^{3+}$  displays two UV emission peaks [3,7]. Schwarz and coworkers [8–10] and Brabier et al. [11] have carried out the optical investigations of alkali rare earth phosphates of the type  $\text{M}_3\text{RE}(\text{PO}_4)_2$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}$ ;  $\text{RE} = \text{La}$  to  $\text{Tb}$ ). Erdei et al. [12,13] prepared  $\text{Ce}^{3+}$ ,  $\text{Tb}^{3+}:\text{LaPO}_4$  green phosphors by a newly developed hydrolyzed colloidal reaction (HCR) technique at room temperature ( $<100^\circ\text{C}$ ) and in atmospheric pressure by utilizing a subsequent calcining

and reductive treatments, respectively. Brixner and Fluornoy have mentioned some of the properties of the  $\text{GdPO}_4:\text{Eu}^{3+}$  phosphors and compared them with other hosts. Over the past few years, we have been actively involved in the preparation and characterization of a wide variety of rare earth doped powder phosphors for their use in color TV monitors, fluorescent lamps and X-ray intensifying screens [14–16]. Keeping in view the commercial applications of red, green and blue emitting phosphors, earlier we have prepared and characterized the  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$ -doped lanthanide oxychloride,  $\text{Na}_6\text{Ln}(\text{BO}_3)_3$  ( $\text{Ln} = \text{La}$  and  $\text{Gd}$ ), lanthanide oxyfluoride and oxybromide powder phosphors [17–21]. The purpose of present paper is to report the synthesis, optical properties and the optimization of dopant ion ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$ ) concentration in lanthanide based phosphors.

## 2. Experimental

Lanthanide phosphates can be synthesized through different reactions and/or in combinations as well. Here, we have adopted a precipitation technique, which involves a direct and clean reaction between the lanthanide oxides and phosphoric acid without any by-products other than the water [22]. For the synthesis of these phosphors, ultra pure gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ), lanthanum oxide ( $\text{La}_2\text{O}_3$ ), yttrium oxide ( $\text{Y}_2\text{O}_3$ ), europium oxide ( $\text{Eu}_2\text{O}_3$ ), terbium oxide ( $\text{Tb}_4\text{O}_7$ ), cerium oxide ( $\text{CeO}_2$ ) and phosphoric acid ( $\text{H}_3\text{PO}_4$ )

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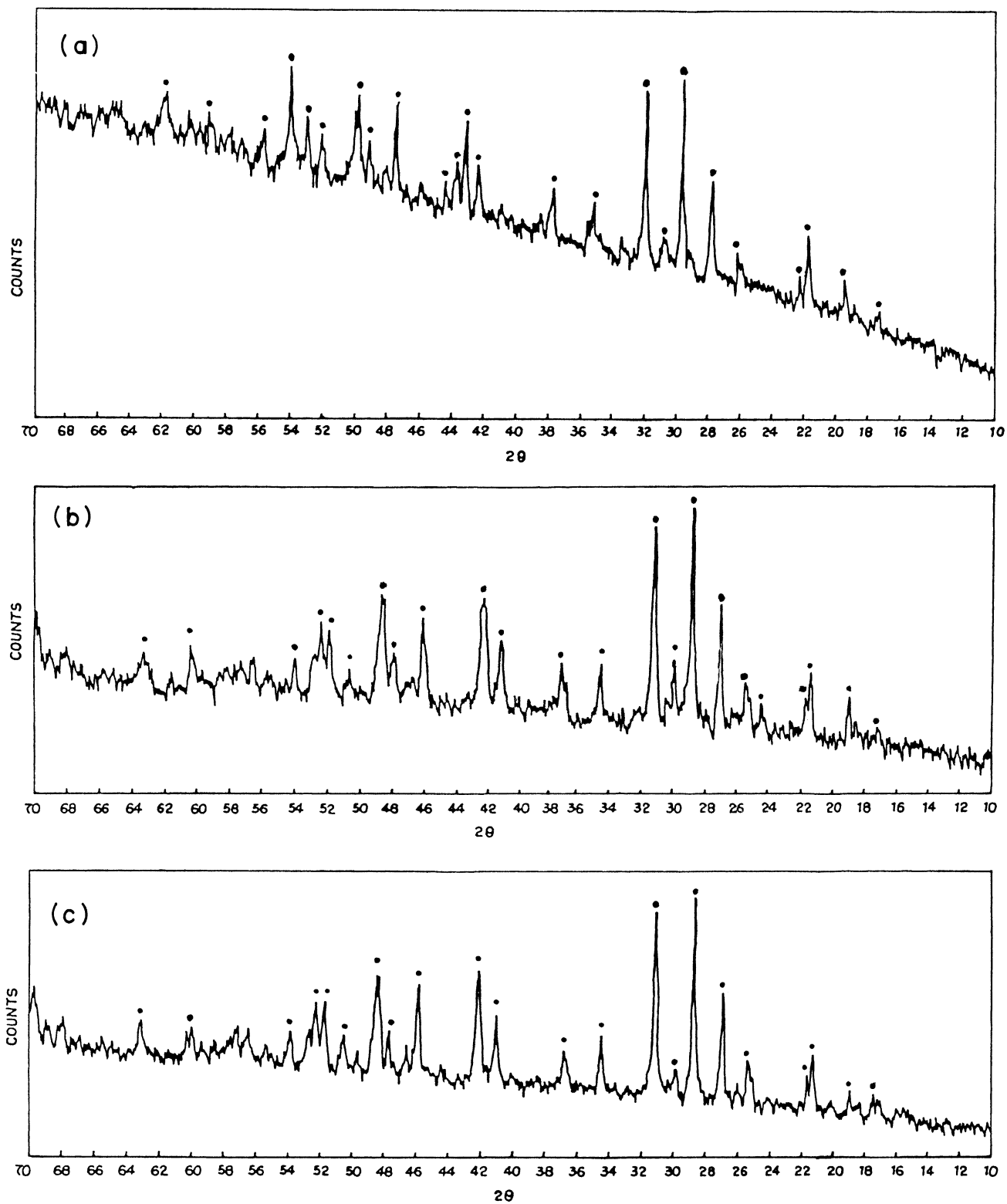


Fig. 1. XRD patterns of (a)  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ , (b)  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and (c)  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  powder phosphors.

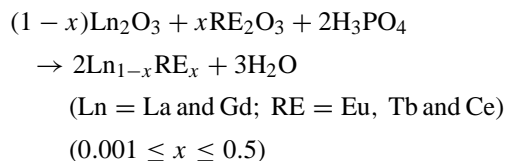
were taken as the starting chemicals. Due to the hygroscopic nature of the lanthanide oxides, the starting oxides were calcined at 700 °C [23]. Initially, chemicals pertaining to following compositions were mixed thoroughly by using acetone as the mixing medium. For labeling purpose, the reddish-orange color emitting ( $\text{Eu}^{3+}$ ) phosphors are abbreviated as RP, green color emitting ( $\text{Tb}^{3+}$ ) phosphors as GP and UV emission ( $\text{Ce}^{3+}$ ) phosphors as UVP with the phosphor sample numbers.

1.  $\text{Gd}_{0.999}\text{PO}_4:\text{Eu}_{0.001}^{3+}$  (RP-1)
2.  $\text{Gd}_{0.995}\text{PO}_4:\text{Eu}_{0.005}^{3+}$  (RP-2)
3.  $\text{Gd}_{0.99}\text{PO}_4:\text{Eu}_{0.01}^{3+}$  (RP-3)
4.  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$  (RP-4)
5.  $\text{Gd}_{0.9}\text{PO}_4:\text{Eu}_{0.1}^{3+}$  (RP-5)

1.  $\text{La}_{0.995}\text{PO}_4:\text{Tb}_{0.005}^{3+}$  (GP-1)
2.  $\text{La}_{0.99}\text{PO}_4:\text{Tb}_{0.01}^{3+}$  (GP-2)
3.  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  (GP-3)
4.  $\text{La}_{0.9}\text{PO}_4:\text{Tb}_{0.1}^{3+}$  (GP-4)
5.  $\text{La}_{0.5}\text{PO}_4:\text{Tb}_{0.5}^{3+}$  (GP-5)

1.  $\text{La}_{0.995}\text{PO}_4:\text{Ce}_{0.005}^{3+}$  (UVP-1)
2.  $\text{La}_{0.99}\text{PO}_4:\text{Ce}_{0.01}^{3+}$  (UVP-2)
3.  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  (UVP-3)
4.  $\text{La}_{0.9}\text{PO}_4:\text{Ce}_{0.1}^{3+}$  (UVP-4)
5.  $\text{La}_{0.6}\text{PO}_4:\text{Ce}_{0.4}^{3+}$  (UVP-5)

The dried lanthanide oxide powders were slowly added to a 85% phosphoric acid. The reaction was vigorous and exothermic in nature. Large precipitates were immediately formed at the reaction site, and then broke into fine particles. The solution was extremely dense and stable and did not separate for a long period of time. The solution was later stirred for 30 min and then separated by centrifuging. Traces of excess  $\text{H}_3\text{PO}_4$  were removed by washing the samples several times with a deionized water. The chemical reaction involved in the present synthesis is as follows:



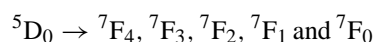
The obtained white powders were collected into quartz boats and fired in a silica tube in the central zone of a high temperature furnace for 3 h at 950 °C in an inert ( $\text{N}_2$ ) atmosphere. Soon after completion of the synthesis, the emission under an UV source is reddish-orange, green and ultraviolet for the  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$  phosphors, respectively. The purity of the synthesized phosphors  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ ,  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  was checked by X-ray diffractometry (XRD). A Philips PW 18140 X-ray diffractometer fitted with a PM 820 3A online recorder was used for this purpose. All diffractograms were recorded with  $\text{Cu K}\alpha$  ( $\lambda = 0.1542$  nm) radiation (Fig. 1(a)–(c)) [22].

Both excitation and fluorescence spectra of these phosphors were recorded on a Hitachi 650 10S spectrofluorimeter using a 150 W xenon arc lamp as the excitation source at room temperature. The recorded excitation spectra are shown in Fig. 2(a)–(c), revealing the stronger lines of excitation,  $\lambda_{\text{exc}} = 398$  nm ( $\text{Eu}^{3+}$ ),  $\lambda_{\text{exc}} = 370$  nm ( $\text{Tb}^{3+}$ ), and  $\lambda_{\text{exc}} = 258$  nm ( $\text{Ce}^{3+}$ ). The fluorescence spectra are shown in the Figs. 3–5. The FT-IR absorption spectra of these samples were carried out on a Perkin-Elmer spectrometer (spectrum 2000) with KBr pellets in the wave-number range of 1400–370  $\text{cm}^{-1}$  given in Fig. 6(a)–(c) [24]. The surface morphological features (shape and grain-size) of the phosphors  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ ,  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  were studied by using Leica stereoscan 440 scanning electron microscope (SEM). SEM photographs are furnished in Fig. 7(a)–(c). For SEM analysis, the samples were pre-coated with a thin layer of gold in a Polaron E5000 coating unit in order to prevent the charging of the specimen. For a comparative study, the electron beam parameters were kept constant while the analysis of the samples was being carried out. The SEM images of the samples with a 20 kV EHT and a 25 pA beam current were recorded by using a 35 mm camera attached on the high resolution recording unit. Thermogravimetric investigations (thermogravimetric analysis, TGA/differential thermal analysis, DTA) were carried out on the phosphor samples of  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ ,  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  by using Mettler Toledo TGA/SDTA 851<sup>e</sup>. The samples were heated from 900 to 1300 °C in a dynamic inert ( $\text{N}_2$ ) atmosphere and with the heating rate of 10 °C  $\text{min}^{-1}$ . TGA/DTA results are produced in Fig. 8(a1/b1), (a2/b2) and (a3/b3), respectively.

### 3. Results and discussion

#### 3.1. $\text{Eu}^{3+}$ :phosphors

The profiles of the fluorescence spectra of all  $\text{Eu}^{3+}$ :phosphors (Fig. 3) show the emission transitions [25]:



The main emission peaks are located at 580–591 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) and at 610–619 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ), respectively. The transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) splits into three components and similarly the other transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) (magnetic dipole in character) is split into two components in all the  $\text{Eu}^{3+}$ :phosphors. The presence of a sensitive forbidden transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ) has been identified in all phosphors with a very weak intensity. The transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) displays more intensity than that of the transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) due to localized energy transfer. Usually, for non-centro symmetrical host-compounds including  $\text{Eu}^{3+}$ -doped lanthanide oxychloride, lanthanide-alkaline earth borates and lanthanide oxybromides, which we studied

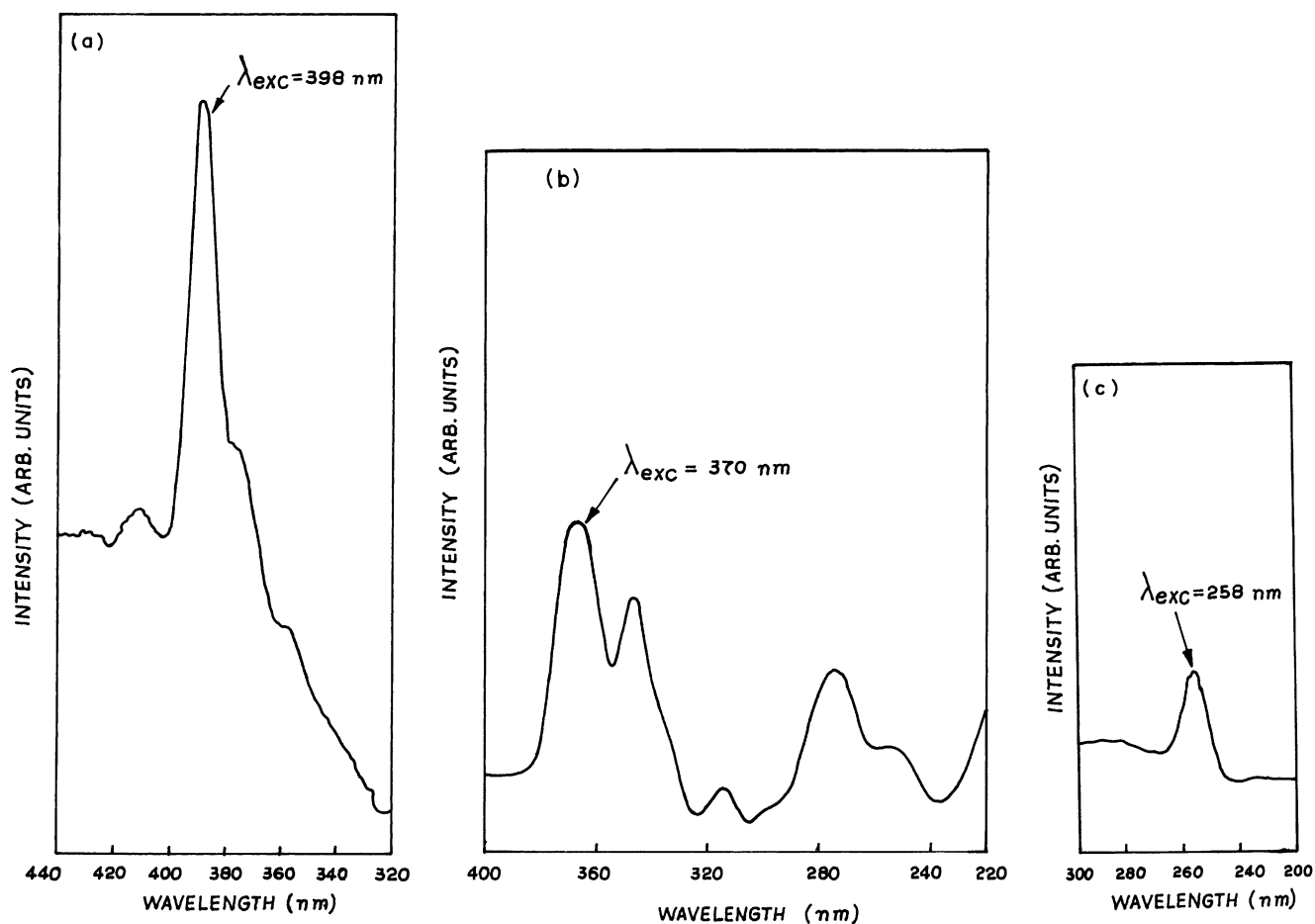


Fig. 2. Excitation spectra of (a)  $Gd_{0.999}PO_4:Eu_{0.001}^{3+}$ , (b)  $La_{0.95}PO_4:Tb_{0.05}^{3+}$  and (c)  $La_{0.95}PO_4:Ce_{0.05}^{3+}$  powder phosphors.

Table 1  
Relative fluorescence intensity ratios ( $R$ ) for the measured emission levels of  $GdPO_4:Eu^{3+}$  powder phosphors

Phosphor	$\frac{({}^5D_0 \rightarrow {}^7F_0)/({}^5D_0 \rightarrow {}^7F_4)}{({}^5D_0 \rightarrow {}^7F_4)}$	$\frac{({}^5D_0 \rightarrow {}^7F_1)/({}^5D_0 \rightarrow {}^7F_4)}{({}^5D_0 \rightarrow {}^7F_4)}$	$\frac{({}^5D_0 \rightarrow {}^7F_2)/({}^5D_0 \rightarrow {}^7F_4)}{({}^5D_0 \rightarrow {}^7F_4)}$	$\frac{({}^5D_0 \rightarrow {}^7F_3)/({}^5D_0 \rightarrow {}^7F_4)}{({}^5D_0 \rightarrow {}^7F_4)}$	$\frac{({}^5D_0 \rightarrow {}^7F_4)/({}^5D_0 \rightarrow {}^7F_4)}{({}^5D_0 \rightarrow {}^7F_4)}$
RP-1	–	1.464	1.071	0.803	1.000
		1.571	0.928		0.857
			0.964		1.000
RP-2	–	1.820	1.179	0.641	1.000
		2.038	0.858		0.743
			0.935		1.038
RP-3	–	1.980	1.200	0.530	1.000
		2.260	0.800		0.680
			0.920		1.050
RP-4	0.232	2.341	1.261	0.295	1.000
		2.785	0.693		0.505
			0.835		1.051
RP-5	0.333	1.993	1.178	0.392	1.000
		2.440	0.720		0.559
			0.845		1.000

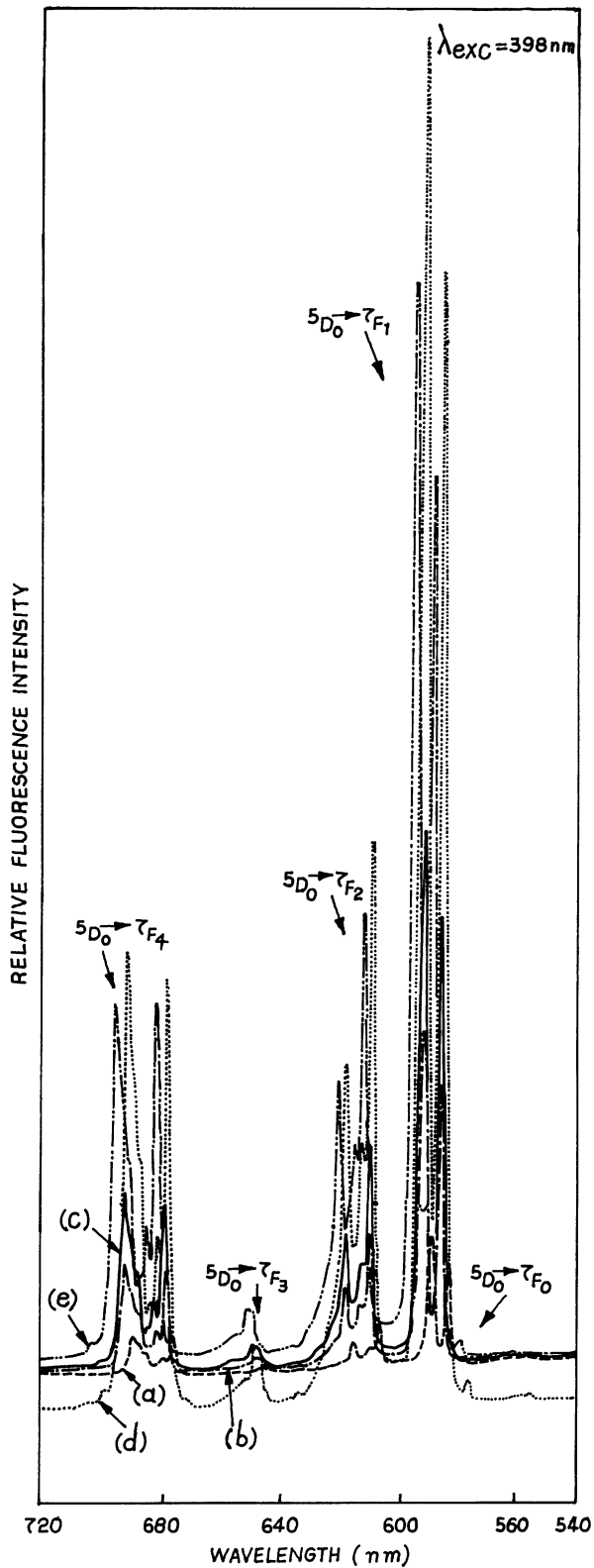


Fig. 3. Fluorescence spectra of (a)  $\text{Gd}_{0.999}\text{PO}_4:\text{Eu}_{0.001}^{3+}$ , (b)  $\text{Gd}_{0.995}\text{PO}_4:\text{Eu}_{0.005}^{3+}$ , (c)  $\text{Gd}_{0.99}\text{PO}_4:\text{Eu}_{0.01}^{3+}$ , (d)  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$  and (e)  $\text{Gd}_{0.9}\text{PO}_4:\text{Eu}_{0.1}^{3+}$  powder phosphors.

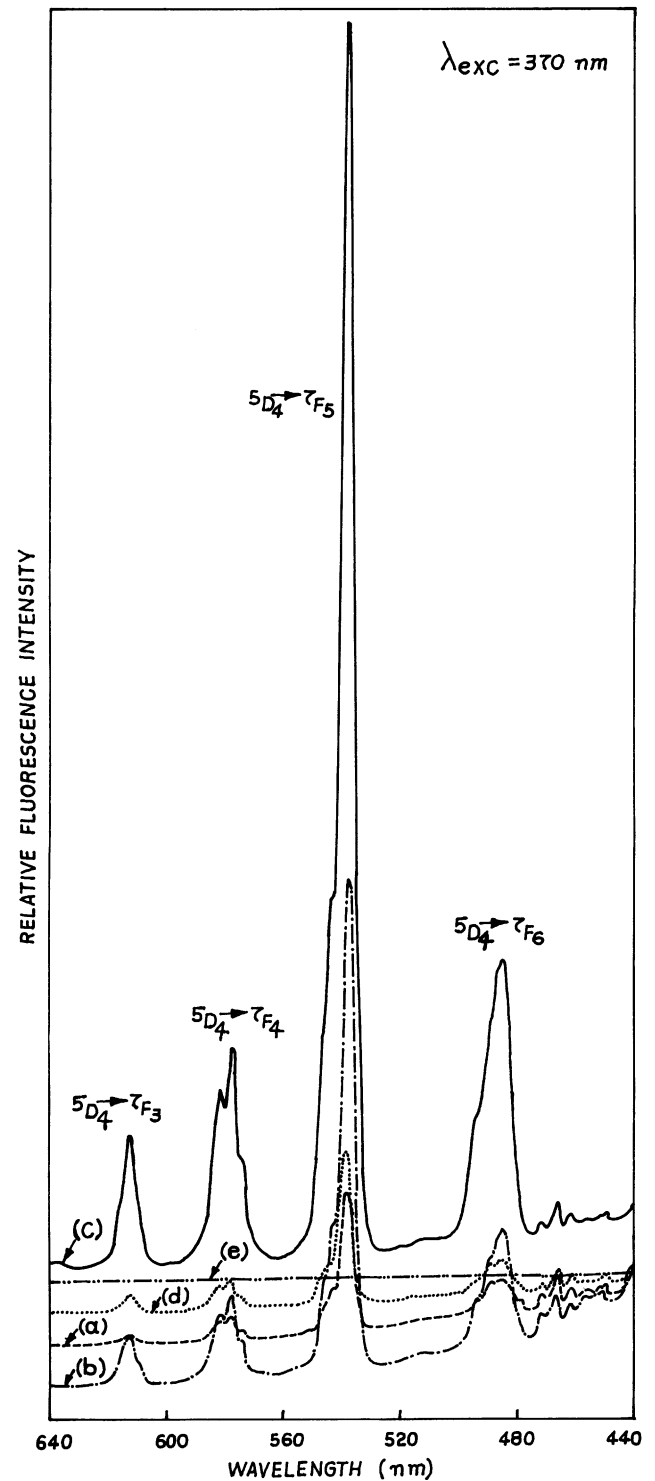


Fig. 4. Fluorescence spectra of (a)  $\text{La}_{0.995}\text{PO}_4:\text{Tb}_{0.005}^{3+}$ , (b)  $\text{La}_{0.99}\text{PO}_4:\text{Tb}_{0.01}^{3+}$ , (c)  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$ , (d)  $\text{La}_{0.9}\text{PO}_4:\text{Tb}_{0.1}^{3+}$  and (e)  $\text{La}_{0.5}\text{PO}_4:\text{Tb}_{0.5}^{3+}$  powder phosphors.

earlier, the ( $5D_0 \rightarrow 7F_2$ ) transition is the most intense one [17–20]. The emission transitions have assigned using the data from the literature [4]. The intensity of the emission transitions was found to increase with an increase in Eu concentration up to 5 mol. Additionally, the emission peak

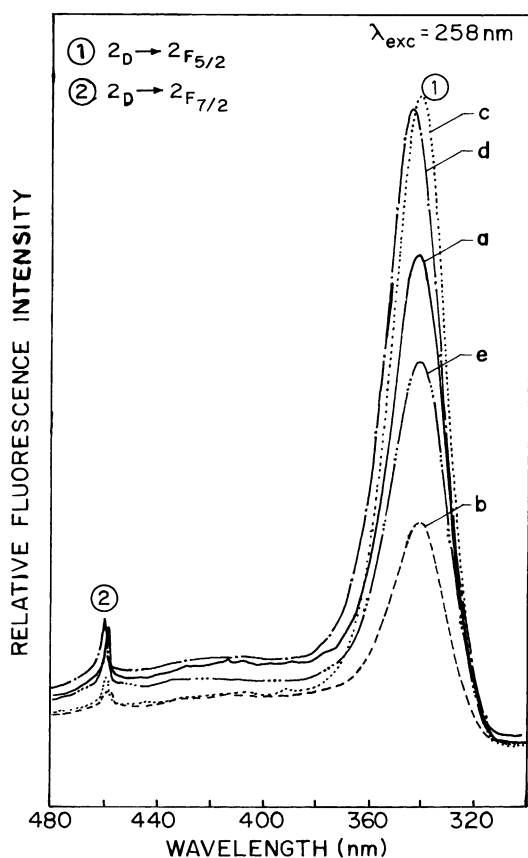


Fig. 5. Fluorescence spectra of (a)  $\text{La}_{0.995}\text{PO}_4:\text{Ce}_{0.005}^{3+}$ , (b)  $\text{La}_{0.99}\text{PO}_4:\text{Ce}_{0.01}^{3+}$ , (c)  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$ , (d)  $\text{La}_{0.9}\text{PO}_4:\text{Ce}_{0.1}^{3+}$  and (e)  $\text{La}_{0.6}\text{PO}_4:\text{Ce}_{0.4}^{3+}$  powder phosphors.

Table 2

The emission level peak positions ( $\lambda_p$ , nm) for the transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ) and color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) of  $\text{GdPO}_4:\text{Eu}^{3+}$  powder phosphors

Phosphor	$\lambda_p$ (nm)	$\bar{X}$	$\bar{Y}$
RP-1	606	0.516	0.450
	614		
RP-2	608	0.621	0.377
	616		
RP-3	609	0.616	0.382
	618		
RP-4	610	0.625	0.373
	619		
RP-5	611	0.657	0.341
	619		

positions are found to be marginally shifted towards the higher wavelength side. The relative fluorescence intensity ratios ( $R$ ), have been calculated and given in Table 1. The emission level peak positions ( $\lambda_p$ , nm) for the transition ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ), is given in Table 2, which are noticed to significantly change with the chemical composition. Color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) are computed according to standard formulations made available by the Commission Internationale de l'Eclairage (CIE), France, and based on the three primary colors red, green and blue (Table 2) [26]. The computed color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) are superimposed in the CIE chromaticity diagram to check the validity of the obtained results (Fig. 9). From Fig. 9, it is clear that the color coordinates of the synthesized powder phosphors are well fitted

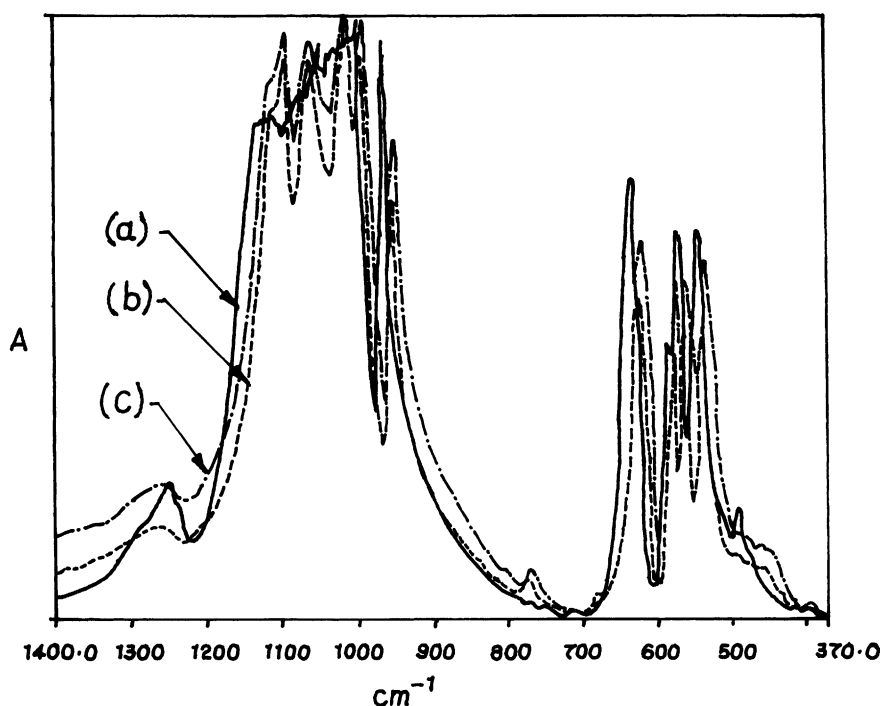


Fig. 6. FT-IR absorption spectra of (a)  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ , (b)  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and (c)  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  powder phosphors.

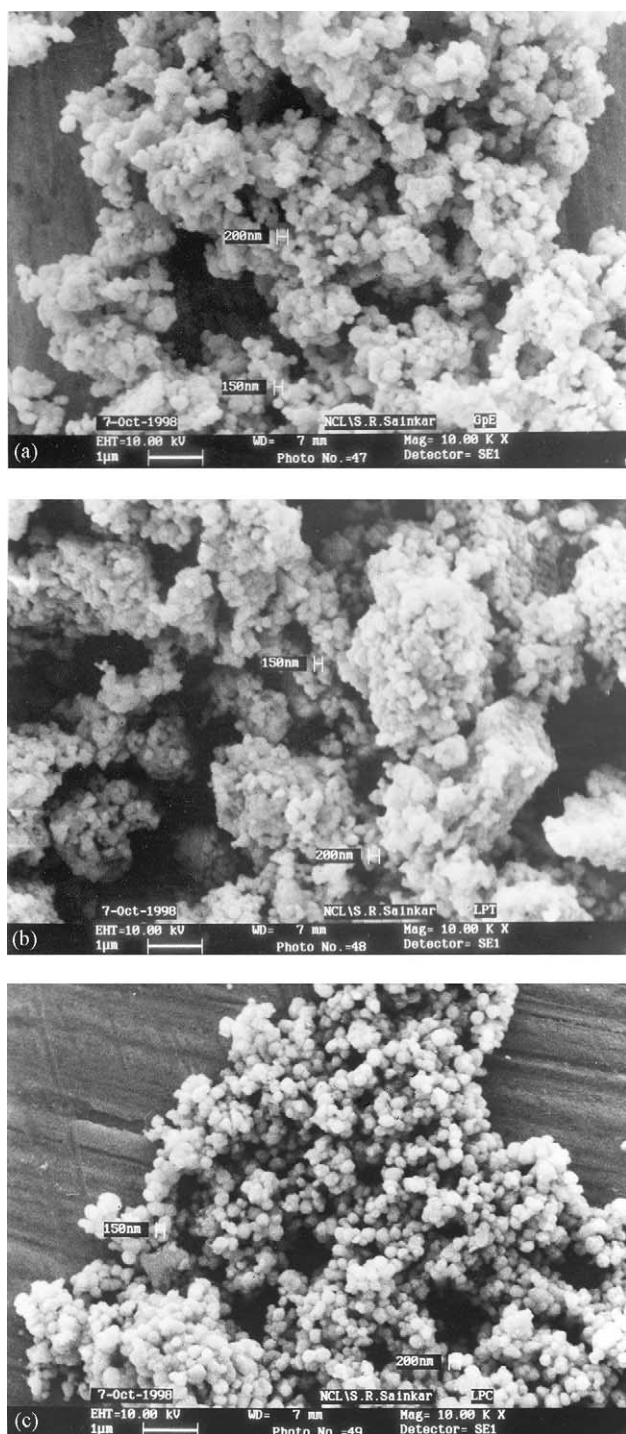


Fig. 7. SEM images of (a)  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ , (b)  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and (c)  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  powder phosphors.

in the reddish-orange region (indicated as a rectangular shaded portion). The recorded FT-IR absorption spectrum of  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$  Fig. 6(a) has been in agreement with the reported literature [24]. The ionic phosphate absorption is reported on the basis of the Raman work to absorb at 1080 and  $980\text{ cm}^{-1}$  [27]. The fundamental frequencies allowed in

the infrared appear at  $500\text{ cm}^{-1}$ . In the pertinent FT-IR spectrum, two bunches of absorption bands have been observed in the wave-number region  $1200\text{--}900$  and  $700\text{--}400\text{ cm}^{-1}$  which are attributed to  $\text{M--OPO}_3$  ( $\text{M} = \text{Gd}$  and  $\text{Eu}$ ) bonds [28]. Thermogravimetry of  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ , indicates the total thermal stability with respect to chemical as well as crystalline phase transformation changes, in a covered temperature range. From the recorded SEM image of  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$  (Fig. 7(a)), it is seen that, the particles are agglomerated and are having a spherical shape with a grain size in the range of  $150\text{--}200\text{ nm}$ . Based on the recorded fluorescence spectral features and from the relative fluorescence intensity ratios ( $R$ ), the optimum concentration of the dopant europium ( $\text{Eu}^{3+}$ ) has been found to be 5 mol.

### 3.2. $\text{Tb}^{3+}$ :phosphors

From the recorded fluorescence spectra of  $\text{Tb}^{3+}$ :phosphors (Fig. 4), the following four emission transitions have been observed [12,29–31]:

- $^5\text{D}_4 \rightarrow ^7\text{F}_6$  (486–484 nm)
- $^5\text{D}_4 \rightarrow ^7\text{F}_5$  (539–537 nm)
- $^5\text{D}_4 \rightarrow ^7\text{F}_4$  (578–577 nm)
- $^5\text{D}_4 \rightarrow ^7\text{F}_3$  (614–612 nm)

Among these, the emission transition  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  is responsible for green color observation as a single peak, and it has been taken as a reference for the comparison of the fluorescence spectral peaks of the  $\text{Tb}^{3+}$ :phosphors studied. From the spectral features, it has been noticed that, the intensity of the emission peaks increases with an increase in terbium concentration up to 5 mol beyond which the fluorescence quenching has been observed. Besides this, positions of the emission peaks have been observed to be varying slightly depending upon the host matrix. Therefore, the  $\text{Tb}^{3+}$  concentration of 5 mol has been found to be an optimum dopant ion concentration. The emission level peak positions ( $\lambda_p$ , nm) of the transition  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  are given in Table 3. As in  $\text{Eu}^{3+}$ :phosphors,  $\text{Tb}^{3+}$ :phosphors were also characterized by computing the color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) (Table 3) and relative fluorescence intensity ratios ( $R$ ) (Table 4). The obtained color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) are superimposed on the CIE chromaticity diagram (Fig. 9) to assess the color richness of the synthesized powder phosphors [19]. From Fig. 9, it is clear that the

Table 3

Emission level peak positions ( $\lambda_p$ , nm) for the transitions  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  and color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) of  $\text{LaPO}_4:\text{Tb}^{3+}$  powder phosphors

Phosphor	$\lambda_p$ (nm)	$\bar{X}$	$\bar{Y}$
GP-1	538	0.245	0.409
GP-2	537	0.225	0.436
GP-3	538	0.271	0.480
GP-4	539	0.262	0.427
GP-5	–	0.283	0.424

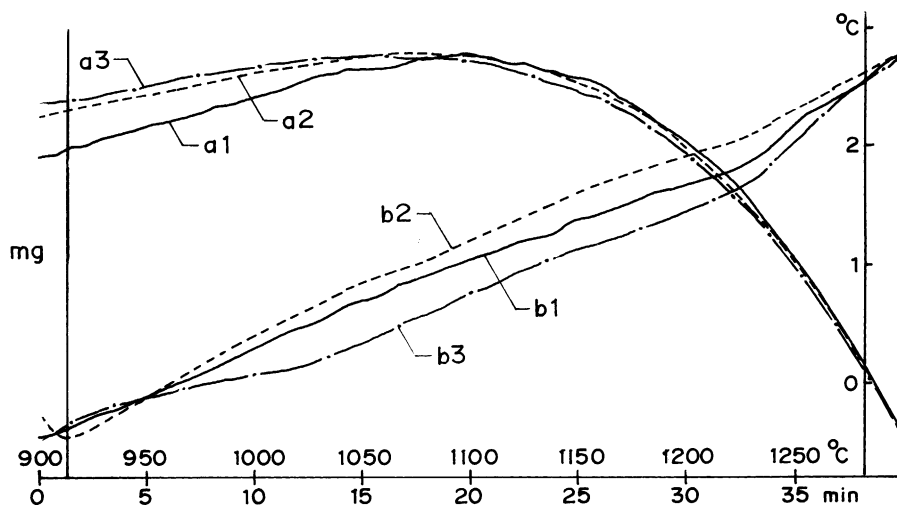


Fig. 8. TGA/DTA curves of (a1/b1)  $Gd_{0.95}PO_4:Eu_{0.05}^{3+}$ , (a2/b2)  $La_{0.95}PO_4:Tb_{0.05}^{3+}$  and (a3/b3)  $La_{0.95}PO_4:Ce_{0.05}^{3+}$  powder phosphors.

obtained color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) are fitted appropriately in the green region (indicated by a marked portion). TGA of  $La_{0.95}PO_4:Tb_{0.05}^{3+}$  indicates the total 0.311% weight loss out of 54.6 mg. No appreciable weight loss in TGA (Fig. 8(a2)) and absence of any noticeable peak in DTA (Fig. 8(b2)) mode indicates thermal stability with respect to chemical as well as crystalline phase transformation changes, in a covered temperature range. As discussed in FT-IR spectrum of  $Gd_{0.95}PO_4:Eu_{0.05}^{3+}$  phosphor, in  $La_{0.95}PO_4:Tb_{0.05}^{3+}$  (Fig. 6(b)), also we have observed two bunches of absorption frequencies attributable to complex  $M-OPO_3$  ( $M = La, Tb$ ) bonds in the wave-number range 1200–900 and 700–400  $cm^{-1}$ , with noticeable little shift in the absorption frequencies [24,28]. From the recorded SEM image of the samples  $La_{0.95}PO_4:Tb_{0.05}^{3+}$  (Fig. 7(b)), it is seen that the individual spherical particles are agglomerated. The grain size is observed to be in the range of 150–200 nm. Based on the computed color coordinates and relative fluorescence intensity ratios ( $R$ ), the optimum

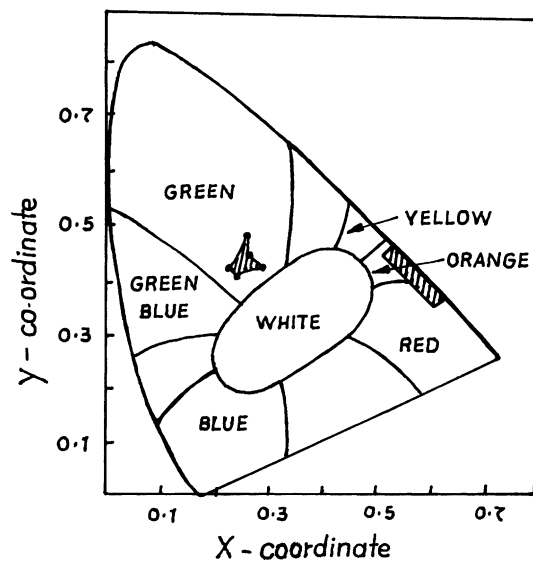


Fig. 9. CIE chromaticity diagram.

Table 4  
Relative fluorescence intensity ratios ( $R$ ) of  $LaPO_4:Tb^{3+}$  powder phosphors

Phosphor	$(^5D_4 \rightarrow ^7F_3)/(^5D_4 \rightarrow ^7F_6)$	$(^5D_4 \rightarrow ^7F_4)/(^5D_4 \rightarrow ^7F_6)$	$(^5D_4 \rightarrow ^7F_5)/(^5D_4 \rightarrow ^7F_6)$	$(^5D_4 \rightarrow ^7F_6)/(^5D_4 \rightarrow ^7F_6)$
GP-1	0.583	0.708 0.750 0.666	1.583	1.000
GP-2	0.437	0.562 0.656 0.437	2.875	1.000
GP-3	0.620	0.721 0.810 0.569	3.025	1.000
GP-4	0.814	0.851 0.888 0.777	1.740	1.000
GP-5	–	–	–	–



Table 5

The relative fluorescence intensity ratios ( $R$ ), emission level peak positions ( $\lambda_p$ , nm) and half width at full maxima ( $\Delta\lambda_p$ , nm) for the transition  ${}^2D \rightarrow {}^2F_{5/2}$  of  $\text{LaPO}_4:\text{Ce}^{3+}$  phosphors

Phosphor	$({}^2D \rightarrow {}^2F_{5/2})/({}^2D \rightarrow {}^2F_{7/2})$ ( $R$ )	$\lambda_p$	$\Delta\lambda_p$
UVP-1	10.22	342	26.10
UVP-2	8.20	341	26.10
UVP-3	24.4	342	24.10
UVP-4	11.9	341	26.10
UVP-5	9.0	341	28.10

concentration of the dopant ion ( $\text{Tb}^{3+}$ ) has been found to be 5 mol.

### 3.3. $\text{Ce}^{3+}$ :phosphors

The trivalent  $\text{Ce}^{3+}$ -ions have an electronic structure containing one 4f-electron and as an activator, they generally result in phosphors having broad band UV emission. In the rare earth phosphates, the emission bands of  $\text{Ce}^{3+}$  are not like those found in other materials [3]. From the measured fluorescence spectra (Fig. 5) of  $\text{Ce}^{3+}$ :phosphors, two bands corresponding to the following electronic transitions are identified [7,32,33]:

- ${}^2D$  (5d)  $\rightarrow$   ${}^2F_{5/2}$  (4f) (342–341 nm)
- ${}^2D$  (5d)  $\rightarrow$   ${}^2F_{7/2}$  (4f) (460–458 nm)

The emission transition  ${}^2D \rightarrow {}^2F_{5/2}$  appears more intense and broader in all  $\text{Ce}^{3+}$ :phosphors. The fluorescence intensity increase with an increase in Ce concentration up to 5 mol, beyond which, the fluorescence intensity tends to quench. It is also noticed that the peak positions of the emission bands have also changed significantly. Since, these phosphors are emitting in the UV region, we could not compute the color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ), however the emission level peak positions ( $\lambda_p$ , nm) and their effective half width at full maxima ( $\Delta\lambda_p$ , nm) are given in Table 5, which significantly change with the chemical composition. The synthesized powder phosphors are also characterized by calculating the relative fluorescence intensity ratios ( $R$ ) (Table 5). TGA of  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  indicates the total 0.344% weight loss out of 66.73 mg. No appreciable weight loss in TGA (Fig. 8(a3)) and the absence of any noticeable peak in DTA (Fig. 8(b3)) mode indicates thermal stability with respect to chemical as well as crystalline phase transformation changes, in a covered temperature range. As has been discussed earlier,  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  also gives same absorption peaks except a few  $\text{cm}^{-1}$  shift in the frequencies (Fig. 6(c)) [28]. From the SEM image of  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  (Fig. 7(c)), it has been noticed that the particles are having spherical shape which tend to agglomerate and size in the range of 150–200 nm. Based on the relative fluorescence intensity ratios ( $R$ ), the concentration of the dopant ion  $\text{Ce}^{3+}$  has been optimized to be 5 mol.

## 4. Conclusions

We have synthesized rich color emitting  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Ce}^{3+}$ -doped powder phosphors by employing a precipitation technique. The phase purity has been verified by XRD and a FT-IR spectral analysis. Based on the color coordinates ( $\bar{X}$ ,  $\bar{Y}$ ) and relative fluorescence intensity ratios ( $R$ ), the optimum concentration of each of the dopant ions ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Ce}^{3+}$ ) has been identified to be 5 mol. From the scanning electron microscopic studies, it has been noticed that the particles are spherical in shape with size varying from 150 to 200 nm, and they tend to agglomerate. From the thermal analysis studies, it has been found that these phosphor materials are quite stable. A systematic studies could therefore result in the formulation of  $\text{Gd}_{0.95}\text{PO}_4:\text{Eu}_{0.05}^{3+}$ ,  $\text{La}_{0.95}\text{PO}_4:\text{Tb}_{0.05}^{3+}$  and  $\text{La}_{0.95}\text{PO}_4:\text{Ce}_{0.05}^{3+}$  phosphors as the three materials in order to observe brighter reddish-orange, green and UV emission from certain electronic display systems.

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