SYNTHESIS RARE EARTH DOPED LAPO$_4$ [X, Y, Z] PHOSPHOR PREPARED USING GREEN CHEMISTRY ROUTE

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Abstract: The present paper reports the synthesis of phosphors using green chemistry route (Solid State reacting Method) and Photoluminescence (PL) of the $LaPO_4$ phosphor doped with Ce Tb, and Eu rare-earth ions, keeping Ce, Tb, concentration constant (0.5mole wt. %) and varying Eu concentration. The phosphors were synthesized using the standard solid state reaction technique and ground using mortar and pestle, fired at 1200^oC for 3 hour in a muffle furnace. We have studied the effect of dopants on the Photoluminescence $LaPO_4$ phosphor was observed at 470 nm. Under the excitation of 254nm wavelength, PL properties of the samples using Spectrofluorophotometer at room temperature. PL emission of doped $LaPO_4$ phosphor shows peaks at 414, 437, 457, 473, 487, 545, 589, 595, 614 and 622 nm with good intensity.

Keywords: Photoluminescence (PL); XRD;; solid state reaction (SSR) ;

Introduction: Various phosphor materials have been actively investigated to improve their photo luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colours.

The applications of rare earth element compounds, especially lanthanide phosphate doped inorganic materials, have been touched upon broadly. Over the past a few years, they have been applied in many fields, such as optical display panels, cathode ray tubes, optoelectronic, sensitive device, nanoscale electronic and plasma display panels[1–4] due to their special chemical and physical properties. Phosphors are widely used in displays and lighting devices.

Experimental: $LaPO_4$ phosphor doped with Ce ,Tb concentration constant and varying Eu concentration were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La_2O_3), Diammonium Hydrogen Phosphate [$(NH_4)_2$ H PO_4),Europium Oxide (Eu_2O_3),Terbium Oxide (Tb_4O_7) and Cerium Oxide (Ce_2O_3) were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200°C for 3 hour in a muffle furnace at the rate of 250°C per hour. The prepared samples were again powdered for taking the measurements. Photoluminescence (PL) of the $LaPO_4$ phosphor doped with Ce ,Tb and Eu rare-earth ions were recorded with Shimadzu 5301R Spectrofluorophotometer at room temperature.

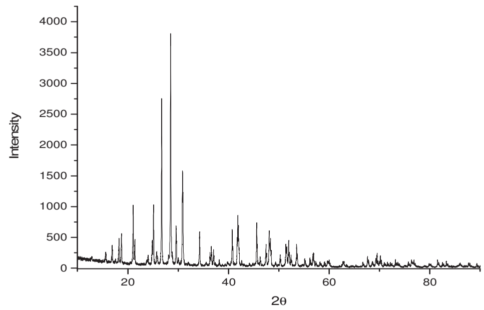


Fig.1. XRD Pattern of $LaPO_4$

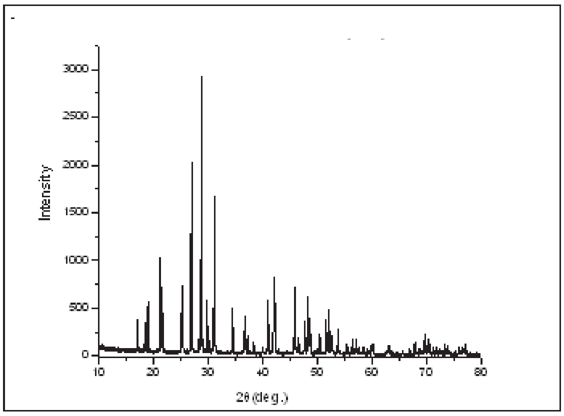


Fig.2. XRD Pattern of $LaPO_4$: Ce Tb, Eu

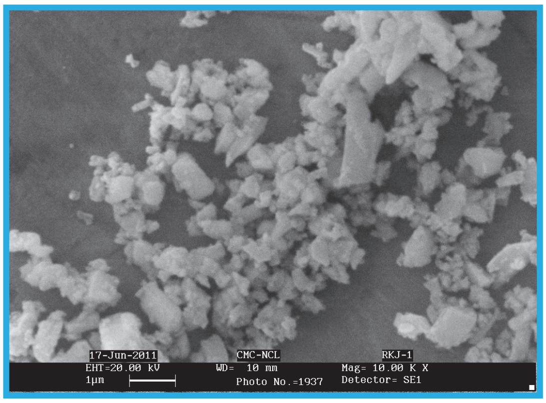
Results And Discussion:

X-ray diffraction study: The crystalanity and phase purity of the phosphors were firstly examined by XRD analysis. Fig 1&2 shows the typical X-ray diffraction (XRD) patterns of synthesized samples of pure

LaPO4 and $LaPO_4$ dopped with Ce.Tb, Eu,. As shown XRD patterns of nanocrystals are in good agreement with the values from JCPDS no.35-731of $LaPO_4$, which shows that all the products are monazite $LaPO_4$ with monoclinic structure. The main peak was found around 28.5^o corresponding to a d value of about 3.11A^o, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate[5-6]. All diffraction patterns were obtained using CuKα radiation (λ = 1.540598 A^o) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. When crystallites are less than approximately 100 nm in size, appreciable broadening in X-ray diffraction lines occurs. The crystallite size of particles of powder sample were calculated by using Scherer equation $D= 0.9 \lambda / \beta\cos\theta$ Where β represents full width at half maximum (FWHM) of XRD lines =0.098

λ = Wavelength of the X-rays.(0.154 nm in the present case),θ = Braggs angle of the XRD peak.=14.35^O

The average crystallite size of $LaPO_4$ phosphors is 59 nm and when doped with RE dopants, the crystallite size becomes 75.04 nm.



Scanning Electron Microscopy

Fig.3. SEM image of $LaPO_4$

SEM image of pure $LaPO_4$ at 1200°C for 4 hours and SEM image of $LaPO_4$: Ce,Tb, Eu, as shown in Figure.3 and Fig.4. respectively. Fig 3.reveals the crystals with irregular shape having an average basal diameter 300 nm and length 1.5 μm.

Fourier Transforms Infrared Spectroscopy: This technique has been used to identify the reaction between solids, by monitoring the vibrational and rotational motion of the molecules during the reaction. The FTIR spectrum of undoped LaPO4 has been depicted in Fig.4. The most of the bands are characteristics of vibration of phosphate group. So the characteristics of monoclinic phase of four bands located at 543,564, 577, 617 cm^{-1} were clearly observed. The data from the graph shows that, the presence of H_2O in the material is detected by the broad peaks 3674, 3730, 3836. These bands may be due to the stretching vibration of hydroxyl (OH) complexes, which is due to the absorbed water molecules on the surface of the phosphor material.The typical bands assigned to the phosphate groups (PO_4^{3-}) can be detected in the spectra.

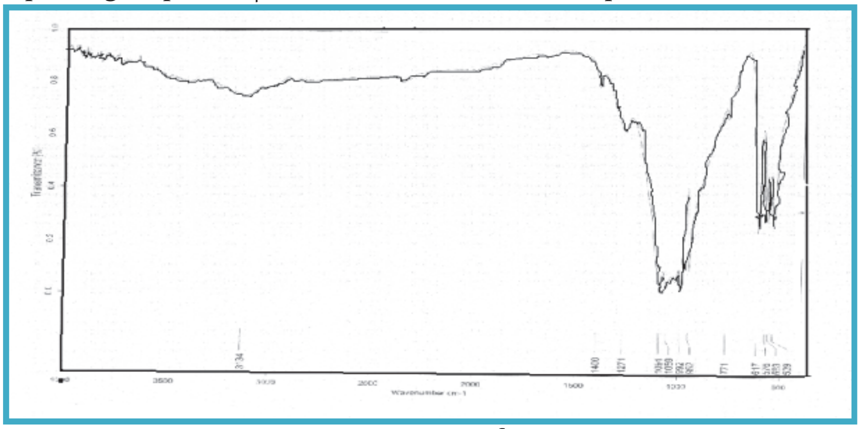


Fig 4.FTIR of $LaPO_4$

The band centered at $1092cm^{-1}$ is a characteristic of the v_3 anti-symmetric stretching of P–O band while the two bands located at between 617 and 543 cm^{-1} can be attributed to the v_4 region of the vibrations of PO_4^{3-} groups. The shoulder at $953cm^{-1}$ can be assigned to the v_1 vibration of PO_4^{3-} groups. These bands are obvious characteristic of the vibrations of the phosphate groups in monoclinic $LaPO_4$. This observation indicates that monoclinic $LaPO_4$: Tb, Eu, Ce, exists in the specimen.

Photo luminescence study: Fig.7 shows photoluminescence of $LaPO_4$ phosphor doped with Ce Tb and Eu rare-earth ions, keeping Ce and Tb concentration constant and varying Eu concentration as were prepared using solid state synthesis method are successfully synthesized. The PL emission of undoped $LaPO_4$ phosphor was observed at 470 nm. Under the excitation of 254nm wavelength, PL emission of doped $LaPO_4$ phosphor shows peaks at 358, 380, 415, 437, 457, 473, 488, 545, with good intensity and three peaks at 589, 594, 613 and 622 with less intensity. The excitation of the material with 254 nm wavelengths generates a strong emission at 545 nm.. It is also observed from the figure, three additional peaks at 488 nm, 613 nm and 622 nm with less intensity.

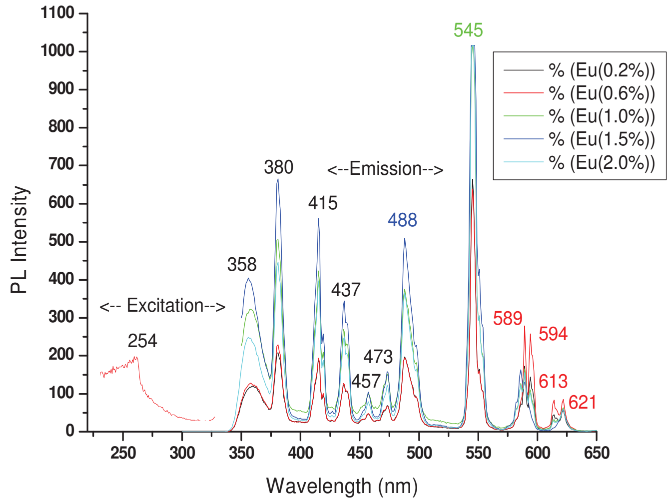


Fig.5. Photoluminescence Spectra of $LaPO_4$:Ce (1.0%),Tb (1.0%), Eu

In $LaPO_4$, La acts as host, Eu, Ce acts as sensitizer, Tb^{3+} acts as activator, and the four emission peaks in emission spectrum are produced by Tb^{3+}. 488 nm ($^5D_4$-$^7F_6$) , 545 nm ($^5D_4$-$^7F_5$) , 588 nm ($^5D_4$-$^7F_4$) , 622 nm ($^5D_4$-$^7F_3$) The transition emission in $^5D_4$-$^7F_5$ level is the strongest emission. Under the excitation of 254nm wavelength, PL emission of doped $LaPO_4$ phosphor shows peaks at 358, 380, 415, 437, 457, 473, 488, 545, with good intensity and three peaks at 589, 594, 613 and 622 with less intensity.

Fig.5 presents the emission spectra of different $LaPO_4$: Ce (1.0%),Tb (1.0%), Eu specimens. The peaks at 588 and 595nm corresponding to orangered color are derived from the allowed magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$), whose intensity is barely affected by the crystal environments surrounding Eu^{3+}. The peaks at 613 and 622nm corresponding to red color are generated from the forced electric dipole transition ($^5D_0 \rightarrow ^7F_2$), whose intensity is hyper-sensitive to crystal fields. Here, Eu^{3+} ion is allowed to occupy a site without an inversion center [20]. Compared with $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$, the intensities of $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ were suppressed greatly. The emission intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu^{3+} ions in the matrix [21,22].

In the trivalent rare earth ions, the luminescence arises mainly due to transactions within the 4 f shell. The efficiency of emission depends on the number of electrons in the 4f shell. The Tb^{3+} ion has 8 electrons in the 4f shell, which can be excited in the 4f-5d excitation band. The electron in the excited $4f^7$ - 5d state remains at the surface of the ion and comes under the strong influence of the crystal field resulting in the splitting of the excitation band. The excitation Spectra thus has multiple peaks. The excited ion in the $4f^7$ - 5D State decays stepwise from this state to the luminescent levels $5D4f_3$ or $5d4f_4$ by giving up phonons to the lattice. Luminescence emission occurs from either of these states, with the ion returning to the ground state. The materials present is very attractive luminescent properties for the generation of the three primary colors, due to the red, green and blue emissions of $LaPO_4:Eu^{3+}$, $LaPO_4:Tb^{3+}$ and $LaPO_4:Ce^{3+}$, respectively. There are in fact multiple emission lines at each of these due to the crystal field splitting of the ground state of the emitting ions. As the Eu concentration increases the PL intensity also increases.

Conclusion: $LaPO_4$ phosphor doped with rare-earth ions, keeping Ce ,Tb concentration constant while Eu varying concentration were prepared using green chemistry route (solid state synthesis method) are successfully synthesized. The PL intensity is very high therefore; the RE doped $LaPO_4$ phosphors can be used in various display.

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