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Synthesis and Characterization of Nano Monazite-Type LaPO₄: Ce, Tb, Eu, Phosphor

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Abstract— The present paper reports the Characterization and Photoluminescence (PL) of the LaPO₄ phosphor doped with Ce Tb, and Eu rare-earth ions, keeping Ce, Tb, concentration constant (0.5mole wt. %) and varying Eu concentration as 0.1,0.5 1.5%, and 2.0% is described. The phosphors were synthesized using the standard solid state reaction technique and ground using mortar and pestle, fired at 1200°C for 1 hour in a muffle furnace. We have studied the effect of dopants on the Photoluminescence LaPO₄ 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 LaPO₄ phosphor shows peaks at 359,363, 380, 414, 437, 457, 473, 487, 545, 589, 595, 614 and 622 nm with good intensity.

It is also found the emitted wavelengths were increased their intensities with increase in Eu concentrations in blue green region.

Keywords— Photoluminescence; XRD; phosphor rare-earth ions; solid state reaction; FTIR: Particle size.

1. INTRODUCTION

Recently various phosphor materials have been actively investigated to improve their uminescent 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 useful applications of rare earth element compounds, phosphate lanthanide doped especially inorganic materials, have been touched upon broadly. Over the past a few years, they have been applied in many fields, such optical display panels, cathode ray as 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. Varioussolution-phase routes, including solid state eaction, sol-gel, precipitation, water oil micro emulsion, polyol-mediated process, ultrasonification, hydrothermal, and mechanochemical method [5-8], have been tried to lower the reaction temperature and obtain high-quality LaPO₄ based nanoparticles. However, the simple and mass fabrication of LaPO₄ nanocrystals with narrow grain size distribution and uniform morphology still remains a challenge [7-10]. We adopted the standard solid state reaction technique to prepare LaPO₄ with good morphologies and fine crystal structures, particle size and its emission and intensity of luminescence were also studied. The present paper reports the Photoluminescence (PL) of the $LaPO_4$ phosphor doped with Ce and Tb rare-earth ions, keeping Ce, Tb concentration constant (1.0 mole wt. %) and varying Eu concentration.

2. EXPERIMENTAL SECTION

LaPO₄ phosphor doped with Ce Tb, and Eu rare-earth ions, keeping Ce, Tb concentration constant and varying Eu concentration as 0.5, 1.0, 1.5 and 2.0 mole wt % were prepared using solid state synthesis method. Stoichiometric proportions of raw materials namely, Lanthanum Oxide (La2O3), Diammonium Hydrogen PO₄), Phosphate $[(NH_4)_2]$ Η Europium Oxide (Eu_2O_3) , Terbium Oxide (Tb_4O_7) and Cerium Oxide (Ce₂O₃) were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200°C for 4 hour in a muffle furnace at the rate of 300°C per hour. The prepared samples were again powdered for taking the measurements. Photoluminescence (PL) of the LaPO₄ phosphor doped with Ce, Tb and Eu rare-earth ions were Spectrofluorophotometer recorded with at room temperature.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Study (Phase Purity and Structure)

The crystallinity and phase purity of the product were firstly examined by XRD analysis. Fig 1&2 shows the

typical X-ray diffraction (XRD) patterns of synthesized samples of pure LaPO4 and LaPO₄ dopped with Ce.Tb, Eu, As shown XRD patterns of nanocrystals are in good agreement with the values from JCPDS no.35-731of LaPO₄, which shows that all the products are monazite LaPO₄ with monoclinic structure [12]. The main peak was found around 28.5[°] corresponding to a d value of about 3.11A[°], followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate[5-7]. All diffraction patterns were obtained using CuK α radiation ($\lambda = 1.540598 \text{ A}^{\circ}$) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. Measurements were made from 2 $\theta = 100$ to 800 with steps of 0.008356[°].

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 62 nm and when doped with RE dopants, the crystallite size becomes 80.04 nm.



Fig. 1: X-Ray Diffraction Pattern of LaPO₄



Fig. 2: XRD Pattern of LaPO₄: Ce Tb, Eu

3.1.1 Scanning Electron Microscopy

SEM image of pure $LaPO_4$ at $1200^{\circ}C$ 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 μ m, while in Fig.4.the crystals appears to be irregular shape having an average basal diameter of 300 nm and length of 1.3 μ m.



Fig. 3: SEM image of LaPO₄



Fig. 4: SEM image of LaPO₄: Ce Tb,Eu

3.1.2 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 and LaPO₄ doped Tb, Eu, Ce, has been depicted in Fig.5 and 6. shows FTIR analysis. 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 H₂O 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. [14-16]. The



Fig. 5: FTIR spectrograph of LaPO₄



Fig. 6: FTIR Spectograph of LaPO₄: Ce, Tb,Eu

typical bands assigned to the phosphate groups (PO4 $^{3-}$) can be detected in the spectra.

The band centered at 1092 cm^{-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 PO₄³⁻ groups. The shoulder at 953 cm⁻¹ can be assigned to the v_1 vibration of PO₄³⁻ groups. These bands are obvious characteristic of the vibrations of the phosphate groups in monoclinic LaPO₄. This observation indicates that monoclinic LaPO₄: Tb, Eu, Ce, exists in the specimen.

3. PHOTO LUMINESCENCE STUDY



Fig. 7: Photoluminescence Spectra of LaPO₄:Ce (1.0%),Tb (1.0%), Eu varying.

Fig.7 shows photoluminescence of LaPO₄ 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 LaPO₄ phosphor was observed at 470 nm. Under the excitation of 254nm wavelength, PL emission of doped LaPO₄ 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 inset in the Fig.7 is the PL emission of Tb in the range 450 - 650 nm. It is also found the emitted wavelengths were increased their intensities with increase in Eu concentrations in blue green region.

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.

In LaPO₄, 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 (${}^{5}D_{4}$ - ${}^{7}F_{6}$), 545 nm (${}^{5}D_{4}$ - ${}^{7}F_{5}$), 588 nm (${}^{5}D_{4}$ - ${}^{7}F_{4}$), 622 nm (${}^{5}D_{4}$ - ${}^{7}F_{3}$)

The transition emission in ${}^{5}D_{4}$ - ${}^{7}F_{5}$ level is the strongest emission.

Under the excitation of 254nm wavelength, PL emission of doped LaPO₄ 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.7 presents the emission spectra of different LaPO₄: 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 $({}^{5}D_{0} \rightarrow {}^{7}F_{1})$, 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 (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$), whose intensity is hyper-sensitive to crystal fields. Here, Eu³⁺ ion is allowed to occupy a site without an inversion center [20]. Compared with ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, the intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ were suppressed greatly. The emission intensity ratio of ${}^5\!D_0\!\!\to\!\!{}^7\!\bar{F_2}$ to ${}^5\!D_0\!\!\to\!\!{}^7\!F_1$ gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu³⁺ 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. [19,20] 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.[21-25]. 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 LaPO₄:Eu³⁺, LaPO₄:Tb³⁺ and LaPO₄:Ce³⁺, 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.

4. CIE COORDINATES



Fig. 8: CIE coordinates on 1931 chart for LaPO₄: : Ce, Tb,(1.0%) Eu

Fig..8. shows the Commission Internationale de l'Eclairage (CIE) coordinates which are calculated using the spectral energy distribution (1931 chart). The CIE coordinates of the undoped LaPO₄ sample are x = 0.16 and y = 0.19. When LaPO₄:, Ce, Tb, Eu powder is excited by 254 nm wave length UV light, its chromatic coordinates obtained are x = 0.266 and y = 0.72

The peak value of wave length = 545 nm,

Half-width = 4 nm,

The color coordinate of the sample is very large and it decreases the level of red color. Therefore LAP green phosphor has good luminescent properties and applications.

5. CONCLUSION

LaPO₄ phosphor doped with Ce, Tb, Eu and rare-earth ions, keeping Ce, Tb concentration constant (0.5 wt. mole %)and Eu varying concentration as 0.5,1.0, 1.5 and 2.0 wt. mole % were prepared using solid state synthesis method are successfully synthesized. The main peak in XRD pattern was found around 28.5° corresponding to a d- value of about $3.11A^{\circ}$, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate. Particle size of the phosphor is about 40 micrometer. As the Eu concentration increases the PL intensity also increases. The PL intensity is very high therefore; the LaPO₄: Ce, Tb, Eu, phosphors can be easily applied in various types of lamp and display.

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