Photoluminescence Investigation of Nano-Monazite-Type Lapo4:Tb and Laypo4:Tb Phosphor

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Abstract— Recent investigations in technology reveal that nanometer sized compounds have attracted considerable attention due to their novel size- dependent characteristics, different physio-chemical and optoelectronics properties compared with the bulk counterparts,[1-4] 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 colors. The present paper reports the synthesis, characterization and Photoluminescence (PL) of the $LaPO_4$: Tb and $LaYPO_4$: Tb (0.5%) phosphor doped with Tb (0.5%) rare-earth ions. The phosphors were synthesized using the standard solid state reaction technique and ground using mortar and pestle, fired at 1200°C for three hours in a muffle furnace. The effect of dopants on the Photoluminescence of $LaPO_4$ phosphor was observed at 470 nm under the excitation of 254nm wavelength, PL of the phosphors are recorded using SHIMADZU Spectrofluorophotometer at room temperature. PL emission of doped $LaPO_4$: Tb (0.5%) phosphor shows peaks at 365, 380,416,437,451,469, 483,545nm whereas. PL emission of doped $LaYPO_4$: Tb (0.5%) phosphor shows peaks 366, 396,451, 469, 589 and 595 nm. The phosphors are also characterized using XRD, SEM, Relative pressure, pore size and Particle Size studies.

Keywords: Photoluminescence, XRD, Phosphor Rare-Earth Ions, SSR Technique, PL, BET Surface Area, Particle Size

I. INTRODUCTION

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 colors. The useful 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 due to their special chemical and physical properties. We adopted the standard solid state reaction technique to prepare $LaPO_4$ and $LaYPO_4$ 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 $LaPO_4$: Tb (0.5%) and $LaYPO_4$: Tb (0.5%) phosphor doped with Tb rare-earth ions, concentration (0.5 mole wt. %).

II. EXPERIMENTAL

$LaPO_4$: Tb (0.5%) and $LaYPO_4$: Tb (0.5%) phosphor doped with Tb rare-earth ions concentration (0.5 mole wt. %) 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], Terbium Oxide (Tb_4O_7), Yttrium Oxide (Y_2O_3) were grinded in an agate motor and mixed and compressed into a crucible and heated at 1200^0C for three hours in a muffle furnace at the rate of 300^0C per hour. The prepared samples were again powdered for taking the measurements. Photoluminescence (PL) of the $LaPO_4$: Tb (0.5%) and $LaYPO_4$: Tb (0.5%) phosphor doped with Tb earth ions were recorded with Spectrofluorophotometer at room temperature.

III. RESULTS AND DISCUSSION

A. *X-ray diffraction study (Phase purity and structure):-*

The crystallinity and phase purity of the product were firstly examined by XRD analysis. (Fig1&2). As shown XRD patterns of nanocrystals are in good agreement with the values from JCPDS no.(35-731) of $LaPO_4$, and (32-0493)of $LaYPO_4$ which shows that all the products are monazite $LaPO_4$ with monoclinic structure. The main peak was found around 29^0 corresponding to a 'd' value of about $3.10A^0$, followed by other less intense peaks corresponds to the monoclinic system of crystal structure of Lanthanum Phosphate[5-7]. Fig.1 $LaPO_4$ doped Tb and Fig.2 $LaYPO_4$ doped Tb (0.5%).The diffraction patterns were obtained using CuKα radiation (λ = 1.540598 A0) at 40 kv and 30 mA, and divergence slit fixed at 1.52 mm. Measurements were made from $2\theta = 10^0$ to 80^0 with steps of 0.008356^0.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-(FWHM) of XRD lines. The average crystallite size of $LaPO_4$: Tb the grain size is 85nm. Whereas the crystallite size of $LaYPO_4$ is 74 nm.

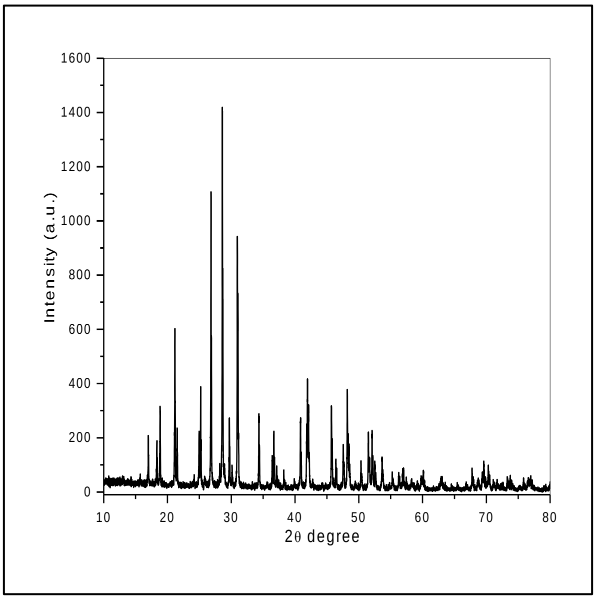

Fig. 1: XRD Pattern of $LaYPO_4$:Tb

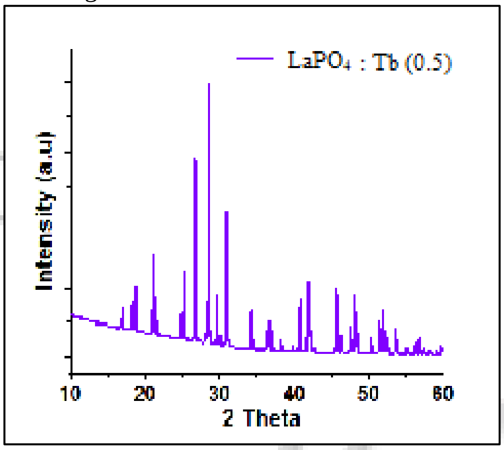

Fig.2. XRD Pattern of $LaPO_4$:Tb

B. *Scanning Electron Microscopy:*

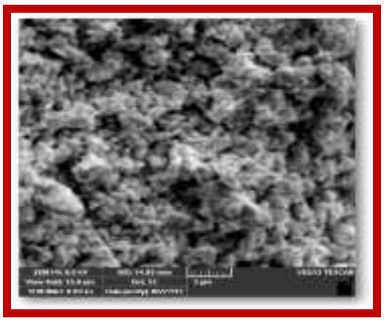

Fig. 3: SEM image of $LaYPO_4$:Tb

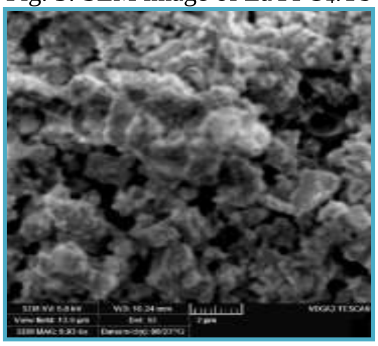

Fig. 4: SEM image of $LaPO_4$:Tb

SEM image of pure $LaYPO_4$:Tb(0.5%) at 1200^{0}C for 4 hours and SEM image of $LaPO_4$: Tb (0.5%) as shown in Figure.3 and Fig.4. respectively. Fig 3.reveals the crystals with irregular shape having an average basal diameter 305 nm and length 1.6 µm, while in Fig.4.the crystals appears to be irregular shape having an average basal diameter of 1.8 µm and length of 1 µm.

C. *Photoluminescence study:*

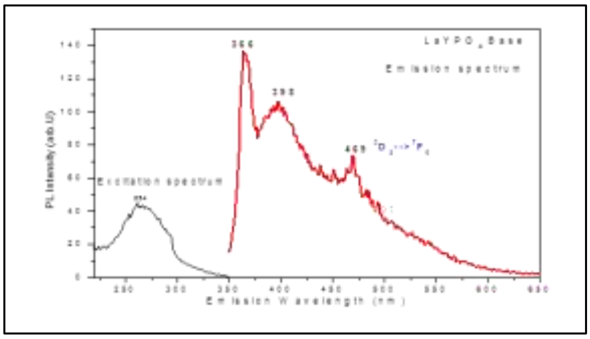

Fig. 5: Photoluminescence spectra of $LaYPO_4$: Tb (0.5%)

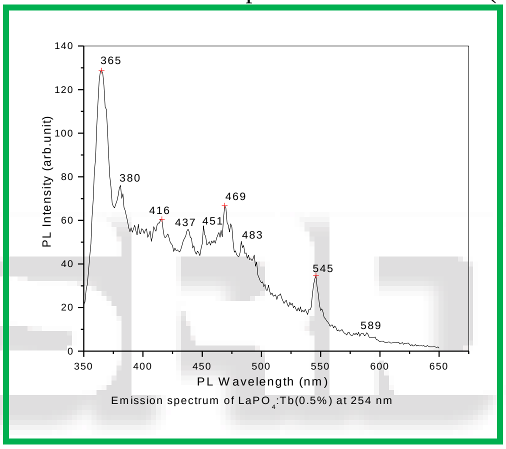

Fig. 6: Photoluminescence spectrum of $LaPO_4$: Tb (0.5%).

Fig.5and Fig. 6 shows photoluminescence spectrum of undoped $LaPO_4$ phosphor and $LaPO_4$ doped with Tb (0.5%) The PL emission of undoped $LaPO_4$ phosphor was observed at 470 nm. Under the excitation of 254 nm wavelength, PL emission of doped $LaPO_4$: Tb phosphor shows peaks at 365,380,416,437, 451,469, 483,545nm with good intensity whereas PL emission of doped LaY PO_4 : Tb phosphor shows peaks at peaks 366, 396,451, 469, 589 and 595 nm.

In $LaPO_4$:Tb and $LaYPO_4$:Tb, La acts as host and Tb^{3+} acts as activator, and the four emission peaks in emission spectrum are produced by Tb^{3+} and assigned to 483 nm ($^5D_4$-$^7F_6$) , 545 nm ($^5D_4$-$^7F_5$) [9,10]. The transition emission in $^5D_4$-$^7F_5$ level gives the emission at 545nm. [11, 12]. 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 [8]. 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 $^5D_4$ F_3 or $^5d_4$- F_4 by giving up phonons to the lattice. Luminescence emission occurs from either of these states, with the ion returning to the ground state [7-9].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. [9].

D. Brunauer Emmett and Teller (BET) analysis (Pore size and relative pressure):

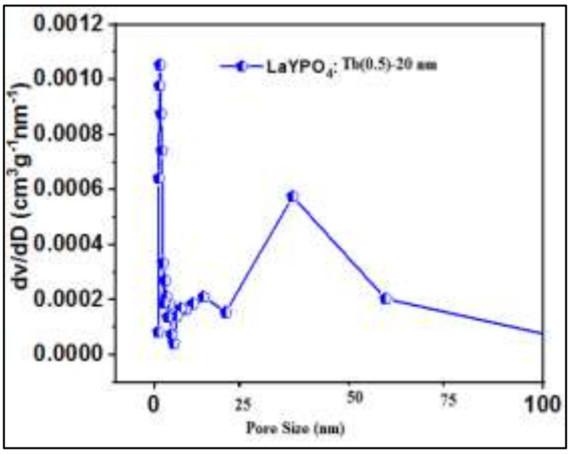

Fig. 7: Pore size of $LaYPO_4$:Tb

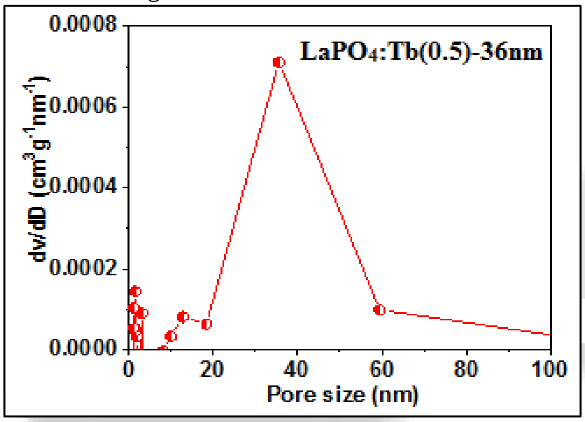

Fig. 8: Relative pressure of $LaPO_4$:Tb

Pore Size: The aim of this study is to give insights on the optimum PSD that can provide accessible surface area and faster diffusion for phosphate adsorption. (Fig.7 and Fig.8). This will thus help in designing an adsorbent that has a high phosphate adsorption capacity along with good adsorption kinetics. Pore size of maximum number of particles of $LaPO_4$: Tb (0.5%) is found to be of 36 nm. Pore size of maximum number of particles of $LaYPO_4$: Tb (0.5%) is found to be of 20 nm

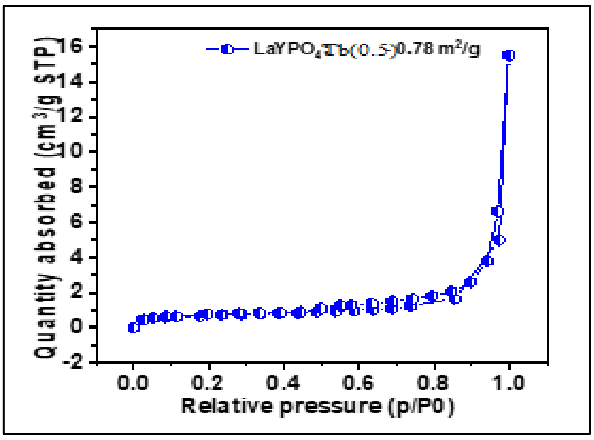

Fig. 9: Relative pressure of LaYPO4:Tb

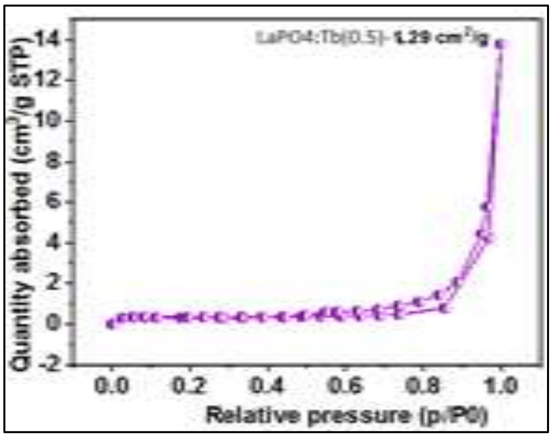

Fig. 10: Relative pressure of LaPO4:Tb

Relative Pressure: These results can be explained by considering the larger surface area to volume ratio of the smallest particles and increased internal surface area of the pores found in the large particles.(Fig.9, Fig.10) For the small particles, the additional surface area hosts adsorbents that lead to non-radiative recombination, and in the porous particles, the pore walls can quench fluorescence. As relative pressure increases the quantity absorbed also increases after relative pressure 0.8 cm^2/g (p/P0) and becomes equal to 1.01 cm2/g.

E. Particle size analysis:

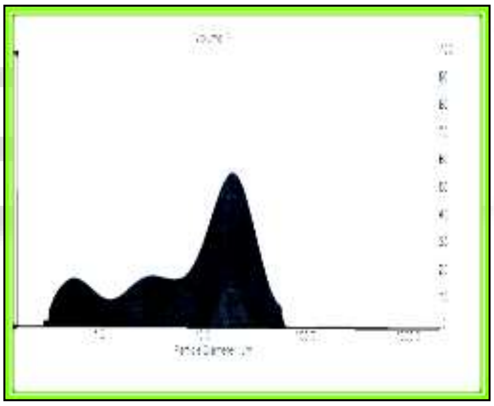

Fig. 11: Particle histogram of $LaYPO_4$:Tb

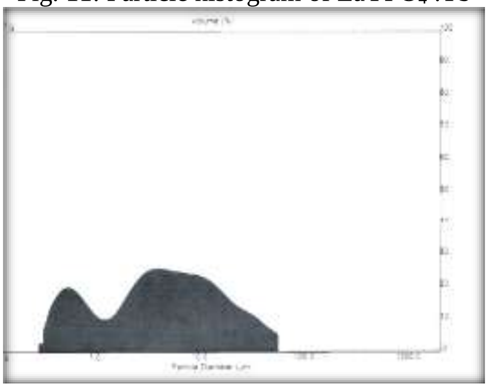

Fig. 12: Particle size histogram of $LaPO_4$:Tb

The Particle size distribution histograms of the $LaPO_4$ and $LaYPO_4$: Tb (0.5%) particles are depicted in Fig.11 and Fig.12. The mean diameter of the particle size of $LaPO_4$ is 0.8 µm and 55 µm while the mean diameter of the particle size of $LaYPO_4$:Tb (0.5%) is 0.6 µm and also around 5 µm. From the data the average surface area of the particle in $LaPO_4$ phosphor was found to be 1.7770 m^2/g. Whereas the average surface area of the particle in $LaYPO_4$: Tb (0.5%) phosphor is found to be approximately 1.1216 m^2/gram.

Therefore it was concluded that, more groundings of the phosphor material is required to get uniform particle size.

IV. CONCLUSIONS

$LaPO_4$: Tb and $LaYPO_4$: Tb phosphor doped with Tb (0.5 wt. mole %) were prepared using solid state synthesis method are successfully synthesized. The main peak in XRD pattern was found around 29^Ocorresponding to a d- value of about 3.10 A^O. The PL peaks $LaPO_4$: Tb (0.5%) sample shows maximum intensity is for 545 and 595 nm as compared to $LaYPO_4$: Tb (0.5%). Therefore $LaPO_4$:Tb (0.5%) phosphors can be easily applied in various types of lamp and display.

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