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Photoluminescence Studies of Tb^{3+} Activated Nano $La_{0.5}Al_{0.2}Y_{0.3}PO_4$ Phosphor

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Abstract— *The present paper reports, synthesis and photo luminescence (PL) studies of the Tb^{3+} (0.5%) doped $La_{0.5}Al_{0.2}Y_{0.3}PO_4$ phosphor and Tb^{3+} (0.5%) doped $La_{0.5}Al_{0.2}Y_{0.3}PO_4$ phosphor with citric acid as flux under 254 nm excitation. The samples were prepared by solid state diffusion reaction method, which is the suitable method for large scale production. The received phosphor samples were characterized using XRD, SEM, PL, FTIR CIE techniques and particle size distribution.For both the phosphors the PL emission mainly concentrates around 544 nm when excited with 254 nm. For $La_{0.5}Al_{0.2}Y_{0.3}PO_4$: Tb^{3+} (0.5%) the ion radius distinction between La^{3+} Al^{3+} and $Y3^{+}$ is so large so it shows the pure monoclinic phase. From the XRD data, using the Scherer's formula, the calculated average crystallite size of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb^{3+}(0.5%) is around 34.5nm and particle size is 5 µm.The present phosphor can act as a single host for green light emission which is used in X-Ray monitoring, imaging, scintillators and bio-medical imaging applications.*

Keywords— *Photoluminescence (PL), Tb^{3+} doped phosphor, Micrometer (µm), CIE coordinates*

1. INTRODUCTION

The phosphors are used in cathode ray tubes (CRTs), Projections Television (PTVs), fluorescent tubes, X-ray detectors and field emission displays (FED), etc. [1] Rare earth ortho phosphates have been extensively applied as phosphors because excellent luminescent properties [2,3]. $LaPO_4$; Ce, Tb Phosphor have been used as green emission component of the Tri-Chromatic Luminescent Lamp [4,5]. Recently a new promising phosphor $La_{0.5}Y_{0.5}PO_4$ was developed by Hydro Thermal Synthesis [6].The luminescence associated with Tb content in different host lattices has found applications related to its green light emission, which is important in the field of displays, sensors and lasers.[7] The past few decades have seen a lot of work reported on the use of Tb as a dopant in Phosphate Phosphors as they have very good optical properties (Green – Orange Regions); which make them part of many display devices. Among all the rare earth ions, Tb^{3+} is the most extensively studied, owing to the simplicity of its spectra and also its use in commercial green phosphors.

For $REPO_4$ phosphor light RE^{3+} with larger ionic radius, the monoclinic crystal phase structure is preferred. For $REPO_4$ phosphor of middle RE^{3+} with intermediate radius a partly hydrated hexagonal structure is favorable. For $REPO_4$ Phosphor heavy RE^{3+} with smaller radius, a tetragonal crystal phase is adopted. Therefore, it is very interesting that what will happen when rare earth ions with different radii are introduced into one $REPO_4$ systems. Mixed ortho phosphates composed of three elements have been investigated indicating that these phosphates can be used as a host lattice for spectroscopic investigations [8-12].In this study, we prepared $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:$Tb^{3+}$ (without and with flux)phosphors that exhibit broad excitation ranges of 240nm – 310 nm and another peak at 360nm using high temperature solid state reaction method. Furthermore, the photo luminescent properties of the powders under 254 nm excitation was investigated. We have investigated the crystal phase structure, micro structures (Morphology and Particle size) of the mixed ortho phosphates. The characterization of the prepared material was done using XRD, SEM, PL, FTIR, CIE studies and particle size distribution.

2. SYNTHESIS OF MIXEDPHOSPHATES

The starting materials Lanthanum oxide (La_2O_3), yttrium oxide (Y_2O_3), Aluminum oxide(Al_2O_3), (NH_4) H_2PO_4, Terbium oxide (Tb_4 O_7) and Citric acid of high purity (99.9%) chemicals were used as starting materials to prepare $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb doped phosphors. Lanthanum oxide (La $_2O_3$), Aluminum oxide(Al_2O_3), Yttrium oxide in stoichiometric proportions is weighed and ground into a fine powder using agate mortar and pestle. The grounded sample was placed in an alumina crucible and fired at 1200°C for 3 hours in a muffle furnace with a heating rate of 5°C /min. The sample is allowed to cool to room temperature in the same furnace for about 20 hours. Rare earth ion Tb was doped 0.5 molar percentage. The sample was found out to be white who is studying for photoluminescence.

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3. PHYSICAL CHARTERIZATION

The X-ray powder diffraction (XRD) pattern of samples is performed on a Rigaku-D/max 2500 using Cu Kα radiation. The microstructures of the sample were studied using scanning electron microscopy (SEM) (XL 30 CP Philips). The particle size distribution histogram recorded and particle size was measured using laser based system Malvern instrument U.K. Spectrofluorophotometer (SHIMADZU, RF-5301 PC) was used for PL studies. All the PL spectra were recorded at room temperature.

4. RESULTS AND DISCUSSIONS

4.1 Crystal Phase and Microstructure of Mixed Rare Earth Phosphate

The present study focuses on the XRD pattern of $La_{0.5}Al_{0.2}Y_{0.3}$ PO_4 doped with Tb^{3+} is shown in figure 1. From the XRD pattern, it was found that the prominent phase formed in $La_{0.5}$ $Al_{0.2}$ $Y_{0.3}PO_4$, after diffraction peaks were well indexed based on MATCH no. 96-900-1650 indicating the monoclinic phase of monazite structure. The main peak was founded around 28.752° corresponding to a d-value of about 3.10A° followed by other less intense peaks corresponds to the monoclinic system of crystal structures of Lanthanum Aluminum Yttrium phosphate. All diffraction patterns were obtained using Cu Kα radiation (λ= 1.54060 A°). Measurements were made from 2θ=10° to 60° with steps of 0.008356°. Li et.al, have studied the crystal phase structure of the mixed rare earth phosphates indicating the pure $LaPO_4$and YPO_4 crystallize in monoclinic phase and tetragonal phase respectively, while the mixed phosphate $La_{0.5}Y_{0.5}$ PO_4 belong to the hexagonal phase [6]. Bing Yan et.al studied with La^{3+} to Y^{3+} of 9:1 molar ratio, the product shows the pure monoclinic phase, just like pure $LaPO_4$ [6].

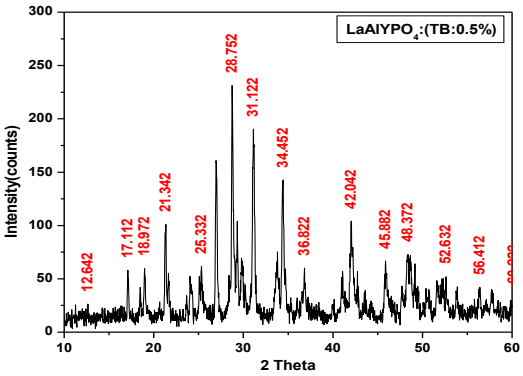


Fig. 1: XRD Pattern of LaAlYPO:Tb (0.5%)

The crystallite size was calculated using the Scherrer equation D=k λ/β cos θ. Where the constant (0.9) λ the wavelength of X-rays (1.54060 A°), β the full-width at half maxima (FWHM) and θ the Bragg angle of the XRD peak. The calculated average crystallite size of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb^{3+} (0.5%) is ~ 34.5nm and particle size is 5 µm. Fig. 1 is the. XRD pattern of $La_{0.5}Al_{0.2}Y_{0.3}$ PO_4 :Tb (0.5%.)

4.2 SEM Study

Characterization of particles, surface morphology and size of nano crystals is done routinely using scanning electron microscope. The main advantage of SEM is that they can be used to study the morphology of prepared nano particles and nano composites. Direct size measurements obtained from images are often used in conjunction with other measurements such as powder, X-ray diffraction (XRD). Figure 2 shows the SEM micrographs of $La_{0.5}Al_{0.2}Y_{0.3}$ PO_4:Tb (0.5%) phosphors. Direct size measurements obtained from images and the average particle diameter is observed. From the Scanning Electron Micrographs of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$: Tb (0.5%) phosphors, it is found the particles are irregular in shape with various sizes from of submicron to few micros and also clusters are found.

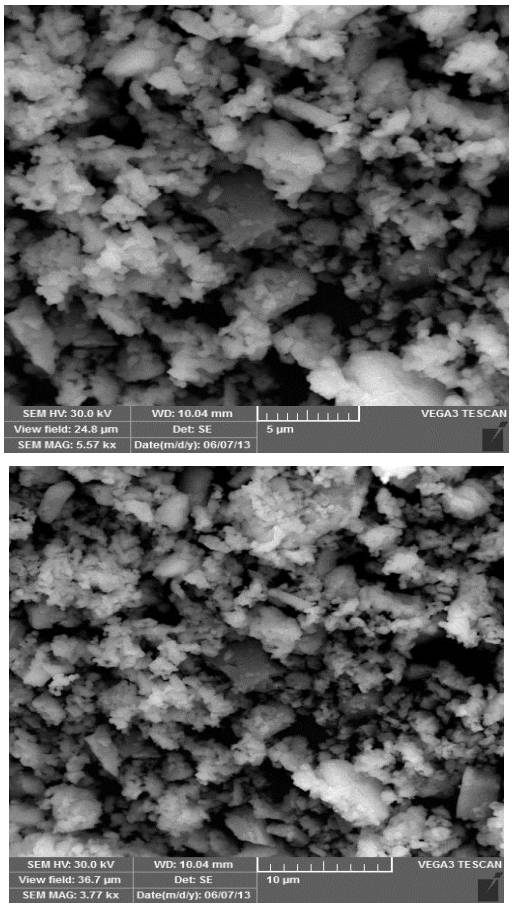
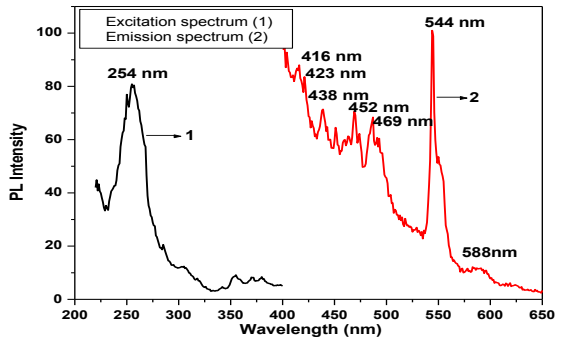


Fig. 2: SEM images of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb (0.5%) under different view fields

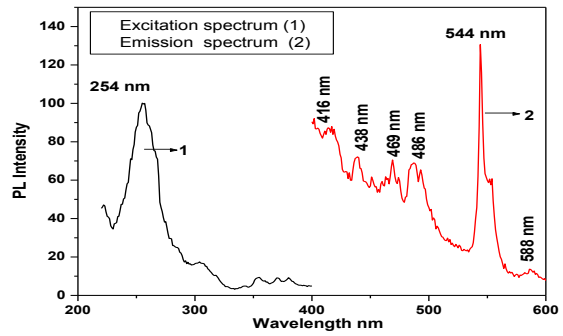
4.3 Photo Luminescence Study

The Photo Luminescence Properties under UV excitation of obtaining mixed ortho phosphates are presented in figure 3a. The excitation spectrum of $La_{0.5}$ $Al_{0.2}Y_{0.3}PO_4$

:Tb^{3+} (0.5%) figures 3a&3b presents a broad, intense band ranging from 240nm – 310 nm related to a ligand-metal charge transfer between PO_4^{3-} groups and RE^{3+} ions. The strong Tb^{3+} intra-configurational $4f^8 \rightarrow 4f^7\ 5d^1$ transitions are also observed in the excitation spectrum. The $4f^8$ line emission of Tb^{3+} is often responsible for the green component in tri – color tube lighting [13]. The emission spectra (fig-3a&3b)of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$: Tb^{3+}(without&with flux) phosphors display the $5D_4 \rightarrow 7F_j$ (j=6, 5,4) Tb^{3+} transitions, besides the weak emission spectrum of $5D_4 \rightarrow 7F_3$ transitions at nearly 588nm. Another weak emission spectrum of $5D_3 \rightarrow 7F_j$ transition at nearly 469nm observed. $5D_4 \rightarrow 7F_5$ emission is predominant because the minimum of the $4f^7\ 5d^1$ curve is fairly low in energy and the Frank – Condon shift is fairly large, there is a possibility that an electron exited to the $4f^7\ 5d^1$ level can relax directly to the $5D_4$, bypassing the $5D_3$ and thus producing only $5D_4$ luminescence [14].. Among the emission lines from $5D_4$ state, the $^5D_4 \rightarrow {}^7F_5$ emission lines at approximately 544 nm is the strongest in nearly all host materials when the Tb^{3+} concentration is few mole % or higher. The reason is that this transition has the largest probability for both electric-dipole and magnetic dipole induced transitions**.** The transition $5D_4 \rightarrow 7F_5$ at ~ 544nm confers a high green color purity for the compound.Both the phosphors give emission lines from$5D_4$ state, the $^5D_4 \rightarrow {}^7F_5$ emission lines at approximately 544 nm is the strongest. 544nm peak intensityof $La_{0.5}\ Al_{0.2}\ Y_{0.3}\ PO_4$:Tb^{3+} (0.5%) with citricacid as flux is maximum when compared to without flux phosphor.40% intensity increment observed with flux. The compounds which are of well established commercial phosphor.



(a)



(b)

Fig. 3: (a) Excitation spectrum of $LaAlYPO_4$: Tb (0.5%) monotiring at 400 nm and Emission spectrum of $LaAlYPO_4$: Tb(0.5%) under 254 nm Ex.; (b) Excitation spectrum of $LaAlYPO_4$:Tb(0.5%) with flux monitoring at 400 nm and Emission spectrum of $LaAlYPO_4$: Tb(0.5%) with flux under 254 nm Ex.

4.4 FTIR Analysis

In order to determine the atomic bonds in a molecule FTIR analysis was carried out. The figure-4 shows the FTIR spectrum of $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb (0.5%). From FTIR spectrum, it is observed that the band in the range 1270-1520 cm^{-1} are attributed to the vibrational modes of oligoperoxide. Weak band around 2015 cm^{-1} is very likely a manifestation of CO_2.Upon increases the synthesis temperature, this band normally diminishes as the CO_2 is removed from the material [15]. The band located near 3382 cm^{-1} can be attributed to O-H stretching modes while the bending mode is at around 1764 cm^{-1}.Some additional bands at higher wave number up to 4000 cm^{-1}, related to water and other technological components remained and or absorbed after synthesis. Peak at 1126 (√3) P-O asymmetry stretch. Most of the other bands are typical for the vibrations of phosphate groups. Free $(PO_4)^{3-}$ion has four normal modes of vibrations of tetrahedral ion. These are $\sqrt{}_1$ (P-O symmetric stretching), $\sqrt{}_3$ (P-O asymmetric stretching), $\sqrt{}_2$and$\sqrt{}_4$ (O-P-O symmetric and asymmetric bending vibrations, respectively) [16]. Neither Tb impurity, nor oligoperoxides affect the structure and the position of these bands. Moreover, for the monoclinic $La_{0.5}\ Al_{0.2}\ Y_{0.3}\ PO_4$, the $\sqrt{}_2$ mode at about 500cm^{-1} can be observed

4.5 CIE Co Ordinates

The CIE co-ordinates calculated by the Spectrophotometric method using the spectral energy distribution of the $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb^{3+}(0.5%) sample is shown in figure 5.The color co-ordinates for the $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb^{3+}(0.5%) sample is x=0.3317 and

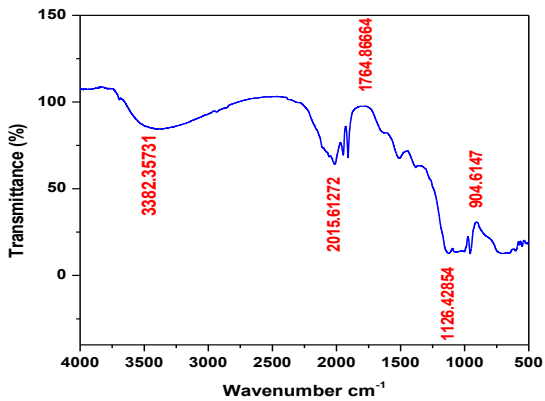


Fig. 4: FT IR Spectrum of $LaAlYPO_4$; Tb(0.5%)

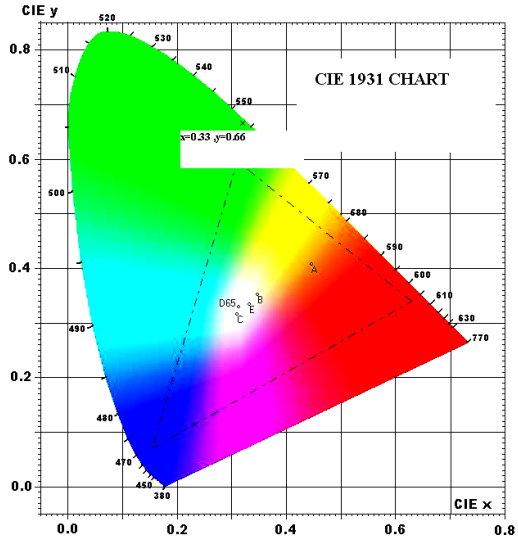


Fig. 5: C.I.E Coordinates

y=0.6628 (these co-ordinates are very near to standard values of Green). Hence this phosphor having excellent color tenability to Green.

4.6 Particle Size

Practical phosphors must be prepared so that they can form a dense, pinhole coating on a substrate.This property is determined mainly by particle size distribution. The optimum coating thickness is roughly proportional to its mean particle size. i.e the smaller the particle size, the thinner the coating can be. Therefore a small particle size advantages for expensive phosphors. [17]. From XRD studies the average crystallite size is around 34.5nm.From particle size distribution data average particle size is 5µm. Many molecular particles agglomerate and form as a crystallite and many crystallite together became a particle

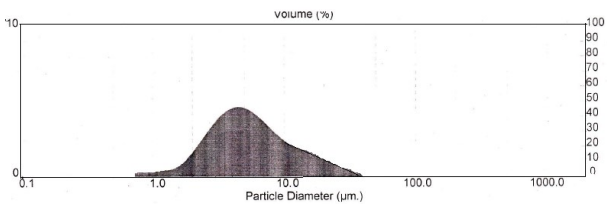


Fig. 6: Particle size histogram of $La_{0.5}Al_{0.2}Y_{0.3}PO_4:Tb^{3+}$ (0.5%) phosphor

5. CONCLUSIONS

Tb doped $La_{0.5}Al_{0.2}Y_{0.3}PO_4$ (without&with flux)nano phosphors were synthesized via high temperature solid state diffusion reaction method. The Crystal phase and microstructure of the products can be favorable for the formation phosphors in pure phase. $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb(0.5%) presents the pure monoclinic phase and nano size crystalline material.The $La_{0.5}Al_{0.2}Y_{0.3}PO_4$:Tb(0.5%) with flux phosphor material presents very attractive luminescent property for the generation of the green color. The color coordinates are very near to standard values of green. Vibrational mode of the monoclinic $La_{0.5}Al_{0.2}Y_{0.3}PO_4$ are influenced neither by dopants nor by Oligoperoxide modifications. Particle size is low when compared with general phosphate phosphors. So this phosphor may be a good candidate for fluorescent lighting, display devices, X-ray monitoring, imaging scintillators and biomedical imaging applications.

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