Synthesis and characterization of RE doped nano Lanthanum Yttrium phosphate phosphor

Physics

KEYWORDS : Photoluminescence [PL], Solid state diffusion reaction [SSR], Mixed rare earth ortho phosphates, Nano phosphors, Rare Earths [RE].

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ABSTRACT

Mixed rare earth ortho phosphates (rare earths = La, Y) have been prepared by solid state diffusion reaction method. The required starting materials were weighed and grounded using agate mortar and pestle followed by at 1200oC for 3 hours in a muffle furnace. The method was employed to obtain Lanthanide activated Lanthanum yttrium phosphates which can be applied as Red (LaxY1-xPO4: Eu3+), Green (LaxY1-xPO4: Tb3+) and Blue (LaxY1-xPO4: Ce3+) phosphors in a display device. The produced phosphor materials were characterized using powder X-ray diffractometry [XRD], scanning electron microscopy [SEM], FTIR, particle size and Photoluminescence [PL] (Emission, Excitation and Chromaticity coordinates). XRD study confirms formation of nano crystallites. Different dopants Ce, Tb and Eu in LaxY1-xPO4 exhibits blue, green and red emissions from the phosphors upon excitation with 254nm. These nano phosphors may be good candidates for display devices.

INTRODUCTION

Inorganic luminescent materials are now a day's widely employed in many quotidian devises and, for this studies on their obtainment, spectroscopic behavior and applications have been remarkable [1, 2]. Mixed rare earth ortho phosphates is very interesting class of host lattices for activator ions due to their physic-chemical inercy (high insolubility, stability against high temperature or against high energy excitations) thus providing durable phosphors. Moreover, these materials can present high excitabilities in ultraviolet region, which enables them in new generation fluorescent lamps (without mercury), cathode ray tubes (CRTS) projection televisions (PTVS) and field emission displays (FED) etc., [3]. Life time and persistence are main concerns in case of phosphors. Efforts are being made to develop better phosphor and replace the existing phosphors [4, 5]. Herein, the fabrication of nano materials will well-controlled dimensionality, morphologies, phase purity and desired properties remains one of the most challenging issues [6]. One simple method to control the particle size and morphology is solid state reaction diffusion method which is extensively employed by the industry in the synthesis of rare earth ions activated inorganic compounds. [7]. The luminescent properties of mixed rare earth phosphates can be conferred by the presence of lanthanide (III) ions as activators due to their intense and narrow emission bands arising from f-f transitions, which are proper for the generation of individual colours in multi phosphor devices [8-10]. So, the red $^5D_0 \rightarrow {}^7F_2$(~613 nm.) green $^5D_4 \rightarrow {}^7F_5$ (~544 nm.) and blue $^1D_2 \rightarrow {}^2F_{7/2}$(~468 nm.) respectively, can be used as navel phosphors. Thus $La_{0.6}Y_{0.4}PO_4{:}Eu^{3+}$, $La_{0.6}Y_{0.4}PO_4{:}Tb^{3+}$ and $La_{0.6}Y_{0.4}PO_4{:}Ce^{3+}$ can be considered as very promising examples of luminescent materials [11]. Ever since Y.S. Patil et.al. has fabricated $LaPO_4$:Eu and $LaPO_4$:Tb nanocrystals by standard solid state reaction method, lots of work have been focused under the study of rare earth phosphate nano crystals [12]. Here Yttrium added to $LaPO_4$ in proportions to overcome blue peak and to increase the life time of phosphate phosphors. Therefore it is very interesting that what will happen where rare earth ions are introduced into $La_{0.6}Y_{0.4}PO_4$:X systems. In this paper we have investigated and discussed the results on the crystal phase, structure, PL, microstructure (morphology and particle size) of the mixed phosphates prepared by standard solid state diffusion reaction method. At the same time Eu^{3+} ions, Tb^{3+} ions and Ce^{3+} have been doped in the mixed rare earth phosphates in order to examine the influence of the hosts on the luminescence of Eu^{3+}, Tb^{3+} and Ce^{3+} whose photo luminescent behaviors are studied in detail.

2. SYNTHESIS OF MIXED PHOSPHATES

The starting materials Lanthanum oxide (La_2O_3), Yttrium oxide (Y_2O_3), $(NH_4)\,H_2PO_4$, Europium oxide (Eu_2O_3) , Terbium oxide ($Tb_4\,O_7$ and CeO_2 of high purity (99.9%) chemicals were used as starting materials to prepare $La_{0.6}Y_{0.4}PO_4$ and Eu, Tb and Ce doped phosphor. Lanthanum oxide ($La\ {}_2O_3$), Yttrium oxide in stoichiometric proportions is weighed and ground into a fine power using agate mortar and pestle. The grounded sample were placed in an alumina crucible and fired at 1200°C for 3 hours in 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 ions Ce, Tb and Eu were doped 0.5 molar percentages. Spectrofluorophotometer (SHIMADZU, RF-5301 PC) was used for PL studies.

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. All the PL spectra were recorded at room temperature.

4.0 RESULTS AND DISCUSSIONS

4.1 Crystal phase and microstructure of mixed rare earth phosphate:

Present study focuses on the XRD pattern of La^{3+} to Y^{3+} of 3:2 molar ratio i.e. $La_{0.6}Y_{0.4}PO_4$ doped with Eu^{3+}, Tb^{3+} and doped with Ce^{3+} is shown in figure 1. From the XRD pattern it was found that the prominent phase formed in $La_{0.6}Y_{0.4}PO_4$, after diffraction peaks were well indexed based on JCPDS no. 96-900-1648 indicating monoclinic phase of monazite structure. The main peak was found around 29.11° 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 Yttrium phosphate. All diffraction patterns were obtained using Cu Kα radiation (λ= 1.54060 A°). Measurements were made from 2θ=0° to 70° 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 [13]. 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 $LaPO_4$[14].

The crystallite size was calculated using the Scherrer equation D=k λ/β cos θ. Where the constant (0.9) λ the wave length 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 $La_{0.6}Y_{0.4}PO_4$: Eu 0.5% is ~ 45 nm, $La_{0.6}Y_{0.4}PO_4$: Tb 0.5% is ~ 45 nm and $La_{0.6}Y_{0.4}PO_4$: Ce 0.5% is ~ 45.6 nm and particle sizes are 3.97 µm, 4.2 µm and 4.2 µm respectively (Histogram not shown). Fig. 1a is the. XRD pattern of A. $La_{0.6}Y_{0.4}PO_4$: Eu 0.5%, $La_{0.6}Y_{0.4}PO_4$:Tb 0.5%, C. $La_{0.6}Y_{0.4}PO_4$:Ce 0.5%. Figure.1 is Comparison of Standard XRD and XRD pattern of A. $LaYPO_4$: Eu 0.5%,

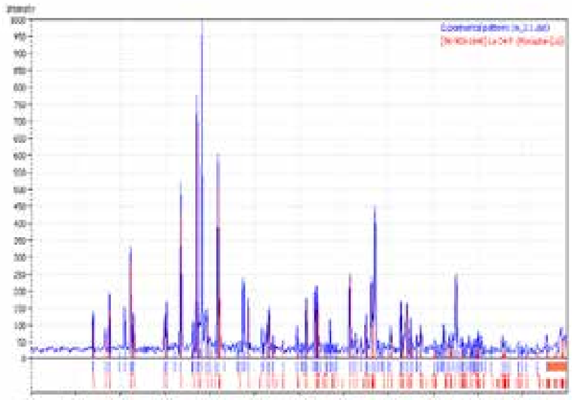


Figure.1: Comparision of Standrad XRD and XRD pattern of A. $LaYPO_4$: Eu 0.5%,

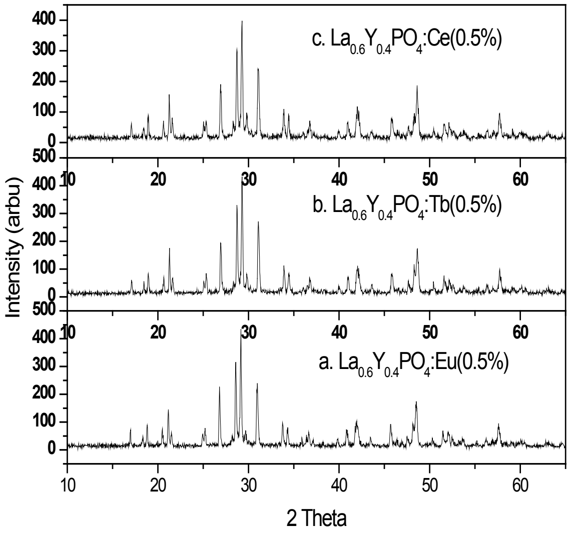


Fig. 1a. XRD pattern of A. $LaYPO_4$: Eu 0.5%, B. $LaYPO_4$:Tb 0.5%, C. $LaYPO_4$:Ce 0.5%

4.2. SEM STUDY:

Characterization of particles, surface morphology and size for 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 a, b and c shows the SEM micrographs of $La_{0.6}Y_{0.4}PO_4$;Eu 0.5%, $La_{0.6}Y_{0.4}PO_4$;Tb 0.5%, $La_{0.6}Y_{0.4}PO_4$: Ce 0.5% phosphors. Direct size measurements obtained from images and average particle diameter is observed. From the Scanning Electron Micrograph of $La_{0.6}Y_{0.4}PO_4$;Eu 0.5%, $La_{0.6}Y_{0.4}PO_4$: Tb 0.5%, $La_{0.6}Y_{0.4}PO_4$: Ce 0.5% phosphors, it is found the particles are are irregular in shape with various sizes from of submicron to few micros and also clusters are found.

4.3. PHOTO LUMINESCENCE STUDY

Fig 2a. SEM images of La $_{0.6}$Y $_{0.4}$PO$_4$:Eu(0.5%)

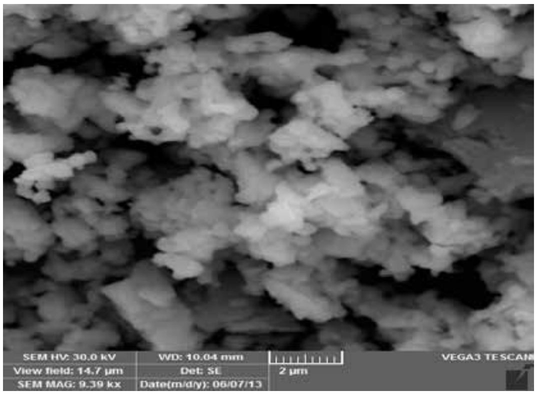


Fig 2b. SEM images of La $_{0.6}$Y $_{0.4}$PO$_4$: Tb(0.5%)

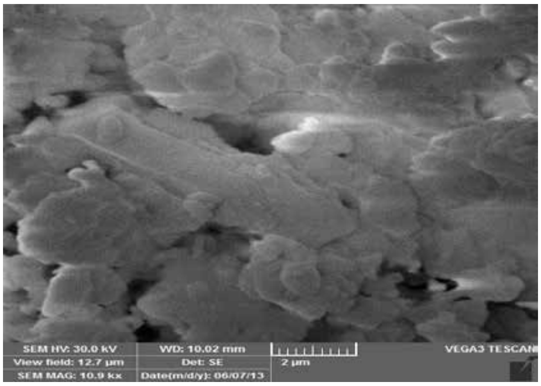
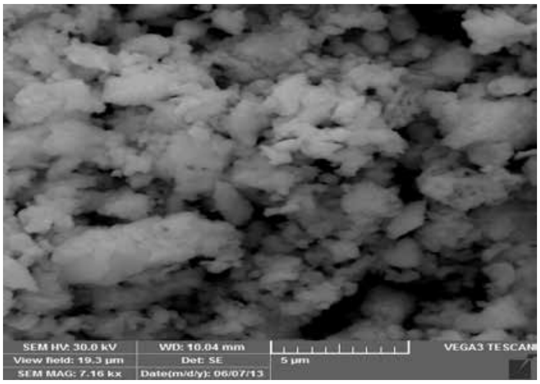
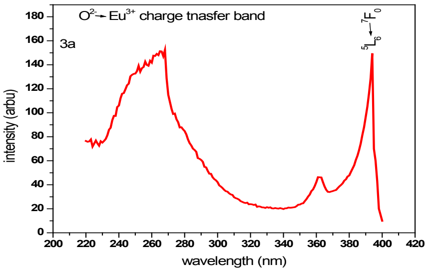


Fig 2c. SEM images of La $_{0.6}$Y $_{0.4}$PO$_4$: Ce(0.5%)

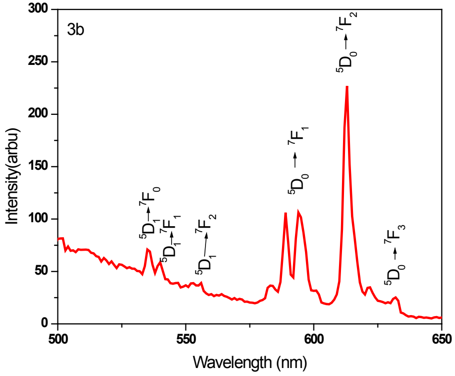


The photo luminescent properties under 254nm UV excitation of obtained mixed ortho phosphates are presented in figure 3. The excitation spectrum of $La_{0.6}Y_{0.4}PO_4$: Eu^{3+}(Figure 3a.) presents a broad intense band with maximum at ~ 254 nm related to a ligand – metal charge transfer between PO_4^{3-} groups and RE^{3+} ions. The strong Eu^{3+} intra configurational f-f transitions are also observed in the excitations spectrum. The peak ascribed to the $^5L_6 \leftarrow ^7F_0$ transition (at 394 nm). The emission spectrum of $La_{0.6}Y_{0.4}PO_4$: Eu^{3+}(Figure 3b) display the characteristic $^5D_0 \rightarrow ^7F_J$ transition of Eu^{3+}. Emissions from the $^5D_1$ state are also observed, accounting for a low rate multiphonon deactivation of upper excited states. The predominance of the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition in the emission spectrum is determinant for the applicability of this phosphor material, which is the only way to get high emission red colour purity. In the present case, the low contributions of the $^5D_0 \rightarrow {}^7F_1$ emissions and the high intensity of $^5D_0 \rightarrow {}^7F_2$ emission results in high colour purities[15-17]. Table -1 is the calculated colour co-ordinates and same is presented in figure-4. CIE 1931 chromaticity coordinates x = 0.6730 and y = 0.3268(Table 1, Fig. 4) that are acceptable for many optical applications [2 & 17].

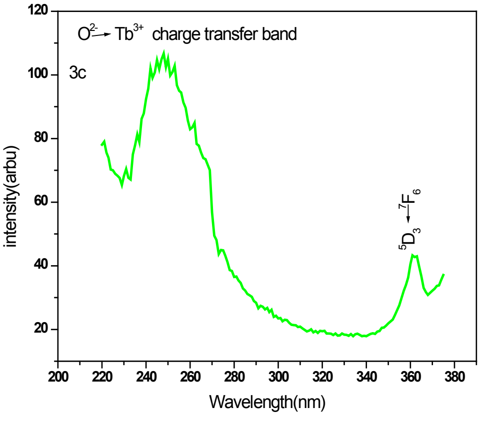
Fig.3a. Excitation spectrum of La $_{0.6}$Y $_{0.4}$PO$_4$:Eu(0.5)



3b.Emission spectrum of LaYPO$_4$:Eu^{3+}(λ_{em}= 613nm ; λ_{ex} = 254nm)



In the La$_{0.6}$Y$_{0.4}$PO$_4$: Tb^{3+} excitation spectrum (figure 3c) some f-f absorption of Tb^{3+} ($^5D_3 \leftarrow {}^7F_6$ and $^5D_4 \leftarrow {}^7F_6$ are observed and the allowed $^5D \leftarrow {}^4F$ absorption at nearly 254 nm is observed. The emission spectrum of this phosphate (figure 3d) displays the $^5D_4 \rightarrow {}^7F_J$ (J=6,5,4,3) Tb^{3+} transitions, besides the weak emissions spectrum of $^5D_4 \rightarrow {}^7F_3$ transition at nearly 590 nm. Although the emission bands are relatively broad (due to the high number of components of Tb^{3+} manifolds and may be due to the high concentration of activator ions), the predominance of the $^5D_4 \rightarrow {}^7F_5$ transition at ~ 544nm confers a high green colour purity for the compound (X= 0.2599 and Y= 0.7289) (Table 1, Fig. 4) which is of a well established commercial phosphor [1, 2, 9].



3c. Excitation spectrum of La $_{0.6}$Y $_{0.4}$PO$_4$: Tb^{3+}

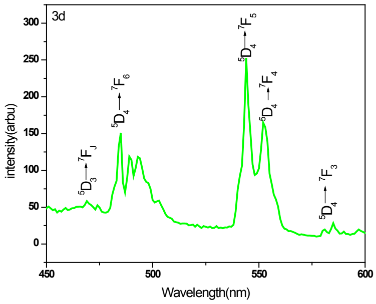


Fig.3d.Emission spectrum of La $_{0.6}$Y $_{0.4}$PO$_4$:Tb(0.5%)

The excitation spectrum of La$_{0.6}$Y$_{0.4}$PO$_4$: Ce^{3+} (Figure 3e) presents the only intra configurational absorption of Ce^{3+} in the near UV region, relative to the $^1D_2 \leftarrow {}^3H_6$ transition at 358nm, beside an intense and broad excitation band with maximum energy, which can be ascribed due to O^{2-} → Ce^{3+} charge transfer band. In its emission spectrum under excitation of 254nm (figure 3f) this phosphate presents a dominant emission at ~ 468 nm, as an outcome of the radiative Ce^{3+} transition. The other Ce^{3+} f-f emissions are weak and do not have a significant contribution to the emissions spectrum. The occurrence of the only one transition with appreciable intensity confers a very high emission blue colour purity for this mixed ortho phosphates (x= 0.1298 and y= 0.0653)

(Table 1, figure 4) which is one of the major features of this study that make La$_{0.6}$Y$_{0.4}$PO$_4$: Ce^{3+} very promising as a blue phosphor.

Figure 3e. : Excitation spectrum ofLaYPO$_4$: Ce^{3+}

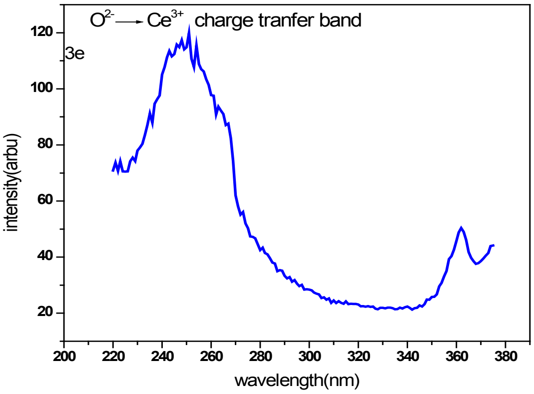


Figure 3f. : Emission spectrum of LaYPO4: Ce3+(λem= 468nm ; λex = 254nm).

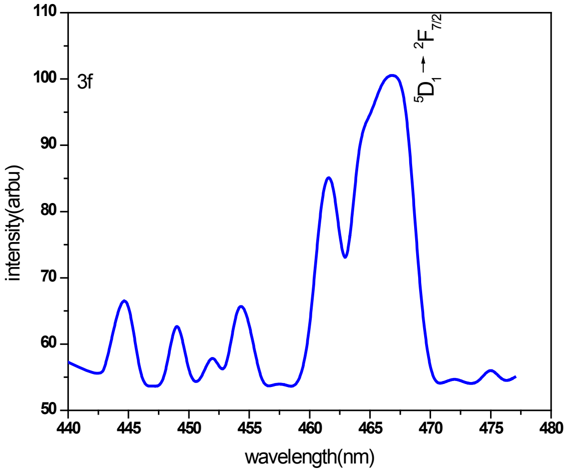
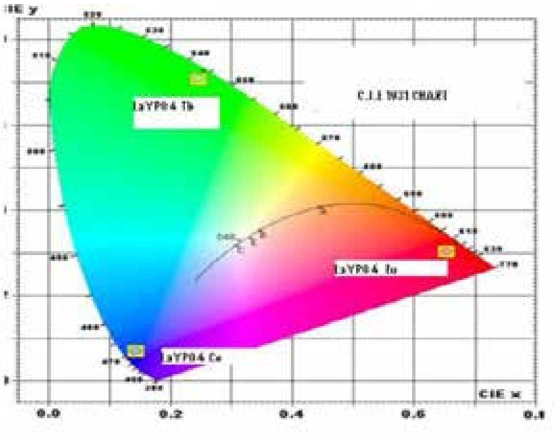


Table – 1 indicates Particle size, chromaticity coordinates and peak half width nm.

Compound name	Particle Size µm	Chromaticity Coordinates X	Chromaticity Coordinates Y	Peak half width nm
$LaYPO_4$: Eu 0.5%	3.97	0.6730	0.3268	8
$LaYPO_4$: Tb 0.5%	4.20	0.2599	0.7289	7
$LaYPO_4$: Ce 0.5%	4.20	0.1298	0.0653	20

Figure 4. CIE coordinates



4.4 FTIR analysis

In order to determine the atomic bonds in a molecule FTIR analysis was carried out. Figure 5 shows the FTIR spectrum of $La_{0.6}Y_{0.4}PO_4$: Eu (0.5%) , $La_{0.6}Y_{0.4}PO_4$:Tb(0.5%),and $La_{0.6}Y_{0.4}PO_4$:Ce (0.5%) From FTIR spectrum it is observed that the band in the range 1270-1520 cm^{-1} and near 2924 cm^{-1} are attributed to vibrational modes of oligoperoxide. Weak band around 2360 cm^{-1} is very likely a manifestation of CO_2.Upon increasing the synthesis temperature, this band normally diminishes as the CO_2 is removed from the material [18]. The band located near 3390 cm^{-1} can be attributed to O-H stretching modes while the bending mode are at around 1630 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 1058(√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 $\surd_1$(P-O symmetric stretching), $\surd_3$(P-O asymmetric stretching), $\surd_2$and$\surd_4$(O-P-O symmetric and asymmetric bending vibrations ,respectively)[19]. Neither Eu, Tb and Ce impurities nor oligoperoxides affects the structure and position of these bands .Moreover for the monoclinic $La_{0.6}Y_{0.4}PO_4$ the $\surd_2$ mode at about 499cm^{-1} can be observed.

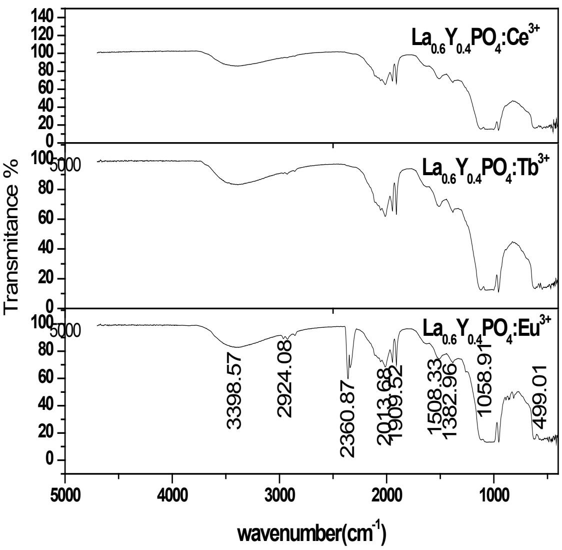


Fig.5.FTIR Spectra of La $_{0.6}$Y $_{0.4}$$PO_4$:Eu(0.5%)
La $_{0.6}$Y $_{0.4}$$PO_4$:Tb(0.5%) , La $_{0.6}$Y $_{0.4}$$PO_4$:Ce(0.5%)

5. CONCLUSIONS

Eu, Tb and Ce doped in $La_{0.6}Y_{0.4}PO_4$ nano phosphor were synthesized via high temperature solid state diffusion reaction. The Crystal phase and microstructure of the product can be favourable for the formation of the phosphor in pure phase. $La_{0.6}Y_{0.4}PO_4$ presents the pure monoclinic phase and nano size crystallite material. The phosphor material presents very attractive luminescent properties for the generation of the three primary colours which are red, green and blue emissions of $La_{0.6}Y_{0.4}PO_4$: Eu^{3+}, $La_{0.6}Y_{0.4}PO_4$: $Tb^{3+}$and $La_{0.6}Y_{0.4}PO_4$: Ce^{3+} respectively. $La_{0.6}Y_{0.4}PO_4$: Eu^{3+} and $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} present a good luminescent behavior and $La_{0.6}Y_{0.4}PO_4$: Ce^{3+} can be pointed as a very promising blue phosphor due to its photo physical characteristics. Vibrational modes of the monoclinic $La_{0.6}Y_{0.4}PO_4$ 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 bio medical imaging applications.

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