Optik 126 (2015) 2390–2393

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Synthesis and characterization of Tb^{3+} activated $La_{0.6}Y_{0.4}PO_4$ phosphor

P. Indira[a,*], S. Kondala Rao[b], K.V.R. Murthy[c]

[a] Department of Physics, Sri ABR Govt. Degree College, Repalle 522265, A.P., India
[b] Department of Physics, QIS Engineering College, Ongole 523002, A.P., India
[c] Display Materials Laboratory, Applied Physics Department, Faculty of Technology & Engineering, M.S. University of Baroda, Vadodara 390 001, India

ARTICLE INFO

Article history:
Received 21 April 2014
Accepted 30 May 2015

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

ABSTRACT

The present paper reports, synthesis and photo luminescence (PL) studies of the Tb^{3+} (0.5%) doped $La_{0.6}Y_{0.4}PO_4$ phosphor under different excitations. 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. The PL emission mainly concentrates around 544 nm when excited with 254 nm, 267 nm, 305 nm wavelengths. Good PL emission intensity was observed when exited with 267 nm. For $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} (0.5%) the ion radius distinction between La^{3+} and Y^{3+} 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 $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} (0.5%) is around 45 nm and particle size is 4.2 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.

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 two rare earth 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 $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} phosphor that exhibits broad excitation ranges of 242–310 nm and another peak at 360 nm using high temperature solid state reaction method. Furthermore, the photo luminescent properties of the powder under different excitations were 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 mixed phosphates

The starting materials lanthanum oxide (La_2O_3), yttrium oxide (Y_2O_3), $(NH_4)H_2PO_4$, terbium oxide (Tb_4O_7) of high purity (99.9%) chemicals were used as starting materials to prepare $La_{0.6}Y_{0.4}PO_4$ and Tb doped phosphor. Lanthanum oxide (La_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 h 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 h. Rare

* Corresponding author. Tel.: +91 9959144807.
E-mail address: polineni1997@yahoo.com (P. Indira).

http://dx.doi.org/10.1016/j.ijleo.2015.05.135
0030-4026/

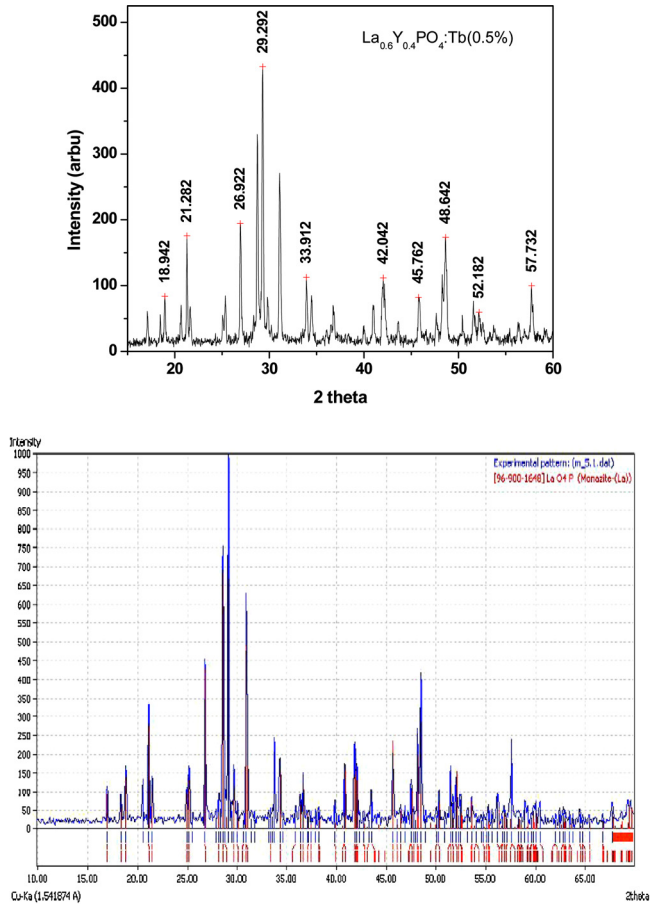

Fig. 1. XRD Pattern of $La_{0.6}Y_{0.4}PO_4$: Tb (0.5%). (A) Comparison of standard XRD and XRD pattern of $La_{0.6}Y_{0.4}PO_4$: Tb (0.5%) phosphor.

earth ion Tb was doped 0.5 molar percentage. The sample was found out to be white who is studying for photoluminescence.

3. Physical charaterization

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 discussion

4.1. Crystal phase and microstructure of mixed rare earth phosphate

The 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 Tb^{3+} is shown in Fig. 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 the monoclinic phase of monazite structure. The main peak was founded around 29.292° corresponding to a *d*-value of about 3.10 Å 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 Å). Measurements were made from $2\theta = 10°$ 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].

The crystallite size was calculated using the Scherrer equation $D = k\lambda/\beta \cos\theta$. Where k the constant($k = 0.9$), λ the wavelength of X-rays (1.54060 Å), β the full-width at half maxima (FWHM) and θ the Bragg angle of the XRD peak. The calculated average crystallite size of $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} 0.5% is ~45 nm. Fig. 1 is the. XRD pattern of $La_{0.6}Y_{0.4}PO_4$: Tb (0.5%). Fig. 1A is comparison of standard XRD and XRD pattern of $La_{0.6}Y_{0.4}PO_4$: 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). Fig. 2 shows the SEM micrographs of $La_{0.6}Y_{0.4}PO_4$: Tb (0.5%) phosphors. Direct size measurements obtained from images and the average particle diameter is observed. From the Scanning Electron Micrographs of $La_{0.6}Y_{0.4}PO_4$: 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.

4.3. Photo luminescence study

The photo luminescence properties under different UV excitations of obtaining mixed ortho phosphates are presented in Fig. 3. The excitation spectrum $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} Fig. 3a presents a broad, intense band ranging from 240 to 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 spectrum (Fig. 3b) of $La_{0.6}Y_{0.4}PO_4$: Tb^{3+} phosphor displays 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 590 nm. Another weak emission spectrum of $5D_3 \rightarrow 7F_j$ transition at nearly 470 nm 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]. The transition $5D_4 \rightarrow 7F_5$ at ~544 nm confers a high green color purity for the compound. For all the excitations the peak positions are the same and intensity maximum observed under 267 nm excitation. The intensity maximum under 267 nm because electric field vector of exited wave interacts electric dipoles of the compound properly. The compound which is of a well established commercial phosphor.

4.4. FTIR analysis

In order to determine the atomic bonds in a molecule FTIR analysis was carried out. The figure shows the FTIR spectrum of $La_{0.6}Y_{0.4}PO_4$: Tb (0.5%). From FTIR spectrum, it is observed that