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Research Paper

Mixed Color Emission from Europium Co-Doped La_2O_3:Bi^{3+} Nanophosphors Material by Polyol Method

Physics

KEYWORDS : Polyol method, Lanthanum oxide, Bismuth, Rare earth co-doping, Phosphorous, Photoluminescence.

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ABSTRACT

Photoluminescence (PL) was observed from prepared Bi3+ and europium (Eu3+) co-doped La2O3 (La2O3: Bi, Eu) nanophosphor powder. The phosphor powders were prepared by polyol method using ethylene glycol as capping agent. The phase formation, functional groups identification of as prepared samples and morphological studies were confirmed by XRD, FTIR and scanning electron microscopy (SEM) and transmission electron microscopy (TEM). PL emission widely changed from green-orange region to approximately blue on heating La2O3:Bi3+, Eu3+ phosphor powders from 700 to 900 o C. The observed emission peaks in PL from phosphor powder materials were assigned to either the broad emission originating from the transition in Bi3+ or the visible emission peaks originating transition from the europium ion. Emission peaks of PL are plotted using CIE coordinates.

INTRODUCTION

Rare earth doped La_2O_3 phosphors have many potential applications in cathode ray tubes, field emission displays, plasma display panels, and vacuum fluorescent display devices [1]. Among various phosphors, materials doped with bismuth ions (Bi^{3+}) have extensively investigated because Bi^{3+} is to be good sensitizers of luminescence due to their band-like absorption character. In using rare-earth (RE) sesquioxides La_2O_3, Y_2O_3, Gd_2O_3 as host materials and doped with Bi^{3+} ions, it has been observed that blue-violet emissions arose from these phosphors [2-4]. Lanthanum oxide (La_2O_3) is a semiconductor material [5] with the largest band gap among RE sesquioxides, with a value of 4.3 eV [6]. Red phosphors lke Eu^{3+} activated phosphors have been extensively investigated in the field of their application [7–10]. Furthermore, Eu^{3+} is often used as a structural probe [11], because of the relative simplicity of its energy-level structure and the fact that it possesses non-degenerate ground ($^7F_0$) and excited ($^5D_0$) states, and because the absorption and emission spectra of this ion show marked dependence on its site symmetry in the host material [12]. Photoluminescence (PL) and electroluminescence (EL) were observed from rare earth (RE^{3+}) co-doped La_2O_3:Bi^{3+} (La_2O_3:Bi^{3+}, RE^{3+}) phosphor thin films [13]. Many preparation techniques such as calcination methods [14], solutions combustion synthesis [15-17], conventional hydrothermal [18] and microwave hydrothermal methods [19] used for preparation of La_2O_3 nanoparticles. To the best of authors knowledge, La_2O_3: Bi^{3+}, co-doped with Eu^{3+} ions (La_2O_3:Bi^{3+}, Eu^{3+}) nanoparticles synthesized by polyol route have not yet been investigated so far.

Polyol method can be used to prepare a variety of materials/compounds including metals, oxides, phosphates, sulphides, fluorides etc. having size in the range of few nanometers to micrometers. Essentially the preparation method involves the reaction of a polyol soluble salt of the metal ions and a precipitating agent. The method offers simple and economic method without using any hazardous or moisture sensitive reagents for preparing a variety of nanomaterials. In this paper, novel La_2O_3: Bi^{3+}, Eu^{3+} nanoparticles were prepared successfully followed by annealing at 700 ° C and 900 ° C temperatures and their luminescent properties were discussed in detail.

EXPERIMENTAL DETAILS

Preparation of the nanoparticles

Starting materials, La $(NO_3)_3.6H_2O$ [Merck, Germany], Bi $(NO_3).5H_2O$ [BDH Laboratory Chemicals Division, India], Eu $(NO_3)_3$ [Alfa Aesar 99.99%], were used for the synthesis of nanoparticles. All the reagents were of AR and were used without further purification. Here ethylene glycol is used as the capping agent and urea for hydrolysis. Initially La_2O_3: Bi^{3+} (1at %) nanoparticles were prepared. Both La $(NO_3)_3.6H_2O$ and $Bi(NO_3).5H_2O$ were dissolved in required amount of distilled water. To this solution, ethylene glycol (25 mL) was added and it was then transferred into a two-necked RB flask. The solution was slowly heated up to 100 °C followed by addition of 2 g of urea and the temperature was increased to 120 °C. At this temperature, the solution became turbid. The temperature was maintained at this value for 2 hours. The precipitate was collected after the reaction by centrifugation and then washed two times with acetone and three times with methanol followed by drying under ambient conditions. The samples prepared thus were finally heated to 700 °C, 900 °C in air at a heating rate of 10 °C per minute. The temperature was maintained at the respective values for duration of 5 hours. After that the furnace was switched off and the sample was subjected to natural cooling to room temperature. The same procedure was used for preparing the rare-earth co-doped La_2O_3: Bi^{3+}, Eu^{3+} nanoparticles. Along with La $(NO_3)_3.6H_2O$ and $Bi(NO_3).5H_2O$, Eu $(NO_3)_3$ was also added. Here in this paper the 1 at % bismuth content is added and 1 at% optimum europium is reported for co-doping due to concentration quenching effect.

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Characterization

X-ray diffraction (XRD) studies were carried out using a Philips powder X-ray diffract meter (model PW 1071) with Ni filtered Cu-Ka radiation. The lattice parameters, unit cell volume were obtained from Rietveld refinement of the XRD patterns using POWDERX software. The average crystallite size was calculated from the diffraction line width based on Scherrer relation D = 0.9λ/βCosθ, where D is the average particles size, λ is the wavelength of X-rays and β is the corrected full width at half maximum (FWHM). All luminescence measurements were carried out at room temperature with a resolution of 5 nm, using Edinburgh Instruments FLSP 920 system attached with a 450 W Xe lamp as the excitation source. A micro second flash lamp was used for lifetime measurements. Transmission Electron Microscopic (TEM) studies were performed using a JEOL JEM 3000F TEM machine. IR patterns were recorded for a thin pellet of the $La_2O3:Bi^{3+}$, Tb^{3+} as prepared nanoparticles made with KBr using a Bomem MB102 machine.

RESULTS AND DISCUSSION

XRD Analysis

The phase of the as-prepared undoped $La(OH)_3$ and doped samples was examined by XRD. Fig.1 (a) shows the XRD patterns of the pure $La(OH)_3$ sample which all the diffraction peaks are attributed to the hexagonal crystal phase, which are in good agreement with the standard PCPDF card [13-0084] with the space group $P6_3/m$. Initially upon heating to 700 ° C the XRD peaks became sharper because of an increase in crystallinity. With increasing temperature, it was deduced that $La(OH)_3$ transforms to La_2O_3. This XRD peaks shows the oxide nanoparticle phase which is in almost close agreement with hexagonal phase (PCPDF 83-1355) with the space group Pm1 Fig.1 (b) [20]

Fig.1 XRD Pattern for as prepared La_2O_3 (a) and 700 °C heated undoped La_2O_3 (b) $La_2O_3:Bi^{3+}$ (c) Co-doped with (d) Eu^{3+}

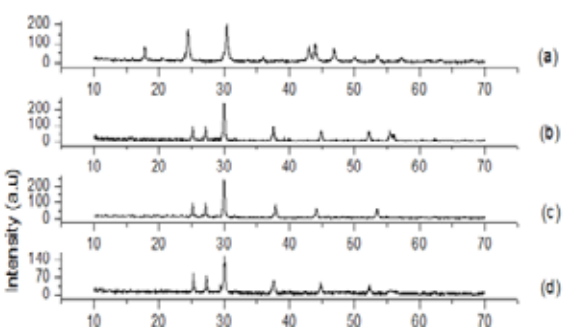
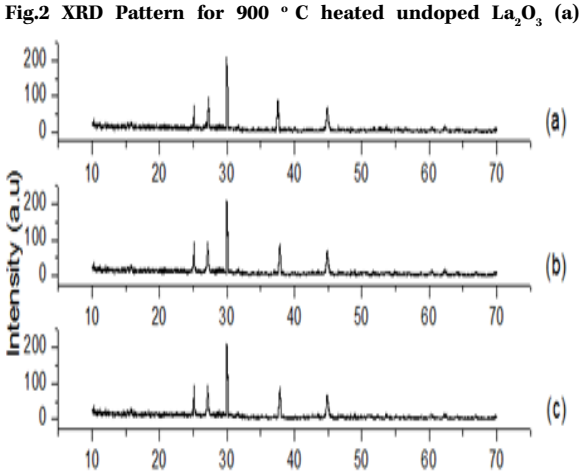
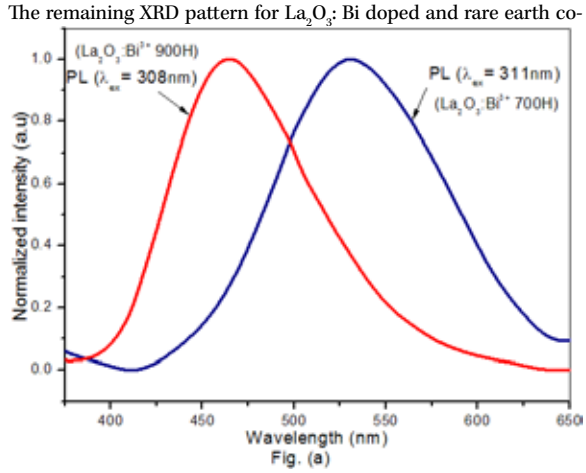


Fig.2 XRD Pattern for 900 ° C heated undoped La_2O_3 (a) $La_2O_3:Bi^{3+}$ (b) Co-doped with (c) Eu^{3+}



The remaining XRD pattern for La_2O_3: Bi doped and rare earth co-



doped samples Fig 1. (a and d) are indexed with the hexagonal form of La_2O_3. For getting pure hexagonal crystal structure, high temperature heating is done at 900 ° C. Hence pure hexagonal phase is attributed with better crystallinity. Fig.2 (a-c) shows 900 ° C undoped La_2O_3, $La_2O_3:Bi^{3+}$ and Eu^{3+} co-doped $La_2O_3:Bi^{3+}$. No diffraction peaks of other impurities were detected, even when co-doping is done to $La_2O_3:Bi^{3+}$. From Figs.1 and 2 a slight shift in peaks is observed due to co-doping. From this result it is noticed that the doped Eu^{3+} and Bi^{3+} ions completely enter into the matrix and occupy La^{3+} sites in these phosphors. According to the Scherrer's equation, the average crystallite size of heated samples is estimated to be 32- 39 nm. The cell parameters of the heated samples at 700 ° C and 900 ° C have also been determined by X-ray diffraction and refined using the POWDERX software. The cell parameters calculated were listed in Table.1 minor changes are observed in lattice parameters on co-doping. Lattice parameters of La_2O_3 for reference are a= 4.057 A° =b and c= 6.430 A°.

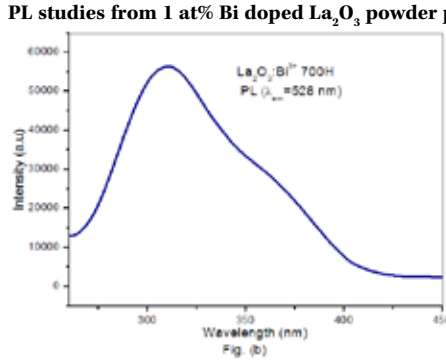
TABLE – 1 & 2

CELL PARAMETERS OF HEATED SAMPLES

Sample	700 ° C Heated			
	a (A°)	b (A°)	c (A°)	V(cc)
Undoped La_2O_3	4.021(3)	4.021(3)	6.541(3)	91.63
La_2O_3: Bi^{3+}	4.018(8)	4.018(8)	6.497(8)	90.54
$La_2O_3:Bi^{3+},Eu^{3+}$	4.027(3)	4.027(3)	6.488(3)	91.16

Sample	900 ° C Heated			
	a (A°)	b (A°)	c (A°)	V(cc)
Undoped La_2O_3	4.023(3)	4.023(3)	6.552(3)	91.44
La_2O_3: Bi^{3+}	4.026(2)	4.026(2)	6.517(3)	91.31
$La_2O_3:Bi^{3+},Eu^{3+}$	4.029(4)	4.029(4)	6.510(4)	91.54

PL studies from 1 at% Bi doped La_2O_3 powder phosphors



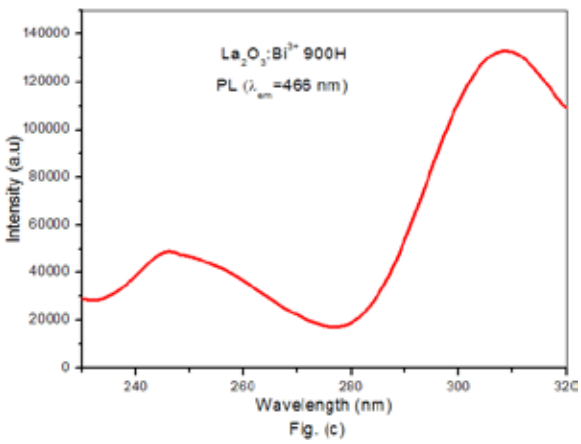


Fig.3 PL emission spectra (a) $La_2O_3:Bi^{3+}$ 700 and 900 °C heated samples (b) PL excitation spectra $La_2O_3:Bi^{3+}$ 700° C heated and (c) PL excitation spectra $La_2O_3:Bi^{3+}$ 900 °C heated samples.

Blue emission from La_2O_3: Bi^{3+} phosphor thin film has been previously reported [21–23]. The emission spectra of 700 and 900 °C heated $La_2O_3:Bi^{3+}$ powder samples are shown Fig.3 (a).The emission peak maximum at 528nm of 700 °C heated sample under excitation of 311nm is observed and corresponding excitation spectra is shown in Fig.3 (b). As for the 900°C sample it is observed a blue shift in emission peak at 466nm and increase in emission intensity when excited at 308nm. During sintering, excited luminescent centers are thermally activated through phonon interactions, which cause thermal release through the crossing point between the excited and ground states according to a configuration coordinate diagram [24].

At higher temperature, the density of phonons increases and electron-phonon interactions dominate, so a blue shift of the emission band is observed for the phosphors as the temperature increases which is in accord with the reported thin film $La_2O_3:Bi^{3+}$ phosphor [25]. In general, the temperature dependence of phosphors used in phosphor-conversion white LEDs is important because it has a considerable influence on the light output and color rendering index. From Fig.3 (c) the excitation spectra of 900 °C consists of two bands, the main excitation band peaks around 308 nm and the weak band peaks around 250 nm, originating from the $6s^2$–6s6p transition in Bi^{3+}.

The lifetime value is found to be significantly lower (0.9 μs) for 700 °C heated sample when compared to the 900 °C sample (8.2 μs) which can be seen from the decay curve shown in Fig. 4(a, b) This is explained based on the general expression for the oscillator strength of an electronic transition (f_{ex}), as given by equation 1, [26]

$$f_{ex} = \frac{2m}{\hbar}\Delta E\,|\mu|^2\,|U(0)|^2 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

Where ΔE is the transition energy, μ is the transition dipole moment and $|U(0)|^2$ is the probability of finding an electron and hole at the same place, m is the effective mass of electron, and h is Planks constant. For nanoparticles, due to their small size, the term, $|U(0)|^2$ is much higher compared to corresponding bulk and hence will have higher transition probability with respect to bulk. Higher oscillator strength (f_{ex}) values suggest shorter excited state lifetime, as both are inversely related. This accounts for the observed decrease in the lifetime values for the 700 °C samples compared to corresponding 900 °C samples. Since the decays are multi exponential average lifetime values are calculated and used for comparison.

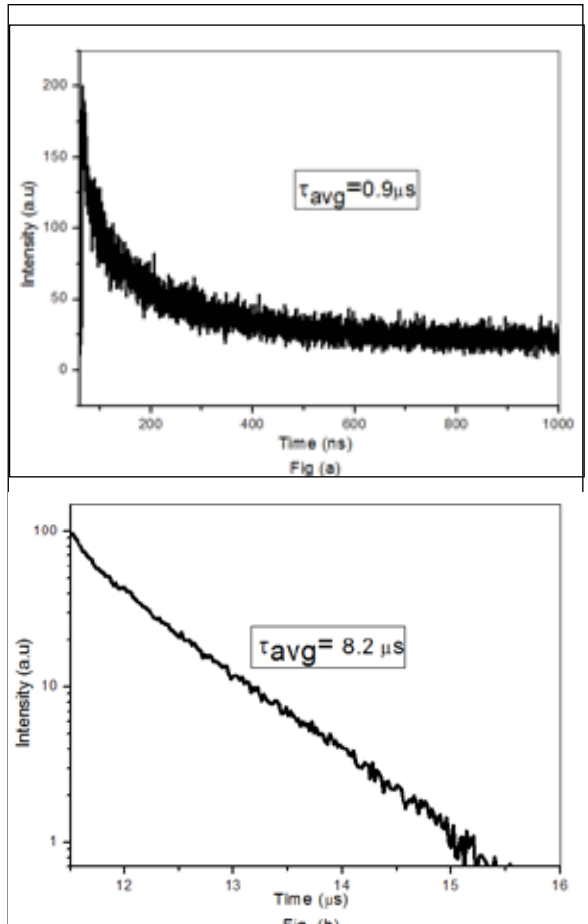


Fig.4 Decay curves corresponding to (a) $La_2O_3:Bi^{3+}$ (700 °C) heated and (b) $La_2O_3:Bi^{3+}$ (900 °C) heated samples.

PL studies from La_2O_3:1 at % Bi, 1 at% Eu powder phosphor

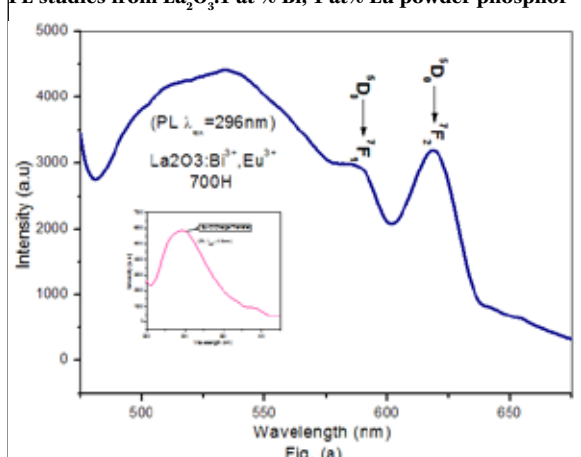


Fig.5 (a, b) shows the excitation and emission spectra of the 700 °C and 900 °C heated Eu^{3+}doped samples. For the excitation spectra Fig. 5 (a) (inset) of the 700 °C (1 at %) Eu^{3+} co-doped sample emission is monitored at 616 nm. Eu–O CT transition band centred at around 296 nm is observed. For the emission spectra (excited at 296 nm) emission peaks centred at 589, 616 nm are ascribed to Eu^{3+} 4f transitions from the excited level $^5D_0$ --- $^7F_2$, $^5D_0$ --- $^7F_2$ in which the strongest emission band at 616 nm is attributed to the transition $^5D_0$ --- $^7F_2$ [27]. Whereas for excitation spectra Fig.5 (b) (inset) of 900 °C heated Eu^{3+} co-doped (1 at%) sample, Eu–O CT transition band centred at around 626

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nm is observed. It is noticed that due to the presence of Bi^{3+} ions $O^{2-}$and Eu^{3+} electron (f-f) transitions are almost null.

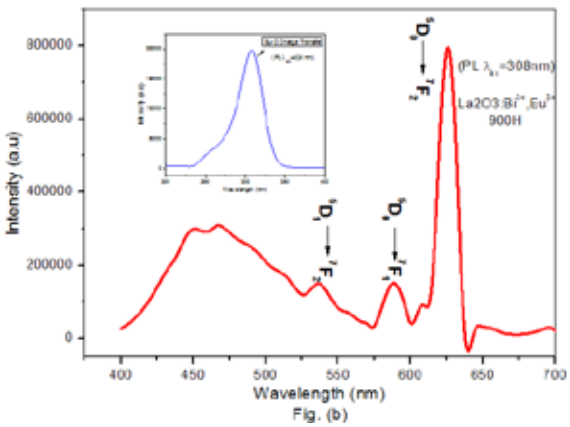


Fig. (b)

In general two excitation bands ranging from 230–275 nm and 275–350 nm are to be observed in La_2O_3:Bi^{3+} doped samples, but with addition of Eu^{3+} the host absorption band centred at 250 nm nearly disappears in both the heated samples. Emission spectra Fig. 5(b) of 900 °C heated sample excited at 308 nm emission peaks centred at 536, 589, 616 nm are ascribed to Eu^{3+} 4f transitions from the excited level $^5D_1$ --- $^7F_2$, $^5D_0$ --- $^7F_2$, $^5D_0$ --- $^7F_2$ in which the strongest emission band at 626 nm is attributed to the transition $^5D_0$ --- $^7F_2$. According to spectra it clearly shows that as on heating to higher temperature the peak intensities increases dramatically due to an increase in crystallinity and a decrease in the number of quenching sites (e.g., adsorbed OH). The OH group quenches the luminescence via non-radiative relaxation processes [28]. For this reason, thermal annealing could eliminate the quenching sites to increase the luminescence efficiency. This result indicates the existence of efficient energy transfer between the Bi^{3+} and Eu^{3+} ions in 900 °C heated sample is more when compared with 700°C heated sample. The corresponding multi exponential life time decay curves are shown in Fig. 6 (a, b) The average life time values of 900 °C and 700 °C heated sample found to be τ_{avg} = 2.13ms and τ_{avg} = 1.09 ms

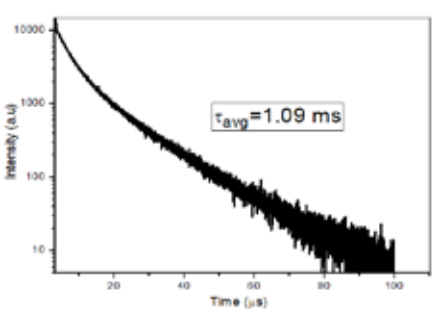


Fig. (a)

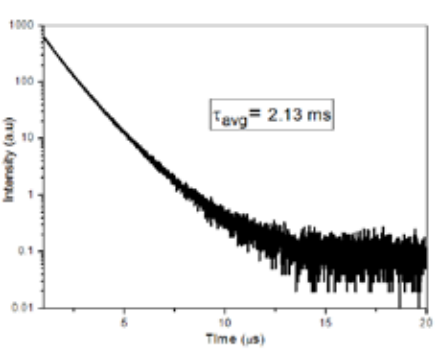


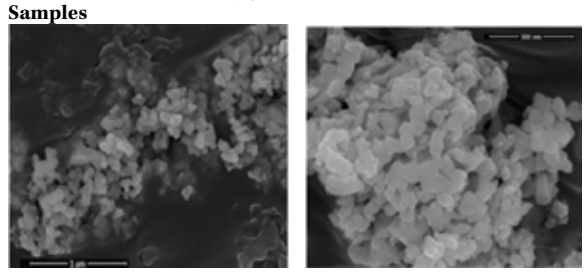
Fig. (b)

Fig.6-Decay curves corresponding to (a) La_2O_3:Bi^{3+},Eu^{3+} (700 °C) heated and (b) La_2O_3:Bi^{3+}, Eu^{3+} (900 °C) heated samples.

Structural and morphological studies

SEM

Fig.7 SEM images of La_2O_3 700 °C heated Undoped an Doped Samples



(a) Undoped La_2O_3 (b) La_2O_3: Bi^{3+}

c) La_2O_3: Bi^{3+}, Eu^{3+}

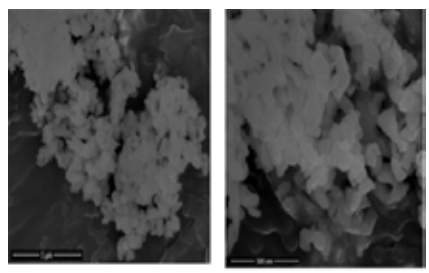
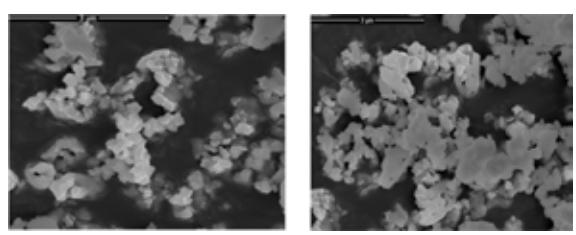


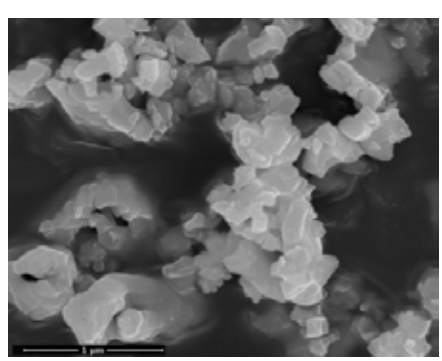
Fig. 8 SEM images of La_2O_3 900 °C heated Undoped and Doped Samples



(a)Undoped La_2O_3 (b) La_2O_3: Bi^{3+}

(c) La_2O_3: Bi^{3+}, Eu^{3+}

The surface morphology and crystallinity of solid host materials are important parameters which determine the emission characteristics of phosphors. The morphological analysis of La_2O_3, La_2O_3:Bi^{3+} and rare earth co-doped heated at 700 and 900 °C samples was performed by SEM examination shown in Figs 7 and 8. It can be seen from images the samples are of sphere-like structure. From these images it is clear that the aggregation and particle sizes of the La_2O_3: Bi^{3+} increases with Eu^{3+} co-doping. Also, it is clearly seen that the particles are in the agglomerated form with their size in the micrometer range.



TEM Fig. 9 (a) TEM image (b) SAED pattern (c) HRTEM of 700 °C La_2O_3 : Bi^{3+}, Eu^{3+} phosphors material

Fig. 10 (a) TEM image (b) SAED pattern (c) HRTEM of 900 °C La_2O_3 : Bi^{3+}, Eu^{3+} phosphors material

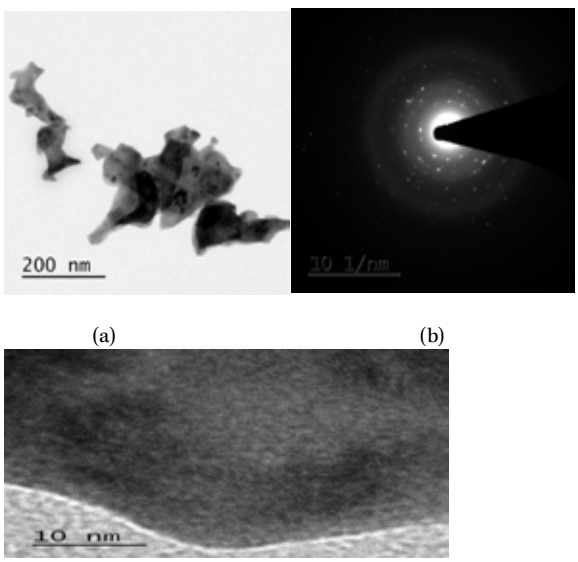


Fig.9 (a)–(c) represents TEM, SAED patterns, HRTEM image of La_2O_3:Bi^{3+}, Eu^{3+} sample after heating at 700 °C which indicates the created oxides are nanocrystalline materials with the average crystalline grain size of about 40-50nm which slightly more when compared with size calculated from Scherrer's relation in XRD. When the calcination temperature was further increased to 900 °C, the nanoparticles became bigger and merged with each other, and the sharpness of the particles completely vanished. The merging is related to the melting process because the surface-to-volume ratio of the nanoparticles is relatively high, and at high temperatures, the surface energy substantially affects the interior bulk properties of the materials. Fig. 10 (a-c) shows TEM, SAED patterns, HRTEM image of 900 ° C. The fine structure of 700 and 900 °C La_2O_3: Bi^{3+}, Eu^{3+} samples was further studied from the HR-TEM images and SAED patterns. The SAED patterns of the heated samples confirmed their nanocrystalline nature by producing a number of bright spots in an irregular manner.

FTIR Spectra

FT-IR spectrum of as-prepared dried samples recorded from 400 to 4000 cm^{-1} shown in Fig.11. The as prepared (undoped) La_2O_3 spectrum Fig.(a) shows an sharp band at 3614 cm^{-1}, corresponding to the stretching and bending O–H vibrations [29] and absorption band at 3481 cm^{-1} results from the O–H vibration of H_2O absorbed by the nanoparticles. The strong broad band at 1450 cm^{-1} is attributed to C-H bending. The FT-IR spectrum is in good agreement with the XRD pattern of as prepared La_2O_3. Whereas from the spectra Fig. 11 (b, c) of La_2O_3: Bi^{3+} doped and europium co-doped samples it is clearly shows the absence of sharp peak at 3614 cm^{-1}[30, 31]. The weak absorption band peak observed at O-H vibration of water molecules that are absorbed by bismuth doped nanoparticles at 3471cm^{-1} and weak broad band assigned at 3462 $cm^{-1}$for co-doped samples. A medium C-H bond stretching is observed at 2892cm^{-1} and two peaks were commonly observed at 1384 and 1464 cm^{-1}, which were assigned C-H bending, respectively in all doped La_2O_3 nanoparticles. Hence, the doped Bi^{3+} and europium ions are soluble in ethylene glycol (EG) homogenously by forming steady metal complexes due chelation between metal ions and EG which is verified from IR spectra.

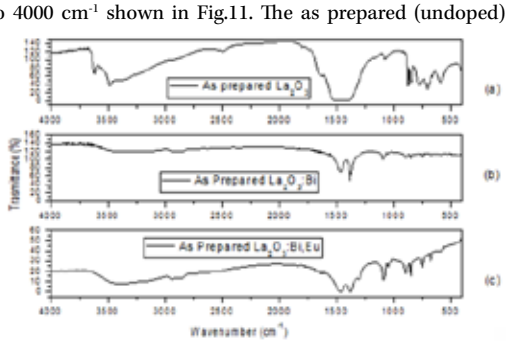
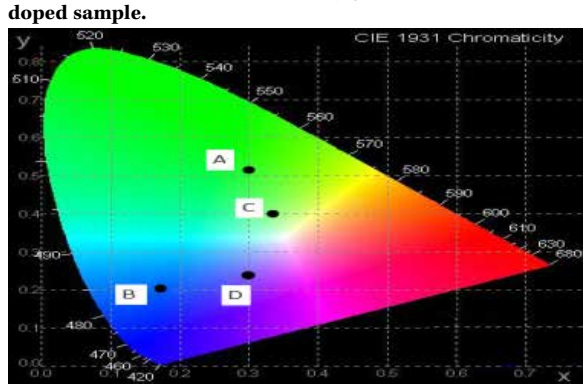


Fig. 11 FTIR spectra of As Prepared La_2O_3:Bi^{3+}, Eu^{3+}

CIE Coordinates

Fig. 12 CIE chromaticity color coordinates in PL emissions from 700 °C and 900 °C heated La_2O_3: Bi^{3+} and europium co-doped sample.



The color of PL emissions observed from La_2O_3:Bi^{3+}, Eu^{3+} powder samples changed to blue color from green colour as the temperature of the powder increased. Fig.12 shows the CIE chromaticity color coordinates of PL emissions from La_2O_3: Bi^{3+} and Eu^{3+} phosphor powder samples. In particular, the color change in PL emission observed from La_2O_3: Bi^{3+}, Eu^{3+} phosphor material is explained as a result that the energy of excited electrons has efficiently transferred from the excited state of Bi^{3+} to that of Eu^{3+} ion. CIE color coordinates have been calculated and found to be (0.30, 0.51), (0.16, 0.20), (0.34, 0.40), (0.30, 0.24), (0.32, 0.52), (0.22, 0.26), (0.17, 0.21) and (0.18, 0.30) respectively for La_2O_3:Bi^{3+} (700 °C), La_2O_3:Bi^{3+} (900 °C), La_2O_3: Bi^{3+}, Eu^{3+} (700 °C), La_2O_3: Bi^{3+}, Eu^{3+} (900 °C) respectively.

CONCLUSIONS

In this paper we have successfully synthesized La_2O_3: Bi^{3+},Eu^{3+} nanophosphors material by polyol method. The XRD patterns exhibited a hexagonal structure, and the FTIR spectra confirmed the presence of OH^- group in all as prepared La_2O_3 undoped and doped samples. After heating the as prepared La_2O_3 and La_2O_3:Bi^{3+} and Eu^{3+}co-doped samples, the XRD pattern con-

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firmed the formation of the pure La_2O_3 hexagonal phase. The effect of heating on the morphology of La_2O_3:Bi^{3+}doped and rare earth Eu^{3+}, co-doped were also examined by SEM and TEM. All the observed emission peaks in PL from La_2O_3:Bi,Eu^{3+}phosphor powder were assigned to either the broad emission originating from the transition in Bi^{3+} or the visible emission peaks originating transition from the Eu^{3+} ions. The shifting of emission from the samples on heating is clearly observed from the CIE color coordinates plot. Finally, from the above studies, we are able to suggest that the La_2O_3:Bi^{3+}, Eu^{3+} nanophosphors powders are promising materials for application in the development of novel optical systems such as FEDs, cathode ray tubes, plasma display panels, fluorescent lamps, etc.

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