

The Role of Bismuth on the Best Red Light Emitting Nanophosphors

Vini.K, H.Padma Kumar, K.M.Nissamudeen



Abstract: This paper explains the role of bismuth in the luminescence enhancement of $Y_2O_3:Eu$ nanophosphors prepared by Combustion method. Bi ions serve as effective sensitizers for visible emitting rare earths for Light Emitting Diodes. From the X-ray diffraction studies, bismuth co-activated nanophosphors exhibit an early crystallization. Bismuth incorporation not only results in the luminescence enhancement at 612 nm, due to 5D_0 to 7F_2 transition but also reduces the processing temperature for intense photoemission.

Keywords : Bismuth, Doping, Luminescence, Nanophosphor.

I. INTRODUCTION

Rare earth activated oxide nanophosphors shows a special attention because of wide range of applications in colour displays, lasers, optical amplifiers, up converters, telecommunication, sensors etc. At present, the main attention was done on some rare-earth metals like Nd^{3+} , Eu^{3+} , Ho^{3+} , Tm^{3+} , and Er^{3+} . These ions are capable to emit light from the visible region to the infrared region. Specifically, Eu^{3+} ions can be introduced into variety of host matrices. Because it emits light in 400-650 nm range that can be enhanced via up conversion processes. Previously, various approaches are used to increase the efficiency of luminescence. The incorporation of post transition metals instead of rare earth or as rare earth sensitizer in oxide host matrices has been suggested. In particular, bismuth is one among them. Because of the chances to be stabilized in various oxidation states which are optically active (0,+1, +2, +3, +5). The optical transitions of bismuth ions are allowed by the dipole selection rules owing to spin-orbit coupling. All the bismuth emission and absorption bands are broader than transitions of lanthanides, because of the unshielded electrons in the outer shell. These specialities provide a lot of favourable circumstances in tuning the optical properties of bismuth by appropriately selecting the host lattice. Bismuth serve as effective sensitizers for rare earths elements that emits light in the visible region (Eu, Sm, Tb) for LEDs [1].

The spectroscopic characteristics of bismuth ions has become an interesting and a hot topic employed in phosphor materials, that can be used as activator or sensitizer. Bismuth

are capable to interact strongly with host matrix that in turn influence their transitions. Thus, materials doped with bismuth ions manifest excellent luminescent property [2]. The bismuth ions are mainly used to activate phosphates, borates and oxide materials. The electronic configuration of Bi^{3+} ions are $6S^2$ with 1S_0 as the ground state and 3P_0 , 3P_1 , 3P_2 and 1P_1 as the first excited state with increasing excitation energies. Thus, it exhibit broad and high absorption at a wavelength of 300- 400 nm through 1S_0 to 3P_1 transition and strong emission at a wavelength of 400-650 nm through 3P_1 to 1S_0 transition when doped with Y_2O_3 host lattice [3]. In this work, an effort was made to synthesize photoluminescent Bi co-activated $Y_2O_3:Eu^{3+}$ nanophosphors by make use of combustion method. The impact of bismuth co-activation and process of annealing on the spectroscopic as well as structural characteristics of nanophosphors have been studied and compared with $Y_2O_3:Eu^{3+}$ nanophosphors.

II. MATERIALS AND METHODS

For synthesis work, yttrium oxide (Y_2O_3), europium oxide (Eu_2O_3), nitric acid (HNO_3) and citric acid ($C_6H_8O_7$) were used as the precursor materials. The procedure is schematically shown in Fig.1.

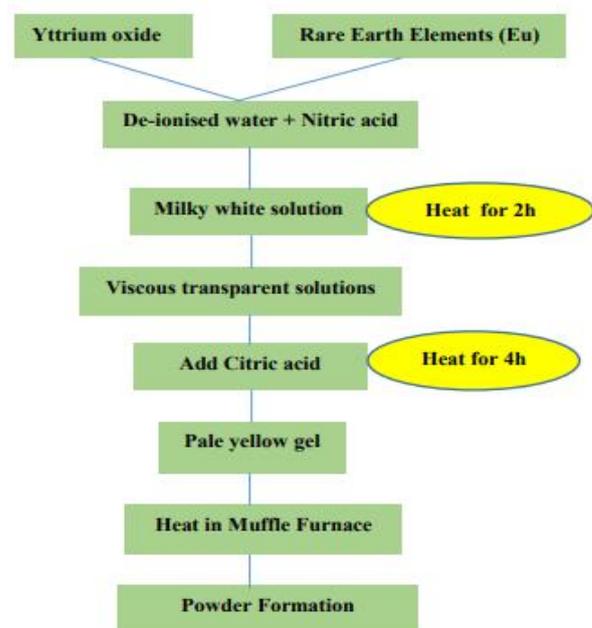


Fig.1: Schematic diagram for the preparation of Eu^{3+} doped Y_2O_3 nanophosphors

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Finally the white colour $Y_2O_3:Eu$ nanopowders are obtained. The PL intensity of 6wt% Eu^{3+} doped Y_2O_3 powders were seem to be maximum when compared to other Eu^{3+} concentrations.

By keeping the value of Eu^{3+} as constant (6wt%), we added different concentrations of Bi^{3+} ions and finally obtained 6wt% of Bi^{3+} as the optimised co-doped value and is shown in Fig.2. So, co-doping of bismuth has been carried out in same quantity (6wt%) in order to synthesize bismuth co-doped $Y_2O_3:Eu^{3+}$ nanophosphors.

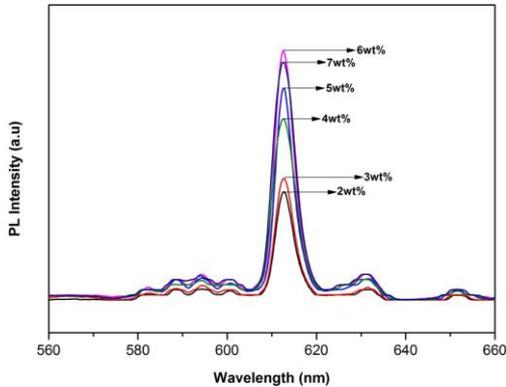


Fig. 2: PL emission spectra of Bi^{3+} co-doped Y_2O_3 prepared at different dopant values.

III. RESULTS AND DISCUSSIONS

A. Structural Properties – XRD Studies

The luminescence intensity of europium doped Y_2O_3 nanophosphors annealed at 1173 K on the basis of dopant concentration which was excited at a wavelength of 260 nm is depicted in Fig.3. It was found that the maximum luminescence intensity is obtained at a dopant concentration of 6wt% i.e 6wt% Eu^{3+} .

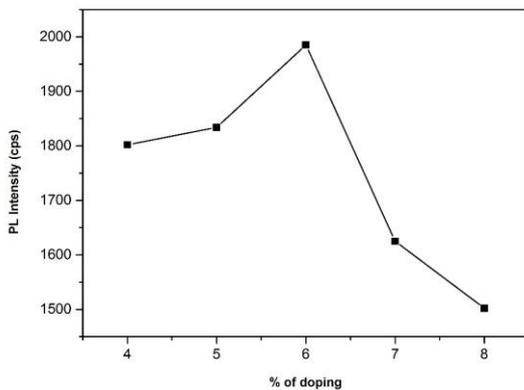


Fig. 3: PL intensity difference of europium doped Y_2O_3 nanophosphors in terms of europium concentration.

Fig.4 exhibits the X-ray diffraction spectra of europium doped Y_2O_3 and bismuth co-doped yttrium nanophosphors in as-synthesized temperature (773 K). As per JCPDS Standard Card No: 43-1036 the structure of the obtained product is cubic with Ia3 as the space group [4]–[6]. The crystal structure of the phosphor was not influenced by the introduction of Bi^{3+} ions [7]. No peaks correspond to europium or bismuth were seem to be present in the XRD pattern [8]. This reveals that the chemical composition of the

compound synthesized by this method are pure [9]. XRD patterns of the nanophosphors exhibit a superior growth on (222) plane of Y_2O_3 . Annealing contribute restructuring of nanophosphors thereby accredited to good crystalline property. In Fig.4 both the samples annealed at 773 K. But it is clear that the primitive crystallization is attained for bismuth co-doped nanophosphors. Structural parameter calculation of europium doped yttrium and bismuth co-doped $Y_2O_3:Eu^{3+}$ nanophosphors annealed at various temperatures are given in Table-I.

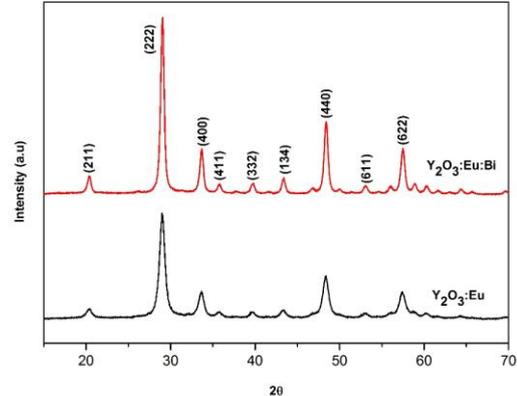


Fig 4: XRD spectra of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors prepared at 773 K.

Table-I: Grain size of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors annealed at various temperatures.

	$Y_2O_3:Eu^{3+}$	$Y_2O_3:Eu^{3+}:Bi^{3+}$
Temperature (K)	Grain size (nm)	Grain size (nm)
773K	9.69	11.70
873K	14.04	19.62
973K	15.46	25.34
1073K	20.57	25.65
1173K	27.51

B. TEM

Fig.5a & 5b shows the transmission electron micrographs of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors in as-synthesized condition. In the case of nanophosphors, particle size increment results in the reduction of surface area, which in turn reduces the surface defects and ultimately attains the luminescence enhancement. Fig.5c & 5d shows the TEM image of $Y_2O_3:Eu^{3+}$ nanophosphors annealed at 1173 K and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors annealed at 973 K (temperature at which optimum intensity is observed). FETEM image of the sample confirmed that in the prepared sample there are small crystallites associated with each other (particles are aggregated) [6],[10],[11].

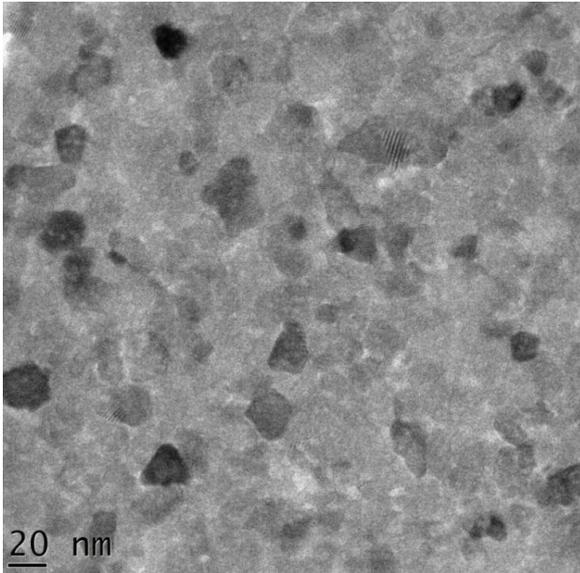


Fig 5a: TEM images of $Y_2O_3:Eu^{3+}$ at 773 K

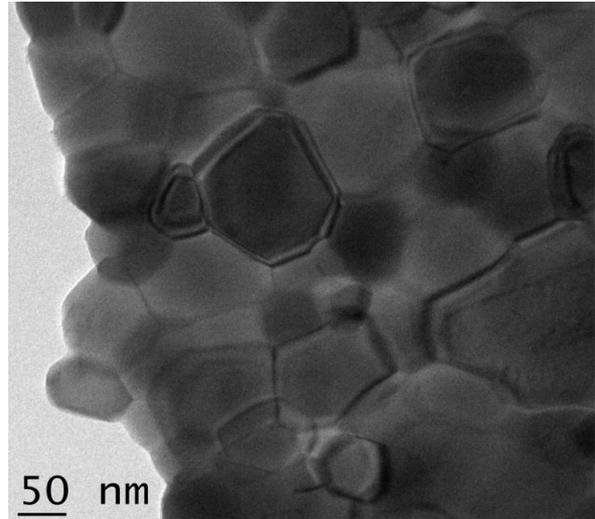


Fig 5c: TEM images of $Y_2O_3:Eu^{3+}$ at 1173 K

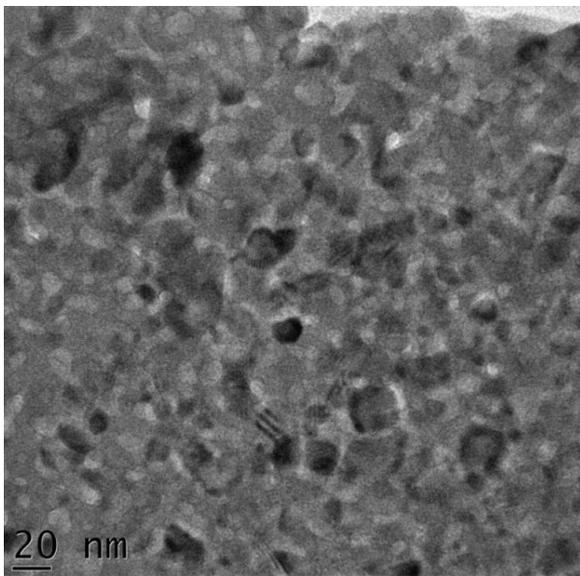


Fig 5b: TEM images of $Y_2O_3:Eu^{3+}:Bi^{3+}$ at 773 K

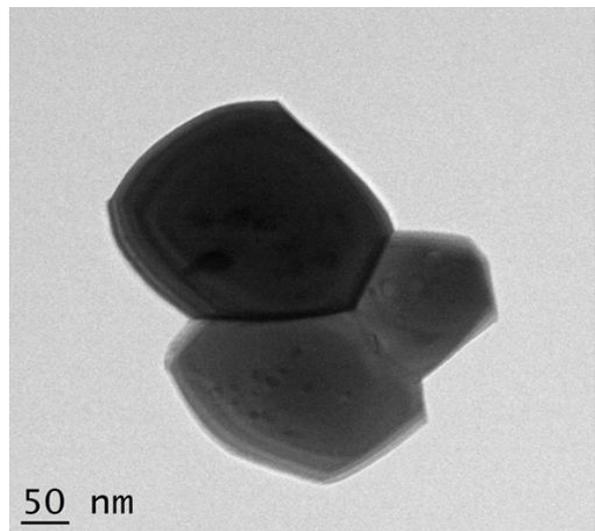


Fig 5d: TEM images of $Y_2O_3:Eu^{3+}:Bi^{3+}$ at 973 K nanophosphors.

It was believed that temperature is an important factor on which quality and crystallinity of the particles depends. In the case of samples, annealed at 1173 K and 973 K, each particle contains many nanocrystals. This is the evolution of structure from amorphous to crystalline state. As the temperature increases, particle size increases which was proved from XRD data and at 1173 K and 973 K, each particle exhibit single crystalline phase. Thus it is quite natural that the PL intensity is stronger [12]. But in the case of lower temperature there occurs decrease in luminescence intensity. Reason may be the formation of killer centers or the activator ions are not perfectly co-operate with host element [12]. When the temperature increases, there will be an increase in the size of the particle. This results in the reduction of surface to volume ratio, reduction in scattering of light which in turn increases the efficiency [12]. Thus we can say that sintering or hard agglomeration plays a significant role in the increase of particle size. Formation of oxygen bridge bonds by the hydrogen bonds which was formed between chemical combination of OH^- can be one of the main reason for hard agglomeration [13].

C. Photoluminescence Studies

Fig.6 indicates the difference in intensity, in the case of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors on the basis of various annealing temperature. It was found that, for $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors, photoemission is saturated when the sample is annealed at 973 K. Thus co-doping with bismuth results in the luminescence enhancement. Moreover, it reduces the processing temperature.

Fig.7 shows luminescence emission of $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors annealed at different temperatures. It was found that the maximum emission intensity is obtained for the samples annealed at 973 K. Fig. 8 shows the emission spectra of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors annealed at 1173 K and 973 K respectively.

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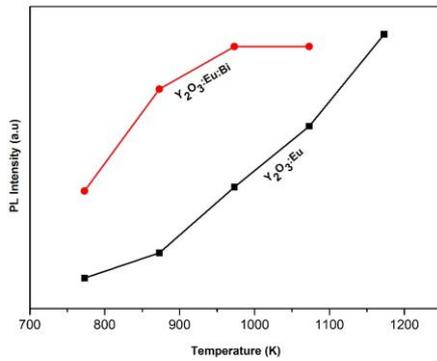


Fig.6: PL intensity difference of $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors in terms of annealing temperature.

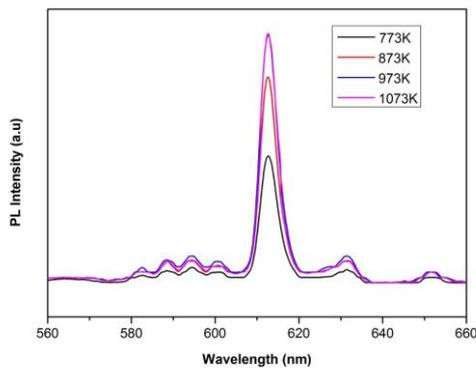


Fig.7: PL emission spectra of $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphors annealed at various temperature.

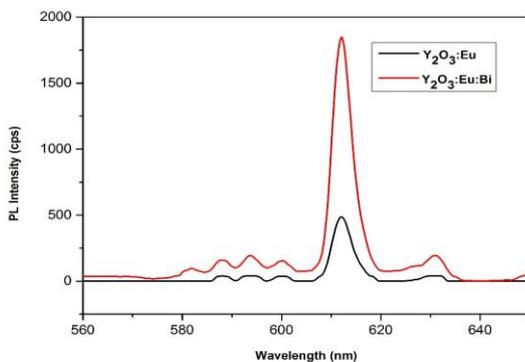


Fig.8: Comparison of PL emission spectra of Eu^{3+} doped sample at 1173 K and Bi^{3+} co-doped samples at 973 K.

These nanophosphors when exposed to UV light results in the charge transfer band whose output is the emission of red colour by 5D_0 to 7F_2 transition of the Eu^{3+} ion. In europium doped yttrium oxide, the charge transfer band that are excited is because of local excitation. O^{2-} has 2p orbital and Eu^{3+} has 4f orbital. An electron get excited from 2p orbital to 4f orbital. In the case of europium, the transfer of energy occurs mainly from two sites namely C_2 and S_6 sites. For europium ions, five emissions should be present corresponds to 5D_0 to 7F_1 transition. Two peaks resides in S_6 sites and three peaks in C_2 site. Only magnetic dipole transitions prevails for S_6 symmetry. Here, the selection rule $\Delta J = 0, 1$ exist. The peaks located at 580-600 nm range are very weak and can be assigned to 5D_0 to 7F_1 magnetic dipole transition [14]. In the case of europium doped yttrium oxide, maximum intense red

emission is observed at 612 nm. Nearby a peak at 630 nm was observed which is very weak. Both the peaks were due to 5D_0 to 7F_2 transitions of europium ions [14], [15], [16]. The ionic radii of Bi^{3+} , Eu^{3+} and Y^{3+} are 0.10 nm, 0.094 nm and 0.090 nm respectively. On comparing the ionic radii, bismuth and europium ions are not expected to take up the distinctive sites in a systematic manner. The incorporation of bismuth ions into $Y_2O_3:Eu^{3+}$ nanophosphors results in the development of defective structure by replacing Y^{3+} with Bi^{3+} . Thus europium sites had better reduced symmetry which is capable of lifting the parity selection rule which in turn results in the enhancement of luminescence. The dawning of this PL enhancement is complex [17]. Intensity increment can be due to many reasons like crystallinity increment, grain size increment and co-doping with bismuth for interstitial oxygen. The substitution of Y^{3+} sites by Bi^{3+} ions normally results in large number of unfilled sites in the oxygen – ion array. It was observed that bismuth plays the role of a lubricant for the perfect incorporation of europium into Y_2O_3 at the time of the sintering process. From the literature review, in the case of europium doped yttrium nanophosphors, co-doping with gadolinium, lithium, holmium, bismuth etc. has been reported. [10]. On comparing the luminescence intensity of $Y_2O_3:Eu^{3+}$ nanophosphors and $Y_2O_3:Eu^{3+}:Li$ nanophosphors, Yi et al., and Jeong et al., reported 2.7 times intensity increment after co-doping. Nissamudeen et al., reported 3 times intensity increment in the case of thin films. Co-doping with Gd ions also exhibit much better results. Bae et al., obtained the intensity increment of 3.1 times after co-doping Gd ions into $Y_2O_3:Eu^{3+}$ nanophosphors. Recently, Nissamudden et al., reported 3.73 times increment by the addition of Gd ions. Bae et al., also communicated the luminescence enhancement by 1.6 times by comparing $Y_2O_3:Eu^{3+}:Li^+ :Gd^{3+}$ and $Y_2O_3:Eu^{3+}$ nanophosphors. In the present study we noted luminescence enhancement of about 3.4 times by the addition of bismuth into $Y_2O_3:Eu^{3+}$ nanophosphors and is shown in Fig.9. The study of role of bismuth has been extended to gadolinium co-doped europium doped yttrium oxide nanophosphors. Earlier we obtained optimized value of co-dopant as 7wt% Gd^{3+} i.e. $Y_2O_3:6wt\%Eu^{3+}:7wt\%Gd^{3+}$. To this we added 6wt% Bi^{3+} (optimized value). Unfortunately we could notice luminescence enhancement of 0.3 times compared to $Y:Eu:Gd$ samples. Here also early optimization is attained at 973 K.

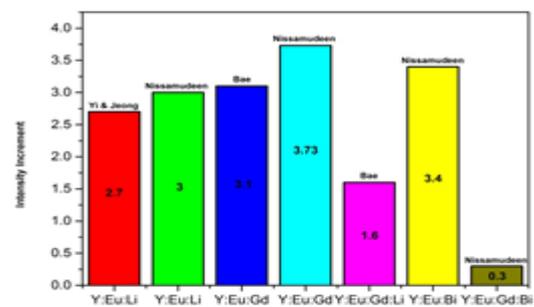


Fig.9: Study of intensity increment by the addition of various co-dopants.

IV. CONCLUSION

Nanostructured $Y_2O_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}:Bi^{3+}$ nanophosphor has been synthesized using combustion method. The changes occur on the morphology, structure and spectroscopic properties after the incorporation of bismuth ions are studied in detail. The XRD studies confirms that the incorporation of Bi^{3+} ions does not make any change in the structure of the Y_2O_3 . PL studies and XRD studies reveals that crystallization depends on annealing temperature and bismuth incorporation. The incorporation of bismuth results in the luminescence enhancement. Moreover, it reduces the processing temperature

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