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Synthesis and Optical Properties of Eu^{3+} Activated $YAlO_3$ Red Phosphor

M.S. Mendhe[1], S.P. Puppalwar[2], S.J. Dhoble[3]

[1, 2]Department of Physics, Kamla Nehru Mahavidyalaya, Nagpur 440009, India

[3]Department of Physics, RTM Nagpur University, Nagpur 440033, India

Abstract: ***$YAlO_3:Eu^{3+}$ phosphor was synthesised by a solution combustion method. Powder X-ray diffraction (PXRD) confirms the orthorhombic phase of yttrium aluminate ($YAlO_3$). The crystal structure, photoluminescence properties and concentration quenching of $YAlO_3:Eu^{3+}$ phosphors were systematically investigated. The excitation spectra indicate that the phosphors can be efficiently excited by 394 nm, which is matched well with the emission wavelength of near-UV LED chip. All the samples show the characteristic red emission of Eu^{3+} ions ($^5D_0$ - ^7F_J, J = 0, 1, 2, 3 and 4). The maximum intensity of luminescence is observed at the Eu^{3+} concentration around x = 0.015. The concentration quenching of Eu^{3+} in $YAlO_3:Eu^{3+}$ phosphor can be mainly attributed to quadrupole–quadrupole interaction. The results indicate that $YAlO_3:Eu^{3+}$ phosphors exhibit potential applications in the field of near-UV LED as an efficient red- emitting phosphors.***

Keywords: $YAlO_3:Eu^{3+}$; XRD; Photoluminescence; Near UV-LED; Red phosphor.

1. Introduction

White light-emitting diode (W-LED) is considered to be the fourth generation illumination lamp over the conventional incandescent and halogen lamp due to advantages of saving-energy, environment protection, long lifetime, reliability [1–3]. Currently, there are mainly two approaches to produce white light. one approach to achieve white light which has become a commercial production in large-scale is to combine cerium-doped yttrium aluminum garnet (YAG:Ce) phosphors with blue InGaN chip, in which a blue light-emitting InGaN chip is used to excite phosphors which emit yellow light and then mix the remaining blue light from the pump to compose desired white light [4]. In order to improve the white light quality, the other approach to obtain white light is proposed to combine UV LED chip with multi-phased (red, green and blue) phosphors, which possesses high color rendering index and superior color uniformity due to white color generated only by phosphors [5, 6]. However, the main red-emitting phosphor for UV LED chip is $Y_2O_2S:Eu^{3+}$ which shows chemical instability and low absorption efficiency in the near UV region [7, 8]. Therefore, it is highly desirable to develop a new stable phosphor that can emit intense red emission with strong excitation band at around 400 nm for near-UV LED chip.

Aluminates have been extensively investigated due to their high thermal, chemical stability and strong absorption in the near ultraviolet region. Rare earth doped aluminate phosphors have considerable practical applications in various devices such as solid-state lasers, optical communication, Plasma display panel (PDP), and LED. Among perovskites, $YAlO_3$ (YAP) is one of the three yttrium aluminium double oxides, together with the $Y_3Al_5O_{12}$ garnet (YAG) and $Y_4Al_2O_9$ monoclinic (YAM) structures. In the present study, a novel phosphor $YAlO_3:Eu^{3+}$ has been prepared by a facile combustion process in which we used the metal nitrates as the base materials and urea as fuel to decompose the metal nitrates. To our best knowledge this is the first report to synthesize $YAlO_3:Eu^{3+}$ by combustion. The orthoaluminates thus obtained by combustion process were then heated at high temperature 800 °C for 2 h producing bright red phosphors.

2. Experimental

Polycrystalline sample $YAlO_3:Eu^{3+}$ were prepared by aqueous combustion method. Solution contains stoichiometric amounts of corresponding metal nitrates, ammonium nitrate and urea. $Y(NO_3)_3$ $9H_2O$ (99.99%), Eu_2O_3 (99.99%), and $Al(NO_3)_3$ $9H_2O$ (A.R. grade) were used as the starting materials. The nitrates and oxide were, respectively, dissolved in deionized water and dilute nitric acid, and corresponding nitrate solutions were obtained, and mixed together, the ratio of ethylene glycol to total metal cation being 1:1. The heat generated in the exothermic reaction between nitrate and urea is used to carry out the synthesis. The starting materials were crushed and ground in a China dish with a minimum quantity of de-ionized water to form a solution. The dish was then introduced into a muffle furnace maintained at 500 ^{0}C. Upon heating of the reactants, there was vigorous evolution of gases with subsequent appearance of flame. As soon as the reaction was over, the China dish was taken out of the furnace and the foam was crushed to yield a porous mass. This powder was used for further characterization. Phase and crystallinity of the prepared material were investigated by powder XRD using PAN-analytical diffractometer with Cu K_α radiation (λ=1.5405 A^0) operating at 40Kv, 30 mA. The photoluminescence (PL) emission spectra of the samples were recorded by using SHIMADZU Spectrofluorophotometer (RF-5301 PC) at room temperature.

3. Results and Discussion

The formation of crystalline phases in the samples prepared by the solution combustion method was confirmed by powder XRD measurements. Fig.1 shows the XRD pattern of $YAlO_3:Eu^{3+}$ phosphor and well matched with the JCPDS data file (No. 70-1677). The PXRD patterns exhibit dominant diffraction peaks due to the orthorhombic phase of

YAlO3 (JCPDS File no.70- 1677). No other phase or unreacted starting materials were observed.

The photoluminescent characteristics of YAG: Eu phosphors were evaluated on the basis of emission (PL) and excitation (PLE) spectra. Fig. 2 presents the excitation spectrum of $YAlO_3$: $0.015Eu^{3+}$ sample, monitored at 617 nm. The PLE spectra recorded between 320 nm and 420 nm contains several weak sharp lines associated to the f–f electronic transitions of Eu^{3+} ions with maxima at 360 nm ($^7F_0\rightarrow{}^5D_4$), 379 nm ($^7F_0\rightarrow{}^5G_{4-6}$), 394 nm ($^7F_{0,1}\rightarrow{}^5L_6$) and 413 nm ($^7F_0\rightarrow{}^5D_3$). In any case, it is a good phenomenon that the as-prepared phosphors can strongly absorb the ultraviolet light, which is matched well with the characteristic emission of the near-UV LED chips. The emission spectra of $YAlO_3$ doped with different Eu^{3+} concentrations are shown in Fig. 3. All of the emission spectra exhibit the similar profile with different relative intensities.

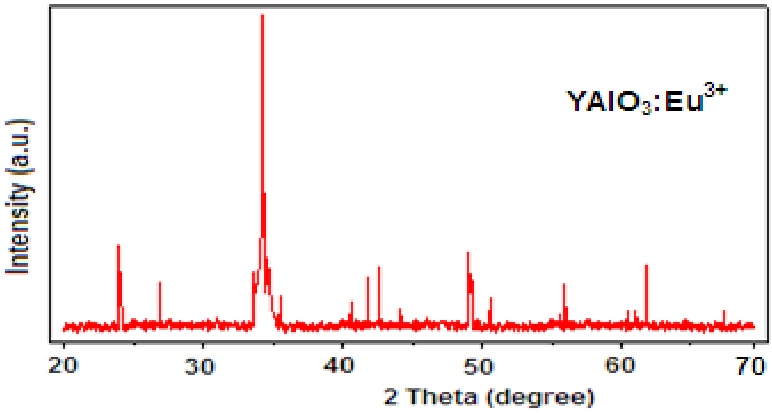

Figure 1: The XRD patterns of $YAlO_3$: $0.015Eu^{3+}$ phosphor.

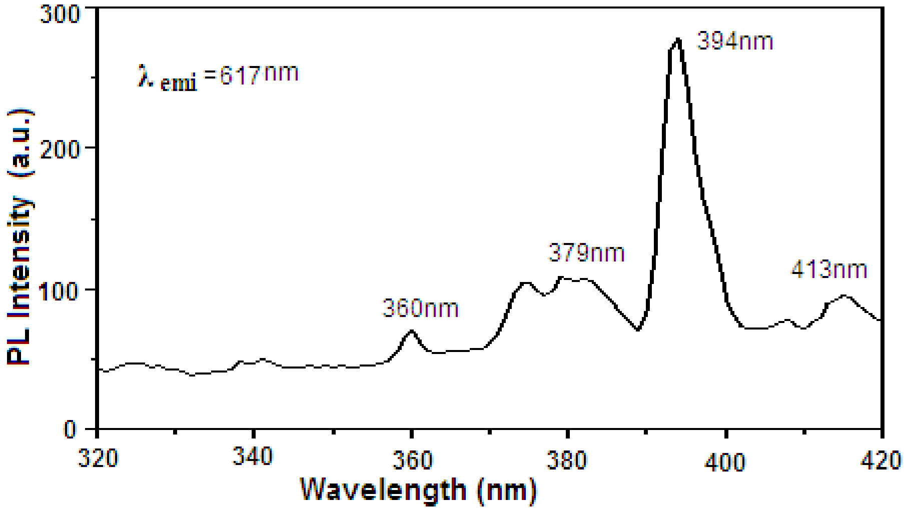

Figure 2: Photoluminescence excitation spectrum of $YAlO_3$: 0.015 Eu^{3+}.

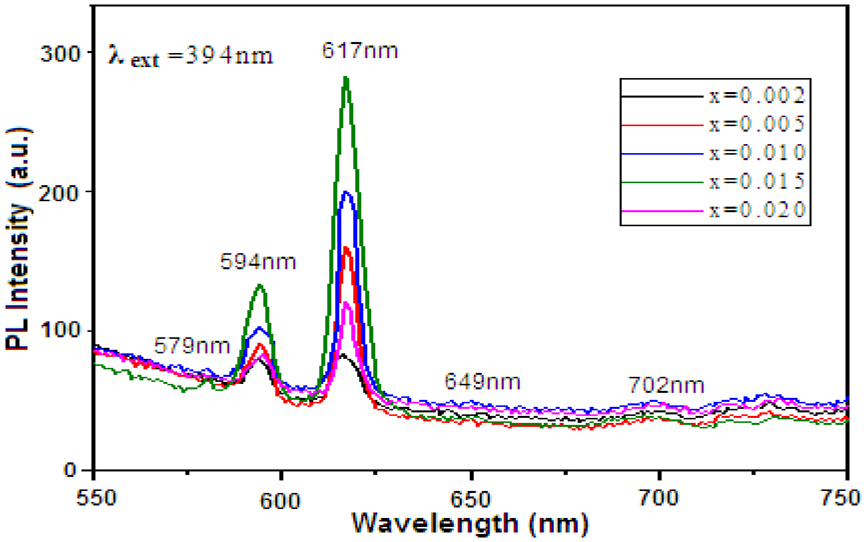

Figure 3: Photoluminescence emission spectra of $YAlO_3$ doped with different Eu^{3+} concentrations.

Each spectrum consists of five typical emission peaks in the range of 550 –750 nm, which result from $^5D_0$ - ^7F_J (J = 0, 1, 2, 3 and 4) transitions of Eu^{3+} ion, respectively. The main peak centered at 617 nm corresponds to electron dipole $^5D_0$ - $^7F_2$ transition which are permitted only when Eu^{3+} ions occupy the low symmetry sites, with no inversion center and the peak at 594 nm ascribes to magnetic dipole $^5D_0$ - $^7F_1$ transition of Eu^{3+} ions, which are located in high symmetry sites in the host lattice and that, are independent on the structure. The other weak emission peaks around at 579 nm, 649 nm and 702 nm are assigned to $^5D_0$ - $^7F_0$, $^5D_0$ - $^7F_3$ and $^5D_0$ - $^7F_4$ transitions of Eu^{3+} ions, respectively. As we all know, when Eu^{3+} ions occupy a low symmetry site, the electron dipole $^5D_0$ - $^7F_2$ transition is dominant [9]. In $YAlO_3$: xEu^{3+} host lattice, the $^5D_0$ - $^7F_2$ electric dipole transition becomes strongest among all these transitions due to the lack of inversion symmetry and the break of parity selection rules, which is benefit for obtaining a pure red phosphors with good CIE chromaticity coordinates. This band is hypersensitive to the environment. Fig. 3 shows the dependence of the peak intensity of the emission centered at 617 nm on Eu^{3+} concentration (x) in $YAlO_3$: x Eu^{3+}. The emission intensity increases initially with the increase of Eu^{3+} concentration and reaches to the maximum at x = 0.015, then gradually decreases due to the internal concentration quenching. The concentration quenching mechanism is generally associated with energy transfer.

While discussing the mechanism of energy transfer in phosphors, it is necessary to obtain the critical distance (R_c), i.e. the critical separation between the donor (activator) and acceptor (quenching site). Blasse suggested that the R_c of energy transfer can be calculated by the critical concentration of the activator ion [10]. The critical transfer distance (R_c) is approximately equal to twice the radius of a sphere with this volume:

$$R_c \approx 2\left[\sqrt[3]{\frac{3V}{4\pi X c\, N}}\right]$$

where, V is the volume of the unit cell, X_c is the critical concentration of the activator ion, and N is the number of host cations in the unit cell. For the $YAlO_3$ host, by taking the values of N = 4 (N = Z x 1, Z is the number of formula per unit cell), X_c = 0.015 and V = 204.10 $A^{\circ 3}$, the obtained R_c value is 18.66 A°. In this case, the exchange interaction will occur in energy transfer process [11]. Thus, in view of the emission and excitation spectra of $YAlO_3$: Eu^{3+}, the radiation reabsorption is unlikely to occur. As a result, the energy transfer process of Eu^{3+} in $YAlO_3$ phosphor would be due to multipolar interaction.

The Commission International del'Eclairage (CIE) 1931 chromaticity coordination of $YAlO_3$:0.015Eu^{3+} phosphor under the excitation wavelength of 394 nm in the CIE 1931 chromaticity diagram is shown in Fig.4. Y_2O_2S: Eu^{3+} is reported to be the mainly commercial red phosphor for near-UV LED [12]. The CIE chromaticity coordinates of $YAlO_3$:0.015Eu^{3+} are (0.680, 0.315) which is closer to NTSC (National Television Standard Committee on Chromaticity) standard values (0.67, 0.33) than that of Y_2O_2S:0.05 Eu^{3+} (0.62, 0.32). So the results indicate that Eu^{3+} doped $YAlO_3$ phosphor have a better color purity and high color saturation. The excitation wavelength and emission band of Eu^{3+} doped $YAlO_3$ phosphor in our work are in the range of the latest Eu^{3+} doped phosphors [13]. Thus, as prepared $YAlO_3$:0.015Eu^{3+} phosphor is promising red emitting phosphor for near UV- LED.

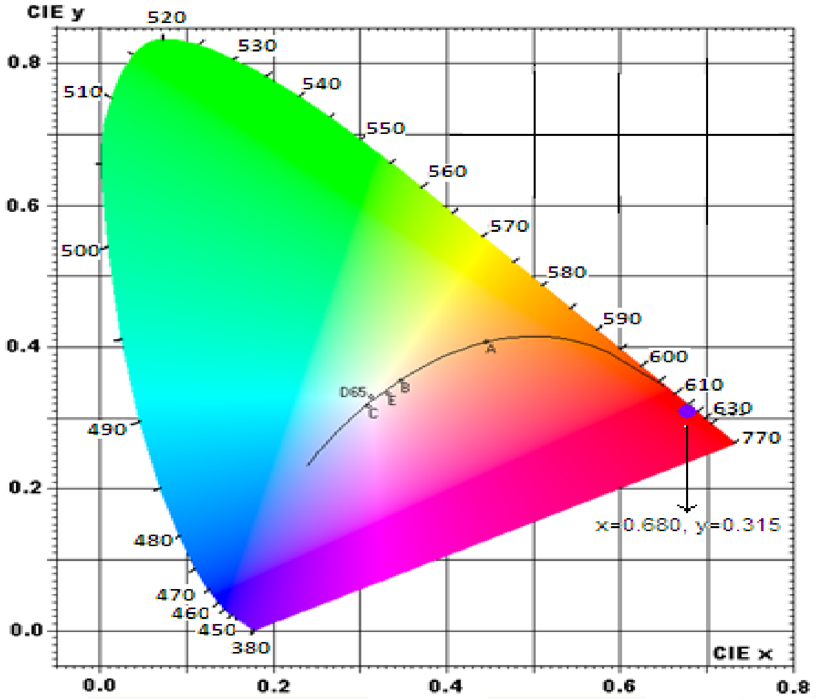

Figure 4: CIE chromatic diagram showing the chromatic coordinates for $YAlO_3$:0.015Eu^{3+}.

4. Conclusion

To conclude $YAlO_3$: xEu^{3+} powder phosphors have been synthesized using facile combustion method. The phosphors can be efficiently excited by 394 nm, which is matched well with the emission wavelength of near-UV LED chip. Under the excitation wavelength of near-UV light, the phosphors show the strong emission peak corresponding to the characteristic emission of Eu^{3+} ions. The main peak in the emission spectra is assigned to the characteristic transitions of Eu^{3+} and centered at 617 nm belonged to the electron dipole ($^5D_0$ – $^7F_2$) transition. These phosphors can be exploited for fluorescent lamp to get better color rendering index and higher lumen output. The results indicate that $YAlO_3$: x Eu^{3+} phosphors are efficient red-emitting phosphors for near-UV LED.

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