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EFFECT OF EUROPIUM CONCENTRATION ON PHOTOLUMINESCENCE PROPERTIES OF NANO CUBIC CRYSTALLINE Y_2O_3:EU PHOSPHOR

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Abstract
Photo Luminescence studies of Yittrium Oxide doped with different Mole percentage (2, 5, 6, 7, 8, 10, 12 & 15) of Europium is studied for nano sized cubic crystalline Y_2O_3:Eu phosphor. Luminescence intensity of yittrium oxide increases from 2 to 6 mol percentage of Eu doping then gradually decreases down from 7-15 mole percentage because of quenching at 6mol% Eu doping. Cubic crystalline nanophosphor is prepared by Urea combustion synthesis keeping U/N ratio as unity. Powder XRD (X-Ray Diffraction) of samples were done and verified with JCPDS 25-1011 data that confirms the nano cubic crystalline structure of Y_2O_3:Eu phosphor. Particle size ranges between 8.3-8.7nm which is well verified with TEM (Transmission Electron Microscopy) images of samples. PL intensity at 2mol% Eu doping in Y_2O_3 has almost similar PL intensity as at 10mol% Eu doping in Y_2O_3 cubic crystalline nanophosphor.

Introduction

Yittrium Oxide doped with Europium is a prominent red phosphors, due to sharp emission of λ=611nm of the europium ion as an activator (Eu^{3+}) in the host lattice (Y_2O_3). It shows efficient luminescence properties under UV and electron beam excitation is therefore been utilized in phosphor application [1]. Solid state method or precipitation method are basic methods that are generally utilized for Commercial production of this phosphor but the crystalline size is of range of μm. Micrometer size of Y_2O_3:Eu phosphor are widely utilized in red light display, tri-chromatic lamps, and projection color TV. Recently nano dimensioned optical properties of Y_2O_3:Eu phosphor has been a field of great interest for researches. Y_2O_3 doped with Eu^{3+} is widely used in lighting and display applications in fluorescent lamp[2,3]. Numerous methods has been tried to prepare nanocrystalline Y_2O_3:Eu with controlled smaller particle size and morphology to improve display and resolution of phosphors. A. Konrad et al. has prepared

10nm size nanocrystalline Y_2O_3:Eu phosphor using chemical vaporization technique[4]. Hergen Eilers et al. used CO_2-Laser vaporization of metal oxide ceramics to obtain monoclinic nanocrystalline structure of Y_2O_3:Eu particles [5]. Lei Yang et al. prepared Y_2O_3 nanotube arrays embedded in anodic alumina membranes (AAMs) with the help of electronic field-assisted deposition method [6]. Nano sized fibers with pure body centered cubic (bcc) Y_2O_3:Eu were prepared using electro-spinning [7]. Comparative study of Y_2O_3:Eu prepared by sol-gel and solid state reaction method were done for 233.5nm excitation spectrum of the 612nm red emission [8], which is attributed to Charger Transfer State (CTS) transition due to Eu-O interaction. PL studies of Y_2O_3:Eu prepared by Urea Combustion and Precipitation method were also done by S. J. Dhoble et al.[9] for 247nm excitation. Luminescence studies of Eu doped yttrium oxide prepared from different synthesis route and effect of temperature were also been studied for different excitation wavelength[10, 11].

This paper reports the preparation of Y_2O_3:Eu nanophosphor using urea combustion synthesis route for different Eu doping mole concentration at definite U/N molar ratio. Effect of doping percentage and quenching of Eu in Y_2O_3 phosphor in cubic crystalline nanophosphor is studied.

Experimental Procedure

Y_2O_3 and E_2O_3 (99.99%), Nitric Acid (80% A.R.), Urea are taken as base materials. Fresh nitrates of Yttrium ($Y(NO_3)_3$) and Europium ($Eu(NO_3)_3$) were prepared by dissolving Y_2O_3 & Eu_2O_3 in nitric acid and warming them at 70-80^{0}C over an electric heater. Heating process involves emission of brown fumes at the beginning with get a clear transparent solution at the end when solution heated for 10-12 minutes.

Sample preparation

Freshly prepared nitrate solutions of $Y(NO_3)_3$ and $Eu(NO_3)_3$ were mixed according to the formula $(Y_{0.94},Eu_{0.06})_2O_3$ in a beaker with the addition of suitable amount of Urea i.e. U/N molar ratio unity. The mixed solution was then heated with continuous stirring till the excess water evaporates. Brownish yellow gel will be obtained when complete water get evaporated. The Gel is taken into a crucible and placed under preheated furnace at 600^{0}C for an 2.5 hour. Combustion processes to prepare Y_2O_3:Eu involves following

$$(2\text{-}2x)Y(NO_3)_3 + 2xEu(NO_3)_3 + 5(NH_2)_2CO \rightarrow (Y_{1-x}Eu_x)_2O_3 + 5CO_2 + 8N_2 + 10H_2O$$

$$6Y(NO_3)_3 + NH_2CH_2COOH \rightarrow 3Y_2O_3 + 20CO_2 + 20H_2O + 14N_2$$

Y_2O_3:Eu samples were prepared for different 2, 5,6, 7,8, 10, 12 & 15 mol% Eu doping concentrations.

Sample Characterization and PL Instruments

The morphology and particle size of prepared Y_2O_3:Eu phosphors samples were observed by using X-Ray Diffraction Spectroscopy & TEM. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The x-rays were produced using a sealed tube and the wavelength of x-ray was 0.154 nm(Cu K-alpha). The X-rays were detected using a fast counting detector based on Silicon strip technology (Bruker Lynx Eye detector).PL testing is done on “Varian-CARY ECLIPSE Fluorescence Spectrophotometer” for Excitation and Emission slit width 1.5.

Result and Discussion

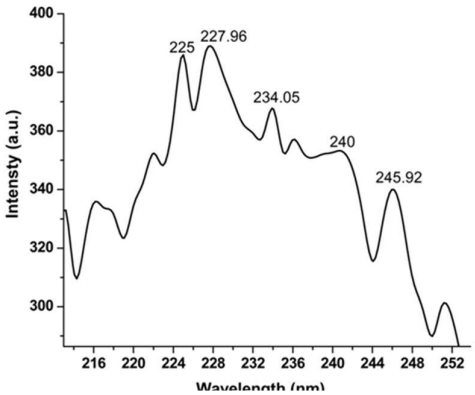


Fig. 1 Excitation spectra for 611nm emission of Y_2O_3:Eu nanophospor

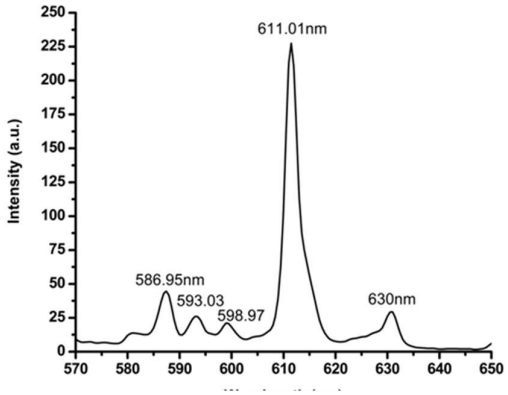


Fig. 2 Emission spectra Y_2O_3:Eu nanophospor at 228nm excitation

Fig. 1 Shows the excitation spectra for Luminescence emission of 611nm emission. It

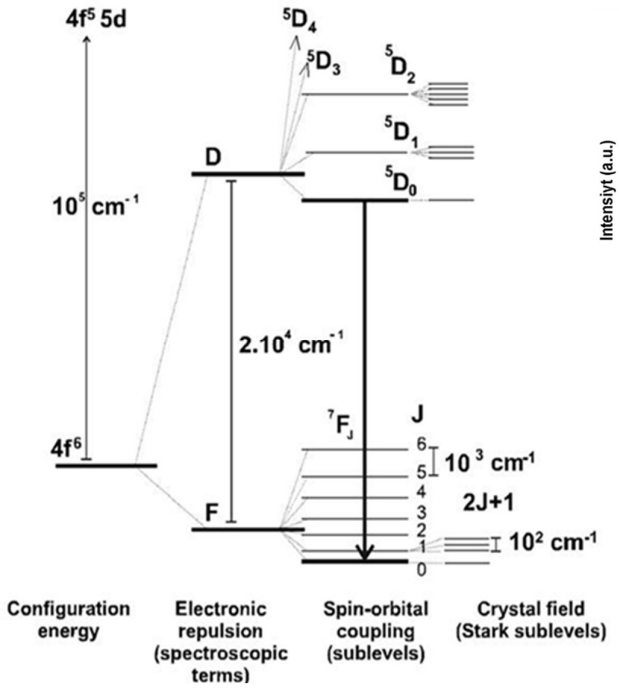


Fig. 3 Energy levels scheme of Eu^{3+}

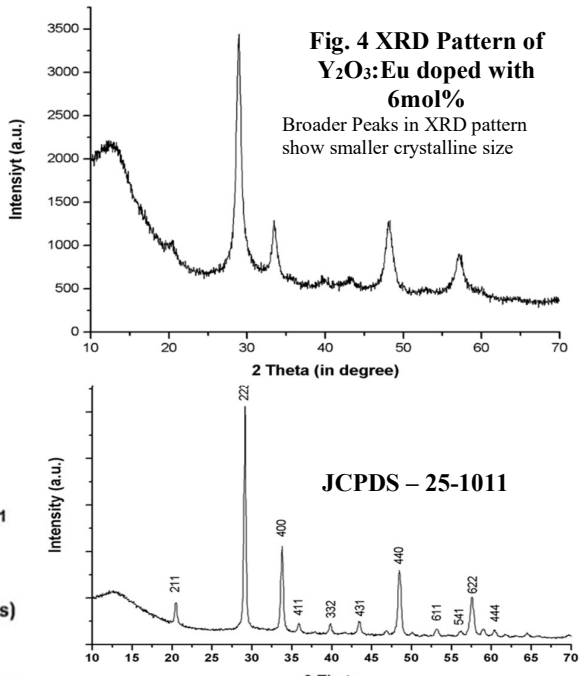


Fig. 4 XRD Pattern of Y_2O_3:Eu doped with 6mol%

Fig. 5 XRD Pattern of Y_2O_3:Eu cubic crystal

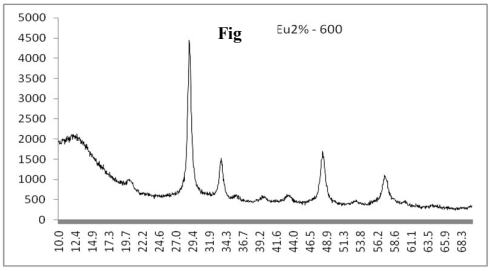
is found that prominent excitation wavelengths for 611nm emission are at 225nm, 227.96nm, 234.05nm, 240nm & 245.92nm. Fig 2. Shows emission spectra of Y_2O_3:Eu nanophosphor at 240nm excitation. Combined The emission bands 586.95nm, 593.03nm, 603nm, 611.01nm and 630nm, seen in the here are due to Eu^{3+} $^5D_0 \rightarrow {}^7F_{J(J=0,1,2,3..)}$ transitions of Eu^{3+} shown in fig. 3. The prominent emission peak is at 611.01nm is hypersensitive $^5D_0 \rightarrow {}^7F_2$ electric dipole forced transition[12-14]. The $^5D_0 \rightarrow {}^7F_1$ transition is magnetic dipole transition because of which small peaks at 586.95nm, 593.03nm and 603nm shows predominant C_2 symmetry site.

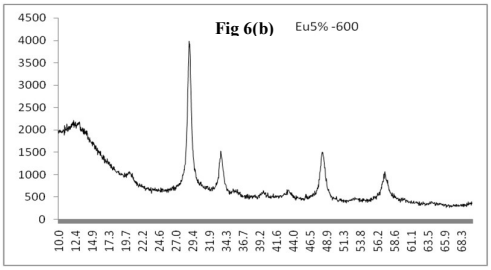
Fig. 4 shows Y_2O_3:Eu nanophosphor XRD pattern is taken for 2θ angle between the 10^0 to 70^0 angle. Highest 2θ peak is found at 29.09^0 which was remained same. XRD data resembles with standard JPDSs data file number 25-1011 (fig. 5), which shows that the samples is cubic crystal system.

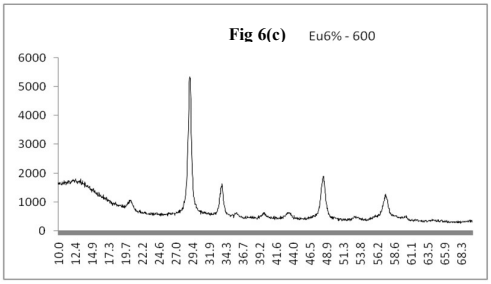
The I_{222} are the intensity of the X-ray peak at 222 direction. The well crystallized Y_2O_3:Eu crystal has preferred orientation of 222 direction indicating the cubic structure means the better crystallization in 222 direction. There is complete absence of monoclinic phases indicating structures of the prepared phosphors are purely cubic in nature. It was also called as Bixyite (C-type) structures which are approximate composition of common CRT red phosphor. The X-Ray diffraction pattern of prepared phosphors matches with the standard JCPDs data.

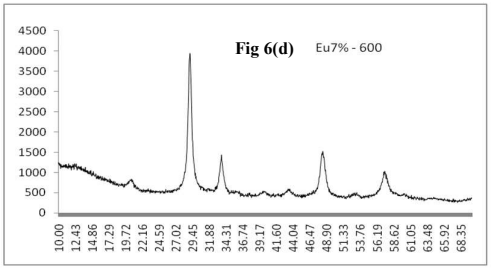
Fig 6(a),(b), (c), (d), (e), (f), (g) and (h) shows individual XRD patterns of Y_2O_3:Eu phosphors with 2, 5, 6, 7, 8, 10, 12 and 15 mol% respectively. The samples shows broader peak, that shows the particals are of nano size. Particle size were calculated by using $D = \frac{K\lambda}{\beta\cos\theta}$(where D= Volume weighted crystallitesize, K = Scherrer constant 0.89, λ= Wavelength of the radiation and β = FWHM (in radians) at 2θ. Fig 7. Shows the comparison of different Y_2O_3:Eu with JCPDS 25-1011 that shows cubic crystalline structure with broader FWHM. Particle size

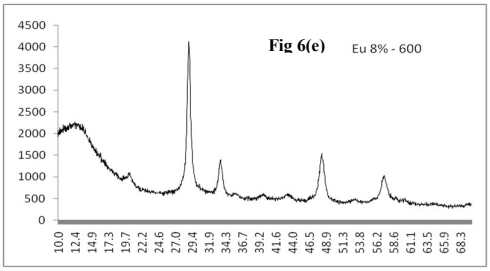
is estimated and is shown in Table 1.

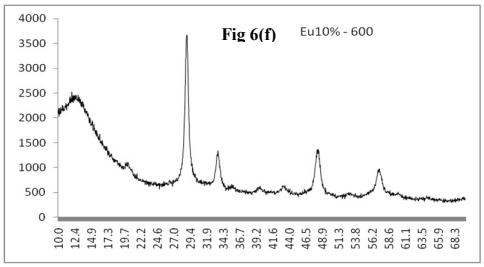


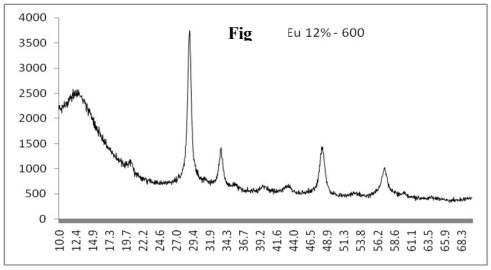


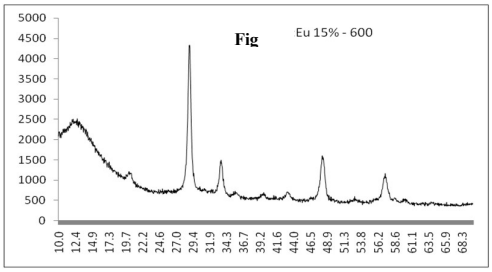












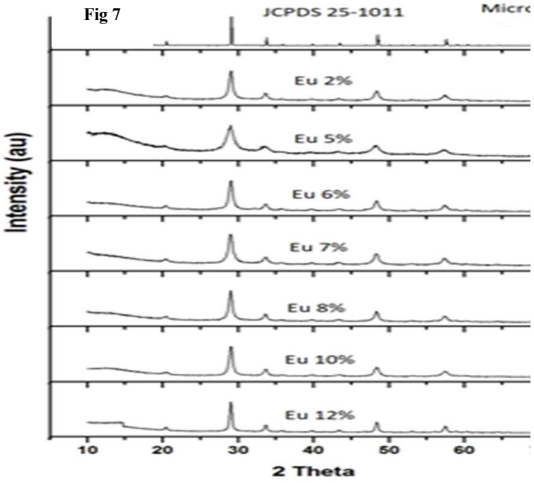


Fig 6(a) Shows XRD pattern of Y_2O_3:Eu with Eu 2% Doping
Fig 6(b) Shows XRD pattern of Y_2O_3:Eu with Eu 5% Doping
Fig 6(c) Shows XRD pattern of Y_2O_3:Eu with Eu 6% Doping
Fig 6(d) Shows XRD pattern of Y_2O_3:Eu with Eu 7% Doping
Fig 6(e) Shows XRD pattern of Y_2O_3:Eu with Eu 8% Doping
Fig 6(f) Shows XRD pattern of Y_2O_3:Eu with Eu 10% Doping
Fig 6(g) Shows XRD pattern of Y_2O_3:Eu with Eu 12% Doping
Fig 6(h) Shows XRD pattern of Y_2O_3:Eu with Eu 15% Doping

Fig 7. Shows the comparison of JCPDS 25 -1011 XRD pattern of Y_2O_3:Eu with the other Y_2O_3:Eu samples prepared with different Eu doping percentage

The average size of particle is found to in range 8.3 to 8.7nm. Fig. 8 (a) & (b) shows TEM Images of Y_2O_3:Eu doped with 6mol% of Eu doping. TEM result resembles with the results of XRD and shows that the cubic crystalline Y_2O_3:Eu doped phosphor is Nano size and is of 8.4nm average size.

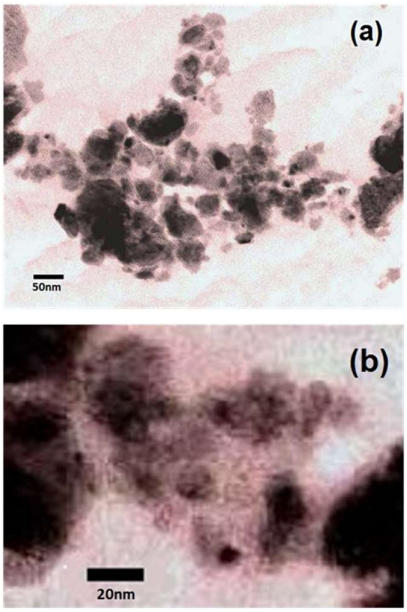


Fig. 8 TEM of Y_2O_3:Eu sample doped with 6mol% Eu

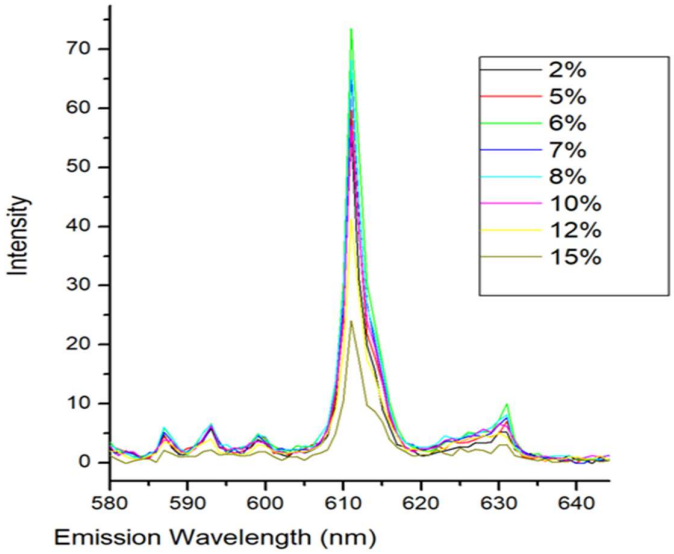
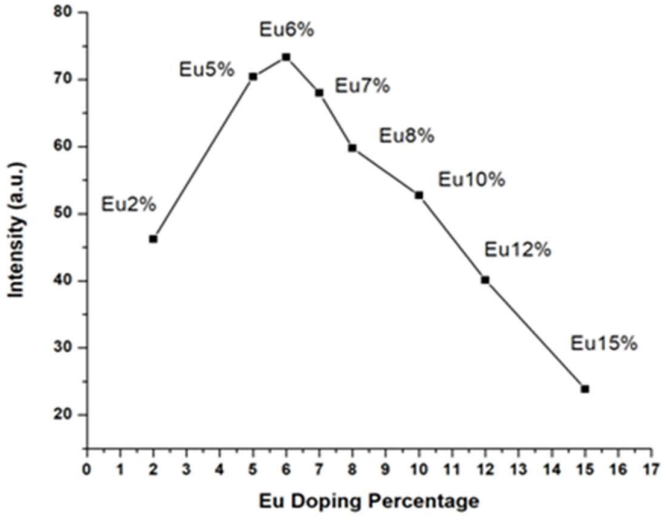


Fig. 9 Shows PL spectra of nano cubic crystalline Y_2O_3:Eu with ıt Eu doping percentage at 228nm Excitation

Fig. 9 shows the variation of PL intensity of Y_2O_3:Eu nano cubic crystalline phosphor with change in Eu doping concentration. It is seen that the PL intensity increases for 2mol% to 6mol% and attains peak value at 6mol% and decreases between 7 to 15mol% of Eu doping. At 6mol% the PL intensity is found maximum and quenching is seen on further increase of Eu concentration that leads to decrease of PL intensity. Table 1 and Fig. 10 shows the variation of PL intensity with the change in Eu doping percentage. PL intensity of Y_2O_3:Eu nano cubic crystalline phosphor at 2mol% Eu doping is similar to 10mol% of Eu doping in Y_2O_3:Eu phosphor.



Conclusion

Y_2O_3:Eu doped nanophosphor prepared with Urea combustion synthesis route have cubic crystalline structure. Phosphor prepared at 600^0Cfor 2.5hrs have definite crystalline size is independent of Eu doping percentage. Photo Luminescence intensity of yittrium oxide increases from 2 to 6 mol percentage of Eu doping and attain peak intensity at 6mol% Eu then gradually decreases down from 7-12 mole percentage. So, at 6mol% of Eu doping in Y_2O_3 nanophosphor quenching effect takes place because of which PL intensity decreases. PL intensity at 2mol% Eu doping in Y_2O_3 has almost similar PL intensity as at 10mol% Eu doping in Y_2O_3 cubic crystalline nanophosphor.

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