

# VUV excited photoluminescence of $\text{Eu}^{3+}$ doped $\text{Y}_2\text{O}_3$ nanoparticles

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## ABSTRACT

Spherical nanoparticles of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  with cubic phase has been synthesized by solution combustion method using glycine as chelating agent and urea as fuel. The 1200 °C annealed sample yield intense red luminescence at 610 nm corresponding to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  ion under vacuum ultraviolet (VUV)/ultraviolet (UV) excitation. Furthermore, the luminescence decay time of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition at 610 nm was also calculated against the 147 nm VUV excitation and found to be ~ 4 ms. These highly luminescent spherical nanoparticles of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  seems to be one of the promising candidates for modern age display devices. Copyright © 2011 VBRI press.

**Keywords:** Nanomaterials; crystal growth; luminescence, VUVPL.



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## Introduction

Recently, rare earth based nanoparticles have engrossed great attention as red light emitter in modern age flat panel display devices, low pressure fluorescent lamps and modern age opto-electronic devices [1-5]. The quality of phosphor is of great importance for the performance of these modern flat panel display devices as they directly influence the brightness and lifetime. From above point of view, the phosphor should have good luminescence efficiency as well as high color purity with long term stability [6]. The  $^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$ , which is responsible for red emission, strongly depends on the crystal field symmetry around  $\text{Eu}^{3+}$  ion [7, 8]. It is found that this red emission becomes relatively strong if the crystal field symmetry around  $\text{Eu}^{3+}$  is low [9-14].

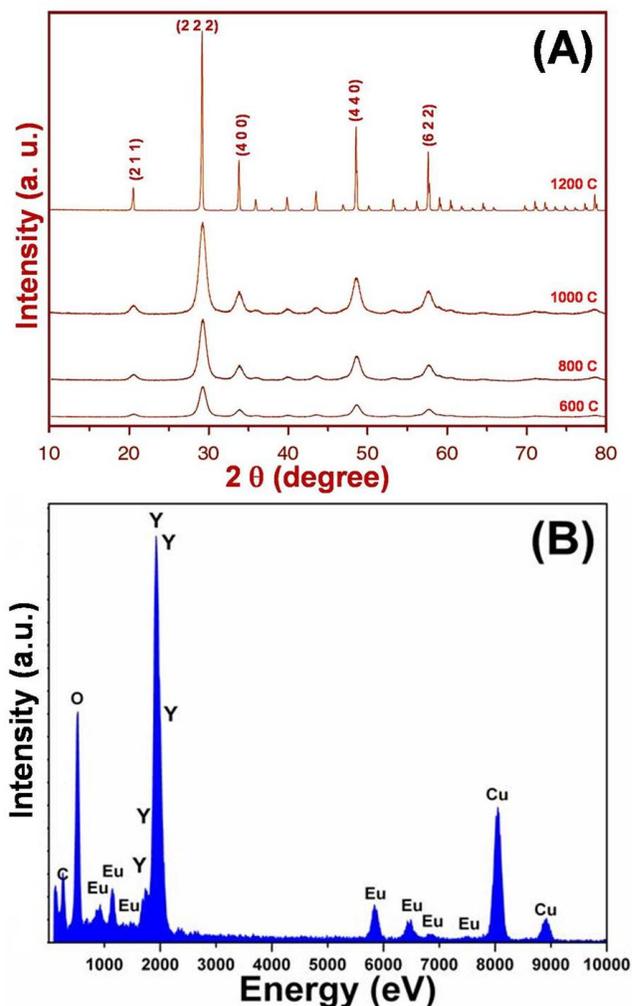
In plasma display panels (PDPs), phosphors are excited by vacuum ultra violet (VUV) radiation, especially by 147 and 173 nm radiations, from inert gas plasma, which shows the unique requirement for PDP phosphors that they can only be excited by the higher VUV excitations. So we have to look on such host materials that are excited by VUV radiation and must have low crystal field symmetry around  $\text{Eu}^{3+}$ . In the same hunt the host "nano-sized  $\text{Y}_2\text{O}_3$ " was found to be one of the promising host material for  $\text{Eu}^{3+}$ , rare earth ions [15-17]. Due to high disorder near the surface, the synthesis of nano-sized  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  phosphor must be potential answer to achieve good chromaticity whereas the lower site symmetry of  $\text{Eu}^{3+}$  in nanosized samples could improve the ratio of red emission to orange emission leading to better chromaticity. Although, several researchers have reported the luminescence characteristics of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticle under UV excitations [15-17], but none of them have explored the luminescence characteristics under higher VUV excitations. In the same pursuit, present letter reveals the solution combustion synthesis of spherical nanoparticles of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  yielding intense red luminescence under higher VUV excitation with relatively shorter luminescence decay time.

## Experimental

### Materials and methods

For the synthesis of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles, analytical reagent (AR) grade metal nitrates i. e. yttrium nitrate  $\text{Y}(\text{NO}_3)_3$ , europium nitrate  $\text{Eu}(\text{NO}_3)_3$ , glycine  $\text{NH}_2\text{CH}_2\text{COOH}$  and urea  $(\text{NH}_2)_2\text{CO}$ , were procured from Merck India. In this reaction glycine is used as chelating agent and urea as fuel. All the metal nitrates, glycine and urea were mixed in double distilled water to form the precursor solution. In this reaction, the glycine and urea mixture was 36mM in concentration while the total metal nitrate concentration was 18 mM. The solution was concentrated by direct flame heating until excess free water

evaporated and spontaneous ignition occurred. The resultant  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles were formed after the combustion was finished. Thus obtained fluffy product was grind to obtain fine powders of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles and were annealed at 600, 800, 1000 and 1200 °C for four hours in air. The europium ion concentration was kept as 20 weight %, as the quenching concentration was found to be ~20 % during the quenching studies (as shown in electronic supplementary information).



**Fig 1.** (A) XRD spectra of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles annealed at 600-1200 °C for four hours; (B) Representative EDAX spectra of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles annealed at 1200 °C; this spectra shows Yttrium:Europium :: 80:19.1 weight % contents.

### Characterizations used

The prepared  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles were characterized by X-ray diffraction (XRD, Rigaku D/max-2200 PC diffractometer operated at 40 kV/20 mA, using  $1.54 \text{ \AA}$   $\text{CuK}_{\alpha 1}$  radiation), transmission electron microscopy (TEM, Tecnai 30 G<sup>2</sup> S-Twin microscope operated at 300 kV), EDAX and photoluminescence spectroscopy (PL, Perkin Elmer LS 55 luminescence spectrophotometer). The Vacuum Ultra Violet Photo Luminescence (VUV-PL) were recorded on McPherson VUV spectrometer system model

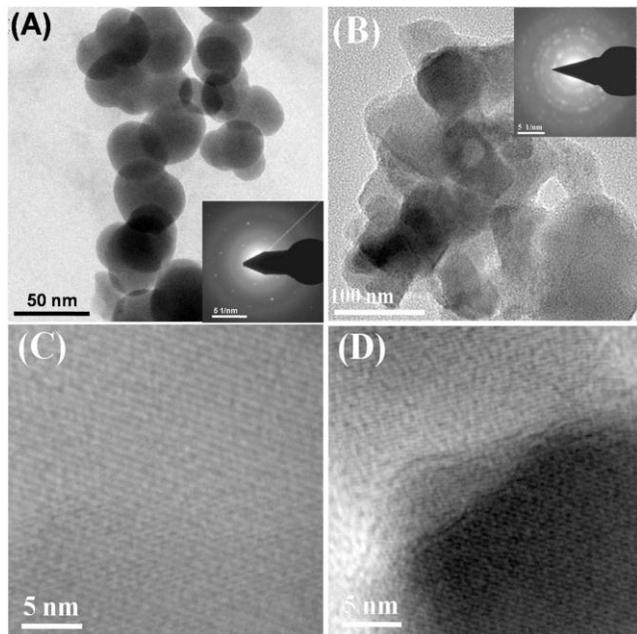
2035, having deuterium lamp as source, which is a Czerny Turner spectrometer having focal length of 360 mm and aperture ratio of  $f/4.8$  and the VUV-PL results were analyzed by Gram suit software.

## Results and discussion

**Fig. 1(A)** show the XRD spectra of the  $Y_2O_3:Eu^{3+}$  nanoparticles after annealing at 600, 800, 1000 and 1200 °C for four hours. These XRD spectra are in well accordance with the standard JCPDS file for  $Y_2O_3$  (JCPDS file No. 86-1326) and can be attributed as the polycrystalline cubic structure having space group  $1a3$  (206). The broadening of XRD peaks (i.e. Scherrer's broadening) can be attributed to nanosized formation of  $Y_2O_3:Eu^{3+}$  nanoparticles. Particle size 'd' of  $Y_2O_3:Eu^{3+}$  was estimated by Debye-Scherrer's Equation (1).

$$d = \frac{0.9\lambda}{B \cos\theta} \text{----- (1)}$$

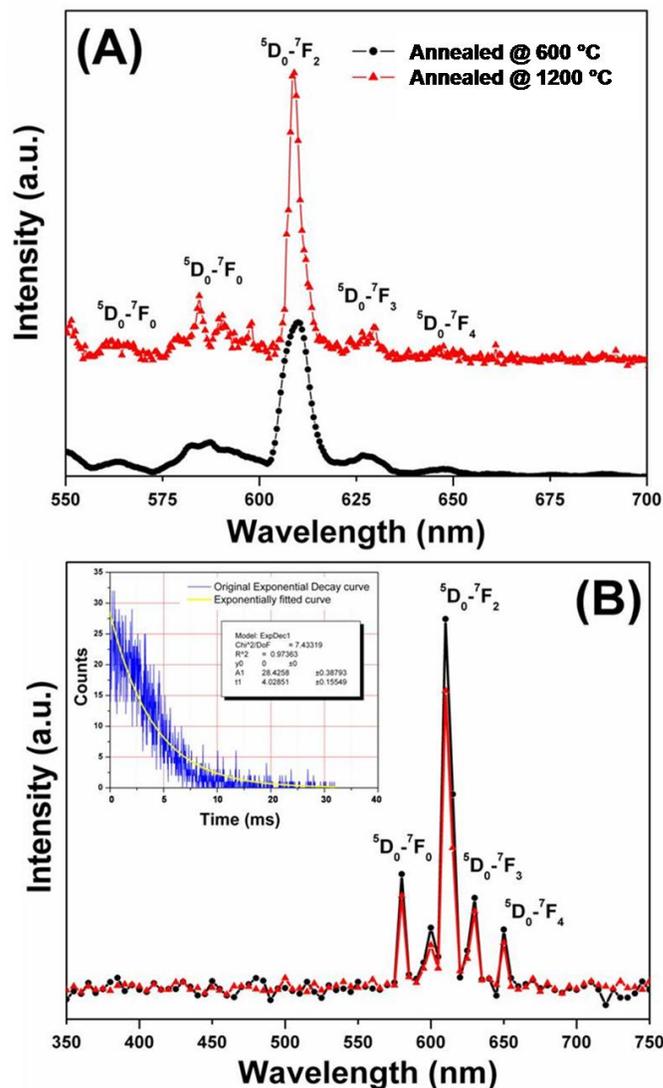
where, d is the particle size,  $\lambda$  is the wavelength of radiation used,  $\theta$  is the Bragg angle and B is the full width at half maxima (FWHM) on  $2\theta$  scale. The average crystallite sizes obtained using Debye-Scherrer's equation were ~30 nm for sample annealed at 600 °C, whereas, 1200 °C annealed sample shows ~50 nm and were found consistent with TEM results (**Fig. 2**). The narrower and much intense XRD peaks at sample annealed at 1200 °C indicates enhancement in crystallinity as compared to those for sample annealed at 600 °C. No peaks attributed to other phases were observed indicating good quality samples.



**Fig. 2.** Representative TEM images and SAED patterns of the  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at (A) 600° C (B) 1200° C. Corresponding HRTEM images are shown in figure (C) and (D) respectively.

**Fig. 2** shows representative TEM images of the  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at (A) 600 °C (B) 1200 °C. The average particle sizes were ~30 nm for sample

annealed at 600 °C; whereas, 1200 °C annealed sample shows ~60 nm particles with little agglomeration. Inset of **Fig. 2 (A)** and **Fig. 2(B)** shows the selected area electron diffraction patterns of  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at 600 °C and 1200 °C, respectively. The corresponding HRTEM images are shown in **Fig. 2 (C)** and **Fig. 2 (D)**, respectively **Fig. 1 (B)** shows the representative EDX spectrum of  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at 1200 °C. The Yttrium:Europium ratio found to be 80:19.1 weight %. This shows that almost all the europium ions were incorporated in the  $Y_2O_3$  host.



**Fig 3.** (A) Photoluminescence spectra of  $Y_2O_3:Eu^{3+}$  nanoparticles,  $\lambda_{ex}=225$  nm. (B) Representative, vacuum-ultraviolet photoluminescence spectra of  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at 1200° C for four hours. For figure (B) black line corresponds to 147 nm excitation and red line corresponds to 173 nm excitation. Inset shows the luminescence decay curve of  $Y_2O_3:Eu^{3+}$  nanoparticle.

In order to study the annealing effect on the luminescence behavior of the synthesized samples, PL studies at 225 nm were performed. The emission spectra of these  $Y_2O_3:Eu^{3+}$  nanoparticles annealed at 600 °C and 1200 °C for four hours are depicted in **Fig. 3(A)**. The PL spectra consists of a number of sharp peaks ranging from 550 nm to 650 nm, associated with forced electric dipole transition

from excited  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0, 1, 2, 3, 4$ ) levels of  $\text{Eu}^{3+}$  activator ions. These luminescence characteristics are very similar to that of our previous work for  $\text{YAG:Eu}^{3+}$  hierarchical nanostructures [18, 19]. The strongest red peak corresponding to 610 nm is attributed to  ${}^5D_0 \rightarrow {}^7F_2$  transition, whereas the 585 nm orange emission originates due to magnetic dipole transition  ${}^5D_0 \rightarrow {}^7F_0$ . For better understanding, the schematic energy level diagram showing diverse paths of excitation and emission from  $\text{Eu}^{3+}$  ions (with the electric dipole transitions of dopant  $\text{Eu}^{3+}$  ion) incorporated in  $\text{Y}_2\text{O}_3$  host are shown in the Fig. 4.

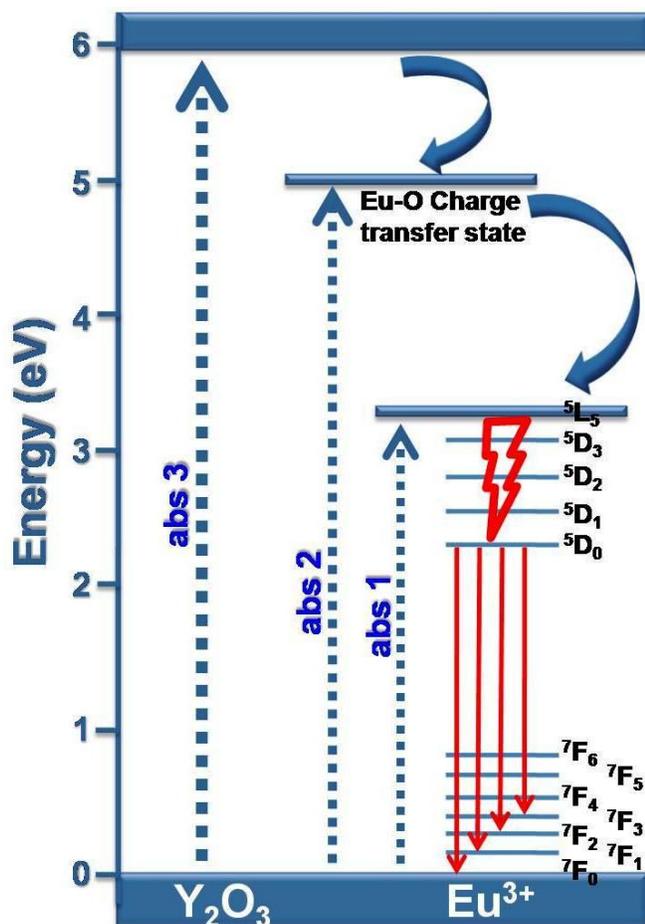


Fig. 4. Energy level diagram of  $\text{Y}_2\text{O}_3$  host and the dopant  $\text{Eu}^{3+}$  with possible electric dipole transitions within energy levels of  $\text{Eu}^{3+}$  ions.

Lower symmetry of crystal field near the activator  $\text{Eu}^{3+}$  ion results in higher ratio of red and orange peak intensity (R/O value) [9-14]. The R/O value strongly depends on local symmetry of activator  $\text{Eu}^{3+}$  ion and as is seen from figure, it remains almost same for both the samples. Due to higher degree of disorder near the surface, nanomaterials generally give better chromaticity and so is the case for synthesized  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles. From Fig 3 it is also clear that the position of emission peaks are unaffected due to annealing, indicating that the environment around the  $\text{Eu}^{3+}$  activator ion is impassive after annealing, where as it is found that maximum luminescence intensity extensively

depend on annealing temperature. At higher annealing temperature the maxima of luminescence intensity is improved due to better crystallization. The luminescence behavior of the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticle significantly depend on the particle size, the growth in grain size at higher temperature and the decrease in the surface area of the particle and the increase in emission intensity may be attributed to the same. Thus, the change in surface to volume ratio, removal of surface defects and non-radiative rates led to improvement in luminous efficiency.

In PDPs, phosphors are excited by vacuum ultraviolet (VUV) radiation, especially by 147 and 173 nm, from inert gas plasma, which shows the unique requirement for PDP phosphors that they can only be excited by the higher VUV excitations. So we have explored the luminescence characteristics particularly by the same excitations. We had recorded the VUV-PL emission spectra only for the sample annealed at 1200 °C because this sample showed the maximum luminescence intensity under UV excitation. Fig. 3(B) is the VUVPL spectra recorded for 147 nm and 173 nm excitations. For the samples excited at 147 nm and 173 nm, emission spectra show one sharp intense peak at the position of 610 nm followed by four other weak peaks at 580 nm, 600 nm, 630 nm and 650 nm, respectively. The intense sharp peak at 610 nm originates due to the forced electric dipole transition for  ${}^5D_0 \rightarrow {}^7F_2$  of  $\text{Eu}^{3+}$  activator. The peak at 630 nm corresponds to  ${}^5D_0 \rightarrow {}^7F_3$  transition and 580 nm and 600 nm peaks were due to  ${}^5D_0 \rightarrow {}^7F_0$  and  ${}^5D_0 \rightarrow {}^7F_1$  transition of  $\text{Eu}^{3+}$ , respectively. In this case, the orange peak intensity almost vanished and only strong red peak appeared. Removal of orange peak in present case suggests that VUV excitation further lowered the crystal field symmetry around the  $\text{Eu}^{3+}$  ion as discussed previously.

The luminescence decay time of the  ${}^5D_0 \rightarrow {}^7F_2$  transition at 610 nm was also calculated against the 147 nm VUV excitation and is shown in the inset of Fig. 3(B). The original experimental decay curve was fitted with exponential decay function,  $I = A \exp(-t/\tau)$ , where,  $I$  is intensity,  $A$  is constant,  $t$  is time and  $\tau$  is the decay time. The calculated decay time for the decay curve shown in the inset of Fig. 3(B) is ~4 ms. Several authors showed that the phosphors with short luminescence decay time are suited more as compared to the long decay phosphors for application point of view in modern days flat panel display devices as it lowers the possibility of luminescence quenching. However, a detailed time resolved photoluminescence (decay) study is crucial to corroborate the tangible rationale behind the observed luminescence-decay behavior.

## Conclusion

In summary, spherical nanoparticles of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  with cubic phase has been synthesized by solution combustion method using glycine as chelating agent and urea as a fuel. The 1200 °C annealed sample yield intense red luminescence, suggesting them to be one of the most feasible candidate for red phosphor and seize great potential in flat panel display application, underlying the importance of the current work.

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