

# Emission spectra of $\text{Eu}^{3+}:\text{Ca}_3\text{Ln}(=\text{Y}, \text{Gd})(\text{VO}_4)_3$ powder phosphors

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This paper reports the results obtained during the investigation of the emission spectra of  $\text{Eu}^{3+}:\text{Ca}_3\text{Ln}(=\text{Y}, \text{Gd})(\text{VO}_4)_3$  phosphors that are prepared by a chemical co-precipitation method. For these phosphors, XRD, SEM and FTIR analysis have also been carried out to understand their structural properties. When these  $\text{Eu}^{3+}$  phosphors were put under an UV source, those were in bright red luminescent. Based on the red color emission richness and also emission spectral measurements,  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor has been found to be a better material compared with  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  phosphor. An energy level scheme has been presented to explain the emission process involved in these phosphors.

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## 1. Introduction

Importance and significance of different phosphor materials have been dealt with in literature [1-3]. We understand that phosphor host materials are based on borates, vanadates, aluminates, silicates etc., containing some appropriate quantities of either transition metal ions or rare-earth ions or sometimes both [4-6]. We have recently reported on the emission properties of  $\text{Ca}_4\text{LnO}(\text{BO}_3)_3:\text{RE}^{3+}$  phosphors [7-10]. It has been a fact that lanthanide vanadates ( $\text{LnVO}_4$ ) have been recognized as good phosphor host matrices [11,12].  $\text{Eu}^{3+}$  Phosphors based on  $\text{YVO}_4$  and  $\text{GdVO}_4$  are evaluated as potential red luminescent materials [13,14]. Keeping in view the useful and important applications, lanthanide based vanadates have now been undertaken as an extension to our previous work. Bulk lanthanide vanadates doped with RE ions are usually prepared by a solid state reaction method at temperatures above  $1100^\circ\text{C}$ , which could possibly change the structural properties of these powder phosphors [15,16]. Recently, development of so-called wet or soft chemical technology, is of considerable importance in the preparation of micron or submicron or nano particles, to produce efficiently luminescent phosphors [17,18]. Therefore, in the present work  $\text{Eu}^{3+}:\text{Ca}_3\text{Ln}(=\text{Y}, \text{Gd})(\text{VO}_4)_3$  phosphors have been chosen to characterize their both emission and structural properties.

## 2. Experimental

$\text{Eu}^{3+}:\text{Ca}_3\text{Ln}(=\text{Y}, \text{Gd})(\text{VO}_4)_3$  powder phosphors were prepared by a chemical co-precipitation method. Adopting the stoichiometric ratio,  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{Gd}_2\text{O}_3$  (99.99%),  $\text{Eu}_2\text{O}_3$  (99.99%) chemicals of analytical reagent (AR) grade were weighed and dissolved in concentrated nitric acid and then each of them was added with an another mixture of di-ethylene glycol (DEG) and de-ionized water

with an appropriate ratio of rare-earth and stirred them well for a half an hour in each case.  $\text{NH}_4\text{OH}$  was added to the above solution in drop-wise until its pH value reaches to 7. At the same time, the  $\text{NH}_4\text{VO}_3$  and  $\text{CaCO}_3$  powders were added in a stoichiometrical ratio to these solutions and were stirred again until homogeneity were obtained. Filtered the precipitate and it was washed with de-ionized water several times. The obtained substances were dried in an oven at  $70^\circ\text{C}$  and calcined at  $900^\circ\text{C}$  for 5 hrs.

To understand the phase purity of these samples, XRD pattern was measured in the range of  $2\theta = 10^\circ - 60^\circ$  in steps of  $0.02^\circ/\text{s}$ , on a powder X-Ray Diffractometer of Xpert PRO equipped with a Ni filter and copper target tube giving a  $\text{CuK}_\alpha$  ( $1.54060 \text{ \AA}$ ) radiation at an applied voltage of 40 kV and with 30 mA as an anode current, calibrated with Si. The morphology of the powder phosphor was observed on a JEOL JSM 840A Scanning Electron Microscope. The samples were gold coated using a sputter coater polaron SC7610 system. FTIR spectrum of the sample was recorded on a Nicolet IR-200 spectrometer with KBr pellet technique from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . The photoluminescence spectra of these phosphors were recorded on a YVON Fluorolog-3 Fluorimeter with a Xe-arc lamp (450 W) as an excitation source and the lifetime of the prominent red emission was measured with a phosphorimeter attachment to the main system which is a computer controlled with a Xe-flash lamp (25 W).

## 3. Results and discussion

Fig.1 shows the photographs of  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  &  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  phosphors under an UV source and the  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor shows a bright red color emission.

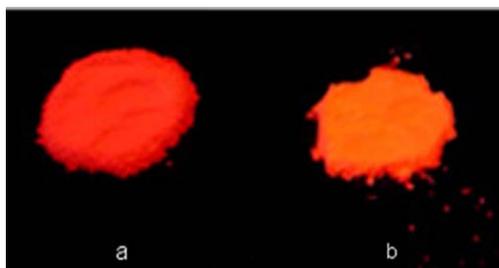


Fig. 1. Photograph of a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors under an UV source.

Fig.2 shows the X-ray diffraction patterns of a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors. XRD patterns of these phosphors are found to be consistent with the tetragonal structures exhibited by the bulk yttrium vanadates [19,6].

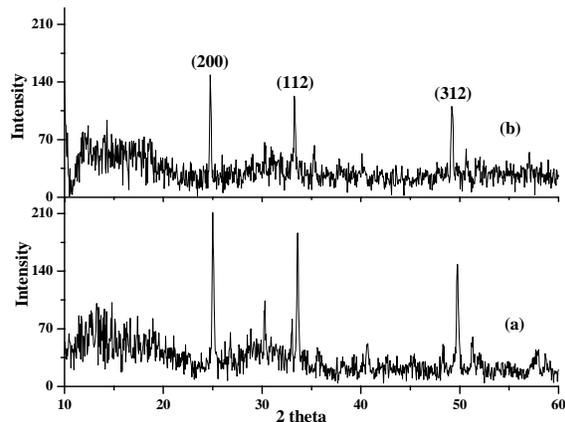


Fig.2. XRD patterns of (a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  (b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors

The average crystallite sizes of these  $\text{Eu}^{3+}$  doped phosphors have been estimated by Scherrer's equation [20]:

$$D_{hkl} = k\lambda / [\beta(2\theta) \cos\theta]$$

Where  $\beta(2\theta)$  is the width of the pure diffraction profile in radians,  $k$  is 0.89,  $\lambda$  is the wavelength of the X-rays,  $\theta$  is the diffraction angle and  $D_{hkl}$  is the average crystallite size along (hkl) direction. Here the diffraction data from (200), (112) and (312) directions were taken to calculate the crystallite size, and the estimated average crystallite sizes are 320 nm and 340 nm for  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  and  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors respectively. Fig. 3 shows the SEM micrographs of the  $\text{Ca}_3\text{Y}(\text{VO}_4)_3$  and  $\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  doped with  $\text{Eu}^{3+}$  powder phosphors to understand their morphology and from this figure we have found that the particles are agglomerated.

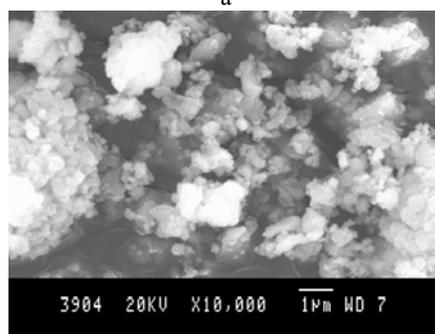
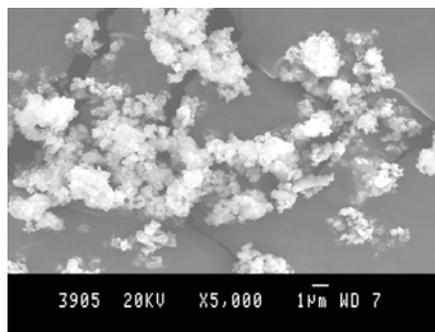


Fig.3. SEM images of (a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  (b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors.

The particle size cannot be measured exactly from the SEM micrographs as shown in Fig.3. It is evident from Fig. 3 that the particles are of  $\sim 0.3 - 0.5 \mu\text{m}$ . It may be mentioned that crystalline powder and micrometer dimension of the powder with a high strength could be useful for applications, as these micro crystalline phosphors can emit high luminescent intensities [21]. Fig.4 shows the FTIR spectra of both  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  and  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors with no considerable changes in both phosphors.

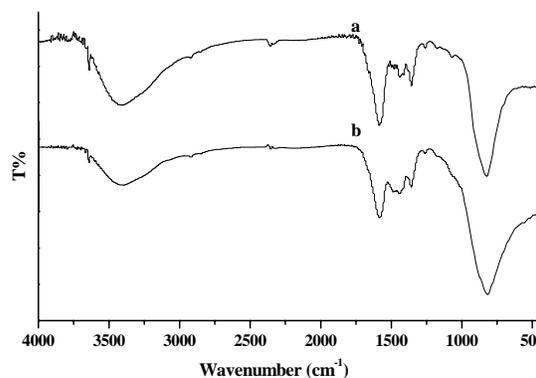


Fig.4. FTIR spectra of (a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  (b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors

Table.1 Assignment of FTIR bands both of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  and  $\text{Eu}^{3+} : \text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors.

FTIR bands ( $\text{cm}^{-1}$ )	Assignment
450	Y(Gd)-O bonds
820	V-O stretching modes
1365	Antisymmetric stretching vibrations of $\text{CO}_3^{-2}$
1430	Bending mode ( $\delta$ ) of $\text{H}_2\text{O}$
1595	Bending mode ( $\delta$ ) of $\text{H}_2\text{O}$
2358	Stretching vibration of O-H
3428	Stretching vibration of O-H

Table.1 presents the data along with the band assignments for the FTIR spectra [22, 23].

Fig.5 shows an excitation spectrum of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  powder phosphor, by monitoring the red emission at 616nm. Datta [24] has carried out a detailed study on the mechanism of absorption and energy transport in vanadate host lattices and concluded that Yttrium based vanadates are host sensitized phosphors, mostly by a non-radiative resonance energy transfer, either by electric multipole or by an exchange interaction. The excitation spectrum reveals a broad excitation band at 225 nm-350 nm, which is attributed to a charge transfer band (CTB) with an existence of oxygen 2p orbital and the particularly filled 4f orbital of  $\text{Eu}^{3+}$  ion along with charge transfer from the oxygen ligands to the central metal atoms inside the  $\text{VO}_4^{3-}$  (V-O) components of the matrix [22,12]. The other excitation bands from 350 nm to 500 nm, correspond to the transitions of  ${}^7\text{F}_0 \rightarrow {}^5\text{G}_3$  (380 nm),  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  (392 nm), and  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  (464 nm). One of the interesting results of this work is that the excitation spectrum of the  $\text{Eu}^{3+} : \text{Ca}_3\text{Ln}(\text{=Y,Gd})(\text{VO}_4)_3$  phosphor could be strongly excited by a near UV radiation, which has the potential as a near-UV LED converted phosphor in solid state lighting technology. The emission spectra of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor have been obtained with excitations at 394 nm, 464 nm and 380 nm as shown in Fig.6. With  $\lambda_{\text{exc}} = 394$  nm, emissions are more intense than at 464 nm and 380 nm respectively. The characteristic emission bands of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor are region of 570 nm-740 nm and which correspond to intra 4f-shell transitions of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  ( $J=0, 1, 2, 3, 4$ ) of  $\text{Eu}^{3+}$ .

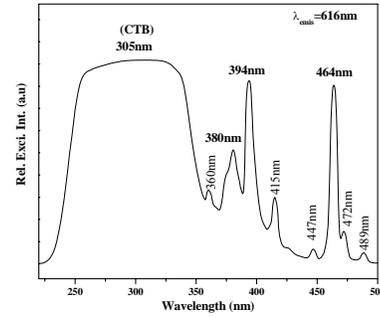


Fig. 5. Excitation spectrum of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  powder phosphor.

A strong red emission of  $\text{Eu}^{3+}$  at 616 nm was obtained due to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition, along with emissions at 583 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ), 593 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ), 649 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ ) and 696 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ ). Most of the f-f transitions of the trivalent lanthanides are little affected by the environment around them.

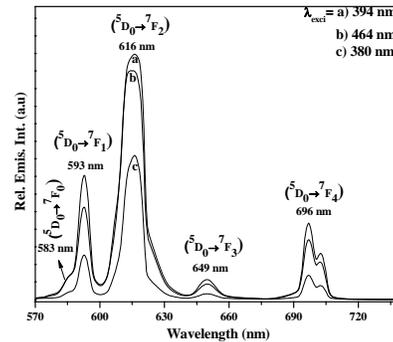


Fig. 6. Emission spectra of  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  powder phosphor.

A few, however, are sensitive to the environment and become more intense and such transitions are known as hypersensitive transitions. The electric dipole transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (616 nm) is considered as a hypersensitive transition [22], which obeys the selection rule  $\Delta J=2$  and hence it is a bright emission. The transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  is moderately bright orange emission with the selection rule  $\Delta J=1$  has been a magnetic-dipole transition. Further, if  $\text{Eu}^{3+}$  occupies an inversion symmetry site in the host matrix, then the orange emission ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) could be a dominant emission. On the contrary, if  $\text{Eu}^{3+}$  does not occupy the inversion symmetry site, the transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  would be a dominant. So the sites in the  $\text{Eu}^{3+} : \text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor are occupied by  $\text{Eu}^{3+}$  ions that have no inversion symmetry.

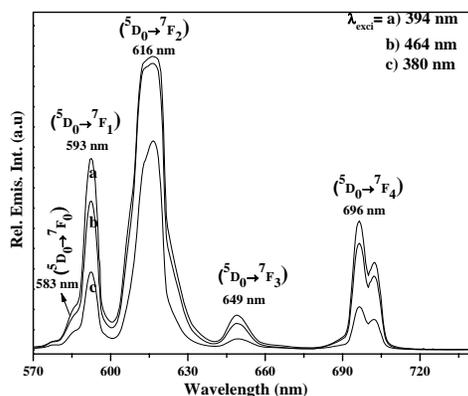


Fig. 7. Emission spectra of  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphor.

The relation between the emission intensities of the transitions ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) ED and ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ) MD could address the richness of the red color emission in comparison with the orange emission. For the  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  phosphor the red ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) /orange ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ) ratio is 1.99. The transition  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  is an electrical dipole (ED) natured and it is sensitive to long range environmental effects.

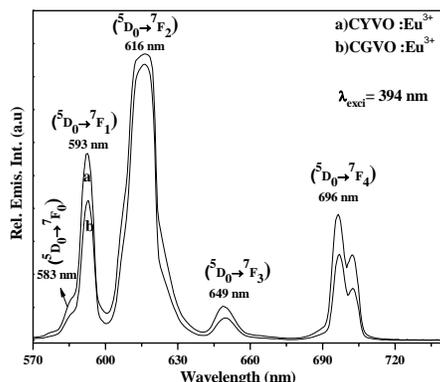


Fig. 8. Emission spectra of (a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  (b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors.

The emission spectra of  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  phosphor are shown in Fig. 7 with excitations at 394 nm, 464 nm and 380 nm. For the  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  phosphor the red ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ) /orange ( $^5\text{D}_0 \rightarrow ^7\text{F}_1$ ) ratio is 1.54. Fig. 8 shows the emission spectra of a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors with an excitation at 394 nm and Fig. 9(i) shows the decay curves of a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors of the emission band  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  with an excitation at 394 nm for a comparison, in order to identify the better material.

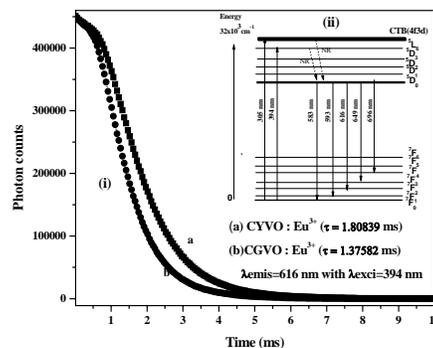


Fig. 9. (i) Decay curves and (ii) Energy Level scheme for Emission processes of a)  $\text{Eu}^{3+}:\text{Ca}_3\text{Y}(\text{VO}_4)_3$  b)  $\text{Eu}^{3+}:\text{Ca}_3\text{Gd}(\text{VO}_4)_3$  powder phosphors.

An energy level scheme is given in Fig. 9(ii) to explain the excitation and emission mechanism of these powder phosphors.

#### 4. Conclusions

It is concluded that by means of a chemical coprecipitation method, couple of red luminescent  $\text{Eu}^{3+}:\text{Ca}_3\text{Ln}(=\text{Y}, \text{Gd})(\text{VO}_4)_3$  powder phosphors have been successfully prepared and their emission spectra have been analyzed along with their structural properties. Based on the results obtained in the present work, we suggest that these luminescent phosphors could be considered as novel optical materials for certain electronic display applications.

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