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Effect of calcination on the optical properties of $YVO_4:Eu^{3+}$ Nano- phosphors

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Abstract

$YVO_4:Eu^{3+}$ nano- phosphors were synthesized by the sol-gel technique and thier size were controlled through calcination. Structural analysis is done by X-ray diffraction (XRD). The optical study is done by photoluminescence (PL) and UV-visible spectroscopy. The PL study shows that the luminescence properties of nano- phosphors are improving with the rise of the calcined temperatur. Luminescence peak at about 618nm corresponds to $^5D_0$-$^7F_2$ electric dipole transitions and a weak band at 594nm is due to $^5D_0$-$^7F_1$ is magnetic dipole transitions in Eu^{3+} ions. The broad band in the range between 250 and 350nm is due to the charge transfer transitions from ligand to Eu^{3+} ion in the UV-visible spectroscopy. This study concludes that with the increase in the calcined temperature of the synthesized phosphors, lumineous intensity increases. The strong emission at the prolonged temperatures make it a potential candidate for the display applications.

***Keywords: Nano*-Phosphors, Luminescence, Calcination, ligands.**

1. *INTRODUCTION*

Nano-phosphor materials have attracted the attention of researchers, because of their tremendous applications in the field of projection displays, nanotechnology and photonics [1-2]. Phosphor materials in the nano range dimensions exhibit improved optical properties as compared to their bulk counterpart. It is due to quantum size effect and increased surface to volume ratio. Most luminescence materials are oxides, sulphides and oxy-sulphides doped with transition metals or rare earth ions [3]. Various methods have been used to prepare YVO_4-Eu^{3+} phosphor such as high temperature solid state reaction, hydrothermal method and precipitation technique. In YVO_4-Eu^{3+} phosphors ultraviolet radiations excites the vanadate group, that is host which is able to transfer efficiently the excitation to Eu^{3+} ion [4-6]. YVO_4 has the Zircon structure. The europium ion substitute for yttrium in the YVO_4 lattice. Thermal treatment, effects the luminescent properties of the phosphors doped with the rare earth elements.

In the present work, we synthesized the $YVO_4:Eu^{3+}$ nano-phosphors by the sol-gel technique and calcined at different temperatures. Samples are characterized by X-ray diffraction (XRD), Photoluminescence (PL) and UV-visible spectroscopy.

2. *EXPERIMENTAL*

2.1 Mateial Used

Ammonium metavanadate (NH_4VO_3), Ytterium acetate [$Y(CH_3CO_2)$] and Europium acetate [$Eu(CH_3CO_2)_3$] materials with the purity 99.99 % were supplied from across company. All the procedure were carried out in dry atmosphere of nitrogen. Besides this Ethylene glycol ($C_6H_6O_2$), Citric Acid ($C_6H_8O_7$) and deionised water were also used.

2.2 Powder Preperation

The Eu^{3+} doped YVO_4 nano- phosphors are prepared by sol-gel method using ammonium metavanadate (NH_4VO_3), Yetterium acetate [$Y(CH_3CO_2)$] and Europium acetate [$Eu(CH_3CO_2)_3$]. 0.01 mole of ammonium metavanadate was dissolved with 20ml of ammonium hydroxide. This solution was added to 100ml of deionised water. (0.01-x) mole of yetterium acetate and (x=0.0005) mole of europium acetate were seperately dissolved in 100ml of deionised water. Second ammonium metavanadate, ytterium acetate and europium acetate solutions were mixed in a round bottom flask. When the precursor were completely dissolved in the solution, 0.02 mole of citric acid and ethylene glycol were added. The citric acid and ethylene glycol were added to the above as chelating and stabilizing agents repectively. The amount of the citric acid and ethylene glycol were determined by the ratio of the citric acid to metal ions [7-9]. The solution was put in the oven at 120^0C for 24 hour to obtain the dried precursor. Dried precursors were calcined at various temperatures between 300^oC and 900^oC for 3 hours.

CHARACTERIZATIONS

The synthesized samples were characterized with X-ray diffractometer (XRD,X'Pert Pro Panalytical Netherland formally called Philips). Optical absorption behaviour of the YVO_4-Eu^{3+} nano phosphor was measured from 250nm to 450nm by UV-visible spectrophotometer (Perkin Elmer Lambda-750). Photo Luminescence of these phosphors has been obtained with He-Cd laser with the wavelength 325nm employing the RENISHAW inVia Raman spectrophotometer.

4. *RESULTS AND DISCUSSION*

4.1 X-Ray Diffraction

Fig. 1 shows XRD pattern of nano- phosphor at different calcined temperatures. The prominent peaks at angle 25.09^o, 33.75^o and 49.82^o in the 2θ range 20°-75° can be indexed to the (200), (112) and (312) Bragg's reflections respectively [JCPDS no. 17-0341]. It shows that the intensity of the peaks keeps on increasing with the rise of calcined temperature. It reveals that the crystallinity is improving at higher calcined temperature. The crystallite size is estimated from the Scherer equation [10] and Williamson-Hall analysis (W-H plot).

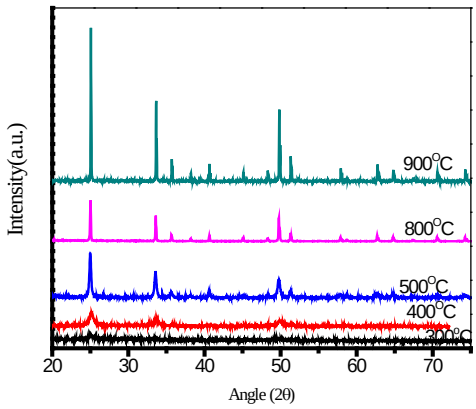

Fig 1. X-Ray spectra of nano- phosphors.

The variation of the estimated crystallite size is summarized in Table 1. The obtained values show that crystallite size increases with the rise in the calcined temperature [11]. The crystallite size calculated from the W-H analysis is slightly higher than those calculated using Scherrer's equation. It is due to neglecting strain component in Scherrer's equation [12].

Table 1: Crystallite size at different calcined temperatures.

S.No.	Temperature(^{0}C)	Crystalite Size(nm)[By Scherrer's Equ.]	Crystallite Size(nm)[By W-H plots]
1.	300	16.95	17.70
2.	400	22.11	32.60
3.	500	33.90	44.10
4.	800	72.00	79.10
5	900	89.09	100.06

4.2 UV-Visible Spectroscopy

Absorbance spectra at different calcined temperatures are shown in the Fig. 2. It shows a broad band from 250nm to 400nm attributed due to a charge transfer state by electron transferred from 2p orbital of the oxygen to the empty 4f orbital of europium, which may be described as ligands- to- Eu^{3+} charge- transfer transitions (LMCT) [13].

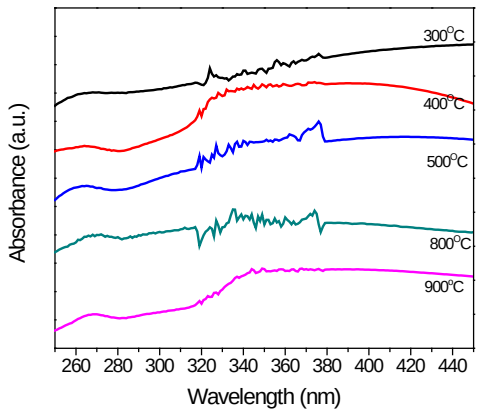

Fig.2: UV-visible graph of nano- phosphors

4.3 Photoluminescence Study

Fig. 3 shows experimental PL spectra of YVO_4-Eu^{3+} nano- phosphor at different calcined temperatures, under the excitation wavelength at 325nm. The PL spectra consist of bands ranging from 590-630nm, which is attributed to electronic transitions of europium ions [9,14]. The most prominent luminescent bands are positioned at 614nm and 619nm and are in quite good agreement with the literature [14].

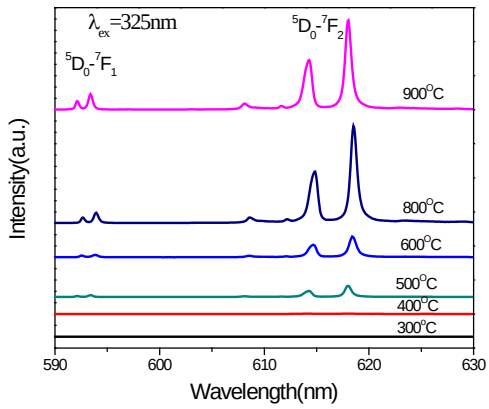

Fig. 3: PL spectra at different calcination temperatures

The intense peak at 619nm is due to $^5D_0$-$^7F_2$ electric dipole transition with energy 2.0154*eV* and it is sensitive to the chemical bond in the vicinity of Eu^{3+} ion. This electric dipole transition split into two bands due to energy level splitting of the $^7F_2$ state by the crystal field. Peak at 594nm is due to $^5D_0$-$^7F_1$ magnetic dipole transition with energy 2.086*eV* and it hardly changes with the crystal field strength around the Eu^{3+}[15]. The intensity of peak at 619nm is stronger than the peak at 594nm confirming that there is no inversion symmetry site for Eu^{3+} ion in the crystal structure.

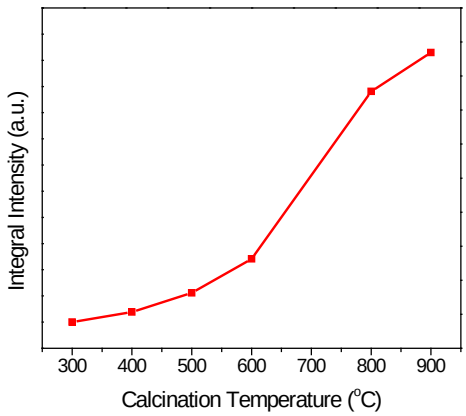

Fig. 4: Integral luminescence as a function of Calcination Temp

The area under the PL spectra is calculated for the nano- phosphors at different calcined temperatures and is shown in the Fig. 4. It shows that the emission efficiency rises with the increase of the calcined temperature. This enhancement in the emission efficiency is due to agglomeration and as well as increase of the crystallite size which is also supported by the XRD results .

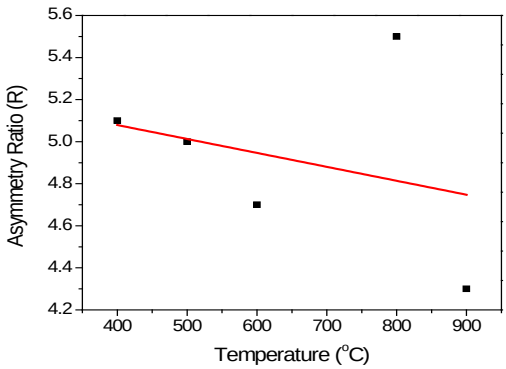

Fig 5 : Asymmetry ratio vs Calcination Temperature.

The asymmetry ratio [Area($^5D_0$-$^7F_2$)/Area($^5D_0$-$^7F_1$)] is estimated from the PL spectra at the various calcined temperatures is shown in the Fig. 5. The straight line reflects that the R is decreasing with the increase of calcined temperature for our sample.

5. Conclusion

We sucessfully synthesized the YVO_4-Eu^{3+} nano-phosphors by the sol-gel method and their size is controlled by thermal treatment. XRD study reveals the increase of the crystallite size of nano-phosphors with the rise of the calcined temperatures from 300°C to 900°C. The absorption spectra reflect the charge transfer transitions. PL study shows that the intense peaks 594nm corresponds to $^5D_0$-$^7F_1$ and at 619nm corresponds to $^5D_0$-$^7F_2$ transition from the YVO_4-Eu^{3+} nano-phosphors. It is concluded that size as well as luminescent properties of synthesized nano-phosphors can be controlled by thermal treatment.

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