

Effect of Synthesis Techniques on VUV Properties of Eu^{3+} Doped YVO_4 Phosphors: A Comparative Study

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ABSTRACT

The europium doped yttrium vanadate ($\text{YVO}_4:\text{Eu}^{3+}$) doped phosphor have been synthesized by two different techniques viz., solution combustion (CM) and solid-state diffusion (SSD) techniques. X-ray diffraction patterns confirm the formation of a pure phase in the samples synthesized by both the methods; however, the luminescence intensities of the samples are different under vacuum ultraviolet (VUV) excitation i.e., 147 and 172nm. The effect of synthetic technique is also seen on morphology of materials studied with the help of scanning electron microscopy, which shows an agglomeration and increase in particle size with increasing calcination temperature in case of SSD. The luminescent properties of the synthesized material have been studied by using synchrotron radiation. The photoluminescence (PL) results clearly show the strongest red emission peak at the wavelength around 618 nm. The highest luminescent intensity is obtained for the sample prepared by the CM method compared to SSD method. It is also noted that wavelength of 172 nm is more efficient than the 147 nm for excitation of $\text{YVO}_4:\text{Eu}^{3+}$.

Keywords: Yttrium Vanadate, Combustion Synthesis, Solid State Diffusion, VUV Luminescence

I. INTRODUCTION

A plasma display panel (PDP) has been regarded as a promising candidate for a display with a large area mainly because its emissive features include a wide viewing angle and high brightness. PDP phosphors are expected to meet the critical requirements to yield a high luminous efficiency on excitation with vacuum ultraviolet (VUV) radiation of wavelengths 147 and 172 nm generated from a plasma of a mixture of He and Xe noble gases¹. Oxide phosphors with aluminate, silicate, vanadate, phosphate, and borate groups generally exhibit strong absorption in the VUV spectral region²⁻³.

The main weakness of red-emitting PDP phosphors currently used are the lack of colour purity, long decay lifetime and colour degradation due to material instability. For these reasons, the optical and luminescence properties such as luminous efficiency, purity of chromaticity and saturation, and decay lifetime of PDP phosphors have been widely investigated⁵⁻⁷. A search for red-emitting PDP phosphors with improved efficiency, brightness, and colour saturation has become an important task for which research is being actively pursued. Several synthesis routes have been described for the preparation of Eu³⁺-doped YVO₄ such as co-precipitation, hydrothermal, solid-state reaction, combustion method⁸⁻¹². However, there is no report on the comparison of structural and VUV properties of Eu³⁺-doped YVO₄ sample synthesized via combustion and solid-state reaction routes. To develop satisfactory red-emitting PDP phosphor, we have thoroughly investigated the effect of preparation method on photoluminescence (PL) properties YVO₄:Eu³⁺ phosphor under VUV excitation. Here, we report the synthesis and VUV PL spectral investigations of red-emitting Y_{1-x}VO₄: Eu_x phosphors in several series and also the dependence of luminescence performance on method of synthesis. The YVO₄:Eu³⁺ phosphor has been prepared by low temperature, low cost and less time-consuming solution combustion method and high temperature conventional solid-state diffusion method. We have also studied the optimized composition of the dopant to obtain red-emitting phosphor with great potential for PDP application.

Pure and Eu³⁺-doped YVO₄ phosphors were prepared following two techniques, namely the solution combustion synthesis and high-temperature solid-state diffusion method. Analytical graded yttrium oxide (Y₂O₃), europium oxide (Eu₂O₃), ammonium meta-vanadate (NH₄VO₃) and urea [CO (NH₂)₂] were taken as starting materials.

II. METHODS AND MATERIAL

2.1. Solution Combustion Method:

In the first step for solution combustion synthesis method, 0.5 mol of Y₂O₃ and xEu₂O₃ (x = 0.02, 0.04, 0.06, 0.08, 0.10) were dissolved in the concentrated HNO₃ (nitric acid) to form respective nitrates. Stoichiometric amount of NH₄VO₃ was dissolved in doubled distilled water and slowly added to the previously formed nitrates, which resulted in a dark brown solution. In this solution, appropriate amount of urea was added as a fuel and ammonium nitrate as an oxidizer was added. The required amount of fuel (urea) and oxidizer (ammonium nitrate) was calculated by the ratio of oxidizing and reducing valencies¹¹. Then, the mixture was stirred until the clear solution is formed. The as-prepared solution of reaction mixture was placed in pre-heated muffle furnace at 550 °C temperature for 5 min and such process resulted in a black powder. Finally, the black powder was annealed at 800 °C for 3 h resulting in the final product.

2.2. Solid State Diffusion Method:

Y_{1-x}Eu_xVO₄ (x = 0.02, 0.04, 0.06, 0.08, 0.10) phosphors were also prepared by conventional high-temperature solid-state reaction method. All the reagents (Y₂O₃, NH₄VO₃ and Eu₂O₃) were taken in stoichiometric ratio and mixed together in mortar-pestle for half an hour and heated at 700 °C for 6h. The last product was again ground properly and maintained in a muffle furnace at 1200 °C for 3h. Finally, the sample was removed out from the furnace and after normal cooling ground appropriately. The X-ray diffraction (XRD) pattern of the sample was recorded on Rigaku miniflex X-ray diffractometer with a scan speed 2.000 deg/min and with Cu K α radiation. The morphology of the phosphor particles was studied by using Hitachi model S-4800 type-2 field-emission scanning electron microscope (SEM) and elemental analysis by Bruker EDS. The VUV spectra were

recorded at Department of Physics, S.G.B., Amravati University, Amravati, by using remote access mode of Beamline 4B8 in Beijing synchrotron radiation facilities (BSRF)¹³ under dedicated synchrotron mode (2.5 GeV, 150 – 60 mA). The vacuum in the sample chamber was about 1×10^{-5} mbar. The effects of the experimental setup response on the relative VUV excitation intensities of the samples were corrected by dividing the measured excitation intensities of the samples with the excitation intensities of sodium salicylate measured simultaneously in the same excitation conditions. The region of excitation spectra was from 100 to 300 nm and the emission spectra recorded at 147 and 172 nm excitation.

III. RESULT AND DISCUSSION

3.1 X-ray Diffraction

The crystallinity and surface morphology have a great impact on optical behaviour such as photoluminescence of the material¹⁴. Fig.1 illustrate the XRD patterns of Eu^{3+} -doped YVO_4 prepared by combustion and solid-state reaction route, respectively. The formation of the crystalline phase of as-prepared products of SSD and CM method was confirmed by X-ray diffraction patterns of YVO_4 (as shown in Figure 1) to verify the phase purity and crystal structure. The X-ray pattern of both method samples indicated a pure phase of the standard YVO_4 and all the peaks are in good agreement with the (ICDD, 01-082-1968). There were no additional peaks found as the concentration of Eu ion was increased to 10%. Thus, it seen that pure phase of YVO_4 could be achieved using CM method at low temperature compared to solid state diffusion (SSD) synthesis, which require higher temperature and time for synthesizing YVO_4 . This agreement indicates that the phosphor has been successfully prepared by using the CM and SSD method. It is also noticed that the crystal diffraction intensity of YVO_4 obtained by SSD is lower than that obtained from the CM method.

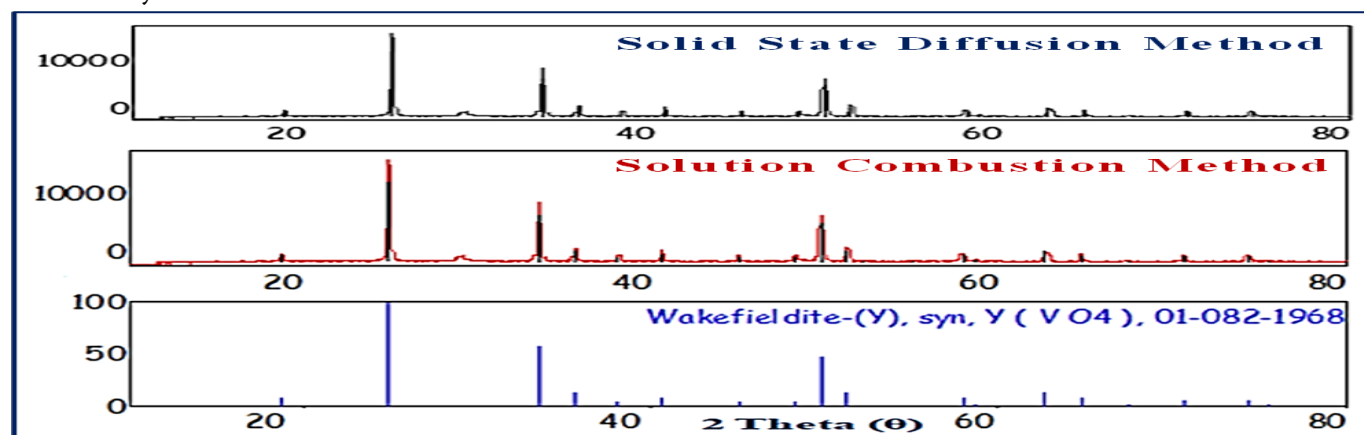


Figure 1: XRD patterns for undoped and Eu^{3+} -doped YVO_4 phosphors prepared by combustion method. Standard JCPDS pattern is also given for reference.

3.2 Scanning Electron Microscopy

The morphologies of $\text{YVO}_4:\text{Eu}^{3+}$ prepared by conventional CM technique and SSD route are shown in Fig. 2(a) and (b), respectively. The $\text{YVO}_4:\text{Eu}^{3+}$ particles prepared by conventional solid-state route have an irregular shape, coarse surface, wide size distribution, and are highly aggregated, whereas the $\text{YVO}_4:\text{Eu}^{3+}$ particles prepared by CM technique have rod shape, smooth surface, narrow size distribution in μm range, and are lowly aggregated. The morphology difference above mentioned should have originated from different preparation conditions and post-treatment techniques. In conventional solid-state reaction route, a high-

temperature calcination is required for obtaining the phosphor materials with high crystallinity, however, high-temperature calcinations make the phosphor particles large and easily agglomerated, thus, milling and grinding appear necessary to obtain suitable particle size for application, but these post-treatment techniques significantly damage the surface quality of phosphor particles¹⁵, as shown in Fig. 2(a). Compared with solid-state reaction route, the CM route needs a lower calcination temperature for the host crystallization and no milling and grinding processes. It is known that the morphology of phosphor particles plays an important role in improving the performance of flat panel displays. The phosphor particles with smooth surfaces are able to increase the screen brightness and improve the resolution¹⁶ because of lower scattering of evolved light and higher packing densities than irregularly shaped particles obtained by conventional solid-state route.

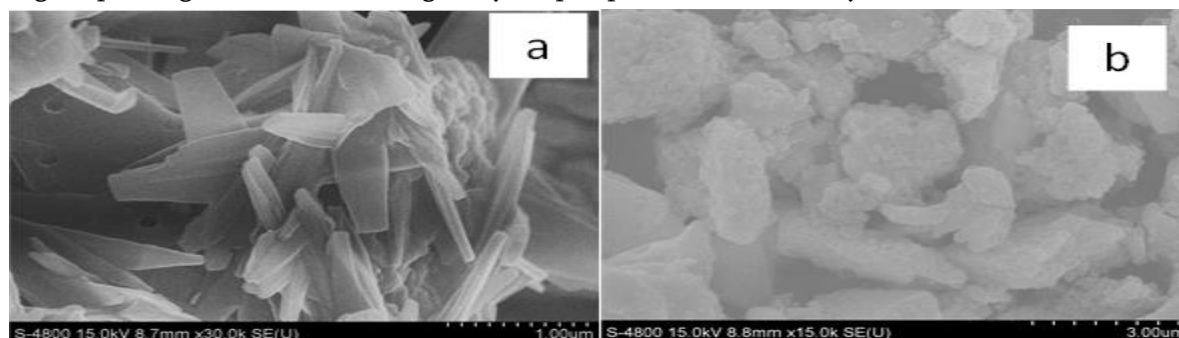


Figure 2: SEM images of 0.8 % Eu^{3+} doped YVO_4 prepared by: (a) CM and (b) SSD Method

Furthermore, recent studies revealed that the VUV energy is absorbed in a very thin layer at the surface of the phosphor particles^{17,18}, so the surface quality of phosphor particles seems to be very important for the luminescent efficiency. Milling and grinding processes are introduced in the phosphor prepared by conventional solid-state route, thus, the surface quality of phosphor is degraded, which is expected to influence the absorption of VUV energy significantly.

3.3 VUV Luminescence Studies

Emission spectra for samples prepared by CM and SSD methods of Eu^{3+} -doped YVO_4 phosphor shown in Fig. 3 along with insets, reveal the characteristic Eu^{3+} emission lines¹⁹⁻²¹. All the samples have been excited by VUV light of wavelength 147 and 172 nm, leading to an efficient energy transfer from the YVO_4 matrix to Eu^{3+} ions with subsequent f-f radiative relaxation ($^5\text{D}_0 \rightarrow ^7\text{F}_j$) transitions. All the emission spectra consist of the characteristic lines from $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($J = 1, 2, 3$ and 4) transitions of Eu^{3+} ion at 596, 620, 653 and 702 nm, respectively, as shown in Fig. 3 along with insets, respectively. In all emission results, red emission line at 619 nm, attributed to the electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} ions, is found to be intense. The excitation spectra of 0.8 % Eu^{3+} -doped YVO_4 sample, prepared by two different methods, recorded at the emission wavelength of 619 nm are shown in the insets of Fig.4. Fig.5 illustrates the plot of Eu^{3+} concentration versus the emission intensity of the red line (at 619 nm) in the $\text{Y}_{1-x}\text{Eu}_x\text{VO}_4$ phosphors synthesized by two different methods. The optimum Eu^{3+} concentration of the samples, synthesized by SSD and CM technique, is observed to be 8 %. As a case, the luminescent efficiency of the Eu^{3+} under the excitation at wavelength 147 and 172 nm depends strongly on the absorption efficiency of the host. As mentioned above, the phosphor powders obtained from CM route have higher luminance than those obtained from SSD route, since they have higher absorption efficiency of energy due to their excellent morphology. The emission spectrum of Eu^{3+} -doped YVO_4 prepared by low temperature method CM method shows very similar characteristics with that from high temperature SSD with difference in emission intensity.

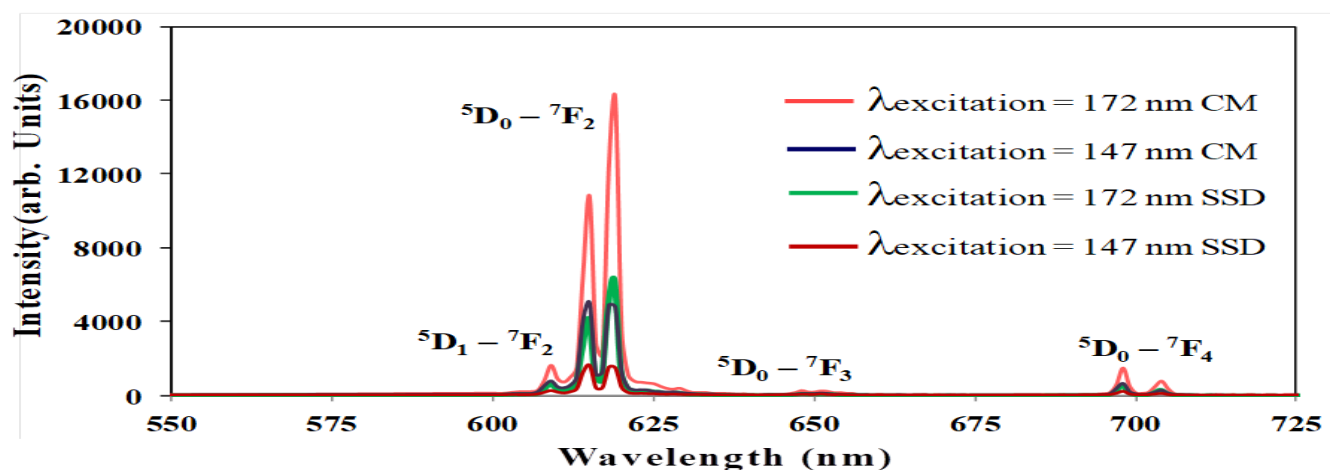


Figure 3: Photoluminescence emission spectra of YVO₄:xEu³⁺ prepared by: (a) CM and SSD method (λ_{ex} = 147 and 172 nm).

The intensity ratio of ⁵D₀ → ⁷F₁ to ⁵D₀ → ⁷F₂ bands varies with the changing of the preparation method at different excitation. It is interesting to note that the emission intensity of Eu³⁺-doped YVO₄ crystals prepared by the CM method is about 2 times as much as that by the SSD method. The difference in the emission intensity of Eu³⁺-doped YVO₄ crystals prepared by different methods can be explained if we consider the morphology of crystals and the phase formation during the processes.

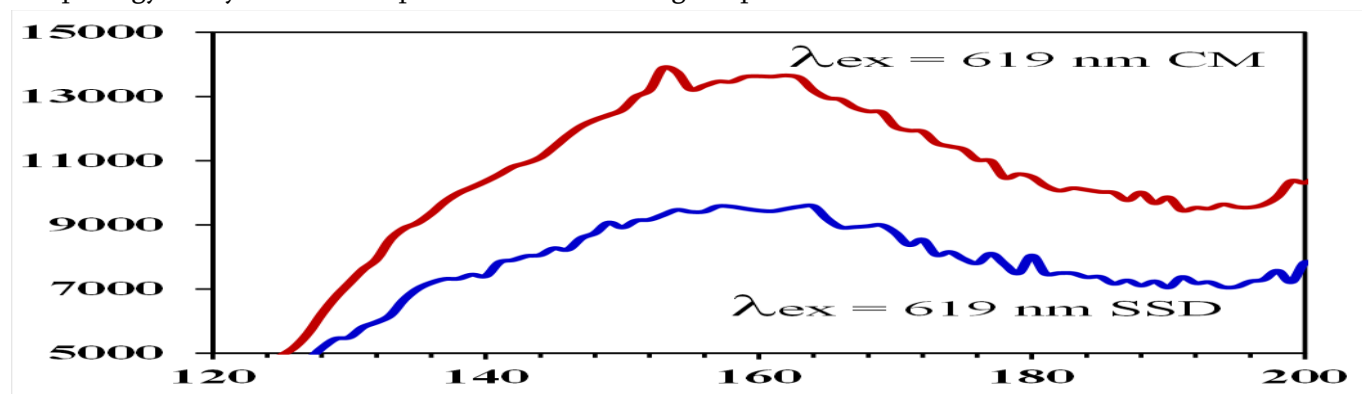


Figure 4: PL excitation spectra of the optimum Eu³⁺-doped YVO₄ samples prepared by CM and SSD route (λ_{emi} = 619 nm)

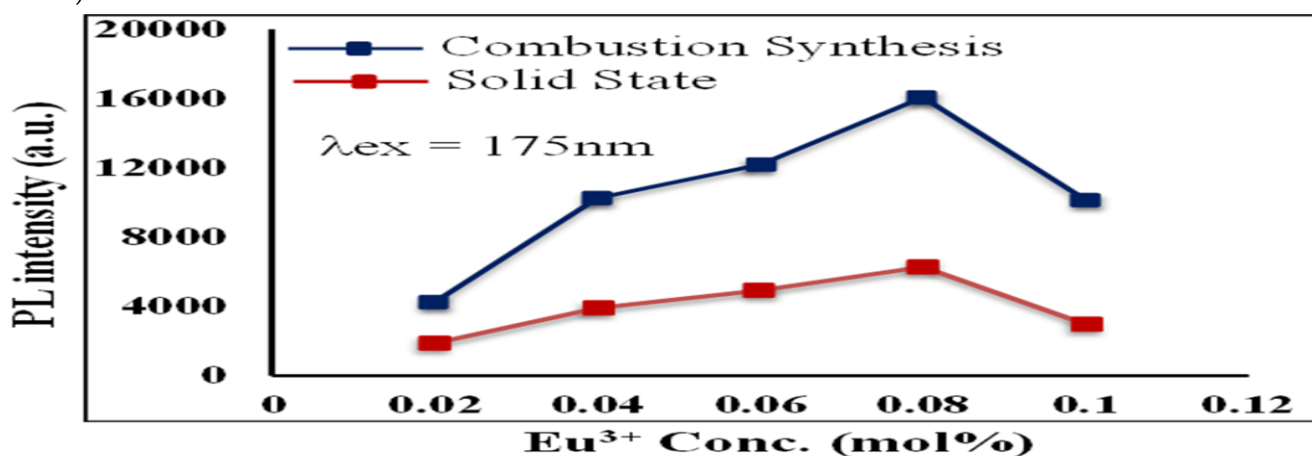


Figure 4: Plot of PL emission intensity as a function of Eu³⁺ concentrations of Eu³⁺-doped YVO₄ prepared by combustion route and solid-state route (λ_{ex} = 172 nm)

The particles of the YVO_4 prepared via the high temperature method were agglomerated (Fig.2b) and the extent of crystallization of YVO_4 prepared from the high temperature process is lower than that obtained from the low temperature CM method (Fig.2a). As mentioned earlier in the process of photoluminescence of Eu^{3+} -doped YVO_4 crystals, the energy is absorbed by the host lattice YVO_4 first and then it is transferred to the activator Eu^{3+} ions then lead to the luminescence. The absorbed energy by the host lattice in the agglomerated Eu^{3+} -doped YVO_4 particles would be lower than that in the YVO_4 crystals with uniform shape. Furthermore, there would be more defects in the crystals with lower crystallization obtained from the high temperature system.

IV. CONCLUSION

Solid-state and solution combustion methods were used to synthesize the red-emitting phosphor for PDP applications. By comparison, advantages of low temperature solution combustion method are summarized as follows: lower calcinations temperature, excellent particle morphology, and higher compositional homogeneity. $YVO_4:Eu^{3+}$ phosphors have strong excitation bands in VUV range, indicating high VUV energy absorption. The phosphors prepared by low temperature solution combustion method have superior luminescence, since they have excellent particle morphology and high compositional homogeneity, compared with those prepared by solid-state reaction route.

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