# Combustion Synthesis of $Dy^{3+}$–doped $YVO_4$ phosphor

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**Abstract**. Dy doped $YVO_4:Dy^{3+}$ phosphors were produced by the combustion method at 600°C. The structure and optical properties of the powders were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL). The XRD patterns showed the tetragonal phase similar to the standard JCPD file (17-0341). SEM shows that the particle sizes were small and agglomerated, and the size increased with the $Dy^{3+}$ dopant concentration and its shape changed to bulk-like particles. In PL, the emission spectra exhibited a weak band at 663 nm for the $^4F_{9/2}$ - $^6H_{11/2}$ transition and a peak at 483 nm (blue) for the $^4F_{9/2}$ - $^6H_{15/2}$ transition and a 574 nm (yellow) peak with higher intensity for the $^4F_{9/2}$ - $^6H_{13/2}$ transition.

## 1. Introduction

Yttrium orthovanadate ($YVO_4$) belongs to the space group $^{19}D_{4h}$ [1] and it is an important optical material that has been given considerable attention due to its outstanding characteristics, such as excellent thermal, mechanical and optical properties. In recent years, significant progress has been made on luminescent materials using $YVO_4$ as host lattice and its emission colors are based mainly on the f–f transition [2]. $Eu^{3+}$ doped $YVO_4$ nanocrystals have been widely used as an important commercial red phosphor. Their applications include color television, cathode ray tube, fluorescent lamps and plasma display panels. Yttrium orthovanadate activated by trivalent dysprosium ($YVO_4$:Dy) is a well-known phosphor material with high efficiency. The emission color of the luminescence is close to white because of the yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) emissions of $Dy^{3+.}$ There are two basic approaches to generate white light from light emitting diodes (LEDs). One is by mixing light of different colours emitted by several chips called multichip LEDs and the other is to convert the light emitted from a blue or ultraviolet (UV) LED to a longer wavelength light using phosphors, which are called phosphor-converted (pc) – LEDs [3]. In order to produce a phosphor that will produce white light for the LED applications $Dy^{3+}$ –doped $YVO_4$ phosphors were produced by a combustion method at 600°C. There are many methods to prepare $YVO_4$ phosphors, such as the chemical co-precipitation method [4], sol–gel method [5] and hydrothermal method [6]. Combustion has for a long time been the major source of energy for heating, transportation and production of electricity [7]. The combustion synthesis is very good because it can provide a product without sintering. In this paper, we report on the synthesis of $YVO_4$ phosphor material doped with different $Dy^{3+}$ concentrations by combustion method. The structure and the luminescence properties of the $YVO_4$: $Dy^{3+}$ is discussed.

## 2. Experimental

$YVO_4$: $Dy^{3+}$ was prepared by the combustion method. The starting materials were yttrium nitrate $Y(NO_3)_3$, ammonium metavanadate ($NH_4VO_3$), urea ($NH_2CONH_4$) and dysprosium nitrate Dy $(NO_3)_3$. The chemical reaction is as follows:

$$Y(NO_3)_3 + NH_4VO_3 + 2NH_2CONH_2 \rightarrow Y(VO_4) + 6H_2O + 4N_2 + 2CO_2$$

All the ingredients were mixed according to the stoichiometric ratio in an agate motar and a pasty solution was formed. The solution was transferred to a crucible and then kept in a furnace maintained at a temperature of 600°C. A combustion process started in a few minutes and a flame was observed. The formation of a foamy powder was observed and a pale yellow powder was obtained. The powder was then characterized by X-ray diffraction (XRD) patterns using a D8 advanced AXS GmbH X-ray diffractometer. The types of chemical bonds were investigated using a Bruker TENSOR 27 Series Fourier transform infrared spectroscopy (FTIR). The morphology was examined by scanning electron microscopy (SEM). The photoluminescence (PL) properties of the phosphor (emission and excitation) were measured using a Carry Eclipse PL spectrophotometer with a 150W xenon lamp as the excitation source.

## 3. Results and discussion

### *3.1. XRD study*

Figure 1 shows the XRD patterns of $YVO_4$ phosphor material doped with different concentration of Dy. The XRD patterns show the tetragonal phase and agreed well with standard JCPD file (17-0341) [8]. It is clear from the XRD patterns that no impurity phases were present which shows that all reactants have reacted completely. The average crystallite size determined from the broadening of the peaks (200), (112) and (312) using Scherrer formula was about 31 nm. The calculated lattice parameters were found to be a=0.711 nm and b=0.628 nm.

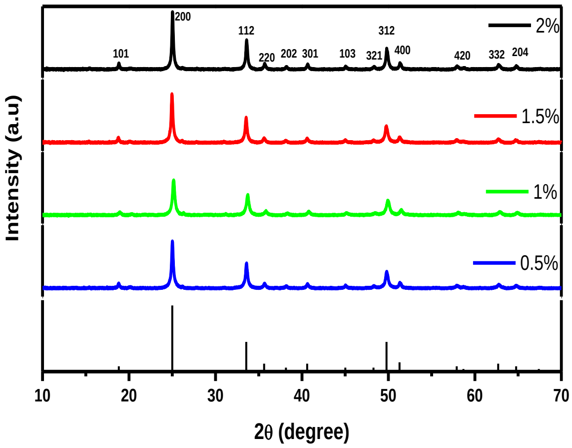

**Figure 1.** XRD pattern for the $YVO_4$ phosphors –doped with different concentration of $Dy^{3+}$ as well as the standard JCPD file (17-0341 ).

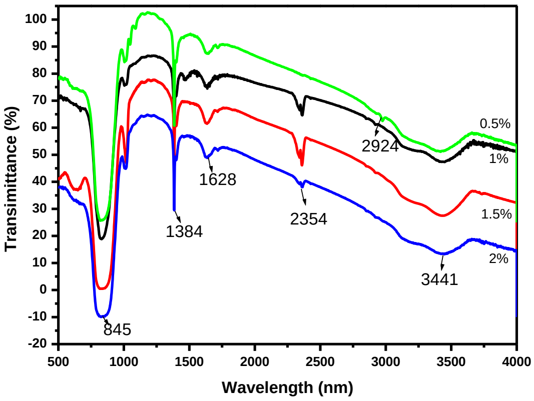

**Figure 2.** FTIR spectra of $YVO_4:Dy^{3+}$.

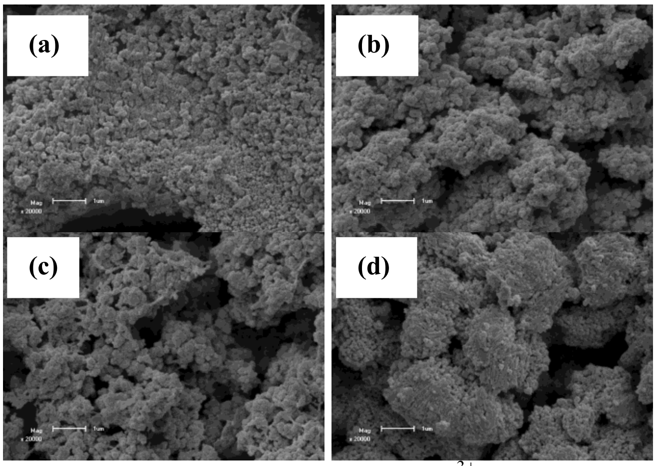

**Figure 3.** SEM image of the $YVO_4:Dy^{3+}$. doped with (a) 0.5, (b) 1, (c)1.5 and (d) 2 mol% $Dy^{3+}$ions

### 3.2. *FTIR study*

Figure 2 shows the FTIR spectra prepared for the combustion method at different concentrations of $Dy^{3+}$. The most intense band shows the characteristics of the V-O bonds with strong band ranges from 776-921 cm$^{-1}$ consisted of a peak at 845 cm$^{-1}$. A broad band centered at 3441 cm$^{-1}$ is assigned to the symmetric stretching vibration of H−O−H ($H_2O$ molecules). The strong peak observed at 1384 cm$^{-1}$ is ascribed to the asymmetrical vibration of the carboxyl groups. It can be seen that the position of the V-O stretching vibration remained the same for all the samples. The two weak bands at 2354 cm$^{-1}$ and 2924 cm$^{-1}$ correspond to the symmetrical and asymmetrical stretching vibration modes of the $CH_2$ group, respectively. The low 0.5% Dy concentration has some influence on symmetrical vibration modes of $CH_2$ since the band on 2.54 cm$^{-1}$ is very weak.

### 3.3. *SEM study*

SEM has been carried out to study the morphological structure of the $YVO_4:Dy^{3+}$ prepared by the combustion method. The SEM micrographs that are shown in figure 3 show the $YVO_4$ doped with (a) 0.5, (b) 1, (c) 1.5 and (d) 2 mol% $Dy^{3+}$ions. In a lower $Dy^{3+}$ concentration the particle size were small and much agglomerated. The particle size seems to increase along with the concentration and its shape changed to bulk-like particles. The surface of the morphology was rough. Table 1 shows the calculated average grain size of the $YVO_4$ doped with the various concentration of $Dy^{3+}$. The grain size decreased to 26 nm for 1 mol% of $Dy^{3+}$, and then increased as the $Dy^{3+}$ concentration increased. When doped with 2 mol% $Dy^{3+}$, the grain size was found to be 35 nm, which is also indicated in the increase in the intensity of the diffraction peaks, as observed in the XRD analysis.

**Table 1:** The average crystallite size for the $YVO_4$ doped with different concentration of Dy calculated by Scherer equation

| $Dy^{3+}$ concentration (mol%) | Average grain size (nm) | Experimental error (±) |
|---|---|---|
| **0.5** | **30** | **±4.5** |
| **1** | **26** | **±3.7** |
| **1.5** | **30** | **±1.2** |
| **2** | **35** | **±2.6** |

### *3.4. PL study*

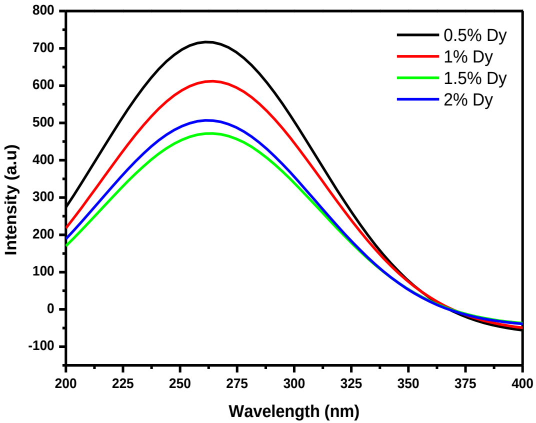

**Figure 4.** Excitation spectra of $YVO_4:Dy^{3+}$

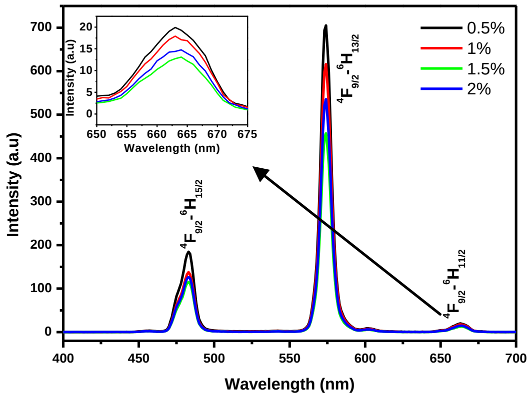

**Figure 5.** PL emission spectra of $YVO_4:Dy^{3+}$.

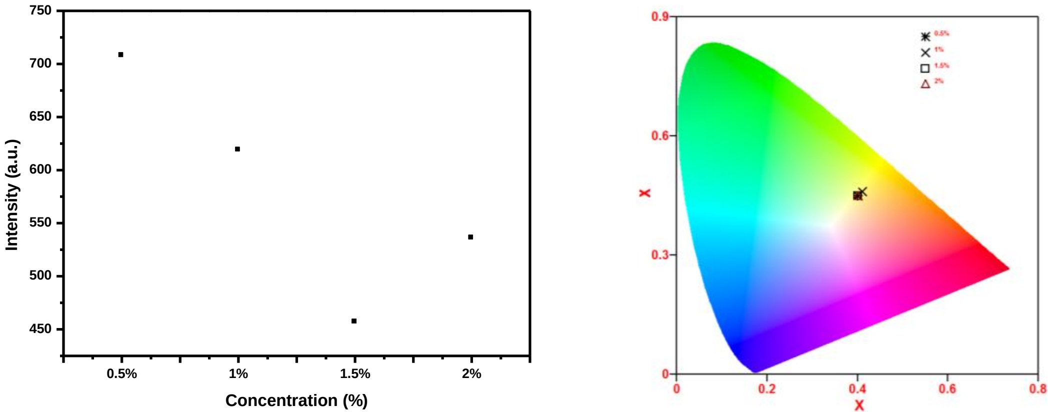

**Figure 6.** (a) 574 nm PL peak intensity vs concentration graph of the $YVO_4:Dy^{3+}$ phosphor, (b) CIE of $YVO_4$:Dy.

The PL excitation spectrum of $YVO_4:Dy^{3+}$ phosphor monitored at an emission wavelength of 574 nm is shown in figure 4. The excitation spectra showed a broad peak around 257 nm. Figure 5 shows the emission spectra of the $YVO_4:Dy^{3+}$ prepared at different concentration of $Dy^{3+}$. The insert shows the enlargement of the 663 nm peak. The spectra show the characteristics of the emission peaks of $Dy^{3+}$. The peaks are located at 483 nm (blue) and 574 nm (yellow). The peaks are related to the hypersensitive transition $^4F_{9/2}$-$^6H_{15/2}$ and the $^4F_{9/2}$-$^6H_{13/2}$, respectively. There is a very weak emission band located at 663 nm which correspond to the $^4F_{9/2}$-$^6H_{11/2}$ transition. The intensity of the yellow emission is stronger than that of the blue emission, because $Dy^{3+}$ is located at a site of the $D_{2d}$, which is deviated from an inverse center in the $YVO_4$ host [9]. The maximum PL intensity was observed for the lower concentration of 0.5%, figure 6 (a). The PL peak intensity showed a decrease in intensity as the concentration of $Dy^{3+}$ increased due to concentration quenching and then the intensity increased again when the concentration reached 2% as shown in figure 6. The reason is when the concentration is far above the critical concentration the intensity of the $Dy^{3+}$ emission will increase quickly as the concentration increase until it reaches another critical concentration, and then the intensity of $Dy^{3+}$ emission will decrease again for the energy transfer among different $Dy^{3+}$ ions [10].

### 3.5. *CIE chromaticity diagram*

The emission color of the $YVO_4:Dy^{3+}$ phosphor can be expressed by Commission Internationale de l'Elcairage (CIE) coordinates as indicated in figure 6(b). The chromaticity coordinate for the $YVO_4:Dy^{3+}$ with different $Dy^{3+}$ concentrations are very similar. It is clear that the $YVO_4:Dy^{3+}$ emitted a more yellowish colour light. The blue part helped to shift it slightly towards the white part of the spectrum. The phosphor can be used as a yellow emitted material in LEDs.

### 3.6. *Lifetime study*

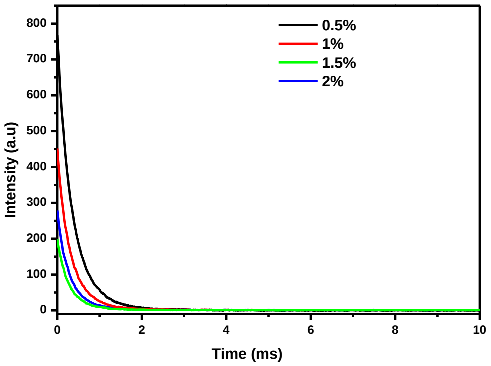

**Figure 7.** Decay curves of $YVO_4:Dy^{3+}$ phosphors with different concentration of $Dy^{3+}$.

Figure 7 shows the decay curves for the different concentration of $Dy^{3+}$ doped $YVO_4$. The logarithmic plots of the curves were fitted by a two order exponential decay equation:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2).$$

Where $I$ represents the phosphorescent intensity, $\tau_1$ and $\tau_2$ correspond to shorter and longer lifetime constants, and $A_1$ and $A_2$ are constants. The parameters for the fitting data are listed in table 2. The phosphorescence decay times as shown in table 2 can be explained by an initial rapid decay and then an intermediate transitional. A decrease in the intensity with an increase in concentration is due to the improvement of the crystallinity as the particle size increased with the concentration [11].

**Table 2**: Lifetime values obtained after bi-exponential fitting to the data of $YVO_4:Dy^{3+}$.

| %Dy | $\tau_1$ (ms) | $\tau_2$ (ms) | $A_1$ | $A_2$ |
|---|---|---|---|---|
| 0.5 | 0.27 | 0.56 | 273 | 493 |
| 1 | 0.26 | 0.89 | 20 | 177 |
| 1.5 | 0.26 | 0.65 | 27 | 267 |
| 2 | 0.28 | 0.64 | 47 | 150 |

## 4. Conclusion

$YVO_4:Dy^{3+}$ phosphors prepared with different concentration of $Dy^{3+}$ have been synthesized by the combustion method at 600°C. The XRD characteristics confirmed the crystalline single phase present in the sample. In SEM images the particle size seemed to increase along with the concentration of $Dy^{3+}$. The emission colour of the luminescence is yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and approaching the white region due to the blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) emissions of $Dy^{3+}$ and has the potential to be used as a phosphor for pc-LEDs. The intensity of the PL was decreasing while increasing the concentration due to concentration quenching.

## Acknowledgements

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