# Combustion synthesis of Eu$^{2+}$ and Dy$^{3+}$ activated Sr$_3$(VO$_4$)$_2$ phosphor for LEDs

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**Abstract.** Combustion synthesis and photoluminescence (PL) characterization of Sr$_3$(VO$_4$)$_2$:Eu,Dy phosphors are presented in this paper. PL emission of Sr$_3$(VO$_4$)$_2$:Eu phosphor shows green broad emission band centring at 511 nm and a red sharp band at 614 nm by excitation wavelength of 342 nm. The PL emission spectrum of Sr$_3$(VO$_4$)$_2$:Dy phosphor exhibits an intense blue emission peak at 479 nm, yellow broad band centring at 573 nm and red band at 644 nm by the excitation wavelength of 426 nm in near visible blue region. The excitation wavelength of Eu (342 nm) and Dy (426 nm) activated Sr$_3$(VO$_4$)$_2$ phosphor are well matched with the excitation of near UV excited solid state lighting and blue chip excitation of light emitting diodes, respectively. The effect of Eu$^{2+}$ and Eu$^{3+}$ ions concentration on the emission intensity of Sr$_3$(VO$_4$)$_2$ was also investigated. The Sr$_3$(VO$_4$)$_2$:Eu is a potential green and red emitting phosphor as well as Sr$_3$(VO$_4$)$_2$:Dy is blue and yellow emitting phosphor for solid state lighting i.e. white LEDs. The XRD and SEM characteristics of Sr$_3$(VO$_4$)$_2$ materials was also reported in this paper.

**Keywords.** Solid state lighting; LED; phosphors; vanadate; Sr$_3$(VO$_4$)$_2$; combustion synthesis.

## 1. Introduction

Luminescent materials are used for various purposes such as making lamps, CR tubes and TV screens, LEDs, detectors, for X-ray imaging, scintillation detectors. Laser crystals have been obtained in the presence of Eu$^{2+}$ ion due to considerable interest in it in the last few years. Recently, interest in solid-state materials of vanadates (Huignard *et al* 2000; Qingli *et al* 2000; Neeraj *et al* 2004a), molybdates (Yi *et al* 2002; Neeraj *et al* 2004b), and tungstates (Macalik *et al* 2004; Pang *et al* 2004) doped with rare earth has expanded significantly, owing to their long-wavelength excitation properties and excellent chemical stabilities (Goutenoire *et al* 2005; Was'kowska *et al* 2005). These compounds have broad and intense charge transfer (CT) absorption bands in the near-UV and are therefore, capable of efficiently capturing the emission over a large range of wavelength. Under photoexcitation, band pertaining to charge transfer from oxygen to metal are very intense and the energy is transferred to the luminescent centre by a non-radiative mechanism (Pode and Dhoble 1997; Neeraj *et al* 2004a; Wang *et al* 2005). In particular, the VO$_4^{3-}$ complexion group in which the central V metal ion is coordinated by four O$^{2-}$ ions in tetrahedral symmetry has been identified as an efficient luminescent centre, similar to other Scheelite-type compounds. Characteristic luminescence of VO$_4^{3-}$ ions is commonly observed in other vanadate complexes such as Mg$_3$(VO$_4$)$_2$, LiZnVO$_4$,

and NaCaVO$_4$. If trivalent rare-earth ions such as Eu$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$ are incorporated into a vanadate host, bright luminescence due to the dopant ions can be observed due to efficient energy transfer processes from the vanadate ions (Shionoya and Yen 1999). Although the luminescence characteristics of various vanadate phosphors have been reported, we have investigated here the properties of Sr$_3$(VO$_4$)$_2$:Eu and Dy phosphors.

In recent years, solid-state lighting technology has been in high demand as the most challenging application to become the replacement of conventional fluorescent lamp by light-emitting diodes (LED). Although the stimulated high-colour rendering potential of the light sources consisting of 360 nm ultraviolet LED (UV LED) and tricolour phosphors was reported and experimentally confirmed, there are currently insufficient studies on the use of phosphors converting UV-LED as illumination sources. Therefore, it is most crucial to study phosphors for UV-LED. At present, more and more researchers are devoting themselves to this work with interest. White light emitting diodes (LEDs) have been widely utilized for backlight of liquid crystal display (LCD), traffic signals and especially for solid state lighting. In comparison with the incandescent and fluorescent lamps, white LEDs have a number of advantages such as higher energy efficiency, reduced power consumption, compactness, long lifetime and lack of pollutant. The strategies involved in developing white light are (i) the combination of blue LED with a yellow phosphor; (ii) the combination of UV-LED with blue, green and red phosphors; and (iii) the combination of blue, green and red LEDs.

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As mentioned above, combining the light of several coloured LEDs can create white light. The use of RGB LEDs promises high efficiencies and flexible, user controlled colour, but this involves complicated electronics, because the amount of red, green and blue light must be carefully controlled since the LED light output (intensity and colour) varies with drive current, temperature and time (device ageing). Homogeneous optical mixing of light is also difficult. Because of the high saturation of the primary LED colours, display with a large colour extent can be made. This can be exploited for the improvement of LCDs, since standard backlight for LCDs are based on fluorescent lamps yielding a smaller colour extent.

$Eu^{2+}$ emission results from two types of transitions. The most common is that due to $4f\ ^{6}5d^{1} \rightarrow 4f^{7}(^{8}s_{7/2})$. As the position of the band corresponding to $4f^{6}5d$ configuration is strongly influenced by the host, the emission can be anywhere from 365–650 nm. Since the $4f$–$5d$ transition is an allowed electrostatic dipole transition, the absorption and emission of $Eu^{2+}$ is very efficient in many hosts, which makes the $Eu^{2+}$ doped phosphors of practical importance.

$Dy^{3+}$ ions, which have luminescence lines in the 570–650 nm region due to the $^{4}F_{9/2} \rightarrow\ ^{6}H_{13/2}^{4}$, $F_{9/2} \rightarrow\ ^{6}H_{15/2}$ transitions, have attracted much attention because of their light emission. Here we concentrated on preparing a vanadate-based system by using low-cost conventional combustion method. The photoluminescence (PL) emission spectrum of $Dy^{3+}$ ion gives emission in the yellow and red regions of the visible spectrum under 426 nm excitation.

In this paper, the $Sr_3(VO_4)_2$:Eu green and red emitting phosphors and $Sr_3(VO_4)_2$:Dy blue and yellow emitting phosphors were synthesized by combustion method and its luminescent properties were investigated. The prepared phosphors were characterized by XRD and SEM techniques.

## 2. Experimental

### 2.1 *Preparation of Sr₃(VO₄)₂:Eu and Dy phosphors*

We prepared $Sr_3(VO_4)_2$:Eu and Dy by typical combustion method, where we used all materials in nitrate form. The starting materials were strontium nitrate ($Sr(NO_3)_2$), ammonium metavanadate ($NH_4VO_3$), urea ($NH_2CONH_2$) and europium nitrate ($Eu(NO_3)_2$) or dysprosium oxide ($Dy(NO_3)_2$).

$$3Sr\,(NO_3)_2 + 2\,(NH_4VO_3) + 4NH_2CONH_2$$
$$\rightarrow Sr_3\,(VO_4)_2 + 12H_2O + 8N_2 + 4CO_2.$$
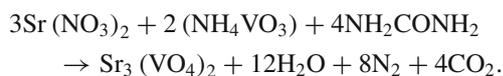
All the ingredients were mixed according to stoichiometric ratio in agate mortar and a pasty solution was formed. The solution was then transferred to silica crucible and kept inside a muffle furnace which was maintained at a constant temperature of 900˚C. If temperature was less than 900˚C,

the combustion process would not start, therefore, by using typical combustion process at 900˚C in this experiment, $Sr_3(VO_4)_2$:Eu and Dy phosphors were prepared. A flame was observed with the formation of foamy powder, the powder so obtained was pale yellow in colour.

We used combustion synthesis because it was an ideal technique used to produce chemically homogeneous and pure, single phase fine powder in the as synthesized condition. Basically the exothermic reaction was initiated at the ignition temperature and it generated heat which was manifested in a maximum or combustion temperature (1000–1650 K), which can volatilize low boiling point impurities, and therefore, resulted in purer products than those produced by more conventional techniques. Smaller particle size was produced from reaction that liberated the greatest amount of gas. The simple exothermic nature of the self-propagating high temperature synthesis (SHS) reaction avoids the need for expensive processing facilities and equipment. The short exothermic reaction time results in low operating and processing costs.

### 2.2 *Measurement procedure*

The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN- analytical diffractometer. The morphology and the composition of product were examined by scanning electron microscopy (SEM, JED-2300). The photoluminescence properties of the phosphor (excitation and emission) were measured using a Shimadzu RF-5301PC spectroflurophotometer at room temperature.

## 3. Results and discussion

### 3.1 *XRD pattern of Sr₃(VO₄)₂*

The formation of crystalline phase in the sample prepared by the combustion method was confirmed by powder XRD measurement. Figure 1 shows the XRD pattern of $Sr_3(VO_4)_2$ material. The X-ray diffraction pattern of $Sr_3(VO_4)_2$ phosphor matched well with the standard JCPDs file[00-019-1289].

The X-ray diffraction pattern did not indicate presence of the constituent nitrate and traces of ammonia gases, which is an indirect evidence for the formation of the desired compound. But these extra lines were observed in XRD pattern due to the initial impurity in the starting materials which we used and the intensity of these lines were negligible as per the comparison with high intensive line of final compound and this extra line did not play any role in luminescence characterization in the present results. The lattice constants (hexagonal setting) of $Sr_3(VO_4)_2$ were determined with the millar indices of (104), (015), (110), (202), (018), (024), (116), (205), (027), (211), (208), (0111), (125), (300), (217). Prepared $Sr_3(VO_4)_2$ phosphor gives the rhombohedral
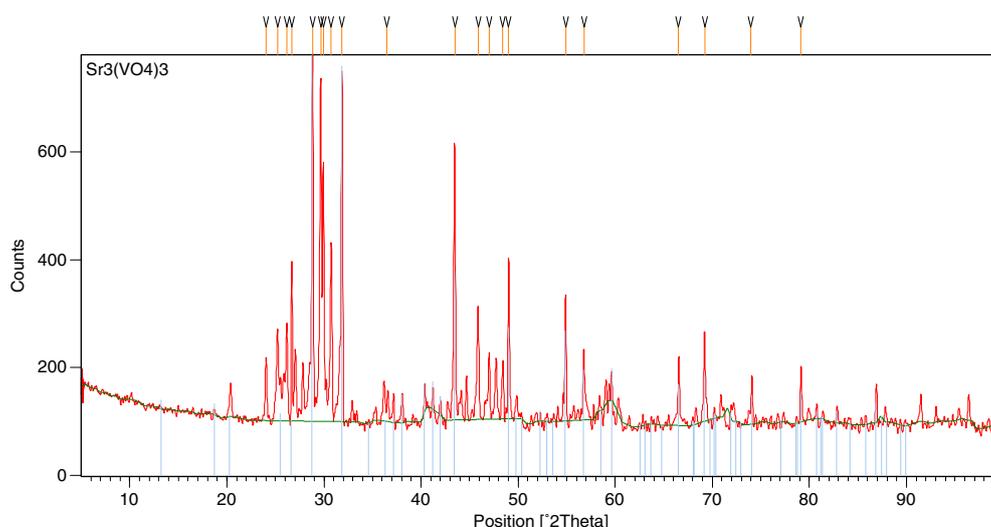
**Figure 1.** X-ray diffraction (XRD) pattern of Sr$_3$(VO$_4$)$_2$ material.

space group R-3m with unit cell a = b = 5·6100 nm and c = 20·0300 nm (hexagonal setting). This result indicates that the final product was formed in homogeneous form with hexagonal unit cell.

### 3.2 *Photoluminescence characterization of Sr$_3$(VO$_4$)$_2$:Eu phosphor*

The PL emission and excitation spectra of Sr$_3$(VO$_4$)$_2$:Eu phosphor are presented in figures 2 and 3, respectively. With an excitation wavelength of 342 nm, the emission spectrum exhibits a green broad band centring at 511 nm due to $f$–$d$ transition of Eu$^{2+}$ ion as well as sharp emission peak is observed at 614 nm in the red region of the spectrum due to $^5D_0 \rightarrow {}^7F_2$ transition of Eu$^{3+}$ ion. PL emission spectra shows 511 nm peak intensity which is maximum for 0·1 mol% and with increasing concentration of impurity above 0·1 mol%, the PL 511 nm peak intensity decreases due to concentration quenching as well as aggregation of activator ions. This result clearly indicates that maximum emission intensity is observed for lower concentration, hence rare earth ions required very less quantities, and therefore, total cost of prepared materials is low.

The emission spectrum exhibits a green broad band centring at 511 nm, which corresponds to the allowed $f$–$d$ transition of Eu$^{2+}$. The 5$d$ energy level of Eu$^{2+}$ and the lower level of 4$f$ state overlap, so the electron of 4$f$ state can be excited to 5$d$ state. The broad luminescence of Eu$^{2+}$ is due to $4f^6 5d^1 \rightarrow 4f^7$ transitions, which is an allowed electrostatic dipole transition. However, the 5$d$ state is easily affected by the crystal field; that is to say, different crystal fields can split the 5$d$ state in different ways. This makes Eu$^{2+}$ emit different wavelengths of light in different crystal fields and the emission spectrum can vary from the blue to the red region. The present results show the emission spectrum exhibits a green broad band observed at 511 nm,
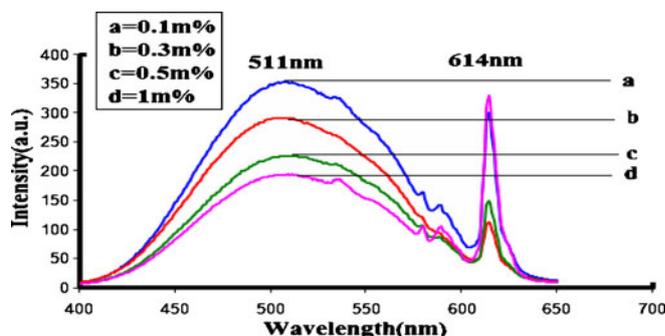


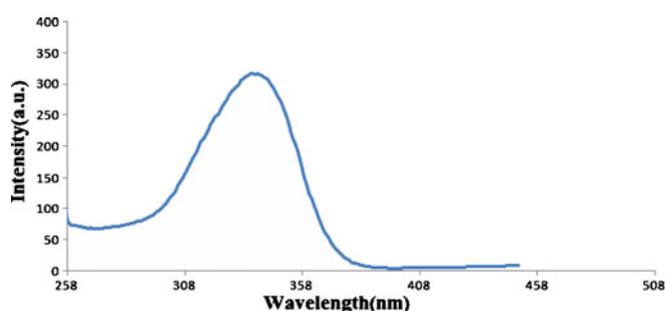**Figure 2.** PL emission spectra of Sr$_3$(VO$_4$)$_2$:Eu phosphor, the excitation wavelength is 342 nm.



**Figure 3.** PL excitation spectra of Sr$_3$(VO$_4$)$_2$:Eu phosphor, the spectra monitored at 511 nm.

it corresponds to the allowed $f$–$d$ transition of Eu$^{2+}$. Therefore, vanadates are excellent matrices for Eu$^{2+}$ activated phosphors. As an activated ion, Eu$^{2+}$ ion with the 5$d$ electron is unshielded from the crystal field by the 5$s$ and 5$p$ electrons, and the spectral properties are strongly affected by the surrounding environment like symmetry, covalence, coordination, bond length, site size and crystal-field strength, etc

(Sun *et al* 2005). So the $Eu^{2+}$-emission band may be changed from blue to green in the visible spectral region by changing the surrounding environment.

The overall emission spectrum consists of a number of prominent peaks induced by the characteristic $f$–$f$ inner-shell transitions of $Eu^{3+}$ ions, similar to other $Eu^{3+}$-activated red-emitting luminescent materials, i.e. $Y_2O_3$, $YVO_4$, etc. The results imply that the absorption of external UV photons by the $VO_4^{3-}$ groups inside the host matrix leads to non-radiative transfer to luminescent centres, $Eu^{3+}$ located in a non-inversion symmetry site. Consequently, the hyper-sensitive electric dipole transition of $^5D_0 \rightarrow {}^7F_2$ at 614 nm displays prominent emission intensity while that of the magnetic dipole transition, $^5D_0 \rightarrow {}^7F_1$, is active under UV excitation conditions.

$Eu^{3+}$ excitation usually occurs through CT band or from host lattice absorption and energy transfer rather than through $4f \rightarrow 5d$ absorption, though this is also possible in some solids by UV radiation in the region 200–250 nm. Sometimes absorption within $4f$ shell also takes place as the spin and parity prohibition are partially lifted by mixing of levels promoted by crystal field. $Eu^{3+}$ emission usually occur from $^5D_0 \rightarrow {}^7F_j$ transitions; there are three transition which are of prime importance: $^5D_0 \rightarrow {}^7F_0$ (around 570 nm), $^5D_0 \rightarrow {}^7F_1$ (around 595 nm), and $^5D_0 \rightarrow {}^7F_2$ (around 610 nm). The first one is strongly forbidden transition and observed with appreciable intensity in some host. $^5D_0 \rightarrow {}^7F_1$ transition is forbidden as electric dipole, but allowed as magnetic dipole, this is the only transition when $Eu^{3+}$ occupies a site coinciding with the centre of symmetry.

PL emission spectrum of $Sr_3(VO_4)_2$:Eu phosphor shows strong $Eu^{2+}$ emission due to the $4f$–$5d$ transition of $Eu^{2+}$ ions at 511 nm wavelength and is the basic characteristic of $Eu^{2+}$ emission. The PL emission shows there is a transfer of energy from $Eu^{2+}$ to $Eu^{3+}$ ions. $Eu^{3+}$ PL emission is also observed in presence of $Eu^{2+}$ ions due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition of $Eu^{3+}$. $Eu^{2+}$ emission gets suppressed 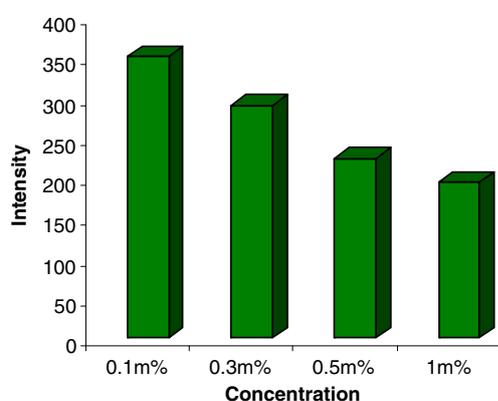*with little* and enhances the $Eu^{3+}$ PL emission in the red region at the same excitation wavelength. The $Eu^{3+}$ emission reaches to the characteristic of red region i.e. 614 nm wavelength. $Eu^{3+}$ emission shows a strong peak at 614 nm wavelength. Figure 4 shows the increase in PL intensity of $Eu^{2+}$ ions at 514 nm with variation in the concentration of Eu ion in $Sr_3(VO_4)_2$ from 0·1 m% to 1 m% concentration. All PL characteristics are obtained at the same excitation wavelength i.e. 342 nm. There is both $Eu^{2+}$ and $Eu^{3+}$ emission observed in the prepared phosphors. Figure 4 shows concentration vs intensity graph in $Sr_3(VO_4)_2$:Eu phosphor. From this it can be seen that 511 nm PL peak intensity goes on decreasing as the concentration of Eu increases in $Sr_3(VO_4)_2$ phosphor. The PL results of prepared $Sr_3(VO_4)_2$:Eu phosphors show the green and red emissions of the phosphors may be applicable in the solid state lighting due to its excitation wavelength around 342 nm.

### 3.3 *Photoluminescence characterization of $Sr_3(VO_4)_2$:Dy phosphors*

Recently, luminescence materials doped with $Dy^{3+}$ have drawn much interest for their white emission (Dominiak-Dzik *et al* 2004; Xiu *et al* 2006; Liang *et al* 2008). In general, $Dy^{3+}$ has two dominant bands in the emission spectra in many host matrices. The band located at 571 nm (yellow) corresponds to the hypersensitive transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and another band located at 478 nm (blue) is due to the transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$. By adjusting the yellow-to-blue intensity ratio (Y/B) value appropriately, it is possible to obtain near-white emission with only $Dy^{3+}$-activated luminescence materials. Therefore, the $Dy^{3+}$-activated phosphors are promising white light phosphors and can be used in mercury-free lamp. For mercury-free lamp, the excitation energy was mainly composed of VUV radiation but VUV energy is mostly absorbed by the host crystal, if the energy can be transferred from host to rare-earth (RE) ions then the rare earth ions can emit visible light. So the host absorption intensity is very important for VUV-excited phosphors applied in mercury-free lamp.

PL excitation spectrum of $Sr_3(VO_4)_3$:Dy phosphor is shown in figure 5 (the spectra monitored at 511 nm). Measurement of emission spectrum was done by monitoring the
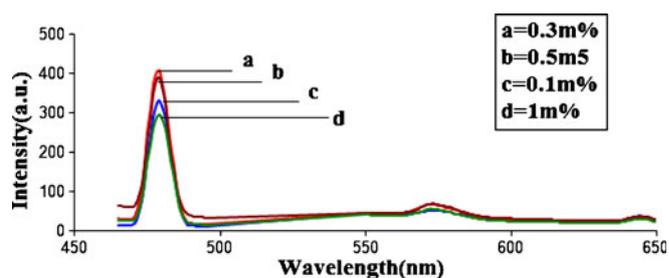


**Figure 4.** PL peak intensity (511 nm) variation with the concentration of Eu ions in $Sr_3(VO_4)_2$ phosphor.



**Figure 5.** PL excitation spectrum of $Sr_3(VO_4)_3$:Dy phosphor, the spectra monitored at 511 nm.

peak wavelength of $Dy^{3+}$ emission of blue, yellow and red regions of the spectrum, respectively (figures 6 and 7). The excitation spectrum in the range 300–450 nm consists of the $f-f$ transition of $Dy^{3+}$ ion, i.e. 426 nm ($^6H_{15/2} \rightarrow$ $^6F_{9/2}$ transition) at the near blue region (figure 5). Nowadays new blue chip excited LED required yellow emitting phosphors by excited blue or near blue wavelength of light. The emission spectra for the $Dy^{3+}$ activated $Sr_3(VO_4)_2$ phosphor shows the emission at 479 nm (blue), 573 nm (yellow) and

644 nm (red). These three different emission bands originated from one origin owing to the fact that they are having the same excitation wavelength. The transition involved in blue, yellow and red bands of $Dy^{3+}$ ion are well known and have been identified as $^4F_{9/2} \rightarrow \ ^6H_{15/2}, \ ^4F_{9/2} \rightarrow \ ^6H_{13/2}$ and $^4F_{9/2} \rightarrow \ ^6H_{11/2}$ transitions, respectively (Kuang and Liu 2006).

Figure 8 shows the concentration vs 573 peak intensity graph of $Sr_3(VO_4)_2$:Dy phosphor. From this it can be seen that the variation in peak intensity is 0·5 m% > 0·3 m% > 1 m% > 0·1 m%. The maximum intensity is at 0·5 m% of $Dy^{3+}$ ion.

Figure 9 shows systematic representation of transition of $Dy^{3+}$ emission around 479 nm ($^4F_{9/2} \rightarrow \ ^6H_{15/2}$) of magnetic dipole and 573 nm ($^4F_{9/2} \rightarrow \ ^6H_{13/2}$) of electric dipole in the $Sr_3(VO_4)_2$:Dy phosphor. 479 nm and 573 nm transitions from $^4F_{9/2}$ energy level to $^6H_{13/2}$ and $^6H_{15/2}$ energy levels, respectively are due to $Dy^{3+}$ ion.



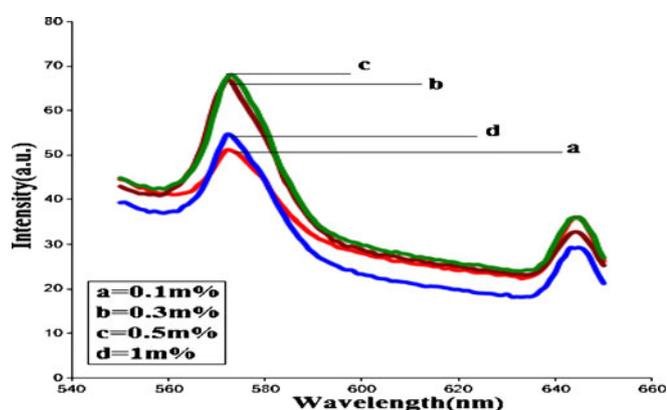**Figure 6.** PL emission spectrum of $Sr_3(VO_4)_3$:Dy phosphor, the excitation wavelength is 342 nm.



**Figure 7.** PL emission spectrum of $Sr_3(VO_4)_3$:Dy phosphor, specially shows the emission of yellow and red regions of the spectrum in the range 550–650 nm, the excitation wavelength is 342 nm.
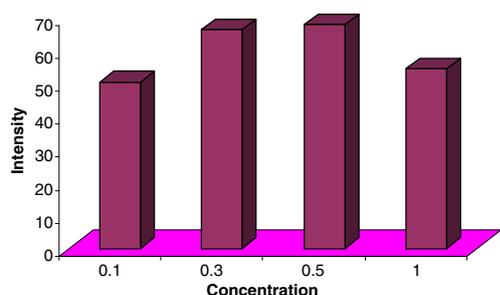


**Figure 8.** Concentration vs 573 PL peak intensity graph of $Sr_3(VO_4)_2$:Dy phosphor.

### 3.4 *SEM photograph of Sr₃(VO₄)₂ phosphor*

Figure 10 shows SEM photograph of $Sr_3(VO_4)_2$:Eu phosphor. In order to study the morphological structure of phosphor prepared by combustion synthesis, scanning electron microscopy has been carried out. SEM photographs show
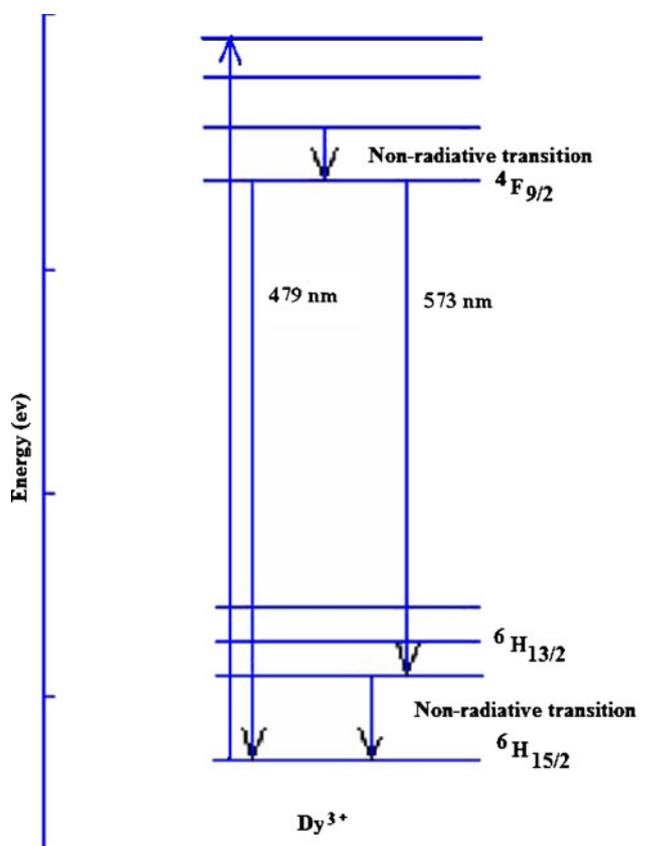


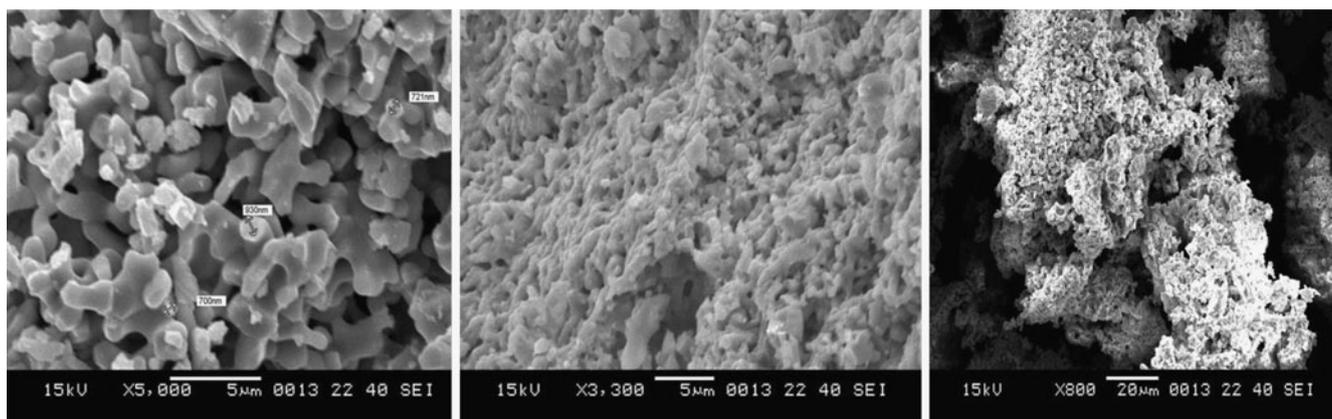**Figure 9.** Schematic energy level diagram of $Dy^{3+}$ ion.

**Figure 10.** SEM photograph of $Sr_3(VO_4)_2$:Eu phosphor.

the particle size of prepared $Sr_3(VO_4)_2$:Eu phosphor to be around or <1 μm. The morphology of particle always indicates the coating of phosphors inside lighting bulb as well as the preparation of chip of LED semiconductor. If particle size is less or in the order of nano-scale, than coating, chemical stability, distribution of particle on surface improved the light output from LED, therefore, quality of LED is enhanced in their application. Particle size in the nano range is indicated in the development of the chemical and physical properties of phosphors as well as coating inside the lamps and fabricating the chip of LED lighting.

## 4. Conclusions

$Sr_3(VO_4)_2$:Eu/Dy phosphors are prepared by combustion synthesis. In Eu activated $Sr_3(VO_4)_2$ phosphor the emission is at 511 (green) and 614 nm (red) and in Dy doped $Sr_3(VO_4)_2$ the emission is at 479 nm (blue) and 573 nm (yellow). The PL emissions are observed by excitation of 342 nm in Eu and 426 nm in Dy activated $Sr_3(VO_4)_2$ phosphors, respectively. The PL results show that prepared phosphors may be one of candidates for LED lamp phosphors as a red, green and blue phosphors. XRD and SEM characteristics confirm crystalline phase present in the sample and morphology of sample.

## References

Dominiak-Dzik, Ryba-Romanowski W, Kova'cs L and Beregi E 2004 *Radiat. Meas.* **38** 557

Goutenoire F, Kodjikian S and Saurd E 2005 *Solid State Chem.* **178** 2811

Huignard A, Gaoin T and Boilot J P 2000 *Chem. Mater.* **12** 1090

Kuang J and Liu Y 2006 *J. Solid State Chem.* **179** 266

Liang X, Zhu C, Yang Y, Yuan S and Chen G 2008 *J. Lumin.* **128** 1162

Macalik L, Maczka M, Hanuza J and Hanuza A 2004 *J. Alloys Compd* **30** 248

Neeraj S, Kijima N and Cheetham A K 2004a *Solid State Commun.* **131** 65

Neeraj S, Kijima N and Cheetham A K 2004b *Chem. Phys. Lett.* **387** 2

Pang M L, Lin J and Yu M 2004 *J. Solid State Chem.* **177** 2237

Pode R B and Dhoble S J 1997 *Phys. Status Solidi (b)* **203** 571

Qingli Z, Changxin G, Chaoshu S and Shaozhe L J 2000 *Alloys Compd.* **309** 10

Shionoya S and Yen W M 1999 *Phosphor handbook* (Boca Raton, FL: CRC press) pp 203–204

Sun J Y, Xia Z G and Du H Y 2005 *Spectrosc. Spect. Anal.* **5** 1760

Wang Z, Liang H, Gong M and Su Q 2005 *Electrochem. Solid State Lett.* **8** H33

Was'kowska A *et al* 2005 *Solid State Chem.* **178** 2218

Xiu Z, Yang Z, LU M, Liu S, Zhang H and Zhou G 2006 *Opt. Mater.* **29** 431

Yi G, Sun B and Yang F 2002 *Chem. Mater.* **14** 2910