

**SOLID STATE SYNTHESIZED  $YVO_4:Dy^{3+}/SiO_2$  COMPOSITES: MICROSTRUCTURES AND OPTICAL CHARACTERISTICS**

In this paper  $YVO_4:Dy^{3+}$  was synthesized via solid state method at  $1100^\circ C$  and effects of different quantities of  $SiO_2$  particles on microstructure and photoluminescence properties were investigated in details. To study the microstructure and properties of these composites XRD, SEM, TEM, HRTEM, XPS and PL equipments were employed. It was found that via addition of  $SiO_2$  particles to  $YVO_4:Dy^{3+}$  phosphors, strong bonding is made between  $SiO_2$  particles and phosphors. Furthermore, based on stronger electronegativity of Si 2p element compared to Y 3d and V 2p elements, increase of  $SiO_2$  causes the increase of binding energy. Moreover, this research showed that the addition of 10 wt%  $SiO_2$  particles to  $YVO_4:Dy^{3+}$  material enhances the excitation and emission luminescence properties, significantly. Further increase of  $SiO_2$  particles results in suppress of emission intensity.

*Keywords:* Solid State, Composite,  $SiO_2$ , Luminescence

**1. Introduction**

Among miscellaneous phosphors, those doped by rare earth ions are very attractive due to their abundant advantages such as the great stability, high efficiency and significant color purity [1-4]. These compounds have many applications including cathode ray tubes, lamps and X-ray detectors [5-10]. As a host lattice,  $YVO_4$  is known as an excellent material [11-13] and especially for the rare earth activators it provides phosphors with noble quantum yields [14-16]. On the other side, since the rare earth materials are very expensive, many researchers have tried to design the phosphors without any rare earth activators [17-18]. As a second alternative, phosphors synthesis in the presence of  $SiO_2$  powder has been introduced since it is cheap, has a good transparency in the visible region and does not affect the peak position of PL spectra [19-21]. There are many reports attributed to the employment of  $SiO_2$  as a coating layer on the surface of phosphors [22-25]. Also in several research works, nanosized  $SiO_2$  has been used to make composite phosphors via different techniques such as sol-gel and spray pyrolysis [19,26-28]. Although it is known that  $SiO_2$  nanoparticles are ideal candidates to improve the optical properties of phosphor materials, but since these nanoparticles are very expensive, their applications are limited to some extent. To best of our knowledge unfortunately there is not enough data about  $YVO_4:Dy^{3+}/SiO_2$  composite materials. Motivated by these backgrounds, in this paper we synthesized  $Dy^{3+}$  doped  $YVO_4$  without /with different quantities of  $SiO_2$  particles via simple solid state method. To study the influence of  $SiO_2$  addition on microstructure and

photoluminescence characteristics of  $YVO_4:Dy^{3+}$ , we employed XRD, SEM, HRTEM, XPS and PL characterizations.

**2. Experimental****2.1. Synthesis of  $YVO_4:Dy^{3+}$  / with or without  $SiO_2$  via solid state technique**

To synthesize  $YVO_4:Dy^{3+}$  phosphor, analytical grades of yttrium acetate ( $Y(CH_3COO)_3 \cdot H_2O$ ), vanadium oxide ( $V_2O_5$ ), dysprosium acetate ( $Dy(CH_3COO)_3 \cdot H_2O$ ) were purchased from Aldrich company. In a typical procedure, 2 g of yttrium acetate, 0.644 g of vanadium oxide and 0.026 g of dysprosium acetate were mixed and stirred vigorously in water for 15 min in an alumina crucible. Then this mixture was transferred to an oven at  $100^\circ C$ . The dried powder was synthesized at  $1100^\circ C$  for 2h to prepare  $SS_0$  compound. In the case of synthesizing  $SS_1$ ,  $SS_2$ ,  $SS_3$  and  $SS_4$ , those introduced in Table 1, specific amounts of  $SiO_2$  powder were mixed with solid state synthesized phosphors and experienced the solid state synthesis, repeatedly.

**2.2. Characterization**

Firstly  $YVO_4:1\%Dy^{3+}$  phosphors were characterized via x-ray diffraction (XRD, Rigaku D/Max-3C, Japan) technique. To study the structure of synthesized phosphor materials and the formed crystallinity, we used scanning electron microscope

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TABLE 1

Compositions of  $\text{YVO}_4:\text{Dy}^{3+}/\text{SiO}_2$  phosphors

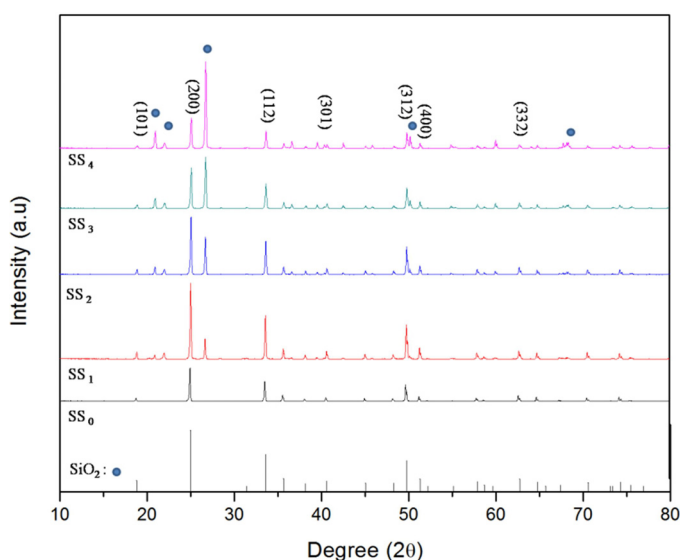
Solid State Synthesized Samples	Composition
SS <sub>0</sub>	$\text{Dy}^{3+}$ doped $\text{YVO}_4/0$ wt% $\text{SiO}_2$
SS <sub>1</sub>	$\text{Dy}^{3+}$ doped $\text{YVO}_4/7$ wt% $\text{SiO}_2$
SS <sub>2</sub>	$\text{Dy}^{3+}$ doped $\text{YVO}_4/10$ wt% $\text{SiO}_2$
SS <sub>3</sub>	$\text{Dy}^{3+}$ doped $\text{YVO}_4/15$ wt% $\text{SiO}_2$
SS <sub>4</sub>	$\text{Dy}^{3+}$ doped $\text{YVO}_4/20$ wt% $\text{SiO}_2$

(SEM, JSM 6360, Japan), transmission electron microscopy (TEM, JEOL JEM 1010, Japan) and high resolution transmission electron microscope (HRTEM, JEOL 3000F, Japan). Also XPS spectroscopy was collected using Al K $\alpha$  source x-ray photoelectron spectroscopy (XPS, Sigma probe, VG scientific, UK) and the photoluminescence behaviors of phosphors were obtained by photoluminescence analyzer (Horiba Jobin Yvon Kyoto, Japan).

### 3. Results

#### 3.1. XRD analysis

Fig. 1 shows the XRD spectra of  $\text{YVO}_4:\text{Dy}^{3+}/$  with or without  $\text{SiO}_2$  particles. It can be seen that in all the samples the trigonal crystal structure (JCPDS No. 17-0341) has been formed successfully. Also, with the addition of  $\text{SiO}_2$  powder, some extra peaks can be observed clearly in XRD spectra. The peaks of  $\text{SiO}_2$  can be seen at 21.05, 22.09, 26.86, 50.24 and 68.26° for the solid state synthesized samples. The most intensive peak of  $\text{SiO}_2$  is seen at 26.86° whereas in the SS<sub>3</sub> and SS<sub>4</sub> samples this peak has a very remarkable intensity.

Fig. 1. XRD spectra of  $\text{YVO}_4:1\%\text{Dy}^{3+}/$  with or without  $\text{SiO}_2$  particles

Evidently, large amounts of  $\text{SiO}_2$  results in a poor crystallinity of  $\text{YVO}_4$  structure. Noteworthy, the relative intensity of (200)

planes to other planes of  $\text{YVO}_4:1\%\text{Dy}^{3+}$  phosphors is gradually decreasing with the increase of  $\text{SiO}_2$  quantity.

#### 3.2. Microstructure observations

Fig. 2 shows the SEM microstructure of  $\text{YVO}_4:1\%\text{Dy}^{3+}$  phosphors. It is seen that the used  $\text{SiO}_2$  particles have sizes approximately from 1 to 5  $\mu\text{m}$  (Fig. 2a). Fig. 2b shows the phosphor particles are in the range of sub micrometers to several micrometers. Accordingly, in the absence of  $\text{SiO}_2$ , the phosphors possess an average size of 4.95  $\mu\text{m}$  that is in a good agreement with the result of our XRD spectra.

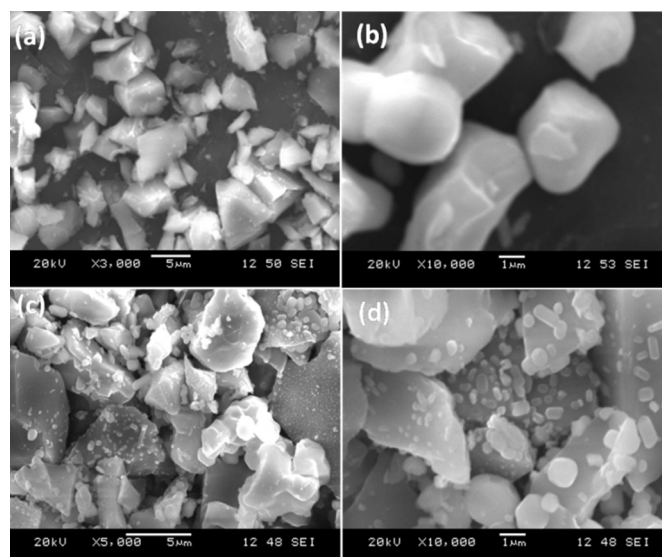
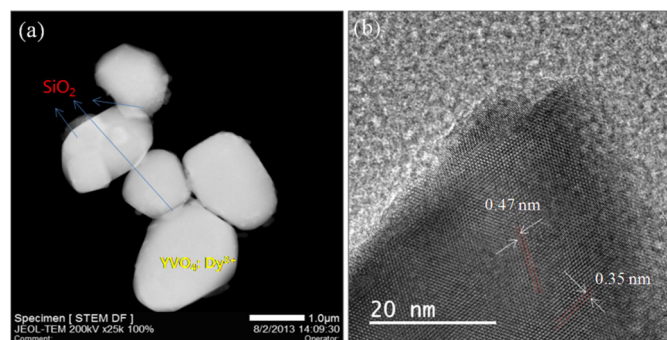
Fig. 2. SEM images of (a)  $\text{SiO}_2$  particles, (b) SS<sub>0</sub>, (c) SS<sub>2</sub> and (d) SS<sub>4</sub> compounds

Fig. 2c,d are attributed to the compounds including 10 and 20 wt%  $\text{SiO}_2$ , respectively. It can be seen that  $\text{SiO}_2$  particles have been distributed on the phosphor particles, homogeneously. Moreover, it seems that a kind of bonding has formed between  $\text{YVO}_4:\text{Dy}^{3+}$  phosphors and  $\text{SiO}_2$  particles. This issue will be characterized and discussed more deeply in this paper.

Fig. 3a shows the TEM images of SS<sub>2</sub> compound. This image shows the presence and distribution of  $\text{SiO}_2$  particles between  $\text{YVO}_4:\text{Dy}^{3+}$  phosphors. According to the appeared

Fig. 3. (a) TEM and (b) HRTEM images of SS<sub>2</sub> compound

fringes in Fig. 3b it is clear that  $\text{YVO}_4:\text{Dy}^{3+}$  phosphors have been crystallized significantly. In this image (200) and (101) planes can be observed clearly and the interspaces between neighbor lattice fringes have been calculated about 0.35 and 0.47 nm, respectively. These distances are agreed with XRD spectra and the results of former investigation [29].

#### 4. XPS Analysis

Fig. 4 shows the XPS spectra of Yttrium and Vanadium elements of  $\text{SS}_0$  and  $\text{SS}_3$  compounds. Fig. 4a,b are related to Y 3d of  $\text{SS}_0$  and  $\text{SS}_3$  compounds, respectively. It can be found that the use of 15 wt%  $\text{SiO}_2$  results in increase of binding energy from 157.16 and 159.19 eV to 157.39 and 159.37 eV, respectively. Also according to Figs. 5(c), (d) that are related to V 2P of the mentioned compounds, it can be observed that the addition of 15 wt%  $\text{SiO}_2$  results in increase of binding energy from 516.8 to 516.86 eV. So it can be easily understood that for both of yttrium and vanadium elements, with the use of  $\text{SiO}_2$  a peak shift occurs to higher levels of binding energies. It can be considered as an evidence for the formation of Y-O-Si and V-O-Si bonds [30]. Since the electronegativity of silicon is higher than those of yttrium and vanadium elements, so while there is a bonding between  $\text{SiO}_2$  and  $\text{Dy}^{3+}$  doped  $\text{YVO}_4$  phosphors, the density of electrons around Y and V will be decreased. Because the shielding effect is reduced, the binding energy in Y-O-Si and V-O-Si bonds is improved. Comparing the XPS spectra reveals that with use of  $\text{SiO}_2$  the amounts of peak shifting for V 2p is remarkably less than Y 3d.

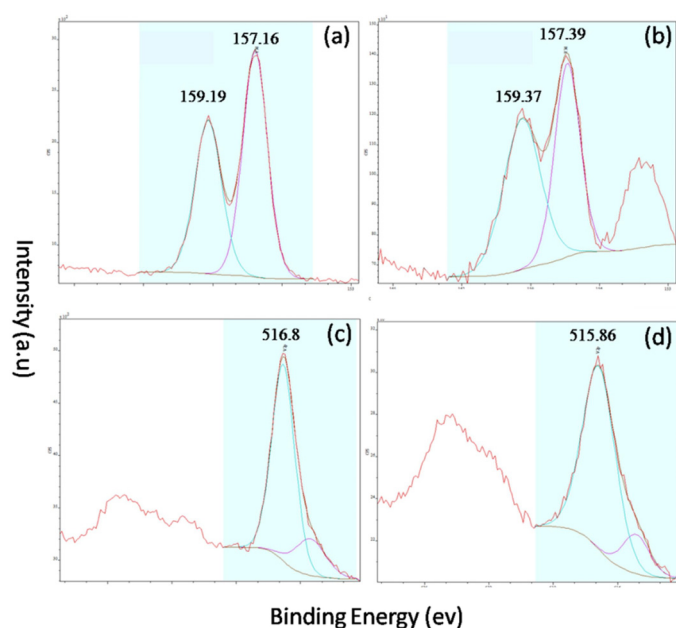


Fig. 4. XPS spectra of (a), (b), yttrium and (c), (d) vanadium elements for  $\text{SS}_0$  and  $\text{SS}_3$  compounds, respectively

In this investigation it was observed that the amount of peak shift depends on the difference of electronegativity between Si

and Y/V. Simply the electronegativity differences of V-Si and Y-Si can be calculated 0.27 and 0.68, respectively. Noteworthy, referring to nephelaxitic effect, the difference of electronegativity between the constituting ions depends conversely to amount of covalency [31]. Then the higher electronegativity difference of Y-Si induces less covalency and it means that the interaction between electrons is enhanced. This fact comes from this key point that in the case of weak covalencies the electrons cannot spread out over wider orbitals significantly [31]. So, the joining of  $\text{SiO}_2$  powder to  $\text{YVO}_4:\text{Dy}^{3+}$  phosphor particles, results in higher peak shifts of yttrium than that of vanadium.

#### 4.1. PL analysis

Fig. 5a shows a strong and wide excitation band in the range of 235 to 350 nm with a maximum excitation at 310 nm. This wide peak is related to the  $\text{VO}_4$  group absorption and  $\text{Dy}^{3+} - \text{O}^{2-}$  charge transfer state (CTS). The wide and strong excitation band of host absorption provides an effective energy transfer and luminescence of  $\text{Dy}^{3+}$  ions. Upon excitation by a wavelength of 310 nm, the emission spectrum appears with two strong bands at 481 and 573 nm (Fig. 5b). Both of the emission peaks correspond to the characteristic emission of  $\text{Dy}^{3+}$  ion due to the transitions of blue ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ ) and yellow transitions ( ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ ), respectively [32].

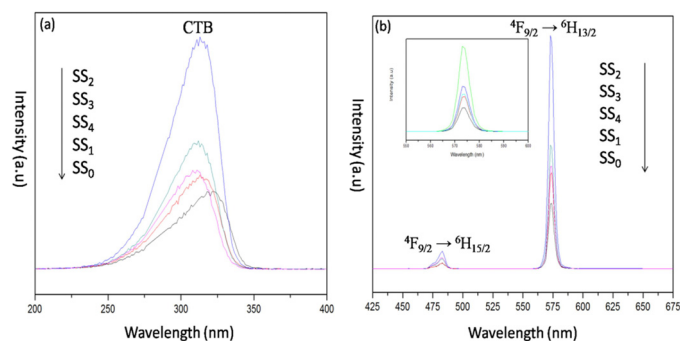


Fig. 5. Photoluminescence (a) excitation and (b) emission of  $\text{SS}_0$ ,  $\text{SS}_1$ ,  $\text{SS}_2$ ,  $\text{SS}_3$  and  $\text{SS}_4$  compound

The synthesized samples with different amounts of  $\text{SiO}_2$  have identical emission band at the mentioned wavelengths. But use of  $\text{SiO}_2$  particles enhanced the emission intensities of 481 and 573 nm peaks. It was already shown that the presence of  $\text{SiO}_2$  particles on the surface of phosphors can play an essential effect on the prevention of exciting light scattering. Takashi Ogi and his colleagues showed that filling the spaces between YAG particles by  $\text{SiO}_2$  decreases the reflection coefficient (R) and then the excitation energy will be improved [19]. In fact the mentioned parameter, R, had been calculated in terms of refractive index of phosphors, air and  $\text{SiO}_2$ . We observed that among the synthesized composites, the strongest emission intensity is related to  $\text{SS}_2$  compound. Further increases of  $\text{SiO}_2$  caused the emission intensities of the phosphor particles to suppress. This

result may be attributed to the XRD analysis of these compounds. As it was explained earlier, when relatively high amounts of SiO<sub>2</sub> particles were added to YVO<sub>4</sub>:Dy<sup>3+</sup> luminescent materials, improper crystallization of the phosphors were obtained obviously. This fact can be considered as an efficient mechanism to suppress the luminescence properties.

### 5. Conclusion

In this paper it was found that via addition of SiO<sub>2</sub> particles to YVO<sub>4</sub>:Dy<sup>3+</sup> phosphors, strong bonds are made between SiO<sub>2</sub> and phosphors particles. Meanwhile, due to higher electronegativity of Si 2p compared to Y 3d and V 2p elements, increase of SiO<sub>2</sub> leads to increase of binding energy. Also, the addition of 10 wt% SiO<sub>2</sub> particles to YVO<sub>4</sub>:Dy<sup>3+</sup> phosphors increased the excitation and emission luminescence properties, significantly. Further increase of SiO<sub>2</sub> results in suppress of emission intensity.

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